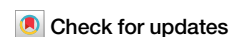


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Floating 3D-PDMS-Iron oxide molecular baskets for decontaminating diverse pollutants and analyzing structural composition impacts

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Novel iron oxide-incorporated porous polydimethylsiloxane sponges were developed using a simple, non-toxic two-step process. Characterized through various techniques, these sponges serve as effective photocatalysts, absorbents, and adsorbents for pollutant removal. They demonstrated nearly 100% degradation of rhodamine B under optimal conditions (~100% with Xe arc lamp, 50 mg, pH 3–9, and 4 h), following a pseudo second-order kinetic model ($r^2 = 0.9999$). The sponges also exhibited good activity for other pollutants, including methylene blue (76–87%), 1,4-dichlorobenzene (57–71%), and azithromycin (82–87%), and maintained high performance over 11 reuse cycles with minimal iron loss. In addition, fresh and used catalysts effectively separated oils (173–680 mg with 50 mg of absorbent, and 10–15 s) and chromium (VI) [~87% with 1 ppm, 50 mg, pH 7, and 24 h] from water. This environmentally sustainable approach produces no toxic waste and allows for simple regeneration, making it a promising solution for the water treatment industry.

Iron oxides (IOs; Fe_2O_3 and Fe_3O_4) have made significant contributions to research on environmental purification through catalysis owing to their unique physicochemical properties, high compatibility, durability, and low toxicity^{1–6}. However, the poor stability, dispersibility, leaching, formation of iron sludge, and recovery of powdered IOs have limited their reusability in catalytic applications^{1,7,8}. Various methods have been developed to address this problem^{8–11}. One effective strategy involves their incorporation into solid host materials, which can either actively participate in catalytic activity or serve as inert carriers to reduce catalyst loss during reactions^{1,12–14}.

Si-based materials have been explored for the surface modification, anchoring, and loading of inorganic nanomaterials^{14–17}. These materials effectively improve the compatibility and performance of the resulting materials for various applications. Recently, silica-based materials have emerged as novel coatings and support materials for IOs^{14,16,17}. They help to overcome the challenges related to dispersibility, stability, recovery, and catalytic rates in aqueous environments of core silicate-iron oxide nanoparticles (NPs). From this perspective, a promising Si-source material is polydimethylsiloxane (PDMS), which is known for its chemical inertness and compatibility under various operating conditions. PDMS sponge is prepared with the help of elastomer (PDMSS) and produces the non-

hydrophilic properties of PDMSS make it suitable for absorbing organic substances and solvents from aqueous mixtures^{18,19}. This spongy characteristic material has gained attention owing to its role as a capping or hosting agent for controlling the stability and durability of metal oxide NPs during catalytic degradation in aqueous solutions^{17,20}.

This study focused on preparing floating three-dimensional (3D) porous PDMS-IO (Fe_2O_3 and Fe_3O_4) sponges (IO-sponges) by incorporating iron oxides (IOs) into the interior and exterior surfaces of the porous PDMS sponge network during synthesis. Specifically, Fe_2O_3 and Fe_3O_4 act as catalysts^{1–8}, while PDMS serves as the host material. The resulting IO-sponges are characterized in detail and applied to various environmental applications, including the catalytic degradation of rhodamine B (RhB), oil absorption and separation, and the adsorption of inorganic Cr(VI) [HCrO_4^-] from the aqueous phase as model pollutants. The outcomes of this study will enhance the stability and reusability of the iron oxides under various working conditions, such as pH, light, and temperature, while reducing the leaching of iron oxides and the formation of iron sludge as secondary waste.

First, the catalytic activity of the IO-sponges was assessed using RhB as a model pollutant under various conditions. RhB is a highly water-soluble

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cationic dye known for its toxicity^{21–23} and various methods and materials were reported in the literatures^{14,17,21,24}. Secondly, the fresh and used IO-sponges were screened for their effectiveness in cleaning oil spills because of harmfulness of the oil spill to the environment and restrictions in the existing reports^{18,25,26}. Third, the ability of the IO sponge to remove carcinogenic Cr(VI) from the aqueous phase was investigated at circumneutral pH to overcome the limits in the works. Both the fresh and used IO-sponges exhibited competent catalytic activity, absorption, and adsorption properties in comparison with the PDMS sponge alone when dealing with a wide range of oils.

In summary, IO-sponge materials offer a simple and environmentally friendly preparation method that does not require toxic reagents or harmful instrumentation. These sponges have demonstrated comparable photocatalytic performance in degrading various organic pollutants, as well as in oil separation and Cr(VI) removal. This indicates that IO-sponge materials are highly suitable for remediating diverse pollutants (inorganic, organic, hydrophilic, and hydrophobic) from aquatic environments. They can be easily separated from the reaction mixture using lab pincers, facilitating reuse. Furthermore, even after a loss of catalytic capacity, IO-sponges can still be employed to eliminate other pollutants through adsorption and absorption, aligning with the goals of a circular economy and environmental sustainability.

Results and discussion

Analysis of prepared sponge materials characterizations

The prepared sponge catalysts with IOs (Fig. 1A) were characterized (Figs. 1B–E2, 2 and Supplementary Figure 1) using various techniques, including water contact angle (WCA), X-ray diffraction (XRD), Attenuated Total Reflection-Fourier Transform Infrared spectrometry (ATR-FTIR), inductively coupled plasma-optical emission spectroscopy (ICP-OES), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). The prepared PDMS sponge materials (Fig. 1A) were subjected to various physicochemical characterization techniques.

First, the measured WCA analysis and the averaged theta (θ) values of six sides of IOs-sponges were 112.90°, 114.62°, 102.64°, and 104.60° for PF2I, PF3I, PF2O, and PF3O, respectively, indicating that all IOs-sponges are hydrophobic (Fig. 1B). The WCA measurements also showed that the PDMS sponge incorporated with IOs on its surface (PF2O and PF3O) exhibited less hydrophobicity than those with IOs incorporated into the PDMS sponge (PF2I and PF3I) (Fig. 1B), suggesting that there is fine PDMS coverage over the IOs in PF2I and PF3I. Furthermore, the hydrophobic properties of the IO sponges were examined by immersing them in a 10 mL of chloroform and water (1:1, v/v) mixture. To distinguish between the two phases, the aqueous phase was colored with a fluorescent dye, and all IO sponges resided in the chloroform phase (Fig. 1C). In addition, the amount of iron (Fe) in PF2I (120.38), PF2O (120.79), PF3I (128.58), and PF3O (128.85) in mg kg⁻¹ were quantified using ICP-OES analysis (the average values of three samples). This confirmed that all sponges contained almost the same amount of iron.

Second, XRD spectra of prepared materials are shown in Fig. 1D. Both the morphology and structure of IOs are in agreement with previous studies^{32–34}. Since the XRD peaks of Fe₂O₃ (PF2I and PF3I) and Fe₃O₄ (PF2O and PF3O) are closely coincide in the same position but XRD spectra of PF2I and PF3I are having more noisy than other two samples due to influence by PDMS sponge backbone, it is difficult to differentiate between Fe₂O₃ and Fe₃O₄. The diffraction peaks for Fe₂O₃ and Fe₃O₄ are closely aligned with JCPDS no. 89-8103 and JCPDS no. 65-3107, respectively, suggesting the coexistence of Fe₂O₃ and Fe₃O₄. In addition, given that the color of Fe₂O₃ is reddish-brown (Fig. 1A, second and fourth samples) while Fe₃O₄ is black (Fig. 1D, third and fifth samples), we can conclude that the XRD peaks correspond to Fe₂O₃ and Fe₃O₄.

Third, the ATR-FTIR analysis clarified the presence of surface functional groups and structural characteristics of the catalysts (Fig. 1E1,2). As discussed in the previous Fig. 1E1,2 paragraph, the catalysts with IOs inside the PDMS sponge (PF2I and PF3I) contain a larger number of Si-based

functional groups, such as Si-O, Si-O-Si, Si-C, and Si-C-H, on the surface than those with IOs on the surface of the PDMS sponge (PF2O and PF3O). Additionally, PF2O and PF3O exhibited an increased intensity of the peaks corresponding to the Fe-based vibrational peaks (Fe-O, Fe-O-Fe, and Fe-OH) compared to PF2I and PF3I, which confirmed that the PDMS surface was fully covered with IOs. These results are in agreement with the WCA results. Finally, SEM-EDS mapping and EDS analysis (Fig. 2 and Supplementary Fig. 1) clearly demonstrate the morphology of the prepared IO sponges, and these images confirm the presence of well-dispersed IOs inside (Fig. 2A, B) and outside (Fig. 2C, D) the PDMS sponges.

In conclusions, the above characterizations confirmed the three-dimensional network structure and the floating spongy properties with strong binding between them. These strong PDMS-IO networks were stable and reduced the leaching of IOs.

Catalytic ability of prepared sponge materials and optimization

Preliminary catalytic tests were conducted using all prepared catalysts in the presence of H₂O₂ under different degradation conditions, including normal stirring (NS), sonication (US), and light irradiation. These tests (Fig. 3A) revealed that the maximum degradation efficiency (~99.99%) of RhB was achieved at different degradation times [NS (48 h) and US (24 h)]. However, when the light-assisted catalytic activity was employed, complete degradation was achieved within 4 h. No RhB could be extracted from either the solid (catalyst) or liquid (reaction mixture) phase after the degradation experiment using SPE for catalysts with water and LLE for aqueous reaction mixtures with DCM. Thus, the results indicated that all the catalysts achieved complete RhB degradation.

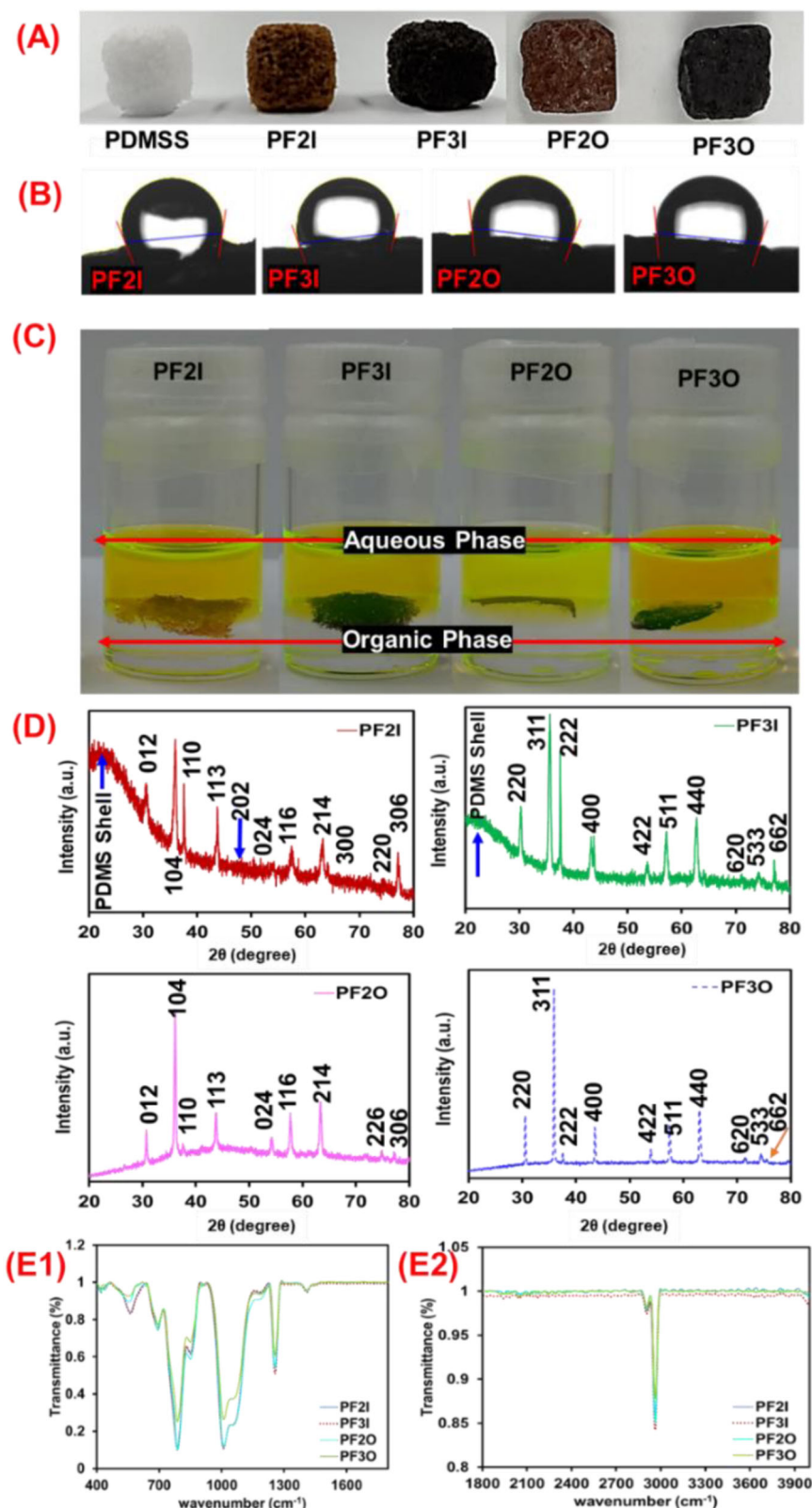
Similarly, to evaluate the possibility of iron loss from the solid catalysts after the degradation experiments, quantification was performed by subjecting both the solid (after extraction with HCl) and liquid phases to ICP-OES analysis. The data for both samples showed that the amount of iron was below the ICP-OES detection limit, indicating no loss of iron from the catalysts into the reaction mixture and the strong attachment of iron to PDMS.

Furthermore, pristine IOs were directly applied to RhB degradation, with the results shown in Fig. 3B, C. These findings demonstrate a relatively less satisfactory performance in terms of the time consumed and the separation of these catalysts after catalytic degradation (Fig. 3B). Separating IOs incorporated into PDMS catalysts is simpler than separating pristine IOs, which minimizes iron loss and secondary contamination. Hence, the catalytic degradation efficiency was optimized using IO sponges as catalysts in the presence of light with H₂O₂.

We conducted control experiments using pure PDMSS (without IOs) and modified PDMSS (with iron oxides), both with and without H₂O₂, under dark and light conditions. As shown in Fig. 3C in the absence of IOs (only PDMSS), RhB degradation (2.36–4.59%) was very low both with and without H₂O₂ under light irradiation. Similar results were obtained for RhB alone, in the presence and absence of H₂O₂ (Fig. 3C). In both cases, this can occur through either an indirect pathway involving the reaction with H₂O₂ or the photocatalytic generation of reactive oxygen species (ROS) from water^{35,36}. These samples did not exhibit significant changes in RhB degradation even after prolonged light irradiation (48 h).

The catalytic activity of the IO-modified PDMS sponge was tested in the presence and absence of H₂O₂ under dark conditions. All samples showed only RhB adsorption (19.1–36.91%) without H₂O₂, and after a 48 h reaction time, coupled adsorption (95%) and minimal degradation (<5%) were observed with H₂O₂ (Fig. 3C, PF2I_dark_H₂O₂, PF3I_dark_H₂O₂, PF2O_dark_H₂O₂, and PF3O_dark_H₂O₂). This is probably because H₂O₂ played an indirect role in the 95% adsorption of RhB. The above results were obtained through Solid Phase Extraction (SPE) and Liquid-Liquid Extraction (LLE) methods for both the solid catalyst and the reaction mixture after degradation, as mentioned in the methods section (Para 2 under the heading of *Evaluation and optimization of catalytic capacity*). The photocatalytic ability of all IOs-sponges was found to be unsatisfactory in the absence of H₂O₂, with only 21.7–31.4% of RhB degraded after 12 h of

Fig. 1 | The prepared sponge catalysts with iron oxide (PF2I, PF3I, PF2O, and PF3O) were systematically characterized using various physico-chemical techniques to understand the properties of these new catalysts. **A** Prepared sponge samples, **B** WCA measurements, **C** hydrophobic vs hydrophilic test, **D** XRD spectra of the freshly prepared samples, and ATR-FTIR of all prepared materials **E1** 400–1800 cm^{-1} , and **E2** 1800–4000 cm^{-1} .



light irradiation. However, satisfactory performance was achieved under light irradiation in the presence of H_2O_2 (Fig. 3A, PF2I_light, PF3I_light, PF2O_light, and PF3O_light). These observations confirm that these catalysts exhibit high reactivity under light irradiation in the presence of H_2O_2 .

The concentration of H_2O_2 was varied up to 1000 μL , and the results, as shown in Fig. 3D, revealed that catalytic activity increased up to 200 μL of

H_2O_2 , followed by a gradual decrease. This is possibly because excess ROS quench themselves through recombination^{37–40}. Therefore, we selected 200 μL as the optimal amount of H_2O_2 for further experiments.

The performance of the prepared catalysts for the photochemical degradation of RhB was investigated over a wide pH range (3–9). The catalytic abilities of all catalysts were ranked in the following order from the

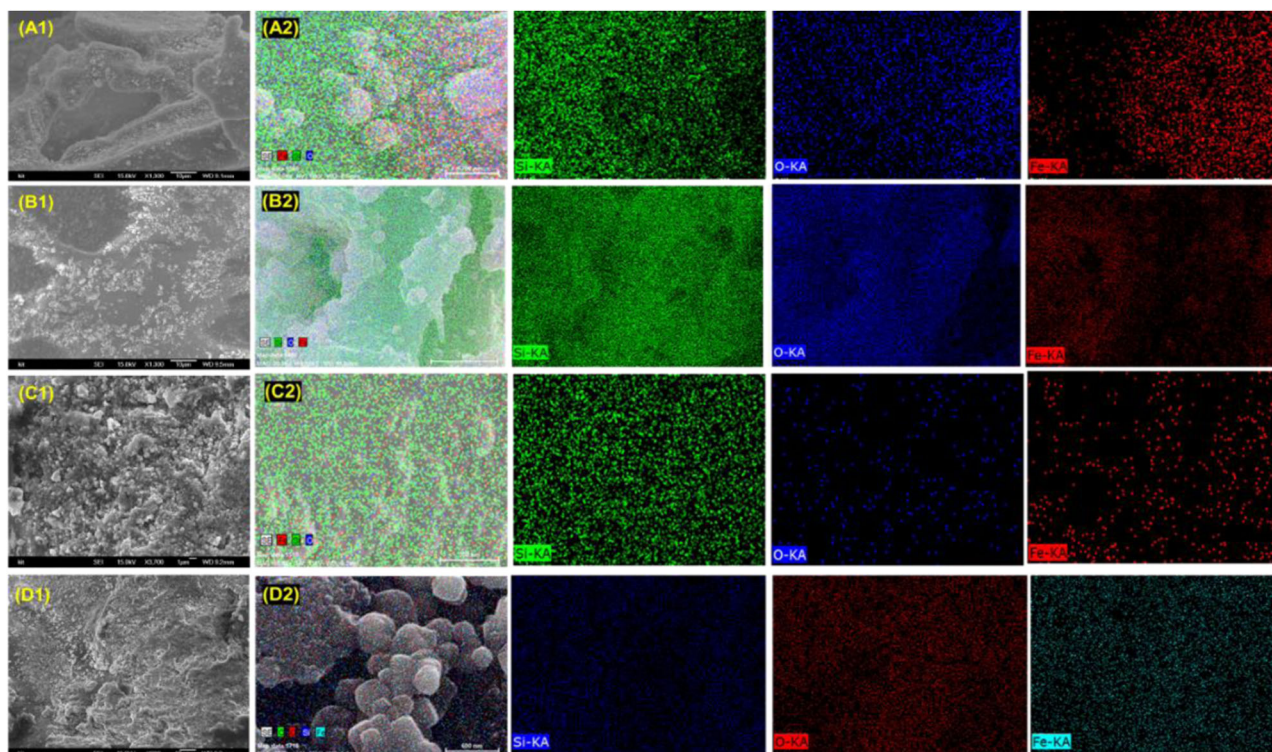


Fig. 2 | The morphology and distribution (SEM-EDS mapping) of iron oxides in the four prepared sponges were systematically investigated to demonstrate the surface properties and the homogeneous distribution of iron oxide in these catalysts. A1-2 PF2I, B1-2 PF3I, C1-2 PF2O, and D1-2 PF3O.

Fig. 3E: high (100%) at pH 5 > (97–99.9%) at pH 9 > (~79–82%) at pH 3 and 7. This clearly indicates the different chemical structural–activity relationships and behaviors of the catalytic surfaces in solution with RhB under varying pH conditions. Furthermore, at pH < 3, removal occurs through partial adsorption and structural distortion of RhB due to the protonated catalyst surfaces. The protonated catalyst surfaces interact less effectively with H_2O_2 and cationic RhB through non-covalent interactions, which also leads to partial structural deformation of RhB. At pH 3 and 7, RhB degradation occurs through Fenton-type degradation at a moderate speed, and the catalyst surfaces exhibit moderate catalytic behavior in generating reactive oxygen species (ROS) due to the equal concentrations of H^+ and HO^- species, as well as the presence of Rh^+ and Cl^- . This leads to significant competition among ionic species with H_2O_2 , affecting the catalyst surfaces and resulting in moderate RhB degradation percentages^{40,41}. At pH 5, RhB degradation occurs through Fenton-type degradation, with the catalyst surfaces favoring the generation of larger amounts of reactive oxygen species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$), which direct RhB towards the catalyst surfaces, leading to an increased RhB degradation rate. At pH ~ 9, approximately 97–99.9% degradation of RhB was observed, which is promising due to the high concentration of OH^- ions in the reaction mixture, favoring the generation of more ROS with the help of the catalyst.

Overall, the order of bond breaking and the generation of intermediates in RhB differ with respect to pH, affecting alkyl bonds, chromophores, and aromatic compounds⁴². They also affect their interactions with competing chemical species, which can lead to unsought and destructive sideways reactions. Furthermore, the catalytic reaction rate was affected at these pH values by the charge (electron) conductivity of the catalysts, which regulated the competence of charge transportation to the surface-reactive sites. Therefore, it is anticipated that the surface properties and electron conductivity connected with the structural composition (geometry) of the catalysts will result in a lower photocatalytic performance^{38–43}. This demonstrates that these catalysts positively influenced RhB degradation and were compatible over a wide pH range. pH changes were not detected after RhB degradation in the solution.

The photocatalytic response of the prepared catalysts was evaluated by varying the amount (20–60 mg). Figure 3F shows that the rate of catalytic efficiency gradually increased with increasing amounts of catalyst until reaching 40 mg, followed by a sudden increase, leading to complete RhB degradation (>99.8%) between 40 and 50 mg. Beyond this range (50–60 mg), the catalytic activity reached saturation.

The effect of RhB concentration on RhB degradation was examined using 50 mg of the catalyst. Figure 3G reveals that all prepared catalysts achieved approximately 100% RhB degradation up to a concentration of 25 mg L^{-1} . Beyond this point, the percentage of degradation sharply decreased owing to a reduction in the availability of catalytic reactive sites and ROS for RhB degradation.

The time required for complete degradation was analyzed, and the results are shown in Fig. 3H, in which complete degradation (~100%) of RhB for all samples was observed at 240 min. From the above observations, we can infer that the rate of catalytic activity of PF2I and PF3I started slowly at different rates compared to the other two catalysts due to the PDMS encapsulation, yet they completed the RhB degradation in the same time frame of 240 min. Therefore, we believe that the catalytic effect of all the iron oxide sponges arises from the trapping of light energy near the pores and surfaces of the catalysts, facilitated by the PDMS component. To further evaluate the catalytic kinetics of RhB degradation, multiple kinetic modeling equations were applied to the experimental data^{44,45}. The results of the kinetic modeling plots are shown in Fig. 4A and Supplementary Fig. 2A, B, and it is evident that the degradation data are well fitted with the pseudo-second-order (PSO) model, as indicated by the higher r^2 values (0.9999), whereas the pseudo-first-order (PFO) model does not match the experimental data well with the lower r^2 values ranging from 0.6669 to 0.9238. Based on the data fitting, the calculated C_e (Q_e) values, representing the degraded RhB concentration, were found to be 15.24 (PF2I), 15.11 (PF3I), 15.10 (PF2O), and 15.13 mg g^{-1} (PF3O), respectively. These values are nearly equal to the initial amount of RhB used in this experiment, which was 15.00 mg g^{-1} (experimental). This suggests that the photocatalytic degradation following the PSO mechanism is likely attributable to the

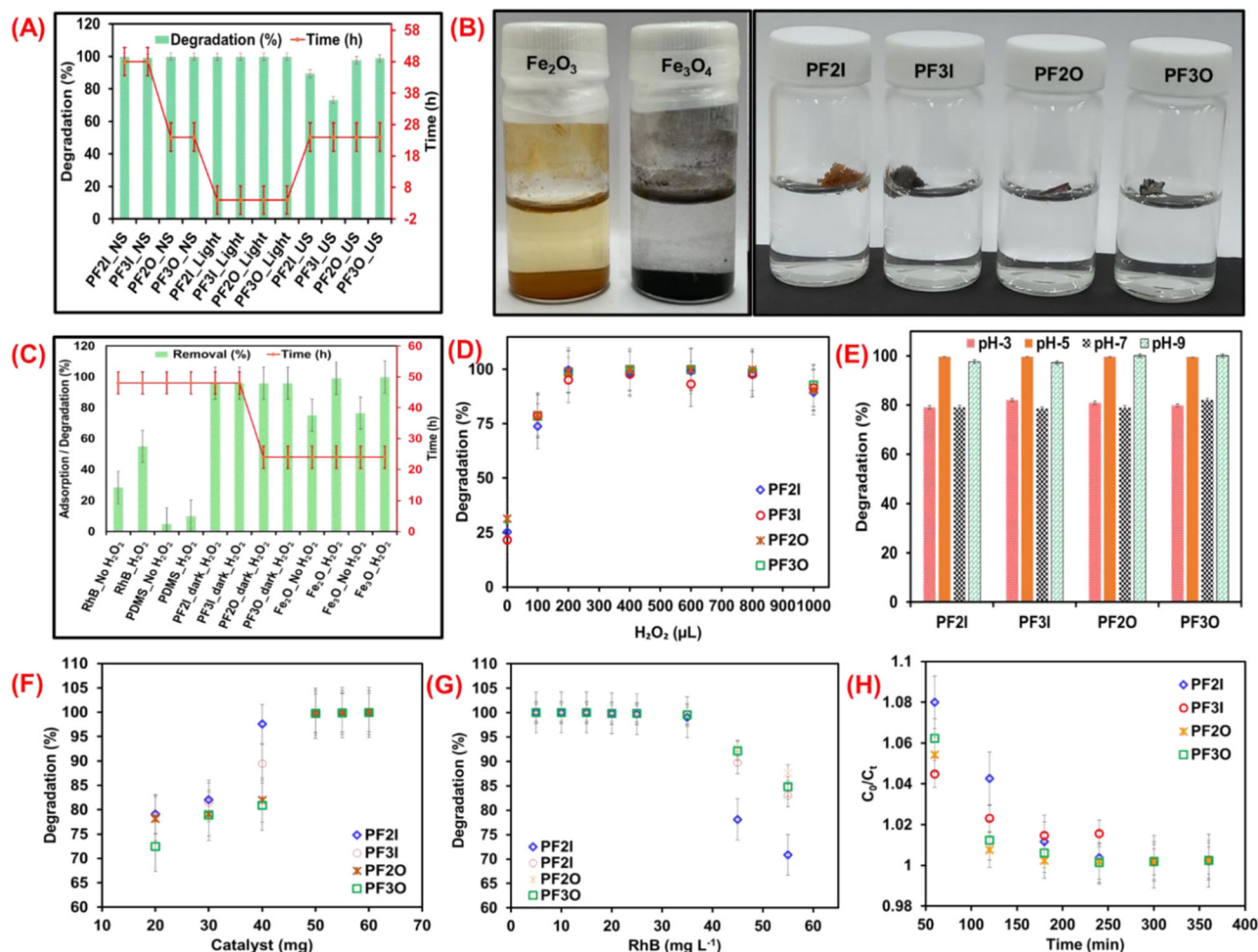


Fig. 3 | The catalytic activity of the prepared catalysts in the oxidative degradation of RhB by light under various reaction conditions was optimized. A Catalytic activity and dynamic behavior of catalyst, **B** photographs of reaction container after

the catalytic reaction, **C** control experiments, **D** effect of H_2O_2 (μL), **E** effect of pH, **F** effect of catalyst amount (mg), **G** effect of RhB concentration (mg L^{-1}), and **H** effect of time (min).

involvement of multiple factors, such as light energy, IOs, PDMSS pores, and H_2O_2 . Furthermore, the detailed mechanism of the catalytic activity and RhB degradation is discussed in the section on possible catalytic and RhB degradation mechanisms.

To further evaluate the formation of radical species during the catalytic oxidation of RhB, glycerol was used as a radical scavenger^{46,47}. Glycerol is a recognized $\bullet\text{OH}$ scavenger. Glycerol (1 mL) was added during the initial (0 min) and middle (60, 180, and 240 min) stages of the reaction. As shown in Fig. 4B, hydroxide radicals ($\bullet\text{OH}$) were identified as the primary ROS responsible for RhB degradation. It is worth noting that there was also the formation of ultra-trace levels of other ROS ($\text{HO}_2^\bullet$ and $\text{O}_2^\bullet$). Therefore, the generation of $\bullet\text{OH}$ in this heterogeneous system likely involves the following steps: (i) light-promoted production of transition/excited $[\text{IOs}]^*$ and (ii) generation of $\bullet\text{OH}$ through $[\text{IOs}]^*$ and the redox behavior of iron in IOs with H_2O_2 and water^{48,49}.

The influence of degradation reaction temperature, coupled with light irradiation, was evaluated within the temperature range of $20\text{--}60 \pm 3^\circ\text{C}$. The catalytic efficiency increased as the temperature increased, resulting in a decrease in the degradation time from 300 to 90 min (Fig. 4C). This suggests that an external supply of thermal energy may have lowered the energy barrier between the start and end points of the RhB degradation¹⁴.

A possible photocatalytic degradation mechanism of the prepared IOs-sponges was derived by optimizing the above parameters. In general, a decrease or shift in its absorbance wavelength due to an increase in the RhB degradation indicates a different mechanism involving N-deethylation

followed by cleavage of the xanthene group, and vice versa^{50,51}. In our system, the absorbance peak of RhB decreased without any shift, and the pink color changed directly to colorless without an intermediate purple color change¹⁴. This indicates that the N-deethylation process ($-\text{C}-\text{N}-$ and $-\text{C}=\text{N}^+$) is accompanied by chromophore cleavage occur during light irradiation, suggesting that the excited state of the catalysts is involved in this process, in which electrons are transferred from the valence band to the conduction band of the IOs^{52–54}. The excited electrons can further participate in reduction reactions, including the generation of ROS along with H_2O_2 (Fig. 4D), followed by RhB^+ molecular interactions through the diethylamino group. Chromophore cleavage is accompanied by N-deethylation under the synergistic effects of IOs, H_2O_2 , and light.

According to the Fenton reaction mechanism, Fe_3O_4 contains Fe(II), which is a good and rapid activator for H_2O_2 , while Fe_2O_3 , containing only Fe(III), is a weaker activator. In this context, Fe_2O_3 acts as a competitive H_2O_2 activator to Fe_3O_4 . Furthermore, Fe_2O_3 is a potential photocatalyst with a narrow band gap (approximately $< 2.1\text{ eV}$) and a high absorption capacity for applied light irradiation. The photocatalytic activity of Fe_2O_3 increases in a concurrent system during real-time applications. The interfacing of other components (e.g., PDMS, co-catalysts, metal oxides, etc.) with Fe_2O_3 is likely to result in a substantial improvement in photocatalytic efficacy. Iron oxide facilitates the trapping of photogenerated electrons and hole pairs within the lattice, thereby enhancing charge separation and improving overall photoactivity⁷. Herein, we can infer that the rate of catalytic activity of PF2I and PF3I started slowly at different rates compared to

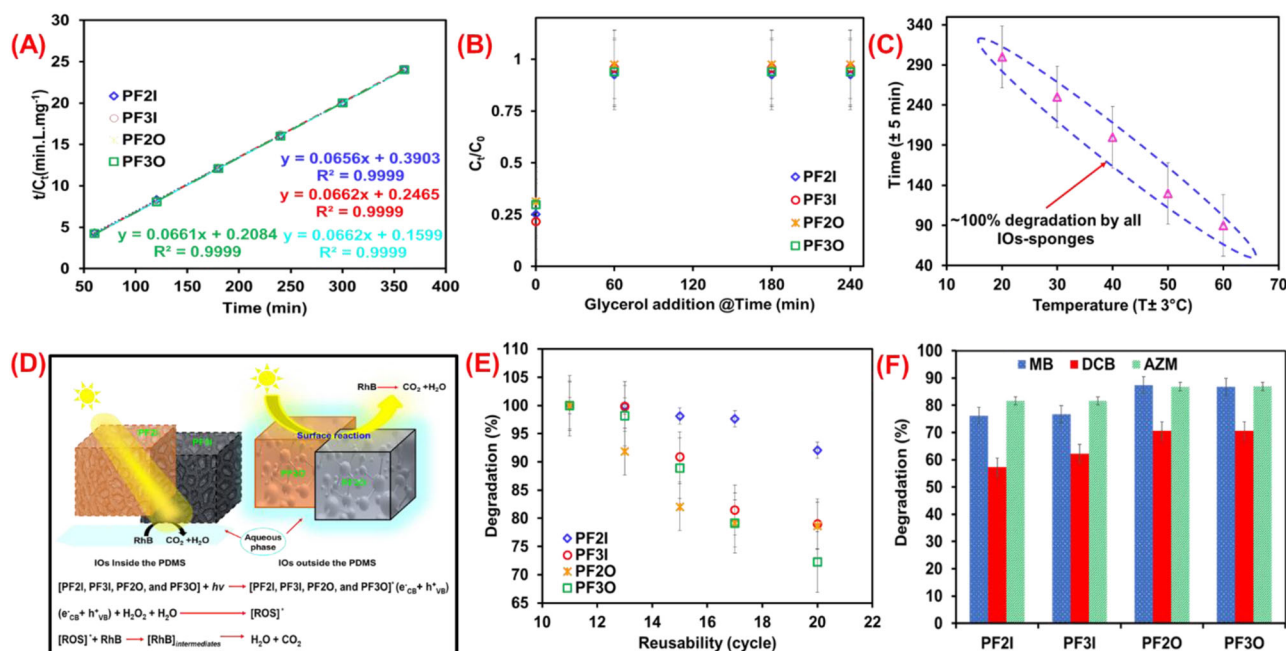


Fig. 4 | An additional series of analytical parameters were optimized to derive the plausible catalytic mechanism for RhB degradation using the prepared sponge catalysts, with further demonstration for the degradation of similar

contaminants. **A** PSO kinetic model, **B** effect of glycerol, **C** effect of temperature, **D** plausible catalytic RhB degradation mechanism, **E** reusability test, and **F** catalytic demonstration to other similar organic micropollutants.

the other two catalysts, likely due to PDMS encapsulation; however, they completed the RhB degradation in the same time frame of 240 min (Figs. 3H and 4A). Furthermore, the activation mechanism of Fe₂O₃ exhibits a different pattern of kinetics, clearly indicating the distinct chemical structure–activity relationships and responses of the catalytic surfaces (Fe₂O₃ and Fe₃O₄) under light irradiation (utilizing a Xe arc lamp with a 300 W output and a light source of 1000 W m⁻²) in the presence of H₂O₂ and varying pH levels. Collectively, this highlights the synergistic effects of Fe₂O₃, light energy, PDMS light scattering, pH, and H₂O₂.

Furthermore, PDMS in the prepared catalysts (PF2I, PF3I, PF2O, and PF3O) does not absorb light itself because of its inertness to light²⁰. Instead, multiple light scattering within the micropores of the catalysts can result in a uniform distribution of light energy over the entire catalyst (PF2I and PF3I). Subsequently, the light scattered inside the catalysts was absorbed by the IOs before escaping the PDMS sponge matrices²⁰, where [PF2I, PF3I, PF2O, and PF3O]*, e_{CB-} , and h_{VB+} are the photoexcited states of the IOs, electrons in the conduction band, and holes in the valence band, respectively. Upon the addition of H₂O₂ to the reaction mixtures, $\bullet OH$ ([ROS]*) is produced by IOs (Fig. 4D), and RhB molecules can be degraded through N-deethylation by $\bullet OH$. Collectively, plausible degradation mechanisms of RhB by photocatalysts with H₂O₂ have been proposed as follows. (i) The responsiveness of the oxidant and catalyst could increase when exposed to light, facilitating electron transfer between them. (ii) The interaction of Fe with the oxidant and RhB shifts the electron density of Fe and the conformation (resulting in different structural spatial arrangements) of RhB in ways that are promising for rapid oxidation. (iii) Redox couples, like Fe (III)/Fe (II), could act as electron shuttle carriers between RhB intermediates and iron species (i.e., Fe-O-, Fe...O-O...Fe, Fe²⁺-O²⁻-Fe²⁺, Fe³⁺-O^{+/+}-Fe²⁺, Fe³⁺...Fe²⁺-O-, etc)^{39,43,55,56}. Therefore, we believe that the catalytic effect of the IO sponges arises from the trapping of RhB near the pores/surfaces of the catalysts, facilitated by light and the oxidant. From the aforementioned discussion, it can be inferred that the oxidative degradation of RhB in this heterogeneous system results in the conversion of RhB into CO₂ and water^{48,57}.

The post characterization of the catalyst after the photochemical degradation was evaluated. The stability, reusability, and dynamic behavior of the IOs-sponges after the photochemical degradation were examined. Initially, ICP-OES analysis solidly confirmed that there was no significant

loss of iron from the IOs-sponges, with an average of 0.0972–0.0733% mg kg⁻¹ in three samples for each. Even this trace amount of loss is not significantly reducing the catalytic activity until the 15th cycle for all catalysts (Fig. 4E). WCA measurements of these samples after catalytic degradation also confirmed that all samples retained their hydrophobicity, with measured theta (θ) values of 111.37°, 113.14°, 93.80°, and 92.69° for PF2I, PF3I, PF2O, and PF3O, respectively (Supplementary Figure 3). In addition, the chemical bonding and functional group changes of the catalysts were not significantly altered but appeared as broader peaks for the -OH group in PF2O and PF3O, as revealed by ATR-FTIR analysis (Supplementary Fig. 4A, B). This indicates that the surface IOs underwent a slight transformation into the corresponding hydroxides; however, these two (PF2O and PF3O) catalysts remained catalytically active. Furthermore, the SEM images showed nearly identical morphologies (Supplementary Fig. 5A–D) compared to the fresh IO sponges. XRD results also supports that the morphology and structures of IO sponges do not change much after RhB degradation, since the XRD peaks of the catalyst after the photochemical reaction (Supplementary Fig. 6, after 11 cycle) are nearly identical to the fresh catalysts, with the possible overlapping and/or disappearance of a few minor peaks due to the IOs partially damaged by reaction components, conditions, and dominance from PDMS.

The reusability of the prepared catalysts was evaluated over 20 cycles, as shown in Fig. 4E). All the catalysts exhibited photoreactivity and remained stable for up to 11 cycles. Afterward, degradation efficiency began to decrease and reached between 70 and 95% in the 20th cycle. The % degradation is decreased significantly (except PF2I) at 4 h degradation time but the degradation time increased (~5–6 h) to other three catalysts to complete the degradation due to the cyclic production and presence of ROS. The values of the degradation efficiency were obtained at the 20th cycle in the following order: PF2I (92.07%) > PF3I (79.03%) ≈ PF2O (78.69%) > PF3O (72.28%). The results shown that there was less significant loss of iron from the IOs-sponges, with an average of 0.0972–0.0733% mg kg⁻¹ in three samples for each. The acceleration of RhB oxidative degradation can be attributed to the catalysis of non-dissolved IOs from the matrix, primarily through the role of an electron shuttle among fresh IOs and transient IOs species (i.e., Fe-O-, Fe...O-O...Fe, Fe²⁺-O²⁻-Fe²⁺, Fe³⁺-O^{+/+}-Fe²⁺, and Fe³⁺...Fe²⁺-O). The catalytic effect, recycled through the cycling of iron

Table 1 | Comparison of catalytic efficiency of synthesized catalysts towards the degradation of RhB with those of other procedures reported in the literature

Catalysts	Amount of catalyst	Method	RhB ^a	Time (h)	pH	Degradation (%)	Ref.
Fe ²⁺ (FeSO ₄)	1 ^b	)))	0.21 ^b	0.12	3	~99	60
Mg (25 wt.%) / SiO ₂	0.70 ^c	UV/V	20	1	7	87/82	61
AgNPs-Fe ₂ O ₃	1.41 ^c	UV/V	24.25	2	10	94.14/58.36	62
TiNPs-Fe ₂ O ₃						88.03/48.36	
Fe ₂ O ₃						77.38/38.03	
Co ₃ O ₄ @CeO ₂	150 ^a	Chemical	30	~0.1–0.23	7	> 98	63
TiO ₂ @RGO	20 mg	Xe Lamp	10	> 7.5	-	> 70	64
PF2I	50 ^d	Visible	35	4	5,9	99.99	<i>This Work</i>
PF3I							
PF2O							
PF3O							

^a: mg L⁻¹^b: mmol L⁻¹^c: g L⁻¹^d: mg;

))) Sonication; UV/V Ultra Violet /Visible light.

between oxidation states (Fe³⁺ and Fe²⁺) coupled with light and ROS^{39,43,48,55–57} was observed both inside and outside the PDMS environment, which is critical for contaminant degradation. In conclusion, these catalyst loss and longer kinetics were observed on and after 16th cycle of the reusability experiments. This performance highlights that these catalysts are competitive, while excelling in terms of reusability, and stability.

Finally, the catalytic efficiencies of these materials for RhB degradation were compared with those reported previously (Table 1). This comparison highlights that these catalysts are competitive with other methods and materials, while excelling in terms of recovery, reusability, and stability.

The catalytic activity and efficiency of the prepared IO sponges were also extended to other similar organic micropollutants, such as AZM, DCB, and MB, using the same degradation reaction conditions for RhB. These molecules are widely used as antibiotics, disinfectants, pesticides, deodorants, medicines, and dyes. However, their presence in both surface and underground water poses risks to the entire ecosystem, including humans^{25,58}. The catalytic degradation percentages (%) were in the range of AZM (81–87%), DCB (57–71%), and MB (76–87%) (Fig. 4F), and the % of non-degraded OMs was verified using the LLE and SPE. The order of catalytic activity towards the above species was PF2I > PF3I > PF2O > PF3O. These observations demonstrate that these catalysts exhibit high activity in the degradation of macromolecular-sized and stable organic pollutants in aquatic environments.

Oils and organic solvents separation/absorption capacity of the prepared sponge materials

The spillage of oil and related substances poses significant health risks^{18,25,29} and necessitates removal from the environment. The oil-cleaning capacity of the prepared IO-sponges was assessed and compared with that of the PDMS sponge and IO-sponges after RhB degradation. The sponges were added to mixtures of water (with fluorescent dye as in Fig. 1C) and oil, followed by gentle shaking, in which the oils had diverse densities ranging from 0.659 to 1.492 g cm⁻³. This suggests that all the catalysts retained their water-repelling and oil-wetting properties. The results, displayed in Fig. 5A, demonstrate that the IO-sponges, before catalytic application, exhibited competitive oil separation capacity compared to PDMSS alone for most oils. Similarly, after 11 cycles, the used catalysts were used for oil absorption, and the results (Fig. 5B) were compared with those of the fresh IO sponges (Fig. 5A). The IOs incorporated into PDMSS (PF2I and PF3I) retained their oil absorption capacity better than the IOs coated on the surface of PDMSS (PF2O and PF3O). This indicates that the oil absorption properties were

retained by PF2O and PF3O, possibly because of the bottom layer of PDMS (Fig. 5C) and possible structural and morphological changes of the IOs by continuous exposure to photochemical reactions.

To verify this, the IOs were removed with HCl from PF2O and PF3O (after degradation), followed by an oil separation/absorption experiment, which resulted in the maximum oil absorption attributed to the PDMS layer. Similar observations were made for the other sponge materials. The above performance is directly linked to the concentration and surface functional groups of the IOs present in the porous PDMS sponges. When the amount of IO is below the PDMS weight/surface ratio, the sorption sites for oils and organic solvents are initially PDMS macrocycles (pores) that eventually occupy the IOs sites/surface. The entire oils and organic solvents phase underwent molecular transfer from the aqueous bulk surface volume into the porous sponges and surfaces of the IOs. In summary, all catalytic materials floated on the surface of water without absorbing any significant amount of water but absorbed a similar amount of the oily layer.

Chromium (VI) removal (adsorption) capacity of the prepared sponge materials

The improper disposal of Cr(VI) into the environment poses significant health risks²⁷, necessitating its removal from environmental samples^{27–30,59}. The carcinogenic heavy metal Cr(VI) ion removal efficiency of the prepared sponges was tested in an aqueous phase under magnetic stirring. The % elimination of Cr(VI) is depicted in Fig. 5D, which illustrates that the prepared IO-sponge materials were capable of removing Cr(VI). Next, these results were compared with those of the IO sponges used 11 times for photochemical RhB degradation.

The experimental results (Fig. 5D) reveal that the % of Cr(VI) elimination is significantly increased (0.5–2.5 times) to that of the fresh IO-sponges, indicating the IO-sponges undergo surface changes such as roughness, IOs, and functional groups, which were supported by ATR-FTIR and SEM analysis of IOs-sponges after the 11 cycles of RhB degradation. Additionally, the supernatant after the adsorption reaction was oxidized with a strong oxidizing reagent, followed by the estimation of Cr(VI) using the standard diphenylcarbazide (DPC) method. The experimental results do not show any reduced chromium in the supernatant. Lastly, the amount of Cr(VI) desorbed from the adsorbent (utilizing pH water) followed by the estimation of Cr(VI) using the standard DPC method³¹, which also does not indicate any reduced chromium on the solid. The possible adsorption mechanism of Cr(VI) by the aforementioned materials involves non-covalent interactions with the IOs (Fe-OH---Cr(VI), Fe-O-OH---Cr(VI),

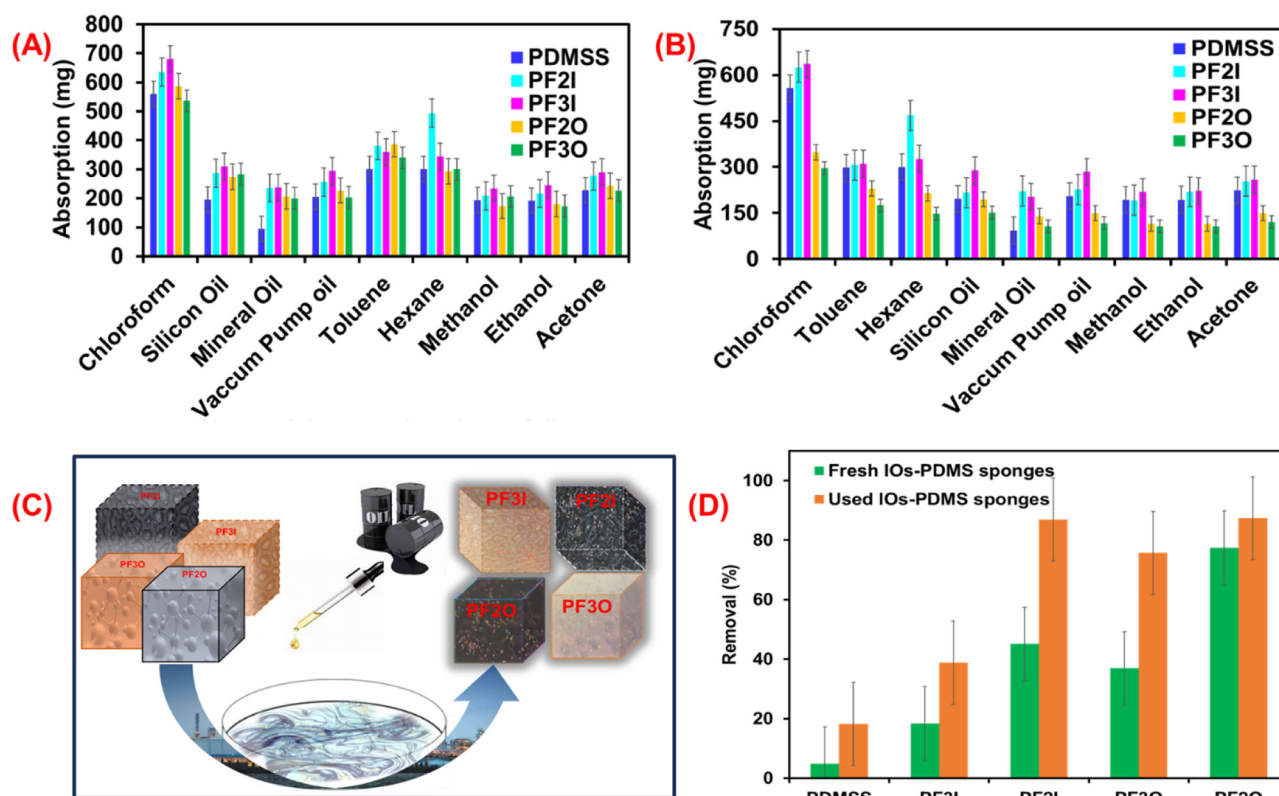


Fig. 5 | The application of the prepared four sponge catalysts for the separation of oil and chromium ions from water was assessed, and their performance was compared with that of four regenerated sponge catalysts after the photochemical

degradation of RhB. A Fresh IOs incorporated PDMSS, **B** used IOs incorporated PDMSS, **C** possible oil absorption mechanism, and **D** optimization of Cr (VI) adsorption with fresh and used IOs incorporated PDMSS.

and $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4\text{---Cr(VI)}$), as well as the rough PDMS surface, which is induced by light irradiation and H_2O_2 (Fig. 5D).

Finally from this study, we derived the following conclusions, first the preparation, characterization, and application of iron oxide-incorporated 3D porous PDMS sponge (3D-PDMSS) were studied for the elimination of hazardous dyes, drug molecules, oils, organic solvents, and Cr(VI) under diverse methods and operating conditions. All the IO sponges showed significantly higher percentages of degradation ($\sim 100\%$), oil ($\sim 100\%$), and Cr(VI) removal ($> 80\%$). Secondly, under the light irradiation, all IO sponges excel faster (4 h) and maximum degradation (100%) of RhB with higher reusability ($\sim 15\text{--}20$) cycles and obey the pseudo second order kinetic with higher r^2 (0.9999). The pollutant comes in close contact with the catalytic surfaces, form conjugations with oxidants and stabilize the iron in the catalysts through dispersion forces inside the pocket of light energy with water molecules and H_2O_2 as the linkers. The extended catalytic activity of the prepared sponges demonstrated to MB (76–87%), DCB (57–71%), and AZM (82–87%) at the similar degradation reaction conditions. Thirdly, all sponges (50 mg) before and after (11 cycles) the photochemical degradation reaction exhibited effective absorption/separation (173–680 mg) behavior of the oils and organic solvents from water (1:1 v/v ratio) in 10–15 s, and this indicates that the sponges retained their competitive absorption/separation capacity even after exposure (11 times) to light and oxidants. Thus, deliberate tuning of the PDMS sponge sorption site to the vicinity of either porous site by simple incorporation/anchoring of the IOs (metal oxides), could shed new light on this open question. Lastly, this study demonstrated that all fresh and used sponge materials were effective in removing carcinogenic Cr(VI) [HCrO_4^-] under the optimized conditions. Importantly, the Cr(VI) removal efficiency (5–77%) increased compared to that of the used catalysts over 11 cycles of RhB degradation (18–87%), demonstrating excellent Cr(VI) removal capacity. This was possibly due to the modification of the IO sponge surface by light and oxidants.

In summary, our findings reveal the intrinsic origin of the superior activity of reusable PDMS-iron oxides for eliminating various types of pollutants. This research will guide the rational design of similar multi-purpose, reusable, and dynamic PDMS-metal oxide materials for wastewater treatment. Finally, the results of this study significantly contribute to the development of eco-friendly, multifunctional, recyclable, and renewable materials-based water treatment systems that deliver high performance and address the growing demand for a sustainable environment and circular economy.

Methods

Preparation of the IOs incorporated PDMSS

All materials and methods of characterizations details were provided in the Supplementary Note 1 and Note 2. The PDMSS, as described by Choi et al.¹⁹, and the PDMSS-IOs-sponges were prepared using a similar method with minor modifications, as reported in the literature by Kalidhasan and Lee¹⁷. To summarize, the catalysts were synthesized using the incipient wetness impregnation (IWI) method.

First, 5% w/v solutions of Fe_2O_3 and Fe_3O_4 were prepared separately in dry methanol (5 mL) and sonicating for 60 min. The preparation of PDMS sponge- Fe_2O_3 (PF2I) involved adding a specific volume of the Fe_2O_3 solution [ranging from 800 to 1200 μL , depending on the size ($\sim 1 \times 1 \times 1$ cm), adsorption capacity, and weight ($\sim 4.6 \text{ g} \pm 0.06 \text{ g}$) of the sugar cube]. A procedure similar to that used for PF2I was used to prepare the PDMS sponge- Fe_3O_4 (PF3I) catalysts. A mixture of the PDMS prepolymer (Sylgard 184, Dow Corning) and a thermal curing agent in a 10:1 (g/g) ratio was then poured onto the sugar cube templates containing the IOs. The samples were degassed in a vacuum desiccator and subsequently cured at 50 °C for 120 min in a hot-air oven. After curing, the samples (PDMS-IO-sugar template) were washed with deionized water, and the sugar components were removed by sonication in an ultrasonic cleaner.

Finally, the resulting products were dried in a hot-air oven (35 °C for 12 h). This process led to the formation of three-dimensional, eco-friendly, and well-interconnected microporous PDMS sponges with IOs. The resulting products were stored until further use.

Preparation of the IOs-coated PDMS

The IO-coated PDMS sponge was prepared using a procedure similar to that described in the previous section with minor modifications to the incorporation of iron oxides. A combination of the PDMS prepolymer (Sylgard 184, Dow Corning) and a thermal curing agent in a 10:1 (g/g) ratio was poured onto the sugar cube templates. The samples were degassed in a vacuum desiccator. Subsequently, the degassed samples were cured at 50 °C for 120 min in hot-air oven. During the curing process (specifically after 45 min), the samples were briefly removed to allow the iron oxides to coat the PDMS surface. This was performed using a pre-prepared 5% w/v solution of each IOs (Fe_2O_3 and Fe_3O_4). Afterward, the curing process is continued. Following the curing process, the PDMS-IO-sugar template were cleaned with copious amount of deionized water (DI water), and the sugar components were removed by sonication in an ultrasonic cleaner. Finally, the resulting products were dried in hot-air oven (35 °C for 12 h). These products were named PF2O (PDMS sponge- Fe_2O_3) and PF3O (PDMS sponge- Fe_3O_4).

The prepared PDMS sponge materials (Fig. 1A) were subjected to various physicochemical characterization techniques. Further information on these techniques can be found in the Supporting Information.

Evaluation and optimization of catalytic capacity

To conduct the experiments, a stock solution of organic molecules (OMs) at a concentration of 100 mg L^{-1} was prepared in ultrapure water. Known amounts (50 mg, with dimensions of $0.1 \times 0.1 \times 0.1 \text{ cm}$) of PDMS sponges (PDMS) and IO-sponges (50 mg, which included the PDMS weight) were mixed separately with a predetermined concentration of RhB ($5\text{--}55 \text{ mg L}^{-1}$), resulting in a total volume of 10 mL. hydrogen peroxide (H_2O_2) at varying volumes (ranging from 250 to 1000 μL) was added to the mixture in vials. These mixtures were then subjected to chemical, photochemical (utilizing a Xe arc lamp with a 300 W output and a light source of 1000 W m^{-2}), and sonochemical degradation (using a Branson ultrasonic bath, Model: CPX3800H-E, 40 kHz) at different time intervals across a various range of pH values (ranging from 3 to 9).

After each experiment, a known quantity of the reaction mixture was analyzed using UV-vis spectrometry (UVS) to calculate the amount of degraded RhB. After the degradation experiment, both the solid (catalysts) and liquid phases (reaction mixture) were subjected to solid-phase extraction (SPE) with water (10 mL for solid catalysts), liquid-liquid extraction (LLE) with DCM (10 mL for the liquid phase), and shaking in an orbital shaker for 30 min, followed by UVS analysis. The kinetics of RhB degradation were measured at predetermined time intervals. The pH values of the reaction mixtures were measured for each experiment. Each RhB degradation test was conducted in triplicates to ensure accuracy.

Control degradation experiments were conducted with above mentioned quantity of reagents under sonication and stirring conditions, both with and without H_2O_2 , and using H_2O_2 alone with OMs. Additionally, the pollutants degradation reaction was executed using the IOs (without the PDMS) under similar conditions.

Photocatalytic experiments were extended to methylene blue (MB), dichlorobenzene (DCB), and azithromycin (AZM). The oxidant and photocatalyst concentrations were maintained as specified for RhB degradation.

To assess the recyclability of all the catalysts after completing the catalytic reaction, they were extracted from the solution using tongs. Subsequently, they were squeezed and cleaned multiple times with DI water and then dried at 60 °C. These catalysts were reused for the fresh degradation reaction of organic molecules (OMs). All subsequent degradation and washing processes were repeated more than 11 times to evaluate recyclability.

Evaluation of oils and solvents separation /absorption capacity

The oil and organic solvent absorption capacities of the IO-sponges were measured before and after photochemical RhB degradation using various organic solvents and oils with different densities from an aqueous mixture and compared with those of the PDMS sponge alone. These included chloroform (C'form, density: 1.492 g cm^{-3}), dichloromethane (DCM, density: 1.330 g cm^{-3}), silicon oil (Si-Oil, density: 0.970 g cm^{-3}), high vacuum pump oil (HVP-Oil, density: 0.880 g cm^{-3}), toluene (density: 0.870 g cm^{-3}), mineral oil (Mi-Oil, density: 0.840 g cm^{-3}), methanol (density: 0.791 g cm^{-3}), acetone (density: 0.784 g cm^{-3}), ethanol (density: 0.780 g cm^{-3}), and hexane (density: 0.659 g cm^{-3}).

For these experiments, a known amount of the prepared sponges ($0.1 \times 0.1 \times 0.1 \text{ cm}$ with a mass of approximately 50 mg) was used before and after catalytic application. The sponge was mixed with an organic solvent or oil in a 1:1 volume ratio ($\sim 500\text{--}1000 \mu\text{L}$) with water for 10–15 s. The total absorption capacity was calculated by measuring the weight of the absorbent before and after the absorption. Weight measurements were conducted rapidly to prevent evaporation of organic molecules.

Evaluation of heavy metal (Cr(VI)) ion removal capacity

Preliminary tests were conducted to assess the capacity of the material to remove Cr(VI) heavy-metal ions. These tests were carried out under the following conditions: [PF2I-PF3O] = 50 mg, time = 24 h, pH ~ 7 , and [Cr(VI)] = 1 mg L^{-1} . These tests were performed without light irradiation (normal stirring) to establish the time required to achieve equilibrium of the Cr(VI) anionic species on the prepared sponge materials. The amount of Cr(VI) removed was quantified using the standard diphenyl carbazide (DPC) method coupled with UVS³¹.

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Competing interests

The authors declare no competing interests.

Additional information

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