Photocatalytic Degradation of Methyl Orange by Magnetically Retrievable Supported Ionic Liquid Phase Photocatalyst

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ABSTRACT: A magnetically retrievable ferrocene appended supported ionic liquid phase (SILP) photocatalyst containing a molybdate anion has been synthesized and characterized by Fourier transform infrared, X-ray photoelectron spectroscopy, transmission electron microscopy, X-ray diffraction, energy dispersive spectroscopy, and vibrating sample magnetometer analysis. The optical properties of the photocatalyst were probed by photoluminescence and UV−vis diffuse reflectance spectroscopy. The discharge of undesirable dye effluents from textile industrial plants in the environment is the major concern of environmental pollution and toxicity. In this context, we employed the as-prepared SILP photocatalyst for degradation of methyl orange (MO) under UV light (365 nm) irradiation, and subsequently, recycling studies were performed. The histological alteration in gills of the fish is employed as a tool for monitoring toxins in the environment. In view of this, the histo-toxicological assessment on freshwater fish Tilapia mossambica gills asserted the damage of secondary gill lamellae due to MO. Conversely, structural modifications in the gill architecture were not observed by virtue of photodegraded products confirming that the degraded product is nontoxic in nature. Additionally, the normal behavior of fishes on exposure to photodegraded products reveals that research findings are beneficial for the aquatic ecosystem.

1. INTRODUCTION

The environmental pollution has become a prominent issue with a detrimental influence on human life. Industries such as textile, dye manufacturing, plastic, rubber, and cosmetics release nonbiodegradable, toxic, and carcinogenic dyes in the nearest water bodies, which provoke environmental pollution causing perilous consequences to human health and aquatic biota.1−4 The discharge of synthetic dyes containing wastewater leads to generation of dangerous by-products through the chemical processes like oxidation, hydrolysis, or other reactions.5 Consequently, the development of efficient processes for removal of dyes from wastewater has gained a great deal of attention. Among the various processes, photocatalysis is a promising tool of dye degradation.6 The design of robust and efficient photocatalytic systems is highly demanded, and efforts have been concerned on applications of metal oxide, sulfide, or nitride based semiconductors and nanomaterials for removal of pollutants.7−23 Moreover, the Fenton process is a propitious way of advanced oxidation processes employed for wastewater treatment. However, the addition of a ferrous salt during the course of dye degradation limits the applicability of the traditional Fenton process. In addition, separation of the catalyst becomes a tedious task as it turns into iron sludge accumulation, which contributes to secondary pollution.24 In order to circumvent these issues, the development of Fenton mimicking heterogeneous processes is the subject of vivid interest in environmental remediation research. Ferrocene is a highly stable, nontoxic, organometallic compound with high catalytic potential due to the electron donor−acceptor conjugated structure serving as a redox switch. Tian et al. reported the applicability of ferrocene in dye degradation.25,26 Recently, the efforts have been focused on designing a heterogeneous version of the Fenton system by immobilization of ferrocene on SBA-1S,27 MCM-41,28 silica,29 and SWCNTs.30

The implementation of green chemistry principles is becoming a central issue in the 21st century. The chemical industry is adopting more sustainable technologies, which is possible through developing the eco-friendly processes for reducing waste and also preventing the toxicity in the environment.31 In this regard, generous interest has been sparked in supported ionic liquid phase (SILP) catalysis involving grafting of ionic liquid like units onto a porous material with high surface area.32 A highly striking stratagem is offered by these advanced materials to overcome the demerits of ionic liquids and opens up a new avenue of powerful green tools for recognizing the goal of sustainable chemical processes.33,34 The motive for designing SILP catalysts instigates from their tempting properties such as facile separation, selectivity, recycling, reproducibility, and activity.

Received: July 3, 2019  
Accepted: October 15, 2019

Published: January 3, 2020
Moreover, the processes employing SILP catalysts can be carried out in continuous fixed bed reactors.35 In the last few years, the field of SILP catalysis has witnessed substantial progress allowing chemical transformations under environmentally benign conditions.36–38

In the past few years, the applicability of magnetic nanoparticles (MNPs) has received significant attention due to their broad applications in the chemical industry.39–41 Amidst them, exploitation of Fe3O4 MNPs in developing magnetically separable catalysts has originated as a frontier horizon that empowers greener and sustainable chemical transformations.42 The low toxicity, easy retrievability by external magnet and high surface area of Fe3O4 MNPs have made them as excellent support materials in the preparation of SILP catalysts.43 Furthermore, in tailoring task specific catalytic systems, ease of surface functionalization of Fe3O4 MNPs with desired substituents has incorporated noteworthy versatility for these materials.44 Owing to these features, a large number of Fe3O4 MNP SILP catalysts have been designed and successfully prepared for catalyzing important organic transformations. However, despite substantial progress, application of Fe3O4 MNP SILP catalysts in photocatalysis is still unexplored and therefore warrants immediate attention.

In view of prior discussion and in continuance of our research associated with green chemistry,45,46 in the present investigation, the advantages of materials that mentioned above are united. This study aims to establish a new heterogeneous ferrocene based Fenton system. We succeeded in preparing a new magnetically retrievable ferrocene appended supported ionic liquid phase photocatalyst containing a molybdate anion, which was reaffirmed by various analyses. The photocatalytic degradation of methyl orange (MO) under UV radiation (365 nm) was investigated in the presence of the as-prepared material as an effective photocatalyst. It is found that incorporation of the ferrocenyl moiety and molybdate anion play a vital role in photocatalysis. On the other hand, MNPs act as magnetic seeds that aid in the separation and reusability of the photocatalyst. The degradation percentage of MO as a pollutant was calculated about 99% within 30 min. Another aim of this study was the histo-toxicological assessment of photodegraded products on the gills of freshwater fish Tilapia mossambica. The normal behavior of fishes and no alterations in the gill architecture confirmed the nontoxic nature of photodegraded products.

2. RESULTS AND DISCUSSION

The preparative route for the magnetically retrievable ferrocene appended supported ionic liquid phase photocatalyst is outlined in Scheme 1. Initially, the chemical coprecipitation method was employed for preparation of Fe3O4 MNPs abbreviated as Mag. (1). Subsequently, the silica layer was coated by the sol–gel process using tetraethyl orthosilicate (TEOS (2)) to afford (SiO2@Mag, 3). The synthesis of 3-chloropropyl modified Fe3O4 MNP (3-Cl.Pr.SiO2@Mag, 5) with efficient organofunctionalization was achieved by taking advantage of the distinctive capacity of Si–OH groups on the surface of 3 to produce strong Si–O–Si bonds with alkoxy silane groups of 3-chloropropyl triethoxysilane (4). The ionic liquid mimicking unit was incorporated in 5 with the aid of the chloropropyl group via quaternization of 1-N-ferrocenylmethyl benzimidazole (6) to give the azolium salt acrnonymed as [FemIL@SiO2@Mag]Cl (7). Afterward, 7 by the anion metathesis reaction with sodium molybdate (8) afforded a magnetically retrievable ferrocene appended supported ionic liquid phase photocatalyst containing a molybdate anion abbreviated as [FemIL@SiO2@Mag]2MoO4 (9).

The surface modifications on pristine Mag. (1) associated with preparation [FemIL@SiO2@Mag]2MoO4 (9) were monitored by FT-IR spectroscopy (Figure 1). The stretching vibration band of Fe–O was observed at 592 cm−1 in the FT-IR spectrum of unmodified Mag. (1).47 The peaks in the FT-IR spectrum at 1060, 957, and 794 cm−1 approved the successful coating of the silica layer on 1, which are ascribed to asymmetric Si–O–Si, symmetric Si–O, and symmetric Si–O–Si stretching modes, respectively.48 The characteristic peak displayed at 2942 cm−1 in the FT-IR spectrum of 3-Cl.Pr.SiO2@Mag (5) is ascribed to C–H stretching modes of the propyl group.49 In the FT-IR spectrum of [FemIL@SiO2@Mag]Cl (7), the strong bands observed at 472 (Fe-Cp stretching), 1564 (C=C stretching), and 1635 (C=N stretching) suggesting covalent anchoring of 1-N-ferrocenylmethyl benzimidazole (6) on 5. Moreover, the stretching vibration of aromatic C–H in benzimidazole and ferrocene
groups is displayed at 3018 cm\(^{-1}\). In the FT-IR spectrum of [FemIL@SiO\(_2@\)Mag\(_2\)]\(\text{MoO}_4\) (9), the absorption peaks observed at 890 and 959 cm\(^{-1}\) are ascribed to Mo=O stretching confirmed the successful immobilization of the molybdate anion [Mo\(\text{O}_4\)]\(^{2-}\) on 9.\(^{51}\)

The loading of the molybdate anion in [FemIL@SiO\(_2@\)Mag\(_2\)]\(\text{MoO}_4\) (9) was probed by energy-dispersive X-ray (EDX) analysis, which affirmed 0.21 mmol of molybdate anion per gram of 9.

Thermogravimetric analysis (TGA) was employed to study the thermal profile of [FemIL@SiO\(_2@\)Mag\(_2\)]\(\text{MoO}_4\) (9) at a 10 °C/min heating rate in air within the 25–1000 °C temperature range (Figure 2). Initially, a weight loss of 1.99% centered at 105 °C was observed in the thermogram attributed to desorption of physisorbed water. Moreover, a steep weight loss of 33.91% up to 340 °C as well as cramped weight losses of 14.99% at 450 °C and 21.78% at 615 °C was due to thermal degradation of covalently bonded organic scaffolds. The large residual weight is ascribed to generation of thermostable metallic oxides and silica.

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) were employed to investigate the size, shape, and morphology of prepared samples as displayed in Figures 3 and 4. The SEM images of different magnetic nanoparticles in this work (SiO\(_2@\)Mag (3), [FemIL@SiO\(_2@\)Mag]Cl (7), and [FemIL@SiO\(_2@\)Mag\(_2\)]\(\text{MoO}_4\) (9)) displayed that the particles are mostly spherical with average sizes of 27 (3), 34 (7), and 35 nm (9). Moreover, SEM images clearly indicate that the sizes of particles changes very slightly after organofunctionalization. So, the influence of surface modification on particle size was found to be negligible.

The TEM micrographs of [FemIL@SiO\(_2@\)Mag\(_2\)]\(\text{MoO}_4\) (9) present spherically shaped granules with a nonsmooth surface (Figure 4a–c). In addition, TEM micrographs display a dark Fe\(_3\)O\(_4\) nanocore encapsulated with a gray shell indicating surface functionalization.\(^{53}\) A bright dotted pattern demonstrated by selected area electron diffraction (SAED) confirmed that the nature of Fe\(_3\)O\(_4\) MNP was single crystalline (Figure 4d), which is in well agreement with X-ray diffraction analysis.

The preservation of the crystalline nature of Fe\(_3\)O\(_4\) MNPs in [FemIL@SiO\(_2@\)Mag\(_2\)]\(\text{MoO}_4\) (9) was ascertained by X-ray diffraction (XRD). The XRD patterns of SiO\(_2@\)Mag (3), 3-ClPrSiO\(_2@\)Mag (5), [FemIL@SiO\(_2@\)Mag]Cl (7), and [FemIL@SiO\(_2@\)Mag\(_2\)]\(\text{MoO}_4\) (9) are shown in Figure 5. The position and relative intensities of all peaks in diffractograms of all the samples coincide with JCPDS card no. 86-1339, confirming the structural preservation of the Fe\(_3\)O\(_4\) nanocore as single phase inverse spinel with crystallinity and high phase purity. All four samples demonstrate diffraction peaks at 2θ values of 30.19, 35.48, 43.12, 57.10, 62.67, and 75.03\(^{\circ}\) assigned to the (2 2 0), (3 1 1), (4 0 0), (5 1 1), (4 4 0), and (6 2 2) crystal planes of Fe\(_3\)O\(_4\), respectively. The sharp and highly intense peak at a 2θ value of 35.48\(^{\circ}\) was assigned to the (3 1 1) plane. With respect to the sharp and highly intense peak, the average crystallite size for 9 was found to be 47 nm according to the Debye–Scherrer equation. Gratifyingly, the multistep functionalization process on the surface of Mag (1) did not induce any phase alteration.

The structural modifications due to functionalization of Mag (1) were investigated by X-ray photoelectron spectroscopy (XPS). The peaks for Mo, C, O, N, Fe, and Si were observed in the survey spectrum of [FemIL@SiO\(_2@\)Mag\(_2\)]\(\text{MoO}_4\) (9) (Figure 6). The peaks at 235.7 (2p\(_{3/2}\)) and 232.4 eV (2p\(_{3/2}\)) displayed in the core-level XPS spectrum of Mo 3d confirmed the existence Mo in 9 with a +6 oxidation state (Figure 6b).\(^{52}\) The photoelectron peak in the C 1s region displayed at 283.1 eV is deconvoluted into peaks at 286.4, 285.0, 284.2, and 283.0 eV (Figure 6c). The peak at 283.0 eV signifies bonding interactions of silicon and carbon. Moreover, the photoelectron peak in the Si 2p region at 100.0 eV is evident to support this fact (Figure 6g).\(^{53}\) The peaks detected in the C1s XPS spectra were assigned to ferrocenyl carbons (284.2 eV), sp\(^3\) C carbon (285.0 eV), and carbon bonded with quaternized nitrogen (286.4 eV).\(^{54,55}\) Dong and co-workers reported that, in the XPS spectrum of Fe, the shifting of core-level peaks toward higher binding energy is observed in the ferrocene anchored material as compared to ferrocene. The successful grafting of the ferrocene moiety is evident from photoelectron peaks of Fe 2p at 723.0 and 708.7 eV (Figure 6f).\(^{56}\) In the N 1s XPS spectrum, two distinct peaks at 398.7 and 401.2 eV were perceived. The photoelectron peak at 401.2 eV is ascribed to wingtip nitrogen in the benzimidazolium cation (Figure 6d).\(^{57}\) The peaks observed in the O 1s XPS spectrum reflects oxygen in Fe\(_3\)O\(_4\) MNPs (528.1 eV) and oxygen bonded with Si (530.5 eV) (Figure 6e).\(^{58}\) Thus, successful formation of 9 is corroborated by these structural investigations.
A magnetic vibrating sample magnetometer (VSM) was employed to scrutinize the magnetic characteristics of bare Mag. (1) and [FemIL@SiO2@Mag]2MoO4 (9). The hysteresis loops of samples at room temperature are depicted in Figure 7. The bare Mag. (1) and 9 illustrate magnetization saturation (Ms) values of 44 and 14 emu/g, respectively. Conversely, a decrease in saturation magnetization was observed after multistep functionalization of 1. This lowering of Ms stems from quenching of surface magnetic moments in 9 due to nonmagnetic groups on the surface of 1. However, Ms illustrated by 9 was sufficient enough such that 9 was effectively retrieved with the aid of an external magnet.

2.1. UV−Visible Diffuse Reflectance Spectra. The optical properties of Mag. (1), SiO2@Mag (3), 3-Cl.Pr.SiO2@Mag (5), [FemIL@SiO2@Mag]Cl (7), and [FemIL@SiO2@Mag]2MoO4 (9) were studied by UV−visible diffuse reflectance spectroscopy and are displayed in Figure 8. The spectra indicate different absorption edges for Mag. (1), SiO2@Mag (3), 3-Cl.Pr.SiO2@Mag (5), [FemIL@SiO2@Mag]Cl (7), and [FemIL@SiO2@Mag]2MoO4 (9). The studies reveal that all the samples (1, 3, 5, 7, and 9) exhibit absorption in the visible region plausibly owing to the presence of Fe3O4 MNPs. In addition, the optical band gap values of Mag. (1), SiO2@Mag (3), 3-Cl.Pr.SiO2@Mag (5), [FemIL@SiO2@Mag]Cl (7), and [FemIL@SiO2@Mag]2MoO4 (9) were obtained by the Tauc plot ((αhv)² vs hv) from the UV−visible spectra using the following equation (Figure 8).

\[
\alpha h\nu = A(h\nu - E_g)^n
\]
where \( n \) is equal to 0.5 for the allowed direct transition, \( h \) is Planck’s constant, \( \alpha \) is the proportionality constant, \( \alpha \) is the absorption coefficient, \( v \) is light frequency, and \( E_g \) is the band gap energy.

The band gap of pristine Mag. (1) was found to be 2.1 eV and is in well harmony with the literature.51 The band gaps of Mag. (1), SiO\(_2\)@Mag (3), 3-ClPr.SiO\(_2\)@Mag (5), [FemIL@SiO\(_2\)@Mag]Cl (7), and [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) are 2.1, 2.26, 2.39, 2.09, and 2.31 eV, respectively (Figure 9). These studies reveal significantly a higher band gap of 9 than 7. The increase in the band gap and decrease in absorption intensity of 9 can be ascribed to the existence of the molybdate anion [MoO\(_4\)]\(^{5-}\) in [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9), which subsequently leads to the decrease in the rate of electron–hole pair recombination.

2.2. Photoluminescence Spectra. The degree of transfer, migration, and reunion rate of photogenerated electron–hole pairs in Mag. (1), SiO\(_2\)@Mag (3), 3-ClPr.SiO\(_2\)@Mag (5), [FemIL@SiO\(_2\)@Mag]Cl (7), and [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) were investigated by photoluminescence (PL) spectral analysis.

The PL spectra were recorded with an excitation wavelength of 292 nm at ambient temperature (Figure 10). The appearances of comparatively strong emission bands at 580 (3-ClPr.SiO\(_2\)@Mag (5)), 583 (SiO\(_2\)@Mag (3)), 584 (Mag. (1)), and 579 nm ([FemIL@SiO\(_2\)@Mag]Cl (7)) indicate rapid reunion rates of the photoinduced electron–hole pairs. It is noteworthy that the presence of [MoO\(_4\)]\(^{5-}\) in [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) causes a significant lowering of the PL intensity compared to [FemIL@SiO\(_2\)@Mag]Cl (7). This is accounted to the improved electron–hole pair separation. On account of this, [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) is envisioned to show excellent photocatalytic activity toward degradation of MO.

2.3. Photocatalytic Activity. The photocatalytic activity, kinetics of reaction, and adsorption ability of [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) were tested for a model pollutant MO degradation under UV-light irradiation (365 nm). UV–visible spectra were used to determine concentrations of the dye at a wavelength of maximum absorbance (464 nm for MO). A mathematical relation for degradation (\( D% \)), final concentration (\( C_f \)), and initial concentration (\( C_i \)) is

\[
D\% = \frac{C_i - C_f}{C_i} \times 100
\]

The photocatalytic reaction was found to fit with a pseudo-first-order. The corresponding slope of the fitting line presents the value of the rate constant \( k \) (min\(^{-1}\)).

\[
\ln \frac{C_i}{C_f} = kt
\]

The photocatalytic performances of as-prepared samples were tested for MO degradation under irradiation of UV light. Initial efforts were focused on optimization of loading of the [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) for MO photodegradation. Accordingly, various quantities of 9 were employed (Figure 11). Use of 0.5 g/dm\(^3\) 9 resulted in 45% MO photodegradation efficiency. Increasing catalyst loading from 0.5 to 0.75 g/dm\(^3\) to 1.0 g/dm\(^3\) enhanced the photodegradation efficiency to 75%. The increase in degradation efficiency can be rationalized on the basis of the increase in the number of active sites that significantly increase the interaction between both light and MO molecules. However, increasing the catalyst quantity beyond 1.0 g/dm\(^3\) had a negative impact as the photodegradation efficiency dropped to 57%. This is attributed to the agglomeration of 9 due to which the surface becomes unavailable for photon absorption. In addition, turbidity of the suspension leads to diminution in the penetration of UV light, thereby decreasing the photodegradation efficiency. It is noteworthy to mention that, in the absence of 9, negligible degradation of MO was observed indicating the decisive role of 9 in the photodegradation process. Further, no shift in the \( \lambda_{\text{max}} \) of MO reveals that the course of photodegradation proceeds without generation of toxic intermediates (Figure 12).62 The photocatalytic reaction was found to fit with a pseudo-first-order along with rate constants \( k \) of 3.124 \( \times \) 10\(^{-3}\), 3.219 \( \times \) 10\(^{-3}\), 7.997 \( \times \) 10\(^{-3}\), and 6.66 \( \times \) 10\(^{-3}\) min\(^{-1}\) for 0.5, 0.75, 1.0, and 1.5 g/dm\(^3\), respectively (Figure 13).

The use of H\(_2\)O\(_2\) is crucial in dye degradation as it leads to the generation of hydroxyl radicals that assist in the dye degradation. In view of this, we decided to probe the effect of H\(_2\)O\(_2\). Accordingly, [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) assisted photodegradation of MO was carried out using various concentrations of H\(_2\)O\(_2\) (Figure 14). The results revealed that increasing the H\(_2\)O\(_2\) concentration from 2 to 10 mmol/dm\(^3\) significantly enhances the MO photodegradation efficiency from 76 to 99% with substantial reduction in photodegradation time to 30 min (Figure 15).

We also investigated the photocatalytic activities of SiO\(_2\)@Mag (3), 3-ClPr.SiO\(_2\)@Mag (5), and [FemIL@SiO\(_2\)@Mag]Cl (7) keeping all the parameters identical (Figure 16). Considerable MO photodegradation was not observed using SiO\(_2\)@Mag (3) and 3-ClPr.SiO\(_2\)@Mag (5) in photocatalytic experiments. However, [FemIL@SiO\(_2\)@Mag]Cl (7) displayed 43% photocatalytic activity, which is due to its lower band gap, as compared to [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) that results in a higher recombination rate of photogenerated electron–hole pairs.

2.4. Plausible Mechanism for [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) Assisted Photodegradation of MO. A tentative mechanistic rational for [FemIL@SiO\(_2\)@Mag]MoO\(_4\) (9) assisted photodegradation of MO under UV light is shown in reactions 4–7 on the basis of the literature.63 In the UV light irradiation, excitation of the electron from the valence band (VB) to conduction band (CB) of 9 occurs leading to the
generation of the electron and hole in the VB and CB, respectively (reaction 4). The electrons transferred in the CB react with H₂O₂ molecules to form oxidative species OH radicals (reaction 5). Furthermore, photoinduced holes left in VB accept electrons from the hydroxyl group forming highly oxidative OH radicals (reaction 6), which are responsible for degradation of MO dye molecules (reaction 7) (Figure 17).

\[
\text{[FemIL@SiO₂]@Mag}_3\text{MoO₄} \rightarrow e_{\text{CB}}^- + h_{\text{VB}}^+ \quad (4)
\]

\[
\text{H}_2\text{O}_2 + [\text{FemIL@SiO₂} ]@\text{Mag}_3\text{MoO₄}(e_{\text{CB}}^-) \rightarrow \cdot\text{OH} + \text{OH}^- \quad (5)
\]

\[
[\text{FemIL@SiO₂} ]@\text{Mag}_3(h_{\text{VB}}^+) + \text{OH}^- \rightarrow \cdot\text{OH} \quad (6)
\]
Dye Molecule + ·OH → Degraded products

Additionally, the appended ferrocenyl group plays a crucial role in photodegradation of MO because it, along with $\text{H}_2\text{O}_2$, forms Fenton catalyst mimic species. Ferrocene is reversibly oxidized; initially, it reacts with $\text{H}_2\text{O}_2$ where it is oxidized forming the ferrocinium cation and ·$\text{OH}$ radical and then regenerated back by transfer of the electron from $\text{H}_2\text{O}_2$ to ferrocinium cation producing $\text{HO}_2$. Both OH and HO$_2$ are key oxidative species, which are primarily responsible for MO photodegradation (reactions 8–9).

$$\text{Fem}^{2+}\text{IL} + \text{H}_2\text{O}_2 + \nu \rightarrow \text{Fem}^{3+}\text{IL} + \cdot\text{OH} + \text{OH}^- \quad (8)$$

$$\text{Fem}^{3+}\text{IL} + \text{H}_2\text{O}_2 \rightarrow \text{Fem}^{2+}\text{IL} + \text{HO}_2^- + \text{H}^+ \quad (9)$$

The recyclability of the catalyst is crucial concerning green chemistry and economical perspectives. MO photodegradation under the optimized reaction conditions was performed to study reusability of $[\text{FemIL}@\text{SiO}_2@\text{Mag}]_2\text{MoO}_4$ (9). After
each cycle, 9 was retrieved magnetically, washed with deionized water, dried at 50 °C in vacuo, and employed directly for another consecutive cycle. The photocatalyst exhibited remarkable recyclability as the photodegradation efficiency of 9 was maintained in the range of 99−93% up to six consecutive cycles (Figure 18).

2.5. Histo-Toxicity Assessment of MO and Photodegraded Products on T. mossambica. Gills play a vital role in the fish body as a respiratory organ. A layer of thin epithelial cells is covered on fish gills, which facilitate discharge of nitrogenous waste, control of acid−base, ionic balance, and exchange of gases.65 The large surface area of gills is sensitive to physical and chemical modifications in aquatic environments. Consequently, histological alteration in gills of the fish is employed as a tool for monitoring toxins in the environment.66 In view of this, we investigated histo-toxicity assessment of MO and photodegraded products on gills of T. mossambica. It was observed that fishes exposed to MO solution showed striking behavioral changes such as restlessness and rapid movement followed by loss of balance and erratic swimming to near water surfaces. However, the fishes exposed to photodegraded MO products displayed normal behavior, which was similar to the control group of fishes.
The histological markers are proven to be useful in assessing toxicity of various compounds including dyes. Therefore, the histopathological examination of gills was performed to assess toxicity of MO and its photodegraded products. In the control group of fishes, the gill showed characteristic histological features like blood vessels (BV), supporting cartilaginous rod (SCR), primary gill lamella (PGL), and overall normal architecture (Figure 19A). However, fishes exposed directly to MO solution showed deformations in the gill architecture such as fusion of secondary gill lamellae (FSGL), desquamation (DSQ), breakdown of pillar cells (BPC), curling of secondary lamellae (CSL), epithelial lifting (EL), and telangiensis (TL). Moreover, the decrease in the gill size was noticed due to shrinkage of the supporting cartilaginous rod (SSCR). Additionally, intracellular vacuolation, severe degeneration (DEG), and necrosis epithelium resulted in gill disruption (Figure 19B). On the contrary, the fishes exposed to photodegraded MO products revealed a normal gill architecture similar to control fishes (Figure 19C). These investigations reveal that the photodegraded MO products are nontoxic.

The summary of various literature reports on photocatalytic degradation of dyes using FeO4-based systems is shown in Table 1. The comparative study reveals that [FeMIL@SiO2@Mag]2MoO4 (9) exhibits better photocatalytic performance.

In continuation with the attainment of this work, the scope of [FeMIL@SiO2@Mag]2MoO4 (9) could be furthermore expanded by evaluating its photocatalytic performance toward mixed proportions of various dyes as well as industrial effluents. Additionally, histo-toxicological assessment of photodegraded products on other aquatic animals may open avenue for applicability of this protocol realizing its environmental fate. Considering these aspects, the work is currently underway in our laboratory.

**3. CONCLUSIONS**

We have successfully prepared a magnetically retrievable ferrocene appended supported ionic liquid phase (SILP) photocatalyst containing a molybdate anion. The photocatalytic potential of the as-prepared SILP photocatalyst demonstrated that the percentage of MO degradation in the presence of H2O2 was up to 99% after UV light irradiation (365 nm) for 30 min. The reusability studies revealed that the photocatalyst could be efficiently recycled for six consecutive runs without substantial loss in activity. These results implying that the as-prepared SILP photocatalyst is a promising material with remarkable potential to be employed for photocatalytic applications under UV light. The presence of the molybdate anion in the SILP photocatalyst was found to be responsible for the lowering of PL intensity improving electron–hole pair separation. As a result, immobilization of the molybdate anion facilitated enhancement in overall photocatalytic performance of the SILP catalyst as compared to its precursor. The fishes exposed to photodegraded MO products displayed normal behavior, which was similar to the control group of T. mossambica fishes. The histo-toxicological assessment on the T. mossambica gills asserted the damage to secondary gill lamellae due to MO. On the contrary, structural modifications in the gill architecture were not observed by virtue of photodegraded products exposure.

**Table 1. Comparative Study of Photocatalytic Performances of FeO4 Based Systems for Degradation of Dyes**

| Sr. No | photocatalyst | pollutant | light source | degradation time | photocatalytic activity | ref |
|-------|---------------|-----------|--------------|-----------------|------------------------|-----|
| 1     | MoS2/FeO4     | methyl orange | 300 W Xe lamp | 100 min | 79.53% | 70 |
| 2     | R-FeO4@m-SiO2@BiOBr | methylene blue | 500 W Xe lamp | 120 min | 96.00% | 71 |
| 3     | FeO4@Ag-WO4  | Fast Green | 300 W Xe lamp | 120 min | 81.11% | 72 |
| 4     | FeO4@MIL-100(Fe) | methylene blue | 500 W Xe lamp | 200 min | 99.77% | 73 |
| 5     | FeO4/BiOBr/BiO | Rhodamine blue | 500 W Xe lamp | 80 min | 99.2% | 74 |
| 6     | TiO2-FeO4-bentonite | Basic blue 41 | UV-high pressure Hg lamp | 161 min | 97.41% | 75 |
| 7     | FeO4@rGO@TiO2 | methylene blue | 300 W UV-vis lamp | 120 min | 99.00% | 76 |
| 8     | FeO4@C@Cu2O | methyl blue | 500 W Xe lamp | 120 min | 100% | 77 |
| 9     | 30 wt % FeO4@WSe2/NG | methylene blue | 500 W Xe lamp | 60 min | 98.8% | 78 |
| 10    | MoS2/FeO4/rGO (0.1 wt %) | Rhodamine B | 800 W Xe lamp | 40 min | 100% | 79 |
| 11    | FeO4/TiO2 (P25) | methyl orange | ultraviolet lamp (UV-C, 96 W) | 60 min | 90.3% | 80 |
| 12    | [FeMIL@SiO2@Mag]2MoO4 (9) | methyl orange | high pressure Hg lamp (HPL-N Philips (250 W)) | 30 min | 99.00% | present work |
products confirming their nontoxic nature. The use of SILP as a photocatalyst for the removal of MO in water affords a significant insight toward dye containing wastewater treatment. In view of green chemistry, this protocol offers precious advantages such as excellent photodegradation efficiency, hassle-free magnetic isolation, recyclability, and nontoxic nature of photodegraded products.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. 3-Chloropropyltriethoxysilane, sodium molybdate, methyl orange (MO), hydrogen peroxide (H2O2, 30% in water), neutral buffered formalin, and eosin–hematoxylin were obtained from Sigma Aldrich. Xylene and DMF were purchased from Sisco Research Laboratories Pvt. Ltd. A PerkinElmer one FT-IR spectrophotometer was employed to record infrared spectra. The KBr discs (~5% w/w) of samples were scrutinized. An energy-dispersive X-ray spectrometer (EDS) connected to the field emission scanning electron microscope (Oxford Instruments) was used to investigate the elemental composition. An SDT Q600 V20.9 Build 20 thermogravimetric analyzer was used for thermogravimetric analysis (TGA) in an air atmosphere. TEM analysis was carried out by a JEOL JEM 2100 (200 kV). An X-ray diffractometer (Philips PW-3710) was used to record X-ray diffraction (XRD) spectra. An FEI PHI 5000 Versa Prob II X-ray photoelectron spectrophotometer (XPS) was used to record XPS spectra. A Lakeshore magnetometer (USA, model 7407) was used for magnetic measurements. A UV–vis spectrophotometer (LABINDIA Analytical UV-3092) was employed to record UV–vis diffuse reflectance spectra (DRS) and to scrutinize the light absorption of samples. A spectrofluorometer (JASCO, model FP,750, Japan) was used to record photoluminescence (PL) spectra. 1-N-Ferrocenylmethyl benzimidazole (6), SiO2@Mag (3), and Mag. (1) were synthesized using the literature procedure. All the chemicals purchased from local suppliers were used as received without purification.

4.2. Preparation of Magnetic Fe3O4 NPs (Mag. (1)). To synthesize Fe3O4 NPs, the chemical coprecipitation method was employed. Typically, 2.0 g of FeCl3·4H2O, 5.2 g of FeCl2·6H2O, and 0.85 mL of HCl (12 mol/L) were dissolved in 25 mL of deionized water to prepare a stock solution. Then the stock solution was added in a dropwise manner to a beaker containing 250 mL solution of NaOH (1.5 mol L−1) with vigorous stirring in a nitrogen atmosphere maintaining temperature at 80 °C. Afterward, the precipitate of Fe3O4 NPs was separated magnetically followed by washing with deionized water. FT-IR (KBr): 2884, 2362, 2314, 1692, 1409, 884, 722, 649, 592 cm−1.

4.3. Synthesis of SiO2@Mag (3). The magnetic Fe3O4 NPs were coated with silica by using the sol–gel technique. In 40 mL of absolute ethanol, a suspension of 0.9 g of Mag. (1) was prepared and subjected to ultrasonication for 0.5 h. Subsequently, 14 mL of TEOS solution (2) (0.2 mL of TEOS in 13.8 mL of absolute ethanol) was added in a batchwise manner. 30% NH4OH solution (6 mL) was slowly introduced into the suspension and stirred for 5 h. Afterward, resultant SiO2@Mag (3) was retrieved magnetically followed by washing with ethanol and dried in vacuo at 80 °C for 10 h. FT-IR (KBr): 2899, 2366, 1060, 957, 935, 794, 553 cm−1.

4.4. Synthesis of 3-ClPr.SiO2@Mag (5). 3-Chloropropyltriethoxysilane (4) (1 mL, 5 mmol) was added to dispersed silica coated Fe3O4 MNPs (3) (1 g) in dry xylene (50 mL), and the mixture was refluxed for 24 h. After the surface modification step, the reaction mixture was allowed to cool and the product was separated magnetically, washed with methanol (3 × 25 mL), deionized water (3 × 25 mL), and xylene (3 × 25 mL), and dried for 12 h at 50 °C in vacuo to give 3-ClPr.SiO2@Mag (5). FT-IR (KBr): 2942, 1651, 1490, 1440, 1375, 1256, 1103, 797, 634 cm−1.

4.5. Synthesis of N,N-Dimethylaminomethylferrocene. Paraformaldehyde (0.06 mol, 1.97 g), N,N,N′,N′-tetramethylicalaminemethane (0.06 mol, 6.37 g), and glacial acetic acid (0.82 mol, 50 g) were mixed and subjected to heat treatment for a few minutes followed by addition of ferrocene (0.12 mol, 23.25 g) with constant stirring. After refluxing for 5 h, the reaction mixture was cooled and water (125 mL) was added with stirring. The residue was isolated by filtration and subsequently washed with dilute acetic acid and water. The sodium hydroxide solution (50%) was used to make the filtrate alkaline while maintaining cooling in an ice bath. Finally, the resultant mixture was extracted thrice with ether. The washing of the collected organic extract with water was performed. Anhydrous Na2SO4 was employed for drying the ether solution and distilled in vacuo to give N,N-dimethylaminomethylferrocene (bp 93 °C).

4.6. Synthesis of Ferrocenylmethyl Trimethyl Ammonium Iodide. N,N-Dimethylaminomethylferrocene (0.05 mol, 12.15 g) in the same quantity of absolute methanol was chilled. To this solution, methyl iodide (0.07 mol, 11.3 g) in the same amount of absolute methanol was added dropwise. The mixture was heated under reflux for 5 min. Subsequently, ether (125 mL) was added. The resultant precipitate was washed thoroughly by ether until washings turned colorless to afford corresponding ferrocenylmethyl trimethyl ammonium iodide (mp 115 °C).

4.7. Synthesis of 1-N-Ferrocenylmethyl Benzimidazole (6). A mixture of ferrocenylmethyl trimethyl ammonium iodide (2 g) and benzimidazole (6.5 mmol, 0.766 g) in dimethylformamide (10 mL) was subjected to reflux for 2 h. Afterward, to the brown solution, 100 mL of H2O was added, and the solution was extracted using ether thrice. The washings of the collected ether layers were performed by H2O twice, dried with Na2SO4, and evaporated on a rotary evaporator to produce N,N-ferrrocenylmethyl benzimidazole (6) (mp 120 °C).

4.8. Synthesis of [FemIL@SiO2@Mag]Cl (7). 1-N-Ferrocenylmethyl benzimidazole (6) (0.94 g, 3 mmol) was added in dispersion of 3-ClPr.SiO2@Mag (5) (1 g) in DMF (25 mL). The resultant mixture was stirred for 72 h at 80 °C. The magnetically isolated product was washed by methanol (3 × 50 mL), DMF (3 × 50 mL), and CH2Cl2 (3 × 50 mL) and dried in vacuo for 24 h at 50 °C to afford FemIL@SiO2@Mag@Cl (7). FT-IR (KBr): 3414, 3018, 2937, 2916, 2947, 2441, 1874, 1635, 1564, 1500, 1470, 1388, 1103, 797, 634, 570, 472 cm−1. Observed elemental analysis: H, 1.98%; N, 4.28%; C, 42.78%; loading 0.43 mmol of benzimidazolium units per gram of 7.

4.9. Synthesis of [FemIL@SiO2@Mag]3MoO4 (9). [FemIL@SiO2@Mag]Cl (7) (1 g) was dispersed in distilled water (10 mL) followed by addition of sodium molybdate (8) (0.205 g, 1 mmol). The obtained mixture was stirred for 24 h. The magnetically separated product was washed with deionized water to furnish [FemIL@SiO2@Mag]3MoO4 (9). FT-IR (KBr): 2927, 2088, 1640, 1443, 1367, 959, 890, 757, 633, 562, 460 cm−1. Observed elemental analysis: N,
4.36%; C, 42.36%; Si, 8.07%; O, 39.45%; Fe, 4.28%; Mo, 1.48%; loading 0.21 mmol of Mo per gram of 9.

4.10. Catalytic Test of [FemIL@SiO2@Mag]2MoO4 (9).
The photocatalytic activities of as-synthesized samples were tested using MO photodegradation under UV light (365 nm) using a high pressure Hg lamp (HPL-N) Philips 250 W. The provision to get enough oxygen for the photochemical reaction was made by keeping the photoreactor open in air. For the photocatalytic experiments in a photoreactor containing 100 mL of aqueous dye solution (MO = 20 ppm), the various photocatalytic experiments in a photoreactor containing 100 g/dm3 were dispersed. To ensure adsorption equilibrium, before UV irradiation, the suspensions were stirred in the dark (30 min). Irradiated aliquots (3 mL) were taken periodically at specific time intervals. The dispersed photocatalyst was magnetically recovered. The residual MO concentration was determined by measuring the absorbance of the dye at 464 nm employing a UV−vis spectrophotometer (Shimadzu, model-UV-3600) during the photocatalytic degradation process. 1 g/dm3 [FemIL@SiO2@Mag]2MoO4 (9) was elected as the optimum quantity. The effect of H2O2 concentration of 2−10 mmol/dm3 was investigated keeping other parameters identical. The optimum concentration of H2O2 was found to be 10 mmol/dm3. Further, the catalytic tests of SiO2@Mag (3), 3-ClPr.SiO2@Mag (5), and [FemIL@SiO2@Mag]Cl (7) were also performed under optimized conditions. To study the recyclability of 9, the model photochemical reaction was performed for photodegradation of MO and 9 was separated magnetically followed by washings with deionized water. The dried photocatalyst was again dispersed in dye solution for consecutive cycles.

4.11. Histo-Toxicological Assessment of Dye on T. mossambica Gills. Histo-toxicity of MO (20 ppm) and subsequent photodegraded products was tested on the gills of T. mossambica obtained from Kalamaba Lake, Kolhapur, Maharashtra, India. Initially, fishes were adapted in a tank of glass containing tap water (26 ± 2 °C, pH = 6.7 ± 0.2) for 12 days. Further, the experiment was performed in glass tanks of 10 dm3 capacity. Three fingerlings per tank with 6.53 ± 1.5 cm body length and 5.6 ± 1.2 g weight were used for histo-toxicity studies. Three experimental groups were set: one control group containing tap water and two treatment groups containing MO (20 ppm) and photodegraded products in tap water. Toxicity was tested for 48 h with a photoperiod of 12 h. Fingerlings were fed once a day with commercial fish feed.

Finally, fishes were sacrificed to remove gills for histological investigations. NBF (neutral buffered formalin) was employed to fix gill tissue for 24 h followed by washing with tap water. Further, tissues were dehydrated in grades of alcohols, cleared in xylene, and embedded in wax blocks for sectioning. Paraffin wax blocks were sectioned with a rotary microtome to obtain 5 micron thick sections. The sections were processed for rehydration and dehydration and cleared in xylene. Eosin−hematoxylin was used to stain the sections, which were subsequently, mounted within, attached camera. The observations and deformities recorded in the gill architecture were based on the considerations and terminology used earlier.

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ACKNOWLEDGMENTS

Authors are thankful for the financial assistance provided by SERB (Science and Engineering Research Board) in the Start-Up Research Grant Scheme (Young Scientist) Chemical Sciences (No. SB/FT/CS-060/2014).

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