Degradation of reactive dye using heterogeneous photo-Fenton catalysts: ZnFe$_2$O$_4$ and GO-ZnFe$_2$O$_4$ composite

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Abstract

Dyes, being potential pollutants, need alarming attention for their degradation from wastewater. Advanced oxidation processes (AOPs) are among the most effective methodology for the degradation of pollutants. In the present study, the heterogeneous photo-Fenton catalysts (ZnFe$_2$O$_4$ and graphene oxide based ZnFe$_2$O$_4$ composite) were prepared and used to study the degradation of synzol red reactive dye. The prepared catalysts were well characterized by using SEM, FTIR and XRD analysis. The effect of various parameters like pH, catalysts dosage, H$_2$O$_2$ dosage, effect of dye concentration and irradiation time during heterogeneous photo-Fenton processes was studied. The results showed 57% and 94% degradation of dye under optimized conditions (e.g. pH = 3, Catalysts dose = 75 mg l$^{-1}$ for ZnFe$_2$O$_4$ and 50 mg l$^{-1}$ for GO-ZnFe$_2$O$_4$, H$_2$O$_2$ dose = 27 mM and irradiation time of 60 min) was observed for ZnFe$_2$O$_4$ and GO-ZnFe$_2$O$_4$, respectively. A comparison of degradation potential of catalysts using various light sources like UV-254 nm, ambient solar light and white LED, was studied. The current findings support the application of solar and LED light for the degradation of organic pollutants in wastewater. The stability and reusability of these catalysts for the degradation of the dye were also studied. The GO- ZnFe$_2$O$_4$ composite showed negligible iron leaching and no considerable reduction in degradation efficiency upto six consecutive cycles of reusability. It has been found that the composite (GO–ZnFe$_2$O$_4$) showed enhanced degradation of dye as compared to ZnFe$_2$O$_4$.

1. Introduction

Dyes are one of the potential environmental pollutants and are under major consideration for environmental scientists. The synthetic dyes and their intermediates cause release of carcinogens, teratogens and mutagens in the life system, that’s why their removal from public sector is very important [1–3]. Azo dyes possess R–N=N–R’ formula units, in which R and R’ can possibly be either alkyl or aryl groups. They consist of broad color range from yellow to red and violet to blue. The parent compound is known as diimide (HNHN), and N = N is called azo group. Synozol red HF-6BN is an Azo representative dye that can be recalcitrant by the implementation of conventional or advanced wastewater treatments.

Advanced oxidation processes (AOPs) have been effectively used for the degradation of various organic contaminants using highly reactive hydroxyl radicals (HO$^\cdot$), as a non-selective oxidizing agent. Heterogeneous (supported metal catalysts, composite of photocatalysts with graphene oxide and other supports) or homogenous catalysts (e.g. Fenton reaction) involves effective utilization of OH radicals from H$_2$O$_2$ [4, 5]. One preferential method of AOPs is Fenton’s process, which uses Fe(II) and H$_2$O$_2$, capable of converting organic pollutants into CO$_2$ and H$_2$O very efficiently [6]. Key step in homogeneous Fenton system is demonstrated as:
Although classical/homogeneous Fenton is highly efficient but it comes with certain drawbacks, which includes lack of recyclability of Fe(II) and Fe(III) ions responsible for sludge formation [7, 8]. To overcome the difficulties caused by homogeneous Fenton, heterogeneous Fenton like systems offer promising role for degradation of organic pollutants under wide pH range [9]. Various heterogeneous Fenton like catalyst have been reported in the literature, which uses iron oxide [10, 11], metal ferrite and their composite materials [12–14].

Now a day’s metal ferrite due to their chemical stability, catalytic behavior, low cost, magnetic, electronic and structural properties have opened a new dimension in the field of AOPs to degrade pollutants [15, 16]. These properties of ferrites offer its application through engineering separation. Iron based nanocomposites have been applied and studied extensively in the literature because it offers effective removal of extensive variety of contaminants (organic and inorganic). Magnetization of the material is basically responsible for the easy separation of these metal ferrites by slight application of magnetic field, making them reusable for longer time. Their efficiency is also because these catalysts offer small size large reactive surface area for adsorption of pollutants.

Being important family member of magnetic metal ferrites, zinc ferrite due to its fascinating electromagnetic properties has attracted significant interests for researchers [17, 18]. For example, the magnetic ZnFe$_2$O$_4$/graphene (ZnFe$_2$O$_4$/G) composite has been synthesized by facile one-pot solvothermal method and used for oxidative photocatalytic degradation of dyes. The synergistic effect of the composite (ZnFe$_2$O$_4$/G) as catalyst as well as hydroxyl radical generator is advantageous for potential degradation of pollutants [19]. Similarly, sadighian and co-workers studied the adsorption kinetics of zinc ferrite-graphene oxide nanocomposite. The nanocomposites possessed good adsorptive properties with suitable recyclability. The researchers also reported the stability of nanocomposite by desorption of pollutants. The superparamagnetic properties of nanocomposite enable their magnetic separation from reaction mixture [20]. The unique catalytic properties of cubic spinal ferrite particles (AB$_2$O$_4$) as compared to other metal oxides is due to the cationic distribution along tetrahedral (A) and octahedral (B) sites. The octahedral metal cations are exposed on the surface and are placed at larger distance, permitting free interactive reaction pathways for reacting molecules. The ZnFe$_2$O$_4$ is an important member of spinal ferrite family. Exceptionally good photochemical stability of ZnFe$_2$O$_4$ promote efficient conversion of H$_2$O$_2$ into highly reactive OH radicals [21]. In order to enhance the catalytic response range of these metal ferrites they have been combined with carbonaceous materials. Graphene oxide serves a role as an excellent candidate in this respect. It has been found that carbon-supported ZnFe$_2$O$_4$ can be prepared and used at lower calcinations temperature with considerable high absorption capacity.

In the present study, a UV light responsive photocatalyst along with graphene oxide based composite (ZnFe$_2$O$_4$ and GO- ZnFe$_2$O$_4$) have been synthesized. The texture and morphology of the prepared catalysts has been characterized by Scanning Electron Microscope while crystallinity and compositional analysis were supported by XRD and FTIR spectroscopy. XPS analysis was made to evaluate the elemental composition of ZnFe$_2$O$_4$ and GO- ZnFe$_2$O$_4$. The band gap of the prepared photocatalysts has been measured using UV–vis diffuse reflectance measurements. Photocatalytic degradation efficiencies of catalysts were investigated by degradation of reactive synozol red dye from wastewater under optimized conditions. Catalyst’s durability has been determined by checking iron leaching in the liquid phase during repeated trials.

2. Experimental section

2.1. Materials and reagents

All the selected chemicals were of analytical grade and used without further purification. Reactive Synozol Red with reagent purity was used for present work. Other reagents were purchased from Sigma-Aldrich which includes ferric nitrate (Fe(NO$_3$)$_3$, 9H$_2$O) (≥99.95% trace metals basis), zinc nitrate (Zn(NO$_3$)2·6H$_2$O) (98%) and sodium borohydride (NaBH$_4$) (99%), were of analytical grade and the solutions were prepared using distilled water which was obtained by water purification system. For the preparation of graphene, Graphite Powder (≥99.99% trace metals basis, <45 μm), NaNO$_3$ (Product Number: S5022, Formula Weight: 84.99 g mol$^{-1}$) (99%), Concentrated Sulphuric acid (clear, assay: 99.999%, vapour pressure: 1 mmHg (146 °C), b.p.:~290 °C), Hydrogen peroxide (concentration 30% (w/w) in H$_2$O, storage temp. 2–8 °C, density: 1.110 g cm$^{-3}$), were used.

2.2. Preparation of graphene oxide

Modified Hummer’s method was used for the preparation of graphene oxide [22]. The graphitic oxide was prepared by mixing powdered graphite flakes (1 g) and sodium nitrate (0.5 g) (2:1) into 23 ml of 98% sulphuric acid and stirred at about 400 rpm using mechanical stirrer at very low temperature in ice bath. Followed by the
addition of 3.0 g of oxidant i.e., potassium permanganate and maintain the agitation for 3 h in an ice bath at less
than 10 °C. The temperature of the suspension was raised to 35 °C by removing ice bath. Then 45 ml water was
added dropwise into the slurry, resulting violent effervescence in exothermic reaction and temperature was

elevated to more than 90 °C. Obtained brown suspension was maintained at this high temperature for about half

an hour. The suspension was then diluted with mixture of water and hydrogen peroxide (2:1). Centrifugation of
the suspension yields a yellow–brown paste and the paste was washed three times with 5% HCl solution, two
times with alcohol, and three times with deionized water in sequence, resulting in GO. Thick slurry of GO was
then poured into petri dish and dried in vacuum at 60 °C [23].

2.3. Preparation of ZnFe2O4 catalyst
The ZnFe2O4 catalyst was prepared according to the following method [24]. Two solutions were prepared
separately: First solution of Zn(NO3)2·6H2O and Fe(NO3)3·9H2O with the mole ratio of 1:2 respectively and
second solution of 0.4 molar NaBH4 was prepared ([Fe3+]/[NaBH4] = 1:2). Following this solution II was
added slowly into solution I within 30 min and was vigorously stirred for 1 h. the obtained slurry was poured
into Teflon-lined stainless autoclave for 12 h at 120 °C. Then the obtained suspension was washed with distilled
water followed by ethanol for three to four times. Solid sample was dried for 24 h at70 °C [24].

2.4. Preparation of GO- ZnFe2O4
The dispersion of GO was ultrasonicated to get clear suspension of GO. This stable suspension was then mixed
with the 1st solution followed by the slow addition of 2nd solution following the same method as described for
the preparation of ZnFe2O4.

2.5. Characterization
The photocatalysts were examined by XRD analysis using X’Pert x-ray powder diffractometer (PW1398, Philips,
Netherlands) equipped with Cu Kα radiation source (λ = 0.154 nm). The crystallite size was calculated using
Debye–Scherrer equation [25].

\[ D = \frac{K\lambda}{\beta\cos \theta} \]  

In the above equation, \( K \) is Scherrer constant having the value of 0.94, \( D \) is the estimated crystalline size, \( \beta \) is
the diffraction angel, \( \beta \) is the full width half maximum of ZnFe2O4 and GO-ZnFe2O4 plane and \( \lambda \) is the
wavelength of x-ray source (0.154 nm) used in XRD. The Fourier-transform infrared (FTIR) spectroscopic
analyses were studied using PerkinElmer (spectrum 100) FT-IR spectrometer to examine the chemical bonding
within the prepared materials. The surface chemical composition and elemental analysis of catalysts were
conducted by x-ray photoelectronic spectroscopy (XPS; Escalab 250 XPS system, Thermo Fisher Scientific UK).
Morphological analyses of photocatalysts were studied using scanning electron microscope (SEM; JSM5910
JEOL JAPAN) at E = 30KV. UV-Visible diffused reflectance spectra were obtained by PerkinElmer UV-Visible
spectrophotometer (750-USA).

2.6. Photocatalytic degradation and analysis method
All the degradation tests were conducted under ultraviolet light using digital UV chamber (model:ZM144W)
fitted with six UV lamps each having energy of 18 W were used for this purpose. The intensity of UV irradiations
was measured using UV radiometer (UVX digital radiometer, Analytic Jena, with probe UVX-25 probe for
254 nm light). Typically, 100 ml of 50 ppm solution of reactive synozole red was selected for UV light assisted
heterogeneous photo-Fenton degradation process. All the experiments were conducted at room temperature. In
order to avoid intensity fluctuation, the distance between the reaction mixtures and UV lamps were kept
constant. Reaction mixtures were constantly stirred by using orbital shaker in order to avoid agglomeration of
catalysts. Various parameters like pH (2–9), catalysts dose (20 mg–200 mg l\(^{-1}\)), oxidant dose (9.8 mM–87 mM),
time (15–160 min), dye concentration (5–60 ppm). In order to investigate the % degradation of the pesticide’s
solutions, the samples were collected after successive intervals and their absorbance were checked by using single
beam spectrophotometer. The % degradation of the solutions was calculated by using formula given below:

\[ \text{Degradation (\%)} = 1 - \frac{C_f}{C_0} \times 100 \]

where

\( C_f \) = final concentration

\( C_0 \) = initial concentration

The comparison of various light sources on the dye degradation was studied using UV-254nm, white LED
and ambient solar light. Digital UV chamber (model:ZM144W, wavelength; 254 nm, 18X8 = 144 W) was used
to study degradation under UV light. Irradiation flux of UV light power was monitored using digital radiometer (UVX; UVP) with 254 nm probe. The light intensity of the above samples during reaction time measured by Lux meter is as follow sunlight = 88000 ± 2000 Lux (ambient solar light) and white LEDs = 77000 Lux (LED chamber, 2 × 2 ft², fitted with the nine LED light, each of 12 W).

3. Results

3.1. Characterizations of prepared ZnFe₂O₄ and GO- ZnFe₂O₄

XRD patterns of graphite, graphene oxide, ZnFe₂O₄ and GO-ZnFe₂O₄ are shown in figure 1. The characteristics peak of graphite at 2θ = 26.6° corresponds to the crystal plane (002), which disappear in XRD pattern of GO and appeared at 2θ = 10.27° thereby confirming the successful oxidation of graphite. The cubic spinal structure of ZnFe₂O₄ is estimated by the observed characteristic peaks at 2θ of 29.9, 35.2, 42.9, 53.2, 56.5 and 64.2 are attributed to the crystal planes of (220), (311), (400), (422), (511) and (440), respectively. Further, the strong intensity diffraction peaks suggest that both pure ZnFe₂O₄ and ZnFe₂O₄ in GO-ZnFe₂O₄ are successfully formed. The average grain size of ZnFe₂O₄ and GO-ZnFe₂O₄ was observed to be 23.5 nm and 22.9 nm, respectively.

FTIR spectra of ZnFe₂O₄ and GO-ZnFe₂O₄ were recorded in the range of 400 to 4000 cm⁻¹ and shown in figure 2. The spectrum of GO-ZnFe₂O₄ shows that the peaks for oxygen function groups in GO are reduced considerably or completely disappeared; and new bands at around 544 cm⁻¹ and 423 cm⁻¹ appeared for GO-ZnFe₂O₄. The band present at 544 cm⁻¹ can be identified to the tetrahedral Zn²⁺ (Zn-O mode) stretching vibration, and the next band at 500 cm⁻¹ can be attributed to the octahedral Fe³⁺ (Fe-O mode) stretching vibration. The below FTIR results verified the successful fabrication of ZnFe₂O₄ and GO-ZnFe₂O₄. Scanning electron microscopic (SEM) analysis of ZnFe₂O₄ and GO- ZnFe₂O₄ were made. The SEM images are shown in figure 3, which clearly shows the formation of ZnFe₂O₄ as well as the spread of ZnFe₂O₄ over the GO support.

The elemental composition of ZnFe₂O₄ and GO-ZnFe₂O₄ was investigated through XPS survey scan as shown in figure 4(a), while the figure 4(b) showing the atomic percentage of the detected elements. The O1s, Zn2p and Fe2p3 were observed in ZnFe₂O₄ with 74.1, 17.5 and 8.4 atomic percentage respectively. The GO-ZnFe₂O₄ has an additional element as C1s, which also confirms the presences of GO in GO-ZnFe₂O₄. The atomic percentage of O1s, Zn2p, Fe2p3 and C1s in GO-ZnFe₂O₄ was 56.3, 15.7, 2.9 and 25.9 respectively. The
variation in the atomic percentage of O1s, Zn2p and Fe2p3 was noticed in GO-ZnFe2O4 as compared to ZnFe2O4 which is attributed to the change in the crystalline structure [25–27] and is also in good agreement to our XRD analysis (figure 1).

The optical band gap of the prepared samples were determined using diffused reflectance spectra obtained from UV-Visible spectrophotometer and are shown in figure 5. The incorporation of ZnFe2O4 on the GO matrix imparts significant enhancement in optical response of the composite. The considerable reduction in optical band gap of GO-ZnFe2O4 (i.e. 2.2 eV) compared to ZnFe2O4 (i.e. 2.9 eV) [28] makes it more responsive photocatalyst, which support the generation of electron-hole pair and resultantly the higher hydroxyl radicals.

3.2. Effect of pH on catalytic activity of ZnFe2O4 and GO- ZnFe2O4
The photo-Fenton and Fenton processes are highly pH dependent [29]. The effect of pH was evaluated on eight pH values viz. 2, 3, 4, 5, 6, 7, 8 and 9 (figure 6(a)). Results are evident that maximum rate of reaction has been achieved on pH 3 with 76.5% and 83% degradation of dye in 60 min with ZnFe2O4 and GO-ZnFe2O4 respectively. The pH value shows critical effect over oxidation potential of OH radicals due to the inverse relationship between pH value and the oxidation potential. In the proposed research, optimum pH was found to be 3. The pH value above or below the optimum values decreases the degradation efficiency of catalyst. The involved reaction at high and low pH are predicted as follows:
3.2.1. Reaction at pH below 3
At pH below 2.5 following are the factors which affect the degradation efficiency of Fenton processes: due to the scavenging effect of OH radicals by excessive H⁺ ions present in acidic media making considerable reduction in the generation of reactive OH radicals for oxidative degradation. Another possibility is the generation of H₃O₂⁺ at pH below 3. The unviability of OH radicals will result the lack of conversion of Fe³⁺ → Fe²⁺.

\[
\text{OH}^+ + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}
\]

\[
\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}_2^+
\]

3.2.2. Reaction at pH above 3
Catalytic efficiency of Fenton process is affected at pH above optimum values too. Due to the stability of H₂O₂ at pH above 3, the reaction of Fe³⁺ with hydrogen peroxide is responsible for the production of iron sludge [FeIII(H₂O₂)]²⁺. Limited availability of H⁺ ions results Limited decomposition rate of H₂O₂ in order to generate OH radicals, is another important reason which alter the efficiency of Fenton process.

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow [\text{FeIII}(\text{H}_2\text{O}_2)]^{2+} + \text{H}^+
\]

\[
\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^- 
\]
3.3. Effect of catalyst dose

Amount of photocatalyst is one of the major parameters, which influence the photo-Fenton processes. In present study various concentrations of catalysts ranging from (20–200 mg l\(^{-1}\)) were used to obtain the optimal amount (figure 6(b)). Results showed that maximum degradation has been achieved at 75 mg l\(^{-1}\) (78% degradation / 60 min) and 50 mg l\(^{-1}\) (91.1% degradation / 60 min) with ZnFe\(_2\)O\(_4\) and GO-ZnFe\(_2\)O\(_4\) respectively. It is evident from the results that by increasing the concentration of catalyst, the degradation efficiency of the process increases up to certain value. The reason for the enhanced efficiency is the enhanced availability of reactive sites. The degradation of synozol red from 50%–90% has been achieved with the composite by increasing the composite dose from 20–50 mg l\(^{-1}\). However, further increase in the catalysts dose was not found to be effective in the present investigation. This is due to the overlapping of reactive catalytic surfaces, making them less available for degradation of dye [30]. In addition, the 'OH may be scavenged by the excessive Fe(II) on the surface of the catalysts making the reactive radicals less frequently available for the oxidative degradation of reactive synozol red. Therefore 75 mg l\(^{-1}\) and 50 mg l\(^{-1}\) for ZnFe\(_2\)O\(_4\) and GO-ZnFe\(_2\)O\(_4\) respectively were found.

Figure 6. Effect of various parameters on degradation of dye (a) pH, (b) Catalysts dose (c) oxidant dose, (d) time and (e) dye concentration.
to be optimum dose for present research.

\[ \text{Fe}^{2+} + \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^- \]

3.4. Effect of \( \text{H}_2\text{O}_2 \)

The impact of \( \text{H}_2\text{O}_2 \) concentration was elucidated by investigating % degradation of dye concentration at various doses. Various concentrations of \( \text{H}_2\text{O}_2 \) (9.8, 12, 15, 27, 37, 47, 57, 87 mM) were investigated (figure 6(c)). It was found that by increasing the oxidant dose form 9.8 mM to 47 mM and 9.8 mM to 27 mM, the % degradation of reactive synozol red showed an enhancement from 45%–63% and from 75%–95% by \( \text{ZnFe}_2\text{O}_4 \) and \( \text{GO-ZnFe}_2\text{O}_4 \), respectively. The enhanced degradation efficiency by increasing the oxidant dose is due to the increased availability of reactive hydroxyl radicals. Beyond the optimum concentration of hydrogen peroxide, \( \text{H}_2\text{O}_2 \) molecules did not participate in oxidative degradation. The peroxyl radicals are formed at higher \( \text{H}_2\text{O}_2 \) concentration and have lower redox potential than that of hydroxyl radical. Excess of \( \text{H}_2\text{O}_2 \) also scavenged the produced hydroxyl radicals present in the solution and thus making them no more available for the oxidative reaction.

3.5. Effect of irradiation time

The effect of time on degradation of dye at different time intervals (10–120 min) at optimized conditions was investigated. The graph (figure 6(d)) shows that the dye degradation increases sharply by increasing the irradiation time. The highest degradation was obtained within first 60 min of reaction time. Hydroxyl ions are furnished in the aqueous dye solution. These generated –OH ions also react with bivalent ions and hence suppressing the Fenton’s reaction. Hydrogen peroxide has become the limiting reactant with the passage of time and the dye degradation rate becomes slower because the required stochiometric amount of hydrogen peroxide is depleted with time [31].

3.6. Effect of dye concentration

From the application point of view, it is very important to analyze the effect of dye doze over degradation rate. Different concentration of dye solutions (5–70 ppm) were prepared and analyzed for photocatalytic degradation of dye. The results are presented on figure 6(e). The 50 ppm dye concentration was observed as optimum concentration for both the \( \text{ZnFe}_2\text{O}_4 \) and \( \text{GO-ZnFe}_2\text{O}_4 \). The dye is effectively degraded (almost with the same extent for both photocatalysts) for the lower dye concentration than optimum value due to readily available hydroxyl radicals. A balance between the dye molecules and the hydroxyl radical is the key requirement for the effective degradation.

It has been observed that \( \text{GO-ZnFe}_2\text{O}_4 \) has shown better dye degradation performance over \( \text{ZnFe}_2\text{O}_4 \), which is attributed to the large specific area provided by composite (\( \text{GO-ZnFe}_2\text{O}_4 \)). Moreover, the high specific surface area (2,630 m\(^2\) g\(^{-1}\)), electronic transportation (200 000 cm\(^2\) V\(^{-1}\) s\(^{-1}\)), thermal conductivity (∼5000 W m\(^{-1}\) K\(^{-1}\)) makes it a promising material for its applications in dye degradation for the waste water treatment [32–37]. In addition to this, the loading of \( \text{ZnFe}_2\text{O}_4 \) particles over GO prevent the agglomeration of GO. The combination of semiconductor material (\( \text{ZnFe}_2\text{O}_4 \)) with GO (graphene-semiconductor composite) results the generation of interphase, which prevent the recombination of excited electrons from semiconductor and transferred it over the graphene surface, where stabilization occurred by π–π conjugation network and hence inhibit charge recombination.

3.7. Effect of various light sources on the degradation of dye

Degradation of synozol red under various light sources (UV-254 nm, ambient sunlight, and white LED) were conducted. The results are shown in figure 7. The ultraviolet irradiation has been found to be the most effective for degradation enhanced degradation of reactive synozol red in case of both \( \text{ZnFe}_2\text{O}_4 \) and \( \text{GO-ZnFe}_2\text{O}_4 \). Remarkable increase in the degradation efficiency is due to the production of charge carriers by the stimulation of UV radiations. The charge carriers are produced by the strong interactions of carbon and photon on carbonaceous surface. This depicts the importance of carbonaceous base in increasing the efficiency of photocatalytic process. Both the LED and sunlight have shown considerable degradation of the dye for the GO based composite (\( \text{GO-ZnFe}_2\text{O}_4 \)) as compare to for \( \text{ZnFe}_2\text{O}_4 \) alone. This shows the role of GO to make visible active photocatalyst by lowering the bandgap of \( \text{ZnFe}_2\text{O}_4 \). Additionally, this also reduce the electron-hole recombination.

3.8. Reusability of the catalyst

The stability and reusability of the catalysts was investigated for both \( \text{ZnFe}_2\text{O}_4 \) and \( \text{GO-ZnFe}_2\text{O}_4 \) under the optimized conditions of pH, catalyst dose, oxidant concentration, dye concentration and irradiation time. The catalysts were easily separated by applying external magnets and reused. After separation of catalysts from
reaction mixtures they were washed, oven dried, reweighed and reused. Results showed that degradation efficiency decreases from 95 to 68% from 1st to 6th cycle as shown in figure 8. The viable applications of heterogeneous photocatalysts (in wastewater treatment) require their stability towards metal leaching from solid to liquid phase. The iron leaching measurements were studied by Atomic Absorption Spectrometer after each run. Low leaching concentration of iron (less than 0.32 mg l$^{-1}$) shows good stability of catalyst and can be used several times without significant lost in photocatalytic efficiency. Iron leaching was found far below than the range (2.0 mg l$^{-1}$ by European Union directives). However, this small but continuous metal leaching leads to the deactivation of catalysts. The decrease in photocatalytic efficiency may also be due to the blockage as well as decrease in number of active sites after multiple uses. These effects may change the structural and functional properties of catalysts.

4. Conclusion

Among all the recently developed adsorbents, GO based zinc ferrite was found to be novel and potential candidates for the photo-Fenton degradation of pollutant. In summary, GO-ZnFe$_2$O$_4$ has been fabricated and used for the degradation of reactive synozol red. The maximum % degradation efficiency of the ZnFe$_2$O$_4$ and

![Figure 7. Effect of various light sources on degradation of Synzol Red.](image1)

![Figure 8. Reusability of catalysts in six sequential runs.](image2)
GO-ZnFe₂O₄ found to be 57 and 96%, respectively within short reaction time of 60 min under optimized conditions using UV-254 nm light. The composite (GO-ZnFe₂O₄) showed enhanced photocatalytic efficiency as compared to the ZnFe₂O₄, which is attributed to multiple factors such as efficient generation of hydroxyl radicals, the decrease in recombination of excited electrons with holes, efficient charge transfer ability of composite, adsorption enhanced degradation, small band gap, etc. The degradation results under various light sources showed that UV light has been most effective as compared to white LED and solar light. The GO-ZnFe₂O₄ has also shown promising degradation under white LED and sunlight. Furthermore, the easy separation of catalysts from reaction mixture after degradation and low iron leaching into the ecosystem prove these photocatalysts as promising candidates for wastewater treatment. These photocatalysts also demonstrate good efficiency and stability up to six cycles, which is advantageous for implementation at industrial scale.

Conflict of interest

All the authors declare no conflict of interest in publication of this research.

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