Visible-light active and magnetically recyclable Ag-coated Fe$_3$O$_4$/TiO$_2$ nanocomposites for efficient photocatalytic oxidation of 2,4-dichlorophenol

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Received 16 November 2017; Accepted 21 April 2018

Abstract

Fe$_3$O$_4$/TiO$_2$/Ag nanocomposites with different amounts of silver were prepared using the sol–gel method. X-ray diffraction, energy-dispersive X-ray spectroscopy, field-emission scanning electron microscopy, transmission electron microscopy, diffuse reflectance spectroscopy, Brunauer–Emmett–Teller surface areas, and the vibration sample magnetometry were used to characterize these nanocomposites. Photocatalytic activity of the nanocomposites was examined via decomposing the solution of 2,4-dichlorophenol (2,4-DCP) exposed to UV/Vis irradiation. Exposing the solution to pure TiO$_2$ and ternary Fe$_3$O$_4$/TiO$_2$/Ag nanocomposite, we obtained 30% and almost 60% degradation of 2,4-DCP after 180 min irradiation, respectively. The excellent photocatalytic activity of Fe$_3$O$_4$/TiO$_2$/Ag samples can be related to the surface plasmon resonance effect of Ag nanoparticles deposited on Fe$_3$O$_4$/TiO$_2$ nanocomposite. The Fe$_3$O$_4$/TiO$_2$/Ag nanocomposites were retrieved from the solution of reaction through a constant magnetic bar, followed by assessing their photocatalytic activity after three repetitive recycling cycles. Afterward, this nanocomposite might be applied as an efficient and reusable photocatalyst.

Keywords: Ag nanoparticles; Plasmonic photocatalysts; Fe$_3$O$_4$; Oxidation; 2,4-Dichlorophenol

1. Introduction

Organic pollutants treatment by the processes of nanomaterials-based advanced oxidation in various wastewaters is among the main environmental concerns [1–3]. To handle this issue via effective procedures for different wastewaters, researchers have focused on advanced oxidation processes because of their ability to generate strongly oxidizing radicals to degrade organic pollutants into harmless chemicals such as CO$_2$ and H$_2$O. Heterogeneous photocatalysis using titanium dioxide (TiO$_2$) is an efficient advanced oxidation method for the fast elimination of organic wastes from the effluent [4–8]. However, the photocatalytic effectiveness of TiO$_2$ nanomaterials cannot satisfy the practical requirements under sunlight irradiation since the great intrinsic band gap (>3.2 eV) of TiO$_2$ severely restricts utilization of the visible light. Besides, the fast electron–hole recombination in TiO$_2$ often results in a low quantum yield and poor photocatalytic activity [9,10]. To use ample and green sunlight appropriately, strategies such as metal/non-metal elements doping and coupling with other functional materials have been selected to generate visible-light-driven TiO$_2$-based photocatalysts through introducing a natural band gap with lower level of energy, suppressing electron–hole recombination rate, and increasing the surface charge carrier transfer rate of TiO$_2$ [11–18]. The composite of TiO$_2$ and metal nanomaterials with a work function lower than the conduction band of TiO$_2$, such as Ag and Au [19,20], has been found to solve the problem and promote the TiO$_2$
photocatalytic activity in the UV or visible light region [21–27]. In the photocatalysis process, these metal nanomaterials can function superior electron acceptor/transport materials to enhance the photo-induced electrons’ migration and inhibit the charge recombination in electron transfer processes. This function is attributed to the electronic interaction between TiO$_2$ and these nanoparticles that promotes the photocatalytic performance [28–32]. Ag has been used to develop plasmonic photocatalyst because of indicating the presence of surface plasmon resonance (SPR) at the visible light region [33,34]. In addition, SPR may accelerate the isolation of electrons and holes in a semiconductor catalyst under exposure to visible light [35–37]. It has been evidenced that Ag coupled with semiconductor plasmon resonance provides an efficient tool in the visible region [19,38–43]. Additionally, Ag has decent physicochemical features and great electrical conductivity [44]. Ag nanoparticles in semiconductors may generate Schottky connections, preventing electrons and holes recombination [45]. A major disadvantage of the application of TiO$_2$ in water treatment is the inconvenience to recycle these photocatalysts due to their good dispersive properties [46–48]. Common isolation techniques, including filtration and centrifugation, can result in catalyst loss and consumption of energy; magnetic separation renders a feasible method for eliminating and recycling materials using external magnetic fields [49–54]. As a typical magnetic material, Fe$_3$O$_4$ can solve the problem of TiO$_2$ photocatalyst recovery when combined with TiO$_2$. The magnetic TiO$_2$/Fe$_3$O$_4$ composites showed a rapid aggregation under the external magnetic field, which can be useful for separation of these particles in application [55–57].

In the present study, we report the synthesis of TiO$_2$/Fe$_3$O$_4$ nanocomposites containing different quantities of silver (FTA samples). Morphological and structural features of the obtained samples were investigated by different analysis techniques including X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM)/energy-dispersive X-ray spectroscopy (EDX), diffuse reflectance spectroscopy (DRS), N$_2$ physisorption, vibration sample magnetometry (VSM), and transmission electron microscopy (TEM) techniques. By employing the photocatalytic oxidation of 2,4-dichlorophenol (2,4-DCP) as a model reaction, we investigated the efficiency of nanocomposites’ photoactivity. Chlorophenols are toxic chemicals used in many industrial applications such as petrochemicals, pesticides, dye intermediates, and paints [58]. Especially, 2,4-DCP is an important chemical precursor for the manufacture of a widely used herbicide, 2,4-dichlorophenoxy acetic acid [59]. However, 2,4-DCP may cause some pathological symptoms and changes in human endocrine systems. These compounds are exposed to the skin and gastrointestinal tract. Chlorophenols persistence and bioaccumulation both in animals and in humans has been recently the subject of intense research [60–62]. So, it would be crucial to seek innovative and effective ways to minimize the harm of chlorophenols in the environment. The outstanding properties associated to the prepared nanocomposites suggests that they can be applied as a novel, visible-light harvesting catalyst for given applications in photocatalysis. The ternary nanocomposites exhibited an improved efficiency for 2,4-DCP photocatalytic oxidation.

2. Experimental methodology

2.1. Materials

FeCl$_3$·6H$_2$O (Merck no. 103943) and FeSO$_4$·7H$_2$O (Merck no. 103965) were used for the synthesis of Fe$_3$O$_4$ nanoparticles (NPs). Tetraisopropyl orthotitanate (TIP, Merck no. 8.21895), anhydrous ethanol, ammonia, and high-purity 2,4-DCP (98%, Merck no. 803774) for photocatalytic experiments as probe molecules were purchased from Merck Company, Germany. Silver nitrate (AgNO$_3$, 99.9%) was obtained from Merck Company, Germany (Merck no. 101510). All the reagents were of analytic grade and applied without additional purification. All aqueous solutions were prepared using double distilled water.

2.2. Preparation of Fe$_3$O$_4$ NPs

Fe$_3$O$_4$ nanoparticles were synthesized by chemical precipitation technique according to the procedure mentioned by Laurent et al. [63]. In this procedure, the Fe$_3$O$_4$ was precipitated under an inert atmosphere (nitrogen 99.999%) and alkaline conditions.

2.3. Preparation of Fe$_3$O$_4$/TiO$_2$ nanocomposite

In this section, 0.1 g Fe$_3$O$_4$ NPs was prepared according to the procedure mentioned in section 2.2. Next, 4 mL TIP was mixed with 70 mL anhydrous ethanol and ultrasonicated (ELMA-Germany, E60H, ultrasound bath) for 1 h to form the solution A. Solution B was prepared by diluting 3 mL acetic acid to 90 mL deionized water. Solution B was added to solution A dropwise at 50°C through the mechanical stirring. Then, the solution was stirred for 30 min. Finally, after cooling to room temperature, the solid product from the suspension was separated by employing a magnet, washed with ethanol and water for several times, and dried in a vacuum at 12 h at 60°C. The resultant powder was annealed at 300°C for 1 h to produce an Fe$_3$O$_4$/TiO$_2$ (FT) nanocomposite. From now on, these samples will be shown as FT. Also, pure TiO$_2$ in the same route was synthesized to control the experiments.

2.4. Ag loading onto TiO$_2$/Fe$_3$O$_4$ sample

The prepared FT sample (section 2.3) was decorated with Ag nanoparticles according to the procedure reported by Huerta Aguilar et al. [64]. For this purpose, 0.5 g of FT was suspended by sonication in 10 mL of deionized water to which AgNO$_3$ (0.5, 1.0, and 2.0 mL, 100.0 mM) was added slowly; the resultant solution was stirred at 20°C for 30 min, and then Na$_2$CO$_3$ (0.5 mL, 1.0% w/v) was slowly added. The obtained slurry was separated and dried at room temperature. These nanocomposites were labeled as FTA (a), where (a) is the quantity of silver achieved by EDX analysis.

2.5. Characterization

Using an X-ray diffractometer (Siemens, D5000, Germany), the XRD patterns were recorded using Cu K$_\alpha$ radiation as the X-ray source. The diffractograms were recorded within the 20 range of 20°–80°. The morphology of the obtained samples was studied using scanning electron microscope (SEM,
Vegall-Tescan Company, Czech Republic) having an EDX. The UV/Vis diffuse reflectance (DR) spectra of the samples were recorded using an Ava Spec-2048TEC spectrometer. The microstructure and morphology of the prepared samples were studied using a TEM device (Philips CM30 300kV). The nitrogen physisorption assessments were done by a Quantachrome Autosorb-1-MP (Micromeritics). The Brunauer–Emmett–Teller (BET) areas were determined by static nitrogen physisorption at −196°C followed by outgassing at 200°C until the pressure was lower than 5 mbar. VSM was manufactured by Meghnatis Daghigh Kavir Company of Kashan, Iran.

2.6. Photocatalytic oxidation of 2,4-DCP

We selected 2,4-DCP as a model of organic pollutant to study the photocatalytic efficiency of the obtained samples. For photocatalytic oxidation experiments, we used a 500 W OSRAM Halogen lamp (ECO) with a wavelength range of 350–800 nm, and the predominant peak at 575 nm. In each photocatalytic oxidation experiment, the baker containing photocatalyst and 100 mL 2,4-DCP aqueous solution (40 mg/L) in the dark was stirred first for 10 min for desorption/adsorption equilibrium, followed by turning the lamp on for 180 min. At certain times, 2 mL of solution were withdrawn and filtered to eliminate the photocatalyst and analyzed using Rayleigh UV-2601 UV/Vis spectrophotometer (λ max = 227 nm).

3. Results and discussion

3.1. X-ray diffraction analysis

Figs. 1 and 2 show the XRD patterns of the synthesized samples. In XRD pattern of FeO4 NPs (Fig. 1(a)), we detected the characteristic diffractions at 2θ = 30.2°, 35.6°, 43.5°, 54.3°, 57.4°, and 63.1° that are indexed to the reflection of cubic spinel structure of the FeO4. This result is consistent with those reported using JCPDS card number 19-0629 [65], suggesting that phase purity of FeO4 and well-resolved diffraction peaks show the good crystallinity of FeO4 NPs. In XRD pattern of pure TiO2 (Fig. 1(b)), the strong diffractions at 2θ = 25.3°, 37.7°, 48.0°, 53.8°, 55.0°, and 62.6° confirmed pure anatase phase formation [66]. In XRD pattern of FT sample (Fig. 1(c)), the diffractions became relatively weaker than those of the pure TiO2 and FeO4 (Fig. 1(b)) but matched well with the XRD patterns of TiO2. Also, we detected some weak diffractions of Fe2O3 nanoparticles in Fig. 1(b), which may indicate that Fe2O3 is coated by TiO2 and confirm that the sample contains Fe2O3 and TiO2. Figs. 2(a)–(c) showed the XRD patterns of FTA samples. Four peaks at 2θ values of 38.048°, 44.133°, 64.303°, and 77.326° corresponding, respectively, to (111), (200), (220), and (311) planes of silver in the standard powder diffraction card of JCPDS file no. 04-0783 were reported. Due to the low amount, high distribution, and small crystalline dimensions of Ag particles, we did not detect the main diffractions of metallic Ag in XRD pattern of the ternary FTA nanocomposites [67]. Fig. 2(d) shows the XRD pattern of TiO2/Ag (TA) sample. We detected the main diffractions for anatase phase of TiO2 in this sample but did not detect the main diffractions for metallic silver.

The mean TiO2 crystal size at 2θ = 25.3° using Scherrer equation for each sample was calculated as follows [68]:

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

(1)

where \( D \) is the mean crystallite size; \( \lambda \) is the X-ray wavelength (1.54056 Å); \( \beta \) is the diffraction full width at half maximum in radian; \( K \) is a coefficient (0.89); and \( \theta \) is the angle’s diffraction at the peak. The TiO2 crystal size in all the obtained nanocomposites is within the nanosized range (Table 1).

The lattice parameters (\( a = b \neq c \)) corresponding to tetragonal crystalline structure were obtained for (101) crystal plane of anatase phase using Eq. (2):

\[ 1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2 \]  

(2)

Considering the interplanar spacing \( (d_{hkl}) \), the distance between adjacent planes in the set \( (hkl) \) can be determined using the Bragg law:

\[ d_{hkl} = \frac{\lambda}{2 \sin \theta} \]  

(3)

The cell volume (tetragonal one) was calculated as:

\[ V = a^2c \]  

(4)
where $a$ and $c$ are considered lattice parameters. Table 1 shows the lattice parameters of prepared samples.

The obtained values of the lattice parameters for TiO$_2$ in the prepared samples matched well with the TiO$_2$’s anatase structure (JCPDS, 78-2486). The diffraction peaks and lattice parameters of TiO$_2$ remain unchanged, confirming that silver atoms do not enter the TiO$_2$ framework and loading on the TiO$_2$ nanoparticles surface and did not change the crystal structure of TiO$_2$.

Table 1
<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Crystal size (nm)</th>
<th>$A$ (Å)</th>
<th>$c$ (Å)</th>
<th>Cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Anatase</td>
<td>10.38</td>
<td>3.77</td>
<td>9.59</td>
<td>136.30</td>
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<td>FT</td>
<td>Anatase</td>
<td>7.11</td>
<td>3.79</td>
<td>9.37</td>
<td>134.87</td>
</tr>
<tr>
<td>TA</td>
<td>Anatase</td>
<td>8.14</td>
<td>3.77</td>
<td>9.76</td>
<td>138.71</td>
</tr>
<tr>
<td>FTA (0.55)</td>
<td>Anatase</td>
<td>8.14</td>
<td>3.78</td>
<td>8.99</td>
<td>127.73</td>
</tr>
<tr>
<td>FTA (2.09)</td>
<td>Anatase</td>
<td>8.31</td>
<td>3.80</td>
<td>9.28</td>
<td>134.40</td>
</tr>
<tr>
<td>FTA (3.56)</td>
<td>Anatase</td>
<td>7.35</td>
<td>3.78</td>
<td>9.14</td>
<td>130.56</td>
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Table 2
<table>
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<th>Sample</th>
<th>$E_{bg}$ (eV)</th>
</tr>
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<tbody>
<tr>
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<tr>
<td>FT</td>
<td>2.70</td>
</tr>
<tr>
<td>TA</td>
<td>3.02</td>
</tr>
<tr>
<td>FTA (0.55)</td>
<td>2.80</td>
</tr>
<tr>
<td>FTA (2.09)</td>
<td>2.60</td>
</tr>
<tr>
<td>FTA (3.56)</td>
<td>2.85</td>
</tr>
</tbody>
</table>

3.2. UV/Vis absorption spectra

The solid-state UV/Vis spectra (Fig. 3(A)) were recorded for all samples. There is a broad intense absorption around 400 nm in the DR spectrum of pure TiO$_2$ owing to the charge-transfer from the valence band made by 2p orbital’s of the oxide anions to the conduction band generated by 3d $t_2g$ orbitals of the Ti$^4+$ cations [69]. In the DR spectra of FTA samples, we can observe the absorption shoulder peak in the range between 360 and 500 nm. These absorption shoulders result from the post-broadening SPR peak [70]. In the visible region, the existence of localized surface plasmon resonance (LSPR) would enable the ternary nanocomposites to show broad and strong absorption [71,72]. The mechanism concerning the interaction of noble metals mechanism with TiO$_2$ consists of several and simultaneous processes: Ag NPs deposited on TiO$_2$ exhibit broad Schottky obstacles functioning as traps of the electron that simplify the electron–hole isolation, improve the process of interfacial electron transfer and also electrons injection into the conduction band, and enhance OH radicals formation efficiency. On the other hand, the spectra of absorption showed that transitions at lower energy are probable since clusters of metal attached to TiO$_2$ surface bring about localized energy levels within the TiO$_2$ band gap. As a result, the electrons of valence band are excited at wavelengths above 370 nm [73,74]. We also measured the energy of band gap of the synthesized samples from the DR spectra according to Eq. (5) [75]:

$$[F(R) \nu]^2 = A (\nu - E_{bg})$$  \hspace{1cm} (5)

where $A$ is a constant, $F(R)$ is the function of Kubelka–Munk, and $E_{bg}$ is the band gap. The $E_{bg}$ data of samples are shown in Table 2. The FTA samples band gap decreased slightly compared with TiO$_2$ (Table 2). Ag nanoparticles loading on the TiO$_2$ surface affect the TiO$_2$ optical properties significantly.

3.3. FESEM/EDX and TEM analysis

Figs. 4 and 5 show the FESEM images of the synthesized samples at two magnifications. The FESEM images of FTA samples show that TiO$_2$ coated the Fe$_3$O$_4$ surface nanoparticles and exhibit the decoration surface of TiO$_2$ by metallic silver nanoparticles. To confirm successful decoration of FT nanocomposites with Ag, the samples were analyzed by electron mapping image analysis (Fig. 6). The images of the same particles were obtained for Ti, O, Fe, and Ag. For FTA samples, Ti had a broader distribution compared with Fe, showing that Fe is set in the interior section of the nanocomposites. In comparison, Ti and Ag lie on the outer layer of the nanoparticles of Fe$_3$O$_4$. These results indicate that Ag nanoparticles are well spread on the surface of the FT nanocomposite. Fig. 7 displays the EDX spectra analysis of the synthesized samples while Table 3 lists their composition. Among the four elements (Ti, Fe, O, and Ag) presented, the higher Ti content compared with magnetite could be resulting from the formation of the TiO$_2$ layer coated Fe$_3$O$_4$ nanoparticles. The Ag signal is around ~3 keV [76], which may indicate the existence of Ag nanoparticles in photocatalyst. Fig. 8 depicts the TEM image of the best photocatalyst FTA (2.09) at different magnifications. The dark grains of magnetite nanoparticles
(Fe$_3$O$_4$) are fully surrounded via grey TiO$_2$ layer that contains TiO$_2$ nanoparticles. Moreover, the TEM images also show that Ag nanoparticles are well dispersed on the FT sample surface.

### 3.4. N$_2$ physisorption analysis

The results of N$_2$ adsorption–desorption isotherms are shown in Fig. 9. The sorption isotherms for the entire prepared samples correspond to the type IV isotherm based on the classification of IUPAC [77]. Textural and structural parameters of the obtained samples are shown in Table 4. Specific surface areas and average pore diameter were calculated according to BET. Pore volumes were extracted from the desorption branch according to the BJH model. The $S_{\text{BET}}$ of the FT sample is greater than the pure TiO$_2$, but the average pore diameter of FT sample is smaller than pure TiO$_2$. This observation may confirm that the nanolayer of TiO$_2$ covered the Fe$_3$O$_4$ nanoparticles. The BET surface area of the ternary nanocomposites (FTA samples) is greater than that of the starting sample (FT sample), indicating the loading of Ag nanoparticles on the FT sample surface.

### 3.5. Magnetic properties of the nanocomposites

The saturation magnetization ($M_s$) of the samples was measured to study the magnetic reaction of the magnetic
photocatalysts are superparamagnetic at room temperature [78]. It is worth noting that the $M_s$ value of the Fe$_3$O$_4$ nanoparticles is significantly higher than that of FT and FTA (a) samples, which is because the Fe$_3$O$_4$ nanoparticles are covered with an anatase TiO$_2$ layer in the FT and FTA (a) samples. The small decrease in $M_s$ value of the FTA (a) samples in comparison with that of the FT sample (Fig. 10) can be explained by the slight increase in mass and size owing to the adherence of Ag nanoparticles to the surface of magnetic composites. Furthermore, no significant variation was seen in the coercivity. Such excellent magnetic properties imply a strong magnetic responsivity on the samples, enabling them to be recycled easily from solution through an external magnetic force. Also, simple, rapid separation and redispersion of the FTA (a) samples can be recognized.

3.6. Photocatalytic oxidation of 2,4-DCP under visible light

To investigate the photocatalytic oxidation activity of the prepared samples for removal of contaminants from wastewater, we selected photocatalytic oxidation of 2,4-DCP as a model reaction. Fig. 11 shows the photocatalytic oxidation of 2,4-DCP under UV/Vis irradiation. Under UV/Vis irradiation, the ternary photocatalyst with 2.09 wt% Ag, FTA (2.09) sample showed the highest performance for 2,4-DCP.
photocatalytic oxidation, and we achieved ~55% degradation after 180 min irradiation. The higher photocatalytic efficiency of ternary FTA (a) nanocomposites compared with other photocatalysts can be explained by the SPR influence of Ag nanoparticles and the lower band gap of ternary nanocomposite (Table 2). Fig. 12 shows the mechanism proposed in the present study for the formation of FTA sample and photocatalytic oxidation of 2,4-DCP over FTA sample. In ternary nanocomposites, high-energy electrons were generated because of LSPR of metallic silver nanoparticles under UV/Vis irradiation. These generated electrons were transferred and excited from Ag nanoparticles to the conduction band of TiO$_2$ and the generated holes remained on the Ag nanoparticles and oxidized the organic target [79]. The adsorbed oxygen molecules on the TiO$_2$ surface trapped the electron from the conduction band of TiO$_2$, and thus, some active species such as OH$^-$ and O$_2$$^•$ radicals were produced. These active species attacked 2,4-DCP molecules and decomposed them. Because of the heterojunction formation, many defects exist in TiO$_2$ that decrease the energy of conduction band of TiO$_2$ [80] in the ternary nanocomposite. Moreover, TiO$_2$ can absorb UV/Vis irradiation and generate electrons and holes.

Fig. 6. Elemental mapping of (a) TiO$_2$, (b) FT, (c) TA, (d) FTA (0.55), (e) FTA (2.09), and (f) FTA (3.56).
Fig. 7. EDX spectra of (a) TiO$_2$, (b) FT, (c) TA, (d) FTA (0.55), (e) FTA (2.09), and (f) FTA (3.56).
Table 3
Elemental chemical analysis of the prepared samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
<th>O (wt%)</th>
<th>Ti (wt%)</th>
<th>Fe (wt%)</th>
<th>Ag (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>8.12</td>
<td>14.24</td>
<td>41.68</td>
<td>35.96</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FT</td>
<td>6.31</td>
<td>9.80</td>
<td>40.15</td>
<td>41.99</td>
<td>1.75</td>
<td>–</td>
</tr>
<tr>
<td>TA</td>
<td>10.26</td>
<td>12.43</td>
<td>37.12</td>
<td>36.13</td>
<td>–</td>
<td>4.06</td>
</tr>
<tr>
<td>FTA (0.55)</td>
<td>8.53</td>
<td>15.34</td>
<td>43.82</td>
<td>31.66</td>
<td>0.09</td>
<td>0.55</td>
</tr>
<tr>
<td>FTA (2.09)</td>
<td>8.73</td>
<td>12.24</td>
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<td>11.73</td>
<td>38.60</td>
<td>35.81</td>
<td>1.53</td>
<td>3.56</td>
</tr>
</tbody>
</table>

Fig. 8. TEM image of FTA (2.09) nanocomposite at various magnifications.
light. These charge carriers can participate in the destruction of 2,4-DCP and produced more oxygen active species like OH$^-$ and O$_2^-$ radicals. Accordingly, the photocatalytic activity was enhanced due to more charge carrier generation. FTA (a) samples can offer a larger surface area (Table 4), contributing to the enhanced photocatalytic function induced by its improved photon absorption [81]. Also, the higher silver loading had shading effect, blocked the light reaching the TiO$_2$ surface, and resulted in a lower photocatalytic performance [82,83].

3.7. The effect of photocatalyst amount

At low photocatalyst loading, the removal of the organic compound 2,4-DCP increased linearly with the catalyst loading. However, the presence of excess photocatalyst in the aqueous solutions could cause a shielding effect in penetration of light [84]. In this regard, the effect of the photocatalyst dose in suspension was investigated for an optimal condition (Fig. 13). The optimal photocatalyst amount is 10 mg/100 mL for 2,4-DCP degradation.

![Fig. 9. N$_2$ adsorption–desorption isotherms for (a) TiO$_2$, (b) FT, (c) TA, (d) FTA (0.55), (e) FTA (2.09), and (f) FTA (3.56).](image-url)
3.8. Kinetic study

The kinetic parameters for the elimination of 2,4-DCP are shown in Fig. 14 and Table 5. The obtained results show the reaction is the first-order type, with its kinetics expressed as \( \ln(C/C_0) = k_{\text{obs}} t \). In this equation, \( k_{\text{obs}} \) (min\(^{-1}\)) is the constant of apparent rate, and \( C_0 \) and \( C \) are the initial concentration and concentration of 2,4-DCP at reaction.

### Table 4
Textural and structural parameters of the prepared sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>Average pore diameter (nm)</th>
<th>Pore volume (cm(^3)/g)</th>
</tr>
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<tbody>
<tr>
<td>T</td>
<td>91.01</td>
<td>7.15</td>
<td>0.17</td>
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<tr>
<td>FT</td>
<td>124.87</td>
<td>4.83</td>
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<tr>
<td>TA</td>
<td>90.61</td>
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</tr>
<tr>
<td>FTA (0.55)</td>
<td>163.65</td>
<td>4.71</td>
<td>0.22</td>
</tr>
<tr>
<td>FTA (2.09)</td>
<td>159.43</td>
<td>5.17</td>
<td>0.19</td>
</tr>
<tr>
<td>FTA (3.56)</td>
<td>160.50</td>
<td>4.34</td>
<td>0.23</td>
</tr>
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</table>

Fig. 10. Comparison of hysteresis curves of (a) FT, (b) FTA (0.55), (c) FTA (2.09), and (d) FTA (3.56).

Fig. 11. Photocatalytic oxidation of 2,4-DCP in the presence of the prepared samples under UV/Vis irradiation (initial concentration of 2,4-DCP, 40 mg/L; volume, 100 mL; catalyst dosage, 10 mg, and 180 min irradiation).

Fig. 12. Our proposed mechanism for (A) formation of FTA sample and (B) photocatalytic oxidation of 2,4-DCP over FTA photocatalyst under UV/Vis irradiation.

Fig. 13. Effect of photocatalyst amount (FTA (2.09)) on degradation of the 2,4-DCP. Irradiation source: UV/Vis, 100 mL 2,4-DCP 40 mg/L, and irradiation time: 180 min.

Fig. 14. The effect of initial concentration on the photocatalytic oxidation rate of 2,4-DCP over FTA (2.09) photocatalyst under UV/Vis irradiation.
Table 5
Kinetic parameters for degradation of 2,4-DCP over FTA (2.09) under UV/Vis irradiation

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>$R^2$</th>
<th>$k_{obs}$ (min$^{-1}$)</th>
<th>Initial reaction rate (mg/L.(min$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.9582</td>
<td>0.0028</td>
<td>0.028</td>
</tr>
<tr>
<td>20</td>
<td>0.9922</td>
<td>0.0034</td>
<td>0.068</td>
</tr>
<tr>
<td>30</td>
<td>0.9939</td>
<td>0.0039</td>
<td>0.117</td>
</tr>
<tr>
<td>40</td>
<td>0.9910</td>
<td>0.0044</td>
<td>0.176</td>
</tr>
</tbody>
</table>

Fig. 15. Recyclability of the FTA (2.09) for photocatalytic oxidation of 2,4-DCP under 180 min UV/Vis irradiation after three successive cycles (photocatalyst dose: 10 mg/100 mL; [2,4-DCP]: 40 mg/L).

time $t$, respectively. The initial reaction rate of 2,4-DCP photocatalytic degradation was faster at higher initial concentration. This result can be clarified further by the short lifetime of active species formed during the reaction. The active oxygen species like OH$^-$ and O$_2$•$-$ were formed on the surface of FTA (2.09). These species did not go far and reacted with the 2,4-DCP molecules near the photocatalyst surface. Thus, the initial degradation rate was faster at high initial concentrations of 2,4-DCP.

3.9. Recyclability of FTA (2.09) photocatalyst

The recyclability of photocatalysts is among the necessities of developing heterogeneous photocatalysis process for wastewater treatment and can decrease the operational expense. The recyclability of the FTA (2.09) ternary nanocomposite was examined using the same 2,4-DCP photocatalytic oxidation in three repeated cycles. The 2,4-DCP photocatalytic oxidation remained unchanged during the first three cycles (Fig. 15). The removal of the photocatalyst was found effective because of magnetic Fe$_3$O$_4$ nanoparticles; thus, removal of FTA (2.09) photocatalyst was recyclable and can be considered a promising candidate for practical applications.

4. Conclusion

In summary, visible-light-driven and magnetically recyclable ternary Fe$_3$O$_4$/TiO$_2$/Ag photocatalysts containing different amounts of silver were prepared by the simple sol–gel method. The photocatalysts were characterized by analysis techniques including XRD, DRS, TEM, VSM, N$_2$ physisorption, and FESEM/EDX. The ternary samples exhibited excellent photocatalytic activity for 2,4-DCP degradation as a model of organic pollutants. The high photocatalytic activity can be attributed to both the high-specific surface areas of them and the silver nanoparticle plasmon resonance. The degradation reactions follow the first-order kinetics. Reusing experiments of the best photocatalyst, FTA (2.09), did not show any reduction in catalyst activity for degradation of 2,4-DCP after three cycles.

Acknowledgments

The authors wish to acknowledge the financial support of University of Tehran for supporting this research. Also, they wish to acknowledge the financial support of Iran Nanotechnology Initiative Council (INIC) Foundation (Grant no. 121833).

References


