Communication

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Novel diatom-FeO_x composite as highly active catalyst in photodegradation of Rhodamine-6G

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Abstract: We report the study of nanoporous silica-iron oxide composite generated from diatom frustules as a highly active catalyst for the photodegradation of the dye Rhodamine-6G. The unique architecture and high surface area of diatoms were utilized to immobilize iron oxide on their surface to form the composite. Photodegradation was carried out under 365-nm radiation and was observed using the absorption spectrum of the dye. The reaction was found to follow pseudo-first-order kinetics. The results were compared with commercially available granular iron oxide. The rate constant K (min^{-1}) for photodegradation by the diatom composite was found to be as high as 0.0584 min^{-1} for diatom-FeO_x composites, which is 52% higher than 0.0273 min^{-1} for granular FeO_x at a dye concentration of 0.02 mM. The unique structural morphology and the synthetic strategy have led to the composites showing superior activity in the degradation of the dye Rhodamine-6G.

Keywords: diatom silica; nanoporous silica; photodegradation; Rh-6G; silica-FeO_x composites.

1 Introduction

Among the numerous organic pollutants released into water [1], various dyes used in the manufacture of textiles are a major concern to public health [2]. These dyes have carcinogenic and mutagenic effects on both aquatic and terrestrial life forms even when present in small concentrations [3]. Their presence in various aquatic bodies decreases the penetration of light and thereby inhibits photosynthesis apart from chelating with other metal ions, which may be present in the ponds and streams and cause microtoxicity to fish and other organisms [4]. In addition, direct inhalation or ingestion of dyes can cause difficulty in breathing and can be fatal in some cases [5]. These hazards call for a rapid and active degradation of these dyes without further production of toxic agents. Unfortunately, many of these dyes are resistant to biodegradation and typical nitrogen-containing dyes undergo reductive anaerobic degradation, during which they release potentially carcinogenic aromatic amines [6]. Consequently, the treatment of effluent-containing dyes has been a challenge.

Besides conventional biological, chemical, and physical treatments, heterogeneous photocatalysis is evolving as an efficient and inexpensive treatment technique for removing dyes from water [7]. Metal oxide nanoparticles have been of great interest, and several nanoparticles such as Al₂O₃, ZnO, and α -Fe₂O₃ have been studied as potential candidates as absorbents and catalysts for dye photodegradation [2, 8]. Semi-conductor photocatalysts such as TiO₂ have been studied extensively, although their large band gaps limit absorption mainly to the ultraviolet (UV) regions [9–11]. This has led to the investigation of materials with narrow band gap, which absorb in the visible (Vis) region of the solar spectrum. Among metal oxides that absorb light up to 600 nm are iron oxides, which are widely available in the earth's crust [12–15], and micro/nano structured iron oxides have been used in the photocatalysis of dyes [16].

Typical photocatalysts are supported on substrates such as silica [17], glass [18, 19], carbon [20], mixed metal

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oxides [21], stainless-steel, alumina, activated carbon, concrete surfaces, and silica gel [22]. There is much interest in using silica as support for heterogeneous catalysts. TiO₂-SiO₂ has been widely used as a heterogeneous catalyst, as it prevents the release of TiO₂ from the surface to the environment [23]. Mesoporous catalysts improve the access to the active sites and consequently increase in their catalytic activity [24].

Diatoms are a class of unicellular microalgae that are found in both fresh and marine environments with size varying from 2 µm to 2 mm. The siliceous cell walls, referred to as frustules, have unique porous structures that have surface area as high as 200 m² g⁻¹ [25]. The silica layer also contains functional groups such as -COOH, -OH, -NH₂, and -SiOH that facilitate the attachment of different molecules [25]. Recently, they have been used in applications such as water treatment, sensing, electroluminescent displays, batteries, solar cells, and drug delivery [26]. Even though there have been reports on metal oxides impregnated on the diatomite [27–32], as referred usually, these composites were not made in the nanoform and have been synthesized after the frustules have been harvested, thereby leading to differential distribution of the metal oxides on the diatomite [33]. Even though these composites have been used to study Fenton and photo-Fenton reactions, they have not been tested for their prowess in the degradation of the dye Rhodamine-6G (Rh-6G). Nano- and micro-sized iron oxides have been used for its photodegradation [16].

In the current study, we present a simple yet scalable technique of synthesis of diatom-FeO_x composites from live cultures of diatoms and their application in the catalytic photodegradation of Rh-6G.

2 Materials and methods

All reagents were of analytical grade and used as acquired. Milli-Q water was used throughout the experiment. Granular ferric oxide was acquired from Sigma-Aldrich, and 30% H₂O₂, NaH₂PO₄, and Na₂HPO₄ were obtained from Merck. Commercially available granular ferric oxide was ball milled for 4 h, and the sub-micron-sized powder (5–10 microns) was used as a control to compare the effectiveness of the nanostructured diatom-FeO_x composite.

Synthesis and characterization of the diatom-FeO_x composite was carried out as reported in our previous paper [34]. The diatom-FeO_x composite was characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM; Leo 1530 VP) equipped with an energy dispersive X-ray spectrometer (EDX),

Scheme 1: Synthesis of diatom-FeO_x composites.

Brunauer-Emmett-Teller (BET) surface area analyzer (Quantachrome Autosorb-I), thermogravimetric analyzer (TGA; Pyris 1; Perkin Elmer Inc.), and Fourier transform infrared (FTIR) spectroscopy (IRAffinity-1; Shimadzu). UV-Vis absorption was monitored with a Shimadzu UV-2450 double-beam spectrophotometer using quartz cells with a path length of 10 mm at room temperature. X-ray photoelectron spectroscopy (XPS) analysis was done using a Surface Science Instruments SSX-100 with operating pressure $\sim 2 \times 10^{-9}$ Torr. Monochromatic AlK- α X-rays (1486.6 eV) were used with beam diameter of 1 mm. Photoelectrons were collected at a 55° emission angle. A hemispherical analyzer determined electron kinetic energy using a pass energy of 150 V for wide/survey scans and 50 V for high-resolution scans. A flood gun was used for charge neutralization of non-conductive samples.

Briefly, FeCl₃·8H₂O was added to the diatom cultures to help the uptake of Fe onto the biosilica in their natural state. The composites were finally obtained by precipitating the iron oxide on the diatoms at alkaline pH followed by thermal treatment with hydrogen peroxide to remove the organics (Scheme 1) [35–37]. The photodegradation experiments were done by adding 3 ml of 0.02 mM solution of Rh-6G and 10 mg of the photocatalyst to a glass vial and sonicated for 10 min. This mixture was transferred to a quartz tube, and 0.225 ml of 30% H₂O₂ was added to it and the absorption spectrum was recorded at time zero. The mixture was irradiated under UV light ($\lambda = 365$ nm, 6 W) at room temperature, and absorption spectra were recorded at 10, 20, 40, 60, 120, 140, 180, 210, and 240 min. The effect of concentration was studied at 0.05, 0.04, 0.03, 0.02, and 0.01 mM concentrations of the dye. pH effects were studied at pH 4.0, 5.0, 6.0, 7.0, and 8.0 using phosphate buffer of 0.2 mM concentration.

3 Results and discussion

The surface of the diatom-FeO_x composite was visualized using TEM and SEM. The TEM images of the original diatom and composite are presented in Figure 1. The

Figure 1: TEM of (A) diatom and (B, C) diatom-Fe composite. SEM of (D) diatom-FeO_x composite, (E) mapping for Si from diatom, and (F) Fe immobilized on diatom surface [26].

treatment made them form a cluster mass rather than remain as single particles. EDX mapping confirmed the presence of Fe on the diatom Si along with its uniform distribution on the surface (Figure 1D–F). The SEM and

TEM images clearly show the presence of FeO_x in the nano form with a uniform distribution across the surface of the diatom silica and in the pores of the silica forming a composite, highlighting the importance of the synthetic route.

Functional group analysis and the presence of iron oxide was also confirmed with the help of the FTIR spectrum (Figure 2). The peak observed at 422 cm⁻¹ was attributed to Fe-O vibration [38], while that at 1624 cm⁻¹ and those between 3300 and 3500 cm⁻¹ were from SiO₂ and free silanol groups [39, 40]. This is expected, as the Si has been derived from diatoms using H₂O₂, which is an oxidizing agent and might lead to the presence of silanol groups. The thermal stability of the diatom-FeO_x composites was determined using TGA (Figure 3). The weight loss below 120°C was attributed to the loss of physisorbed water, and that between 120°C and 300°C was due to loss of chemisorbed water [41]. The weight loss in the 400–600°C range was attributed to the decomposition of organosilanes and

Figure 2: FTIR spectra of diatom and diatom-FeO_x composite: (A) between 300 and 4000 cm⁻¹ and (B) expanded view from 300 to 800 cm⁻¹.

Figure 3: TGA of diatom-FeO_x composite.

Figure 4: XPS spectra of diatom-FeO_x composites and granular FeO_x.

dehydration of silanol groups. The weight loss between 400°C and 800°C may also be attributed to the dehydroxylation of the silica surface [42, 43]. The diatom-FeO_x composites displayed good thermal stability. The BET surface area analyzer gave the surface area of the composites as 70 m² g⁻¹ as compared to the 200 m² g⁻¹ of the pure diatom silica. This is expected, as N₂ does not adsorb onto the metal oxide surfaces and can be viewed as a confirmation of the presence of FeO_x on the surface of the silica.

The analysis of the XPS spectra (Figure 4) clearly proved the presence Fe²⁺ in the sample. The peaks for Fe2p at 706 and 721 eV clearly showed the presence of Fe²⁺. The shift is expected due to the lack of charge neutralization of the non-conductive samples. That is, due to the evolution of electrons, the sample accumulates a positive charge on the surface, which is neutralized by the surrounding stray electrons in that area of the sample when a non-monochromatic X-ray source is used. However, the use of a monochromatic X-ray source releases controlled electrons, which does not neutralize the positive charge, causing the XPS peaks to shift to higher binding energies. The atomic percentage of the Fe²⁺ in the composite was 22.12% and that in the granular ferric oxide was 4.18%, which acts as a factor for the higher activity by the diatom FeO_x composite compared to granular FeO_x.

The various characterization techniques used have brought forth the fact that the composites are naturally functionalized due to their biological origin. SEM imaging has shown the porous nature of the sample, and EDX mapping has proved that the iron oxide is uniformly distributed on the Si substrate. The XPS data have proved that the Fe²⁺, the main species that catalyzes the reaction, is available abundantly in the composites that have

nano-FeO_x when compared to granular bulk FeO_x. This uniform distribution and better availability of the active species in the composite is responsible for the better degradation activity by the composite material when compared to granular bulk Fe. It is also clear that the current synthetic procedure has given rise to composites that has nano-FeO_x distributed uniformly on porous silica.

3.1 Photodegradation in the presence of diatom-FeO_x

Rh-6G in aqueous medium has a yellow color and absorbs strongly at 525 nm. The comparison of the absorption spectra of Rh-6G with catalyst, with granular FeO_x, and in the absence of catalyst are shown in Figure 5A. In each case, the absorption spectra were recorded after a 201-min irradiation. The color disappeared completely in case of the diatom-FeO_x composite, while significantly less photodegradation was seen in the case of granular FeO_x and none in the case of the diatom control.

Figure 5B shows not only decrease in the absorption intensity of the dye with increase of irradiation time but also a slight bathochromic shift of the λ_{max} . This indicates a change in the chromophore of the dye pointing out toward complete destruction of the aromatic rings in the dye [44]. The spectra clearly demonstrate that the diatom-FeO_x composites effectively catalyzed the photodegradation of the dye Rh-6G. This is attributed to the large surface area of the composites available for catalysis and the unique architecture of the diatom frustules, leading to the uniform distribution of the catalyst.

The kinetics of photodegradation is presented in Figure 5. The absorbance at λ_{max} of 525 nm reduced gradually with increase in the irradiation time. The solution containing the diatom-FeO_x composites as catalysts showed complete reduction of the dye at 210 min when compared to granular FeO_x. Figure 5B and C show the kinetics of the photodegradation of the dye Rh-6G by diatom-FeO_x composites and by granular FeO_x, respectively. Figure 6A shows degradation as a function of time, and Figure 6B shows that the reaction followed pseudo-first-order kinetics with the rate constant (K) being 0.0584 and 0.0273 min⁻¹, respectively, for diatom-FeO_x composites and granular FeO_x at a dye concentration of 0.02 mM.

3.1.1 Mechanism of photodegradation

The photodegradation of Rh-6G followed pseudo-first-order rate kinetics, which was in line with what has been

Figure 5: (A) Photodegradation of Rh-6G in aqueous solution using different catalysts. The irradiation time was 210 min for each. Kinetics of photocatalytic degradation of Rh-6G. (B) Diatom-FeO_x composites and (C) granular FeO_x. All experiments were carried out in 3 ml of 0.02 mM dye solution to which 10 mg of the catalyst was added.

reported [45]. The proposed mechanism of photodegradation in the presence of diatom-FeO_x composites is as follows. The FeO_x on the diatom composite absorbed the

Figure 6: (A) Plot of C/C_0 versus time. C_0 is the initial concentration of the dye and C is the concentration of the dye at a given time t (3 ml of 0.02 mM dye solution and 10 mg of the catalyst loading). (B) Plot of $\ln(C_0/C)$ vs. time with best fit and R^2 value proving that the reactions follow pseudo-first-order kinetics for diatom-FeO_x composites.

UV radiation and generated an electron-hole pair [16]. This electron was scavenged by H₂O₂ in a Fenton mechanism or was captured by the Fe³⁺ to generate Fe²⁺ back [46]. The Fe²⁺ reacted with H₂O₂, forming OH* radicals. This was confirmed by carrying out the reaction in the absence of H₂O₂, which showed negligible reduction in the absorbance spectrum of Rh-6G. These radicals reacted with the dye and oxidized it [47]. The OH⁻ ions combined with the holes and further generated hydroxyl radicals to assist the reaction:

3.1.2 Effect of pH

It has been reported that pH plays an important role in the rate of dye photodegradation [48]. The photodegradation of Rh-6G was carried out at different pH for both diatom-FeO_x composites and granular FeO_x. The results are presented in Figure 7. It was seen that the catalysis was most effective at pH 5.0. The higher reaction rates can be associated to two reasons. The pK_a of H₂O₂ is 11.7 and thus the dissociation of H₂O₂ was maximum at around pH 5.0, leading to higher OH* radical formation at this pH. Additionally, the higher surface area of the catalyst along with the pH content played a role in the adsorption of the dye on the surface of the catalyst [49]. The structure of the dye allows a more facile hydrogen-bond-based adsorption on the catalyst surface in acidic pH when compared to basic. The OH* radicals that are formed by reaction with positive holes acted as the main oxidizing agents at lower pH [50]. The observed trend could be explained by the scavenging of the OH* radical by the H⁺ ions at pH <4.0. At a slightly acidic pH of 4.0–5.0, the OH* radicals are at an optimum level and hence show better activity. At pH >5.0, near pH 6.0–7.0, the FeOOH precipitated out to block out the surface pores, leading to a decrease in catalytic activity [51–53]. However, as the pH increased, more OH* radicals were produced and a slight increase in the activity was observed [54]. It was also noted that the granular iron oxide showed a somewhat different trend because it had significantly lower Fe²⁺ concentration (4.18% compared to the composite, which had 22.12%), which led to the generation of relatively lower numbers

of OH* radicals. Consequently, its activity was less compared to the diatom composite, also limiting its response to change in pH.

3.1.3 Effect of concentration

In order to investigate the effect of concentration of the dye on photodegradation, the concentration of the dye Rh-6G was varied, keeping a constant amount of catalyst. Figure 8 clearly shows that the rate of the degradation by diatom-FeO_x composites was higher than that of granular FeO_x at all concentrations, although both systems showed similar trends. This is in line with what has been reported before [2, 55]. In case of the granular FeO_x, the rate reached its minimum at a concentration of 0.03 mM, as all the active sites were occupied at this concentration. However, in case of the diatom composite, the rate was somewhat stable even up to a concentration of 0.04 mM and thereby decreased at 0.05 mM concentration of the dye. This is explained by the fact that the composite material is porous, has uniform distribution of the catalyst on its surface leading to significantly more active sites available for the reaction, and hence is able to deal with larger concentration of dyes. Three individual effects explain the general trend in decrease in the activity with increase in the dye concentration. The increase in the dye concentration leads to the increase in the amount of the dye adsorbed on the catalyst surface, leading to the decrease in number of active sites that produce the OH* for catalysis [55, 56]. In addition to this, the increase in the dye concentration

Figure 7: pH dependence of diatom-FeO_x composite and granular FeO_x in photocatalysis of Rh-6G (3 ml of 0.02 mM dye solution and 10 mg of the catalyst loading).

Figure 8: Concentration studies of diatom-FeO_x composite and granular FeO_x (3 ml of the dye solution and 10 mg of the catalyst loading at pH 5.0).

Figure 9: Recycling ability of the diatom-FeO_x composites.

Table 1: Comparison of the rate constants with different materials in the literature.

Material	K (min ⁻¹)	References
ZnO (nanometer sized)	0.0128	[2]
α-FeOOH (micro rods)	0.0195	[16]
TiO ₂ -silica	0.00327	[17]
TiO ₂ -glass	0.0326	[18]
Ti-Sn composites	0.0054	[21]
SiO ₂ @TiO ₂	0.00473	[58]
TiO ₂ -films	0.01173	[59]
Diatom-FeO _x composite	0.0584	This paper

decreases the path length of the photon entering the dye solution and also leads to higher absorption of light, thereby decreasing the photocatalytic activity by lowering the light absorbed by the catalyst to produce the active species [57]. Table 1 compares the performance of different materials with diatom – FeO_x composite, in their ability to degrade the dye.

3.2 Recycling ability of the catalyst

The ability of the catalyst to catalyze the reaction multiple times was tested by using the same amount of the catalyst for multiple solutions, and the data are presented in Figure 9. The catalyst showed stable degradation rates up to five cycles and thereby decreased in the sixth cycle. This might be due to the adsorption of the products of degradation on the catalyst surface and thereby reduction in the availability of the reaction sites for the degradation to occur.

4 Conclusion

The diatom-FeO_x metal composite showed high activity in catalyzing the photodegradation of Rh-6G, which is a well-known pollutant in the textile industry. This high activity could be attributed to the high surface area available from the composite, the nanostructuring of iron oxide on the frustule surface, the uniform distribution of the catalyst on the Si surface, and also the large amount of Fe²⁺ available for catalysis as compared to granular FeO_x. The reaction mechanism followed pseudo-first-order kinetics. A pH of 5.0 and a dye concentration of 0.04 mM were found to be optimum for dye photodegradation. The catalyst was found to be active for five cycles before decrease in its activity occurred.

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