


 Cite this: *RSC Adv.*, 2025, 15, 6668

# Lead ferrite-based heterogeneous photocatalysis: a green approach for rhodamine 6G dye remediation

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Improper dye disposal pollutes the environment and endangers living species, underlining the need for more effective pollution detection systems. Therefore, the current study is focused on developing reliable methods for monitoring and controlling dye release in water using lead ferrite nanoparticles (PbFe<sub>12</sub>O<sub>19</sub>-NPs) as the most efficient iron-based material. In the current study, PbFe<sub>12</sub>O<sub>19</sub>-NPs were synthesized by a sol-gel method and characterized by advanced analytical techniques. The obtained finding revealed that the PbFe<sub>12</sub>O<sub>19</sub>-NPs possess a hexagonal structure with a negative surface charged smooth surface. They have an average particle size of 13.8 nm. The photocatalytic activity of PbFe<sub>12</sub>O<sub>19</sub>-NPs for the degradation of rhodamine 6G (RG) dye was evaluated under optimized conditions using UV-visible spectroscopy. The PbFe<sub>12</sub>O<sub>19</sub>-NPs-based developed method showed a degradation efficiency greater than 95% with LOD and LOQ of 0.0043 and 0.014 mg L<sup>-1</sup>, respectively. Moreover, the PbFe<sub>12</sub>O<sub>19</sub>-NPs as nano-catalysts showed active reusability and ease of separability due to their magnetic nature. The PbFe<sub>12</sub>O<sub>19</sub>-NP-based developed method was applied to real water samples and the RG degradation was found to be greater than 90% with an RSD of less than 3.0%.

 Received 29th December 2024  
 Accepted 31st January 2025

DOI: 10.1039/d4ra09072a

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## 1 Introduction

The rapid growth of the textile industry has significantly contributed to water pollution due to the excessive use of synthetic dyes.<sup>1</sup> Because of the overuse of synthetic dyes, the explosive rise in the textile industry has greatly increased water contamination.<sup>2-5</sup> An estimated 7 × 10<sup>5</sup> tons of dyes undergo production each year, of which 10–15% are released as effluents.<sup>6</sup> These effluents include toxic organic pigments that are poisonous to aquatic life, frequently non-biodegradable, and carcinogenic.<sup>7-11</sup> Commonly used dyes including Eriochrome Black-T, Methylene Blue, and rhodamine B can have a negative environmental impact even at low quantities (<1 mg L<sup>-1</sup>) in water bodies.<sup>12-14</sup>

The wastewater treatment techniques, such as adsorption, filtration, and biological degradation, have some drawbacks such as high costs, generation of secondary waste, and insufficient dye degradation.<sup>15</sup> However, the photocatalysis process has been the

most efficient, and affordable green solution for dye degradation in recent years.<sup>16</sup> The current studies have observed a significant rise in interest in nanomaterials, particularly metal oxide-based nanoparticles due to their unique properties like large surface area, high stability, and efficient photocatalytic activity.<sup>17,18</sup> Among metal oxides, ferrite-based nanomaterials have shown outstanding potential for environmental remediation.<sup>19,20</sup> There have been several studies on iron-based photocatalysts, and structural changes can significantly impact their catalytic effectiveness.<sup>17-20</sup>

The distinctive family of hexagonal ferrites known as lead hexaferrite (PbFe<sub>12</sub>O<sub>19</sub>) is well-suited for photocatalytic applications due to its unique magnetic and optical characteristics. The modification of Fe-based catalysts to improve photocatalytic efficiency is still being researched, despite much work on ferrite nanoparticles.<sup>21-24</sup>

In this study, PbFe<sub>12</sub>O<sub>19</sub> nanoparticles were synthesized *via* the sol-gel method and characterized using UV-visible spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), zeta potential (ZP), zeta sizer (ZS), and vibrating sample magnetometry (VSM). The photocatalytic activity of the synthesized PbFe<sub>12</sub>O<sub>19</sub> nanoparticles in degrading rhodamine G (RG) dye under exposure to sunlight was assessed. This work seeks to contribute to the development of effective and environmentally acceptable photocatalysts for wastewater treatment by filling the gap in the current ferrite-based nanomaterials and improving their practical application.

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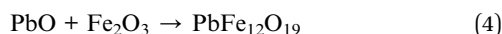
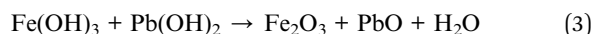
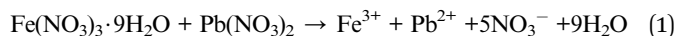
## 2 Experimental

### 2.1 Chemicals

Iron nitrate [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O], lead nitrate Pb(NO<sub>3</sub>)<sub>2</sub>, citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>), ammonium hydroxide (NH<sub>4</sub>OH), rhodamine 6G (RG; C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub>Cl), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were obtained from Fluka (Buchs, Switzerland). The Centre of Excellence in Analytical Chemistry, located in Jamshoro, Pakistan, provided the deionized (DI) water.

### 2.2 Synthesis of PbFe<sub>12</sub>O<sub>19</sub>-NPs by sol-gel method

PbFe<sub>12</sub>O<sub>19</sub>-NPs were synthesized by a sol-gel method. Stoichiometric amounts of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Pb(NO<sub>3</sub>)<sub>2</sub> were mixed in deionized water in 1 : 2 molar concentrations with continuous stirring with the addition of citric acid (2 M) to prevent aggregation (eqn (1)). The pH was maintained at 7 with NH<sub>4</sub>OH and promoted hydrolysis and condensation of Fe<sup>3+</sup> and Pb<sup>2+</sup> ions (eqn (2)). The resulting mixture was slowly evaporated at 80 °C until a gel was formed. The gel was further heated in an electric oven to remove organic residues and produced Fe<sub>2</sub>O<sub>3</sub> and PbO (eqn (3)). The resulting product was calcined in the furnace in an air atmosphere at 900 °C for 3 h to form PbFe<sub>12</sub>O<sub>19</sub> nanoparticles (eqn (4)).<sup>25</sup>



### 2.3 Instrumentation

The pH meter (Eutech, Malaysia) was employed to maintain the pH of the solutions. The XRD and SEM analyses were accomplished by D-8 Bruker and JSM-6380 JEOL instruments to determine the average particle size and surface morphology of the PbFe<sub>12</sub>O<sub>19</sub> nanoparticles. The zeta potential and zeta size were studied by a zeta potential analyzer (ELSZ-2000). The nitrogen absorption and desorption of samples were performed

at liquid nitrogen temperature (78 K) and gas saturation vapour tension was measured by the Brunauer–Emmett–Teller (BET) surface area analyzer of Quantachrome (Boynton Beach, Florida, USA). The UV-visible spectrophotometer (UV-2600, Shimadzu, Japan) was employed to investigate the band gap of PbFe<sub>12</sub>O<sub>19</sub> nanoparticles and to evaluate the catalytic activity of RG dye.

### 2.4 Photocatalytic analysis

The photocatalytic degradation of RG was performed at room temperature in a designed photo reactor using sunlight with stirring (450 rpm) for photoreaction. The concentration of PbFe<sub>12</sub>O<sub>19</sub>-NPs (used as a photocatalyst) was studied ranging from 1 to 5 mg in 20 mL of pollutant (RG) with a concentration range of 5–20 mg L<sup>-1</sup>. The estimated solar irradiance during the experimental period was ranging from 600 to 900 W m<sup>-2</sup> (regional meteorological data). The initial absorbance was recorded before equilibrium and the final absorbance was recorded after achieving photodegradation equilibrium at 527 nm.<sup>26–28</sup> The sunlight was applied to start the photoreaction with continuous stirring for 20–80 min. After the completion of the reaction, an aliquot of 5 mL was drawn to check the degradation efficiency on the UV-visible spectrophotometer. The schematic diagram of photocatalytic analysis is shown in Fig. 1. The synthesized PbFe<sub>12</sub>O<sub>19</sub> nanocatalyst was recycled 12 times to check the efficiency after every experiment. The experiments were performed with repeated washing using water and ethanol.<sup>29</sup> The photodegradation efficiency (%) of RG was determined by the following equation (eqn (5)):

$$\%D = 1 - \frac{C_f}{C_i} \times 100 \quad (5)$$

Where  $C_i$  and  $C_f$  (mg L<sup>-1</sup>) represent the initial and final concentrations of RG at 40 min respectively.

### 2.5 Sampling

The industrial wastewater samples ( $n = 5$ ) were gathered from different sites of the Jamshoro industrial area close to the discharge points. The collected water samples were filtered with Whatman no. 1 filter paper and stored in glass bottles (soaked in 10% HNO<sub>3</sub> and washed with DI water) at 4 °C.

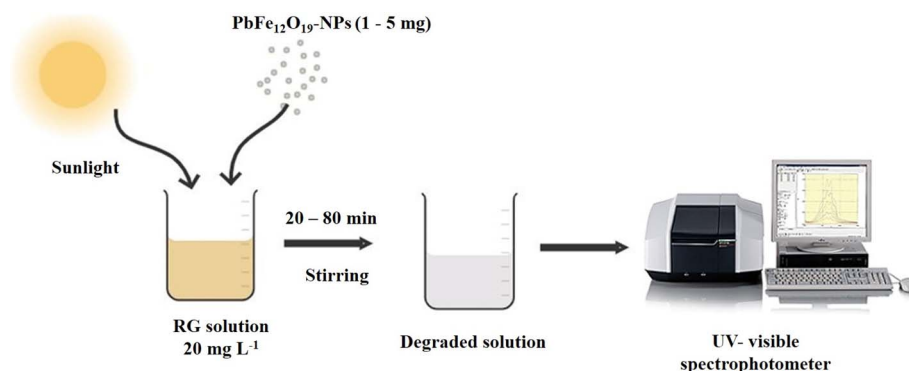


Fig. 1 Schematic diagram of photocatalytic degradation of RG using PbFe<sub>12</sub>O<sub>19</sub>.



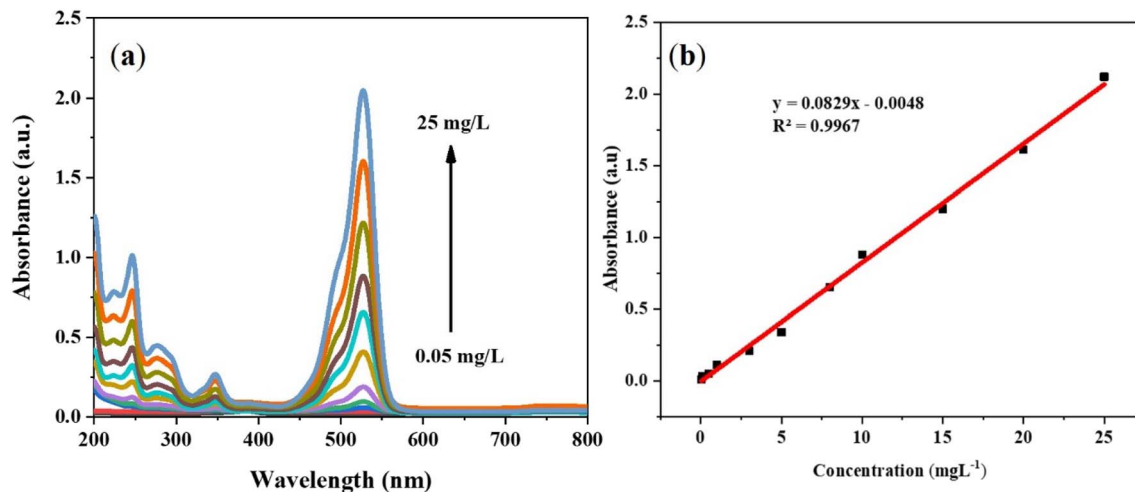


Fig. 2 (a) Calibration curve of RG at different concentrations ranging from 0.05 to 25 mg L<sup>-1</sup> and (b) the linear relationship between absorbance and concentration.

## 2.6 UV-visible spectroscopy analysis of RG

The quantitative analysis of RG was conducted by UV-visible spectroscopy technique. The experiments were carried out in DI water. The  $\lambda_{\text{max}}$  (wavelength maximum) of RG was found at 527 nm due to  $\pi$ - $\pi^*$  transitions in their aromatic rings.<sup>30,31</sup> The calibration was drawn by increasing RG concentrations from 0.05 to 25 mg L<sup>-1</sup> (Fig. 2(a)). Good linearity was observed between the absorbance and varying concentrations of RG with the coefficient of determination ( $R^2$ ) of 0.9967 (Fig. 2(b)). The limit of detection (LOD) and limit of quantification (LOQ) was found 0.0043 and 0.0145 mg L<sup>-1</sup>, respectively.

## 3 Results and discussion

### 3.1 Characterization of PbFe<sub>12</sub>O<sub>19</sub> nanoparticles

The band gap of synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs was studied using the UV-visible spectroscopy technique. The absorption band at 355 nm was observed in the obtained spectrum of synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs (Fig. 3(a)), confirming particle formation. The band gap of PbFe<sub>12</sub>O<sub>19</sub>-NPs was calculated by the following equation (eqn (6)).

$$E_g = \frac{1240}{\lambda} \times 100 \quad (6)$$

where  $E_g$  is the band gap energy in electron volts (eV), 1240 represents the constant (product of Planck's constant  $h$  and speed of light  $c$  in eV nm) and  $\lambda$  is the wavelength of the absorption gap in nanometers (nm). By applying this equation, the band gap was found 3.49 eV indicating that the PbFe<sub>12</sub>O<sub>19</sub>-NPs have potential optical activity and can be applied as photocatalysts for the degradation of RG.<sup>32</sup>

The XRD technique was applied to study the structure, size and degree of crystallinity of PbFe<sub>12</sub>O<sub>19</sub>-NPs. Fig. 3(b) shows the XRD patterns of PbFe<sub>12</sub>O<sub>19</sub>-NPs in the range of 2 $\theta$ -80°. The diffraction peak pattern at 2 $\theta$  matched with the hexagonal phase (JCPDS no. 31-0686).<sup>33</sup> The absence of extraneous peaks in the XRD patterns confirmed the successful removal of all

unreacted materials and impurities. The average crystallite size of PbFe<sub>12</sub>O<sub>19</sub>-NPs was assessed using the Debye-Scherrer equation as reported in literature.<sup>34</sup> The average crystallite size of PbFe<sub>12</sub>O<sub>19</sub>-NPs was found 13.8 nm.

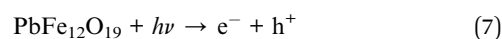
The SEM image of synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs showed hexagonal flake shape with smooth surface as shown in Fig. 3(c). Further, the surface of the particles is smooth and the particles are uniformly distributed.<sup>35</sup>

The ZP of synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs was investigated and the average ZP of synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs was found -31.2 mV which confirmed its stability (Fig. 3(d)).<sup>36</sup> The zeta size of PbFe<sub>12</sub>O<sub>19</sub>-NPs was also studied (Fig. 3(d)) and the zeta size was found within the nanometer range with an average size of 35.7 nm.<sup>36</sup>

The BET technique was employed to study the specific surface area, pore size and pore volume of synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs.<sup>32</sup> The average surface area of synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs was found 158.3 m<sup>2</sup> g<sup>-1</sup> which is very effective for degradation applications. Further, the average pore size and pore volume of PbFe<sub>12</sub>O<sub>19</sub>-NPs were found 15.94 nm and 45.71 cm<sup>3</sup> g<sup>-1</sup> respectively. As the average pore size was calculated at 15.94 nm, so the synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs are mesoporous (materials having pore sized 2-50 nm) in nature.<sup>37</sup>

### 3.2 Photocatalyst oxidation mechanism

The applications and outstanding properties of PbFe<sub>12</sub>O<sub>19</sub>-NPs are due to the excitation of its electrons by absorption of sunlight resulting in the production of the electron-hole ( $e^-$ - $h^+$ ) pair. This pair contains high oxidizing-reducing potentials that make them able to initiate the first series of chain reactions.<sup>38</sup> Once the PbFe<sub>12</sub>O<sub>19</sub>-NPs interact with UV light ( $\lambda \leq 355$  nm) which is equivalent to or greater than the band gap (3.49 eV), valence band (VB) electrons are excited towards the conduction band and form a positive hole ( $h^+$ ) in the VB (eqn (7)).



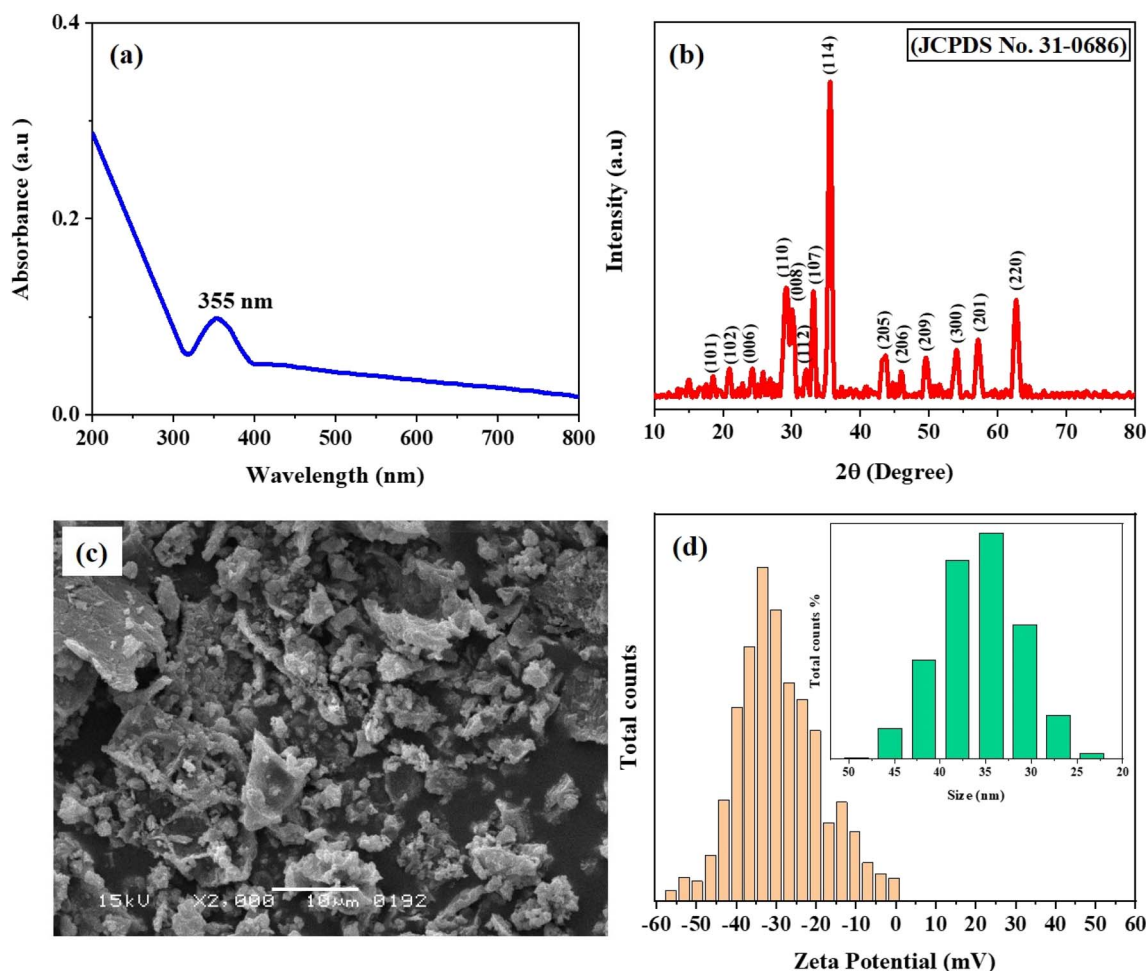
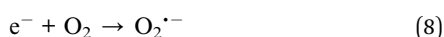


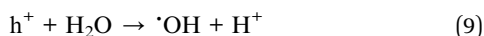
Fig. 3 (a) UV-visible spectrum, (b) XRD spectrum, (c) SEM image, and (d) zeta potential along with zeta size analysis of synthesized  $\text{PbFe}_{12}\text{O}_{19}$  nanoparticles.

The excited electrons ( $e^-$ ) in the conduction band and the holes ( $h^+$ ) in the valence band can participate in reduction and oxidation reactions.<sup>39</sup>

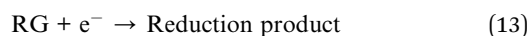
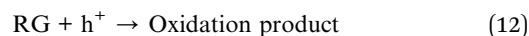
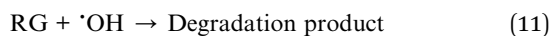
The excited electrons ( $e^-$ ) in the conduction band can reduce adsorbed oxygen ( $\text{O}_2$ ) molecules, forming superoxide radicals ( $\text{O}_2^{\cdot-}$ ) (eqn (8)).<sup>40</sup>



The holes ( $h^+$ ) in the valence band can react with water molecules ( $\text{H}_2\text{O}$ ) or hydroxide ions ( $\text{OH}^-$ ) to generate highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ) (eqn (9) and (10)).<sup>41</sup>



The generated reactive oxygen species such as hydroxyl radicals ( $\cdot\text{OH}$ ) and superoxide radicals ( $\text{O}_2^{\cdot-}$ ) play a crucial role in the degradation of RG (eqn (11)–(13)).<sup>42</sup>



The RG molecules are attacked by these reactive radicals, which cause them to fragment into smaller, less hazardous pieces, which eventually result in entire mineralization into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

### 3.3 Optimization study for the degradation of RG using $\text{PbFe}_{12}\text{O}_{19}$ -NPs

Various factors that affect the rate of photocatalysis may include light source, the initial concentration of RG, catalyst dose, pH, and irradiation time.<sup>43</sup> Therefore, in the present study, these factors were investigated under different operating parameters as discussed below.

Solar lights and artificial lights have been used in dye photodegradation, but mostly artificial light sources can be used to maintain stable intensities away from clouding and other environmental factors.<sup>44</sup> The intensity and wavelength of UV light greatly affect aqueous medium photodegradation. Sunlight irradiation is an alternative and economical light



source due to its abundance, availability and non-hazardous nature.<sup>45</sup> Sunlight consists of 5% UV light (200–400 nm), 43% visible light (400–800 nm) and 52% IR (>52%). Visible light has lower photon energy than UV light. Therefore the experiments were conducted under various conditions including dark, tungsten UV light, and sunlight and excellent results were obtained in sunlight. Fig. 4(a) shows the photodegradation efficiency of 3.0 mg PbFe<sub>12</sub>O<sub>19</sub>-NPs towards 10 mg L<sup>-1</sup> RG in different conditions for 40 min. The results indicate that the maximum % degradation was found with sunlight.

Research has shown that the initial degradation rate of RG solution is directly related to photocatalyst concentration. It has also been observed that there is a specific concentration range of photocatalyst for the photocatalyst degradation of each particular pollutant. At the same time, it is considerable that a larger amount of the designated portion can reduce the rate of photocatalyst activity.<sup>46</sup> The main reason behind this fact is that by increasing the amount of photocatalyst, an increase will be caused in the number of active locations that exist on the molecular levels and results in enlarging the number of hydroxyl and superoxide radicals. When the photocatalyst concentration is higher than the optimal amount, a decrease in

the rate of photocatalyst degradation is induced, which is related to the light blockage that is created by the raised mass of particles in the suspension.<sup>47</sup> In addition, increasing the concentration of photocatalysts beyond the optimum amount could result in the coagulation of catalyst nanoparticles; therefore, there would be less surface area and consequently less photon absorption, which reduced the rate of photocatalyst degradation. The obtained results of RG degradation compared to various concentrations for sunlight irradiation in 20 min are illustrated in Fig. 4(b) indicating that the maximum degradation efficiency was found at 10 mg L<sup>-1</sup>.

The degradation of RG was investigated by varying the dosage of photocatalyst (PbFe<sub>12</sub>O<sub>19</sub>-NPs) ranging from 1.0–5.0 mg. The obtained results of RG degradation at different concentrations of photocatalyst PbFe<sub>12</sub>O<sub>19</sub>-NPs under sun light irradiation for 40 min are illustrated in Fig. 4(c).

One of the effective factors in the photocatalyst degradation of RG by PbFe<sub>12</sub>O<sub>19</sub>-NPs in aqueous solutions is known to be the pH. It is a complicated procedure to determine the influence of pH on the efficiency of the optical degradation process of dye materials since it could cause multiple effects on photocatalysis. Moreover, pH can affect the ionization level of

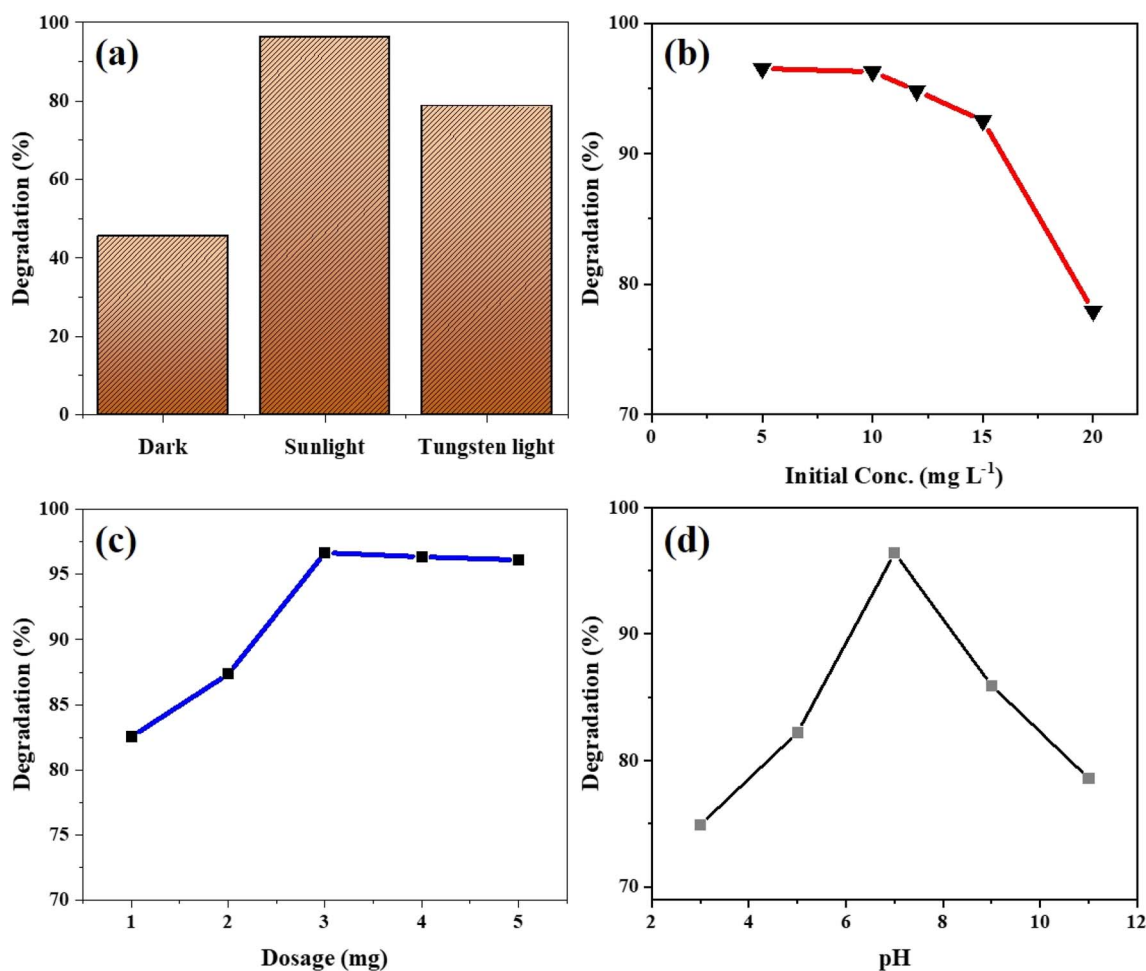


Fig. 4 (a) Effect of irradiation and (b) RG initial concentration, (c) catalyst dose and (d) pH on the degradation efficiency of PbFe<sub>12</sub>O<sub>19</sub>-NPs towards RG.



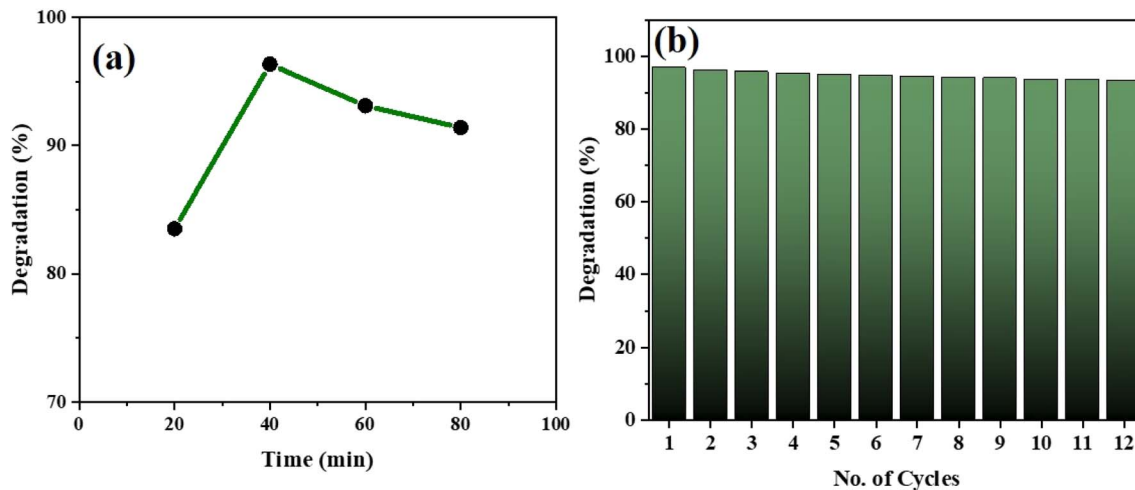


Fig. 5 (a) Contact time and (b) reusability of  $\text{PbFe}_{12}\text{O}_{19}$ -NPs over the degradation efficiency towards RG.

photocatalysts, and the nature of reactive dyes. Therefore, it could be stated that the variations of pH have an impact on the absorption of dye molecules, which stands as a crucial stage in the photocatalyst oxidation process.<sup>48</sup> On the other hand, hydroxyl radicals have been observed to be composed of the reaction between hydroxide ions and positive holes. Positive holes are recognized as vital oxidizing species that exist in the lower pH, whereas hydroxyl radicals are the dominant species in neutral or higher pH.<sup>49</sup> In base solutions, the hydroxide ions that are positioned on the surface of  $\text{PbFe}_{12}\text{O}_{19}$ -NPs are oxidized, while the hydroxyl radicals are produced through a more natural procedure and consequently, increase the efficiency of the photocatalyst process. There are negative charges between the photocatalyst level and hydroxide anions within the base solutions, which can prevent the production of hydroxyl radicals and therefore, reduce the efficiency of the photochemical process.<sup>50</sup> The performed studies have indicated that  $\text{PbFe}_{12}\text{O}_{19}$ -NPs contain a tendency to agglomerate in acidic conditions while in this case, they have been causing a reduction in the surface area. In general, high pH values can prevent the absorption of anionic dyes that are present on the surface of the photocatalyst and contain a negative charge.<sup>48</sup> At low pH, the induced reduction by conduction electrons seems to have an essential role in the procedure of dye degradation. Therefore, it can be suggested that pH stands as a principal agent in the photocatalyst degradation of textile sewage. The results of RG degradation at different pH from 3–11 of photocatalyst  $\text{PbFe}_{12}\text{O}_{19}$ -NPs under sunlight irradiation for 40 min are demonstrated in Fig. 4(d).

Time exposure to sunlight is one of the foremost factors in determining the photodegradation capacity of photocatalysts toward RG degradation.<sup>51</sup> It is reported that as irradiation time for photocatalytic reaction increases photodegradation and decolorization of dye increases, which can be attributed to the formation of  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  with increasing irradiation reaction time.<sup>52</sup> Initially, the degradation rate is faster and slows down upon increasing the irradiation time. 5 displays the outcome of sunlight irradiation time on the photocatalysis of RG. It was

found that percent degradation increased with increasing irradiation time. The  $\text{PbFe}_{12}\text{O}_{19}$ -NPs degraded 95.5 RG, respectively under sunlight irradiation within 40 min. The percent degradation was progressively increased by increasing the time duration and intensity of light are illustrated in Fig. 5(a).

### 3.4 Kinetic study

Since photocatalysis is a surface phenomenon the adsorption of dyes onto the surface of the photocatalyst is a crucial step to enhance the photodegradation efficiency.<sup>32</sup> To describe the kinetics of solid/liquid systems, usually, pseudo-kinetic models like pseudo-first-order and pseudo-second-order kinetics are employed.<sup>53</sup> So, the experimental data for the photodegradation of RG dye were fitted to pseudo-first-order and pseudo-second-order kinetic equations to find the appropriate model which represents the kinetics of degradation. In a pseudo-first-order reaction, a straight-line graph is obtained by plotting the logarithm of the ratio of the initial concentration of RG dye to their concentration after photocatalytic degradation ( $\log(q_e - q_t)$ ) against the irradiation time.

The straight-line equation of pseudo-first-order reaction kinetics is given in eqn (14). The slope of the plot represents the first-order rate constant  $k_1$ . The regression coefficients for pseudo-first-order reaction kinetics were found 0.96 for RG, respectively.

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (14)$$

Where  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are the amount of dye removed (degradation capacity) at time  $t$  and at equilibrium, respectively,

Table 1 Kinetics parameters study for the degradation of RG by  $\text{PbFe}_{12}\text{O}_{19}$ -NPs under sunlight

	Regression equation	$q_e$	$k$	$R^2$
Pseudo 1st order	$y = 0.0056x + 0.3723$	2.69	0.0130	0.7538
Pseudo 2nd order	$y = 0.0171x - 0.0436$	22.9	0.0171	0.9991



Table 2 The comparative study of PbFe<sub>12</sub>O<sub>19</sub>-NPs-based degradation of RG with reported studies

Catalyst	Light	Time (min)	Removal%	Reference
5-wt%CuO NPs/ZIF-8	UV-visible	105	96	58
CaMn <sub>3</sub> O <sub>6</sub>	Visible	240	83.1	59
TiO <sub>2</sub>	Visible	240	64	60
ZnO/Zn film	UV	30	34	61
PbFe <sub>12</sub> O <sub>19</sub> -NPs	Sunlight	40	>95	Current study

and  $k_1$  (min<sup>-1</sup>) represents the rate constant of the pseudo 1st order model.

The degradation of RG on the surface of PbFe<sub>12</sub>O<sub>19</sub>-NPs was also analyzed using the pseudo 2nd order kinetic. The equation for the pseudo 2nd order reaction is provided in equation eqn (15).

$$t/q_e = 1/k_2q_e^2 + t/q_e \quad (15)$$

Where  $q_t$  and  $q_e$  are the same as described above and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of the pseudo 2nd order model.

The co-efficient of determination was found 0.9991 RG for pseudo-second-order chemical reaction kinetics as described. The  $R^2$  values of pseudo 2nd order kinetics are closer to unity for RG dye. Therefore, the photocatalytic degradation reaction of RG by PbFe<sub>12</sub>O<sub>19</sub>-NPs belongs to pseudo 2nd order kinetics. So, the reaction mechanism is found to be chemically rate-controlling.<sup>53,54</sup> The kinetics parameters for the degradation of RG by PbFe<sub>12</sub>O<sub>19</sub>-NPs is given in Table 1.

### 3.5 Reusability

The PbFe<sub>12</sub>O<sub>19</sub>-NPs nanocatalyst demonstrated effective reusability in successive catalytic experiments, with repeated washing using water and ethanol.<sup>29</sup> The photocatalyst was tested in RG degradation efficiency from 93.3% to 96.8% (Fig. 5(b)). This minor decline in performance (less than 10%) underscores the strong reusability of the catalyst. The reduction in photocatalytic activity may be attributed to: (a) loss of catalyst during the recovery process (washing and drying), which could lead to reduced dosage and subsequently lower surface activity in subsequent cycles;<sup>55</sup> and (b) changes in the photocatalyst properties, such as agglomeration (leading to fewer active sites and lower surface area) and fouling, over repeated cycles.<sup>56</sup> Furthermore, the reduction in adsorption capacity, due to pore blockage by dye molecules (RG) and their intermediates, may contribute to the decline in catalytic activity after multiple cycles.<sup>57</sup> Despite this slight reduction, the PbFe<sub>12</sub>O<sub>19</sub>-NPs

photocatalyst retains significant reusability, making it a promising candidate for long-term industrial applications.

### 3.6 Comparative study and real sample analysis

The analytical performance of PbFe<sub>12</sub>O<sub>19</sub>-NPs-based degradation of RG was compared with reported studies. Table 2 shows that the degradation of RG is better than that of currently reported studies. Further, to validate the practical applicability of the developed method, it was applied to real samples and the percent degradation was found greater than 90% with a percent relative standard deviation of less than 3. This indicates that the developed method is reliable for the monitoring of dyes in water (Table 3).

## 4 Conclusion

PbFe<sub>12</sub>O<sub>19</sub>-NPs were successfully synthesized using the sol-gel method, resulting in the soft magnetic material, average size of 13.8 nm with a hexagonal crystal structure and negatively charged surface. The synthesized PbFe<sub>12</sub>O<sub>19</sub>-NPs were employed as photocatalysts for the degradation of RG under optimized conditions including sunlight source, initial concentration of 10 mg L<sup>-1</sup>, 3 mg of photocatalyst dosage, pH 7, and 40 min contact time. The PbFe<sub>12</sub>O<sub>19</sub>-NPs demonstrated outstanding recovery rates (>90%) for the analysis of water samples which confirmed its practical applicability for environmental monitoring. PbFe<sub>12</sub>O<sub>19</sub>-NPs was found to be highly efficient for the photodegradation of rhodamine 6G dye, with more than 95% removal.

## Approval of ethics

The present experimental studies do not involve any animal/human participants.

## Data availability

Access to the information that supports the current study will be provided at the official request.

## Author contributions

The current study is a result of the visionary work of Dr Jameel Ahmed Baig, along with Dr Imam Bakhsh Solangi, whose role was in supervision, project management, review, and editing. A committed MPhil. student, Ms Sara Abbasi, was instrumental in the original draft's creation, formal analysis, data curation, and

Table 3 Application of the developed method to real water samples

Samples	Initial conc. (mg L <sup>-1</sup> )	Final conc. (mg L <sup>-1</sup> )	Degradation (%)	RSD (%)
01	8.05	0.54	93.3	2.54
02	5.42	0.23	95.7	2.43
03	4.12	0.13	96.8	2.65



methodology. The PhD candidates Khalil Akhtar, Saima Perveen, Sajjad Hussain, Fahad Abbasi and Shakoor Ahmed Solangi expertly managed the technical parts, which included software use, research, and visualization.

## Conflicts of interest

The authors state that none of the work presented in this study may have been influenced by any known conflicting financial interests or personal ties.

## Acknowledgements

The University of Sindh, Jamshoro's National Centre of Excellence in Analytical Chemistry (NCEAC) has been recognized for providing well-equipped laboratory facilities for research projects. The authors acknowledge and extend their appreciation to the Researchers Supporting NRP Project No.14503 of HEC Islamabad, partially support by Türkiye Bursları Research Fellowship Program sponsored by the Prime Ministry of Turkey Presidency 2023 and National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro.

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