Research Article

Characterization of Newly Synthesized ZrFe$_2$O$_5$ Nanomaterial and Investigations of Its Tremendous Photocatalytic Properties under Visible Light Irradiation

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High functional ZrFe$_2$O$_5$ nanoparticles were synthesized using coprecipitation technique. The chemical composition of nanomaterials was studied by energy-dispersive X-ray (EDX). To observe the morphology, field emission scanning electron microscopy (FE-SEM) was used. X-ray diffraction (XRD) technique was utilized to appraise the structure of the synthesized material. The photocatalytic behavior of ZrFe$_2$O$_5$, nano-particles was investigated by measuring the degradation rate of toluidine blue O (TBO) dye in aqueous solution in the presence of ZrFe$_2$O$_5$ nano-particles under visible light irradiation. A steady decrease in absorption peak under visible light irradiation was observed by increasing exposure time. The degradation efficiency was observed as 92% after 140 min of exposure to visible light. Besides, ZrFe$_2$O$_5$ nanophotocatalyst could be recovered and recycled easily. The rate of TBO and total organic carbon (TOC) removal under visible light irradiation decreased by only 5% and 10%, respectively, after seven cycles of use, demonstrating the high photostability of the synthesized nano-photocatalyst material.

1. Introduction

Over the past few decades, environmental and water decontamination issues have become the foremost area of the scientific research [1–3]. To cope with such issues, there has been great interest among scientists in developing semiconductor photocatalysts with great prospective for environment protection applications such as air purification and water disinfection [1–7].

Among various photo-catalysts, transition metal oxides, such as TiO$_2$ [6] and NaNbO$_3$ [7], constitute a fascinating and promising class of semiconducting photocatalyst materials that have been widely studied for their photocatalytic activities under UV/Visible light. However, their industrial use in waste water treatment is limited due to their poor visible light absorption capability, reclaiming, and low quantum yield due to fast recombination of charge carriers generated by visible light irradiation [8]. In general, to utilize the visible part of the electromagnetic spectrum ($\lambda > 400$ nm), the bandgap of a photo-catalyst material must be narrow (up to 3.0 eV), and the preferred range of ionic character is between 20 and 30% [9–12].
Searching for new types of potential photo-catalytic materials that can be exploited by solar irradiation particularly under visible light (\(\lambda > 400\) nm) along with providing better stability by separating the electron-hole pairs more effectively has become an imperative issue in current photocatalysis and environmental research areas [1–10]. In this regard, better photo-catalytic activity has been observed on a few semiconductor composites combining ZrFeO\(_5\) with secondary semiconductor, such as TiO\(_2\) under visible light irradiation [13].

Therefore, we were motivated to prepare ZrFeO\(_5\) with the expectation of improved catalytic performance. Furthermore, to the best knowledge of authors, ZrFeO\(_5\) has neither been synthesized, nor its photocatalytic behavior has been reported in the literature. Hence, bridging the research gap in photocatalysis using novel ZrFeO\(_5\) nanomaterial is imperative. Hence, in the present work, we report synthesis of ZrFeO\(_5\) nanoparticles by coprecipitation technique and the investigation of their photo-catalytic properties under visible light irradiation for the degradation of toluidine blue O dye.

## 2. Experimental

### 2.1. Materials

All the chemicals (\(\text{ZrOCl}_2\cdot8\text{H}_2\text{O}, \text{FeCl}_3\cdot6\text{H}_2\text{O}, \text{NH}_3\cdot\text{OH}, \) and toluidine blue O 85% dye contents) used in the synthesis were purchased from Sigma Chemical Co. (St. Louis, MO, USA) and were used without further purification.

### 2.2. Synthesis of ZrFeO\(_5\) Nanoparticles

The ZrFeO\(_5\) nanoparticles were synthesized by chemical co-precipitation technique [14], in which 50 mL solution A of \(\text{ZrOCl}_2\cdot8\text{H}_2\text{O}\) was prepared by dissolving “a” grams in deionized water \(\text{FeCl}_3\cdot6\text{H}_2\text{O}\) and solution B was prepared by dissolving “b” grams in 50 mL as shown in Table 1. Solutions A and B were mixed slowly and stirred for 30 min at 65°C. To precipitate chloride precursors, the pH of the solution was raised to 10 by adding 3.5 M \(\text{NH}_3\cdot\text{OH}\) dropwise with continuous stirring; this process took about 120 min. The resulting mixture was left stirred for another 60 min. The precipitate of ZrFeO\(_5\) was filtered and washed with de-ionized water till chloride became free. The precipitate obtained was dried at 100°C for 90 min in an oven and calcined at 400°C for 4 hours in a muffle furnace.

### 2.3. Characterization

The structural analysis of ZrFeO\(_5\) nano-photocatalyst was performed using field emission scanning electron microscope (JEOL JSM 7401 F), energy-dispersive X-ray analysis, and X-ray diffractometer (D8 FOCUS 2220 Bruker AXS) with Cu K\(\alpha\) radiation (\(\lambda = 1.5418\) Å). Photocatalytic degradation studies were performed by using UV-Vis spectrophotometer (Shimadzu 3600, Japan).

### 2.4. BET Specific Surface Area Determination

BET specific surface area was determined by \(\text{N}_2\) adsorption at (77 K) with a Micromeritics ASAP 2000 system following the overnight treatment to degas the sample in vacuum at 130°C.

### 2.5. Photocatalytic Activity Test

The reaction mixture was prepared by adding the ZrFeO\(_5\) nanopowder catalyst (6 mg/L) to TBO dye solution having an initial concentration (\(C_o\)) of 0.05 mM. The mixture was then shifted into a glass reactor, where it was stirred for 30 min in dark to attain the adsorption equilibrium [10]. After the adsorption-desorption process, the reaction mixture was irradiated with visible light under constant stirring in oxygen atmosphere. In the photoreaction, the mixture was exposed to visible light (\(\lambda \geq 510\) nm) using a visible lamp (150 W) and a UV cut-off filter. After starting the irradiation process, 3 mL suspension was taken out (with 20 min time intervals) from irradiated mixture and immediately centrifuged at 4000 rpm for 5 min to separate the catalyst nano-particles from the suspension. Absorption of clear solution was taken using UV-Vis spectrophotometer (Shimadzu 3600, Japan) at 30°C and ambient pressure.

The percentage of degradation \(D\%)\) was calculated using equation [10]:

\[
D\% = \frac{A - \hat{A}}{A} \times 100, \tag{1}
\]

where \(\hat{A}\) and \(A\) are the absorbance of the mixture before and after degradation, respectively.

### 2.6. Stability and Reusability Test

Photo-catalyst activity of same ZrFeO\(_5\) nanomaterial was tested repeatedly for seven (7) times. After each use, photo-catalyst was separated, washed, dried and 3 mg of fresh photo-catalyst was added at the end of each cycle to compensate for the loss of catalyst during use.

### 2.7. Total Organic Carbon (TOC) Removal Test

TOC removal was estimated to check mineralization of TBO with ZrFeO\(_5\) (Figure 6). The values of TOC were determined from illuminated mixture of 0.05 mM dye concentration and catalyst load of 6 mgL\(^{-1}\) using TOC analyzer (Thornton 770 Max with 5000TOC sensor).

The degree of TBO mineralization was estimated by determining the decrease in TOC in the reaction solution [10].

## 3. Results and Discussion

### 3.1. Characterization of ZrFeO\(_5\)

FE-SEM images of the as-synthesized ZrFeO\(_5\) nano-particles (\(\text{ZrO}_2 : \text{Fe}_2\text{O}_3 = 1:1\)) are shown in Figure 1. FE-SEM analysis showed that

| Sample no. | \(\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}\) “\(a\)” g/50 mL in solution A | \(\text{FeCl}_3 \cdot 6\text{H}_2\text{O}\) “\(b\)” g/50 mL in solution B | \(\text{ZrO}_2 : \text{Fe}_2\text{O}_3\) (molar) |
|------------|-------------------------------------------------|-------------------------------------------------|----------------------------------|
| S1         | 1.62                                            | 2.72                                            | 1:1                               |
| S2         | 1.62                                            | 2.04                                            | 4:3                               |
| S3         | 1.62                                            | 1.36                                            | 2:1                               |
| S4         | 1.62                                            | 0.68                                            | 4:1                               |
ZrFe$_2$O$_5$ nano-particles comprise a mean diameter of 30 nm. The chemical composition of the ZrFe$_2$O$_5$ nano-particles was appraised by energy dispersive X-ray analysis (EDX) as shown in Figure 2. It is clear from Figure 2(b) that for the 1:1 molar ratio, the average composition of Zr/Fe is 68:32.

The phase and crystallinity of ZrFe$_2$O$_5$ nano-particles before and after the calcinations were examined by X-ray diffraction technique on an MX Labo powder diffractometer using Cu Ka radiation (40 kV, 20 mA), at the rate of 2°/min over the range of 20–80°. The XRD patterns showed that ZrFe$_2$O$_5$ nano-particles were amorphous prior to calcinations (Figure 3(a)). However, after calcinations at 400°C for 4 hours, the nano-particles had transformed into a crystalline ZrFe$_2$O$_5$ phase (Figure 3(b)).

3.2. Bandgap Energy. Prior to investigating the photocatalytic action, it is imperative to appraise the optical absorption of the ZrFe$_2$O$_5$ nano-particles for the motive that the UV Vis absorption edge is associated with energy band of the semiconductor catalyst [15]. The optical bandgap (E$_g$) of ZrFe$_2$O$_5$ nano-particles estimated from the Tauc plot is 2.4 eV, signifying that the synthesized nanomaterial can absorb visible light.

3.3. UV/Vis Absorption Spectra of TBO Degradation. UV/Vis absorption spectra of TBO degradation with ZrFe$_2$O$_5$ over a period of 120 min by absorbing visible light are shown in Figure 4.

3.4. Mechanism of Photocatalytic Reactions. The photocatalysis using visible light/ZrFe$_2$O$_5$ is based on adsorption of photons with energy higher than 2.4 eV ($\lambda \geq 510$ nm), resulting in initiating excitation related to charge separation event. High-energy excited states of electron and hole pairs arise when semiconductors possessing wide band gap are subjected to irradiation higher than their band gap energy. The outcome is the promotion of an electron in the conductive band ($e_{CB}^-$) and a positive hole electron in the valence band ($h_{VB}^+$) as shown in (2). The $h_{VB}^+$ and $e_{CB}^-$ are powerful oxidizing and reducing agents, respectively. The $h_{VB}^+$ reacts with TBO dye resulting in its oxidation. Consequently, CO$_2$ and H$_2$O are produced as end products (7). The $h_{VB}^+$ can also oxidize organic compounds by reacting with water to generate $^\cdot$OH (8). Due to electron preferring nature of hydroxyl radical ($^\cdot$OH), it can oxidize almost all electron rich organic dyes, ultimately converting them to CO$_2$ and water (9). The conductive band $e_{CB}^-$ can react with O$_2$ forming an anion radical superoxide as shown in (3). Further reactions can lead to the formation of hydrogen peroxide which leads to the formation of $^\cdot$OH. Consider the following:

$$ZrFe_2O_5 + h_v (\lambda \geq 510 \text{ nm}) \rightarrow ZrFe_2O_5 (e_{CB}^- + h_{VB}^+)$$

(2)

$$\begin{align*}
(O_2)_{ads} + e_{CB}^- & \rightarrow \cdot O_2^- \\
O_2^- + H^+ & \rightarrow HO_2 \\
2HO_2 & \rightarrow H_2O_2 + O_2 \\
H_2O_2 + h_v & \rightarrow 2^\cdot OH
\end{align*}$$

(3–6)

$$h_{VB}^+ + TBO \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O$$

(7)

$$H_2O + h_{VB}^+ \rightarrow ^\cdot OH + H^+$$

(8)

$$^\cdot OH + TBO \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O$$

(9)
During photo-catalytic degradation, the presence of dissolved oxygen restricts the recombination process on ZrFe$_2$O$_5$ (e$_{CB}^-$ / h$_{VB}^+$) which results in maintaining the electroneutrality of the ZrFe$_2$O$_5$ particles. Hence, effective photocatalytic degradation of TBO dye is achieved by the reduction process of oxygen and the oxidation of TBO simultaneously to avoid the accumulation of electron in the conduction band and thus reducing the rate of recombination of e$_{CB}^-$ and h$_{VB}^+$.  

3.5. Evaluation of Photocatalytic Activity. TBO dye was taken as a test pollutant. The photo-catalytic activity was evaluated by studying the disintegration rates of TBO dye in the presence of samples S1, S2, S3, and S4 under visible light irradiation through a cut-off filter ($\lambda \geq 510$ nm). A 0.05 mM solution of TBO decomposed rapidly under visible light when sample S1 was used, highlighting their photo-catalytic activity. The dye solution was degraded by approximately 92% in 140 min under visible light for sample S1 (Figure 5). However, degradation of dye decreased with the increase in the amount of zirconium in the nano-particles which shows consistency with the optical absorbance results (Figure 4). For comparison we also studied the photo-catalytic behavior of bulk ZrFe$_2$O$_5$ as shown in Figure 5. The enhancement in the photo-catalytic behavior of ZrFe$_2$O$_5$ nano-particles can be ascribed to considerably higher specific surface area of nano-particles compared with the bulk ZrFe$_2$O$_5$ (Table 2).

By contrast, the TBO without ZrFe$_2$O$_5$ nano-particles as a catalyst under visible light was stable, and only 2% had degraded after 140 min. It is clearly seen from Figure 5 that under visible light, sample S1 of the ZrFe$_2$O$_5$ nano-particles shows 92% degree of mineralization after 140 min. This is the first report on photo-catalytic degradation of TBO with ZrFe$_2$O$_5$ nano-particles in a relatively shorter time with a high stability suggesting its reusability. Previously, Shakir et al. [10] observed degree of mineralization as 85% after 3 hours of degradation of TBO with Cu$_{0.33}$MoO$_3$ nanorods under visible light irradiation. In a new study reported by Ito et al. [16], zirconium ferrite particles were used for elimination of phosphate from water of sewage treatment plants to avert eutrophication of semiclosed bay of Tokyo. They further discovered good adsorbance of phosphate ions onto zirconium ferrite particles. Magnetic separation characteristic indicated that 90% of phosphate in the discharge water of sewage plants could be eliminated in 5 min [16]. Besides, the zirconium ferrite adsorbent could be used repeatedly.

3.6. Stability Evaluation of ZrFe$_2$O$_5$ Nanophotocatalyst. The photo-catalytic stability and long-term use of these ZrFe$_2$O$_5$
Figure 5: Photo-catalytic degradation profile of the TBO mineralization concentration in the solution (50 mL) with samples S1, S2, S3, and S4 and bulk ZrFe$_2$O$_5$ versus the exposure time to visible light irradiation.

Table 2: Specific surface area of ZrFe$_2$O$_5$ nanoparticles of different molar ratios calcined at 400°C and % age degradation of TBO dye.

| Sample no. | ZrO$_2$ : Fe$_2$O$_3$ (molar) | Crystallite size (nm) | BET specific surface area m$^2$/g | Degradation of TBO dye |
|-----------|-------------------------------|----------------------|----------------------------------|------------------------|
| S1        | 1 : 1                         | ~23                  | 83.14                            | 92%                    |
| S2        | 4 : 3                         | ~26                  | 74.65                            | 81%                    |
| S3        | 2 : 1                         | ~29                  | 63.11                            | 69%                    |
| S4        | 4 : 1                         | ~33                  | 56.92                            | 53%                    |

nano-particles were also evaluated by recycling the photocatalyst for up to seven reaction cycles and measuring the degradation rates of TBO, as shown in Figure 7. After each photo-catalytic reaction, aqueous solution was centrifuged at 4000 rpm for 5 min to isolate the catalyst from aqueous solution and redispersed it in fresh TBO solution for another cycle. The ZrFe$_2$O$_5$ nanomaterial showed stable photocatalytic behavior even after seven (7) cycles of reactions, demonstrating the high photostability of the ZrFe$_2$O$_5$ nanoparticles. The total organic carbon (TOC) was also measured to evaluate the total destruction of TBO (Figure 6). The rate of TBO and TOC removal under visible light irradiation decreased by only 5% and 10%, respectively, after seven cycles, demonstrating the high photostability of the synthesized photo-catalyst against visible light.

One of the factors that improved the photo-catalytic performance of ZrFe$_2$O$_5$ to a great extent is the size shrinkage of ZrFe$_2$O$_5$, thereby enlarging its specific surface area, due to which it could adsorb more TBO to photodegrade on its surface. From the electronic structure point of view, the band potentials of ZrFe$_2$O$_5$ accomplish a straddling gap, which may make possible the transfer of charge carriers and retard the e$^-$h$^+$ recombination, ensuring the superior photo-catalytic performance [15, 17–19]. Furthermore, the superior reactivity of the ZrFe$_2$O$_5$ was observed on samples with appropriate 1 : 1 molar ratios of ZrO$_2$ : Fe$_2$O$_3$, suggesting that there is a critical ratio for such a positive synergistic effect. Above this critical ratio, excessive zirconium covers the active sites and hinders the visible light penetration in the sample to excite ZrFe$_2$O$_5$. This correspondingly deteriorates the photo-catalytic activity, as a consequence of increased recombination of the photogenerated charges on ZrFe$_2$O$_5$. However, optimum molar ratios of ZrO$_2$ : Fe$_2$O$_3$ became the...
cause for a quicker separation of electron-hole pair resulting in slower recombination.

4. Conclusions

A new type of photo-catalyst ZrFe$_2$O$_5$ nano-particles has been synthesized by co-precipitation technique, and its photo-catalytic properties were investigated. The photocatalytic measurements showed that ZrFe$_2$O$_5$ nano-particles under visible light could be efficiently used for the photocatalytic degradation of toluidine blue O dye. Photodegradation efficiency in the absence of ZrFe$_2$O$_5$ nano-particles showed no significant change in the absorption maximum of toluidine blue O. Although bulk ZrFe$_2$O$_5$ exhibits the photo-catalytic ability to decompose TBO dye under visible light irradiation, however, degradation with ZrFe$_2$O$_5$ nanoparticles is tremendously more efficient than that of bulk ZrFe$_2$O$_5$.

Conflict of Interests

Authors have no direct financial relation with the commercial identities mentioned in the paper that might lead to a conflict of interests.

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