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A Comparison Study of Photocatalytic Activity of Fe_3O_4/TiO_2 and Ag/TiO_2 on the Degradation of 2, 4-Dichlorophenol

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Abstract In this work, pure TiO_2 and binary nanocomposites of Fe_3O_4/TiO_2 and Ag/TiO_2 were synthesized in order to improve photocatalytic performance of these samples for degradation of 2, 4-dichlorophenol (2, 4-DCP) as an organic pollutant. A range of analytical techniques including XRD, DRS, SEM/EDX, and elemental mapping were employed to reveal the crystal structure, morphology and property of the nanocomposites. XRD data demonstrated that the prepared samples are purely in TiO_2 anatase phase and cubic spinel Fe_3O_4 exist in the synthesized nanocomposite. We calculated the TiO_2 crystal size from XRD patterns, in the range of 8.35-11.09 nm. The presence of Ag, Fe, O, and Ti atoms in the synthesized nanocomposites was confirmed by SEM/EDX. We obtained 30.43, 32.02 and 42.40 % degradation of 2, 4-DCP (100 ml 2, 4-DCP 40 ppm and 0.01 g catalyst) for pure TiO_2, Fe_3O_4/TiO_2 and Ag/TiO_2, respectively, after 180 min of irradiation under visible light. Similar conditions were employed for 2, 4-DCP degradation under UV irradiation, we obtained 53.05, 51.00 and 71.50 % degradation of 2, 4-DCP pure TiO_2, Fe_3O_4/TiO_2 and Ag/TiO_2, respectively. Thus, the synthesized binary nanocomposites exhibited higher photocatalytic activity compared to pure TiO_2 under visible light.

INTRODUCTION

World's population growth and drinking water scarcity has made drinking water supplementation, one of the fundamental problems of today's world. Therefore, water recycling will provide access to a suitable source for various uses. Recently, advanced oxidation processes (AOPs) have been proposed as a wastewater treatment solution. Among advanced oxidation processes, heterogeneous photocatalytic processes have been used as a successful method for the decomposition of various organic pollutants. Photocatalysts are environmental cleaners that can degrade many environmental pollutants through oxidation by using sunlight or artificial light, especially ultraviolet light. Titanium dioxide (TiO_2) is one of the photocatalysts that has been used to degrade organic pollutants. TiO_2 is an ideal photocatalyst with non-toxic nature, high oxidizing properties under UV radiation and low cost, which is stable under various reaction conditions and is also environment friendly [1].

There are two distinct defects in the performance of TiO_2 for the destruction of environmental pollutants. The first is the high energy of its separation band (3.2 eV), which requires UV radiation to generate the electron-cavity pair, but UV radiation forms only about 4% of the sun's emission. In order to utilize a larger part of the radiation emitted from the sun, it is necessary to make special changes in this semiconductor system. The presence of metals such as silver at TiO_2 surface would reduce the separation band energy and expand its absorption spectrum towards the visible light region. The presence of these metals decreases recombination rate of electron-cavity pair and also increases the

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free radicals formation rate [2]. The second defect is the recycling of nano-sized photocatalysts, which is very difficult and costly. An operational solution for photocatalyst recycling is magnetizing TiO_2 by Fe_3O_4 so that it can be separated and reused by employment of an external magnetic field [3]. In this study, (Ag/ TiO_2) and (Fe_3O_4 /TiO_2) binary nanocomposites as well as pure TiO_2 will be synthesized by sol-gel method. The synthesized samples will be identified with various techniques such as DRS, SEM/EDX and XRD, and eventually photocatalysts are used for photocatalytic degradation of 2, 4-dichlorophenol as an organic pollutants both under visible and ultraviolet light.

EXPERIMENTAL

Materials

$FeCl_3 \cdot 6H_2O$ (Merck No. 103943), $FeSO_4 \cdot 7H_2O$ (Merck No. 103965) were used for synthesis of Fe_3O_4 nanoparticles (NPs). Tetraisopropylorthotitanat (TIP) (Merck No. 8.21895), anhydrous ethanol, ammonia, and High-purity 2, 4-DCP, 98%, (Merck No. 803774) was used as a probe molecule for photocatalytic tests were purchased from Merck Company. Silver nitrate ($AgNO_3$), 99.9%, was supplied by (Merck, No.101510), Acetic acid (CH_3COOH), 99.9% (Merck No. 1.00063). All the reagents were of analytic grade and used without further purification. Double distilled water was used for preparation of all aqueous solutions.

Preparation of Fe_3O_4 and TiO_2 NPs

We synthesized Fe_3O_4 nanoparticles by chemical precipitation technique according to Mentioned procedure in ref [4] and for synthesis of TiO_2, the method reported in reference [5] will be used with some modifications. Subsequently, the obtained nanoparticles identified by various analysis.

Synthesis of binary (Fe_3O_4/TiO_2) and (Ag/TiO_2) nanocomposites

(Fe_3O_4/TiO_2) nanocomposites Synthesis: We mixed 0.1 g of the Fe_3O_4 nanoparticles with 4 ml of titanium isopropoxide (TIP) (as a titanium source) and 70 ml of water-free ethanol and placed it in an ultrasonic bath for one hour (Solution A). Solution B prepared by mixing 3 ml of acetic acid and 90 ml of distilled water. Then solution B was added to solution A, stirred at 50 °C for 30 min. Finally, after cooling to room temperature, we separate the synthesized solid from the suspension by centrifugation. Rinsed with ethanol and dried for 12 h at 60 °C. For the final step, the obtained solid is heated under atmospheric pressure at 300 °C for one hour.

(Ag/TiO_2) nanocomposites Synthesis: 1 g of TiO_2 is spread in 20 ml of deionized water by ultrasound waves and subsequently, 1 ml of $AgNO_3$, 100 mM, was slowly added to mixture. The solution was stirred at room temperature for 30 min, then 1 ml of Na_2CO_3 (1% w / v), was slowly added. The slurry was filtered and dried at room temperature [6].

Characterization

The XRD patterns were recorded on a Siemens, D5000 (Germany). The morphology of the prepared samples were characterized using scanning electron microscope (SEM) (Vegall-Tescan Company) equipped with an energy dispersive X-ray (EDX). The diffuse reflectance UV–Vis spectra (DRS) of the samples were recorded by an Ava Spec-2048TEC spectrometer.

Photocatalytic degradation of 2, 4-DCP

In a typical run, the suspension containing 10 mg photocatalyst and 100 mL aqueous solution of 2, 4-DCP (40 mg/L) was stirred first in the dark for 10 min to establish adsorption/desorption equilibrium. Irradiation experiments were carried out in a self-built reactor for 180min irradiation. UV illumination was performed with a 400 W Kr lamp (Osram). A visible (Halogen, ECO OSRAM, 500W) lamp was used as irradiation source. At certain intervals, small aliquots (2 mL) were withdrawn and filtered to remove the photocatalyst particles. These aliquots were used for monitoring the degradation progress, with Rayleigh UV-2601 UV/VIS spectrophotometer (λ_{max}= 227nm).

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RESULT AND DISCUSSION

X-ray diffraction analysis

Figure 1. A shows the X-ray diffraction pattern of the synthesized Fe_3O_4 nanoparticles in the present study. The diffractions at 2θ = 30.2°, 35.6°, 43.5°, 54.3° , 57.4° and 63.1° are observed, which are related to the cubic spinel structure of Fe_3O_4, reported by JCPDS reference number 0629-9, thus synthesis of magnetic nanoparticles is confirmed [7].

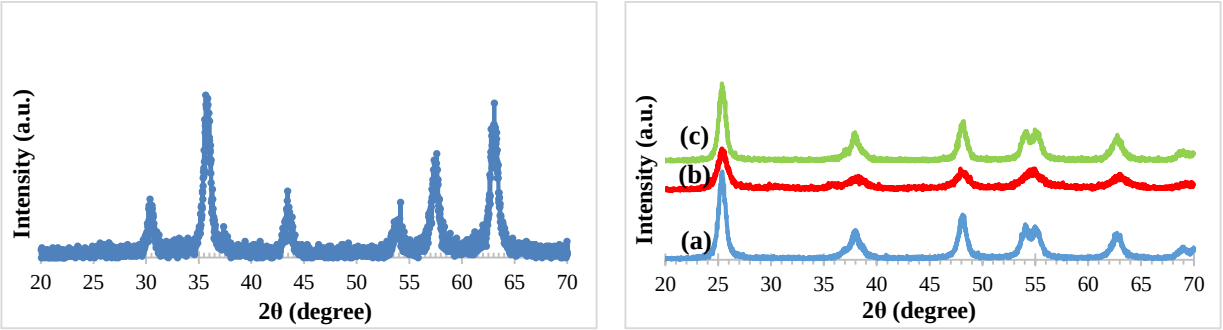

FIGURE 1. XRD patterns of A) Fe_3O_4, B) a) TiO_2, b) Fe_3O_4/TiO_2 and c) Ag/TiO_2

Figure 1. B shows the XRD patterns of the pure TiO_2 and binary nanocomposite. All the observed diffractions are related to the anatase phase according to the reference (PDF 24-1272) [8]. The reason for the low intensity of Fe_3O_4 nanoparticles and silver atoms diffraction is that they are very small in comparison to TiO_2, and because of the high TiO_2 crystallinity, most of the Fe_3O_4 diffraction is not visible.

The size of the TiO_2 crystal was calculated using first diffraction width and Scherrer's equation. Which varies between 8.35 to 11.09 nm [9].

$$D_{(hkl)} = 0.9\lambda / \beta \cos\theta$$

In this equation, D (hkl) is the crystal size based on Miller's index (101), λ is the wavelength of the X-ray, β is the width of the peak at half of its height, and θ is the Bragg's angle for the desired diffraction. Also, to calculate the parameters (a = b ≠ c), 101 crystalline location of anatase phase is used from the following equation.

$$1/d^2 = \left(h^2 + k^2\right)/a^2 + l^2/c^2$$

In this equation, D, the distance between neighboring places, is calculated by Bragg's law

$$D_{(hkl)} = \lambda / 2\sin\theta$$

To calculate a = b and c, respectively, the angles of the third (2 0 0) and first (1 0 1) diffractions of the anatase phase are used respectively [10]. Table 1 shows the unit cell parameters and volume for the anatase phase TiO_2 in the synthesized samples and confirmed the formation of pure anatase phase.

TABLE 1. Phase, crystal size and lattice parameters of the prepared samples

Sample	Phase	Crystal size (nm)	a=b (Å)	c (Å)	Cell volume (Å^3)
TiO_2	Anatase	10.38	3.77	9.59	136.30
Fe_3O_4/TiO_2	Anatase	7.11	3.79	9.37	134.87
Ag/TiO_2	Anatase	8.14	3.77	9.76	138.71

FESEM/EDX analysis

In order to investigate the surface morphology of the synthesized samples, FESEM studies were performed. The SEM images of pure TiO_2, Fe_3O_4/TiO_2 and Ag/TiO_2 samples are shown in Fig. 2. The EDX results were used to examine the elemental composition of the pure TiO_2, Fe_3O_4/TiO_2 and Ag/TiO_2 nanocomposites (Fig. 3 and Table 2).

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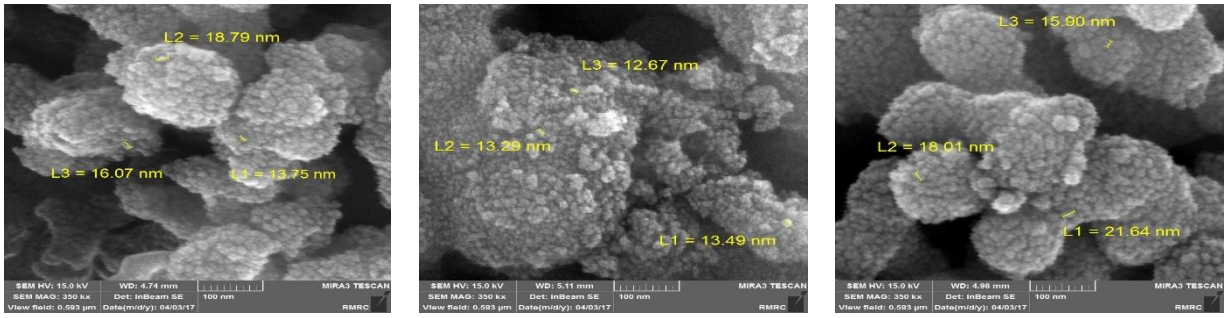
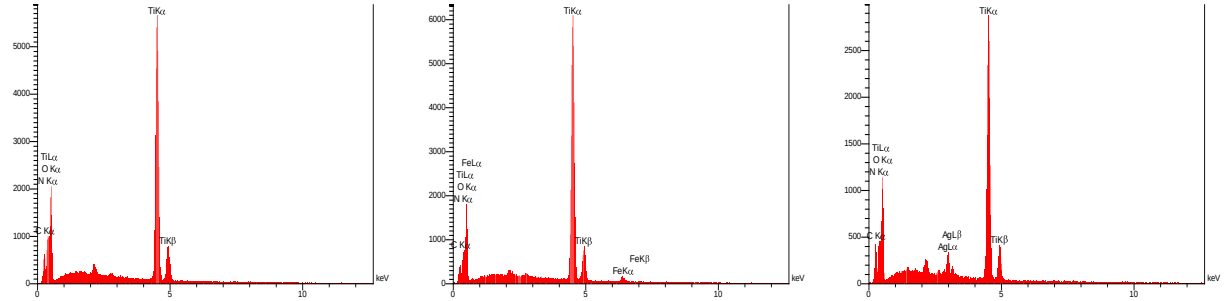


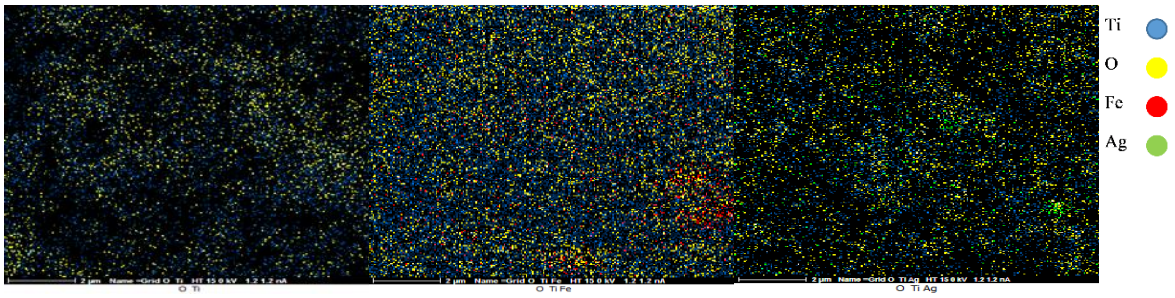
(a) (b) (c)

FIGURE 2. FESEM images of a) TiO_2, b) Fe_3O_4/TiO_2 and c) Ag/TiO_2



(a) (b) (c)

FIGURE 3. EDX spectra of a) TiO_2, b) Fe_3O_4/TiO_2 and c) Ag/TiO_2



(a) (b) (c)

FIGURE 4. Elemental mapping of a) TiO_2, b) Fe_3O_4/TiO_2 and c) Ag/TiO_2

TABLE 2. Elemental chemical analysis of the prepared samples.

Sample	C wt%	N wt%	O wt%	Ti wt%	Fe wt%	Ag wt%
TiO_2	8.12	14.24	41.68	35.96	-	-
Fe_3O_4/TiO_2	6.31	9.80	40.15	41.99	1.75	-
Ag/TiO_2	10.26	12.43	37.12	36.13	-	4.06

The EDX result confirms the presence of C, Ti, O, Fe Ag and N elements in these samples. In the EDX spectra of Ag/TiO_2 sample, the absorption peak at 3 keV is for metallic silver and confirms the presence of silver nanoparticles in the prepared sample. Figure 4 shows elemental mapping images of the prepared samples.

DRS analysis

The diffuse reflectance spectra of the prepared samples over the wavelength range of 200–800 nm are shown in Fig. 5. A. The DR spectrum of pure TiO_2 consists of a broad intense absorption around 400 nm, due to the charge-transfer from the valence band formed by 2p orbitals of the oxide anions to the conduction band formed by 3d t_{2g} orbitals of the Ti^{4+} cations [11]. We calculated the band gap energy from the DR spectra according to below equation [12] for the prepared samples.

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$$[F(R)h\nu]^{0.5} = A(h\nu - E_g)$$

Where A is constant, F(R) is the Kubelka-Munk function and E_g is the band gap. The band gap of the binary nanocomposites decreased slightly compared with TiO_2 (Table 3).

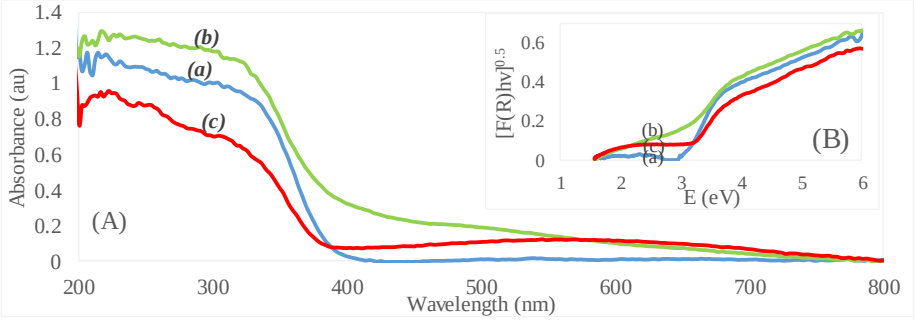

FIGURE 5. A): Diffuse reflectance spectra and B) Kubelka-Munk plots for the band gap energy calculation of a) TiO_2, b) Fe_3O_4/TiO_2 and c) Ag/TiO_2

TABLE 3. Band gap energy of the prepared samples.

Sample	TiO_2	Fe_3O_4/TiO_2	Ag/TiO_2
E_g (eV)	3.05	2.70	3.02

Photocatalytic performance of the prepared samples

To evaluate the photocatalytic activity of the synthesized samples a set of experiments for 2,4-DCP degradation with an initial concentration of 40 mg L^{-1} under visible light and UV irradiation at room temperature was carried out in aqueous suspension using TiO_2, Fe_3O_4/TiO_2 and Ag/TiO_2 catalysts, and the experimental results are shown in Fig. 6. The experimental results demonstrated that among the prepared samples, the Ag/TiO_2 catalyst showed the highest efficiency of the 2, 4-DCP degradation under visible light (42.40% degradation obtained after 180 min irradiation).the results show that the photocatalytic activity of pure TiO_2 is lower than that of Fe_3O_4/TiO_2 and Ag/TiO_2 samples. It implies that the Ag dopant promotes the charge pair separation efficiency for TiO_2 catalysts. The electron transfer from the TiO_2 conduction band to Ag particles at the interface is thermodynamically possible because the Fermi level of TiO_2 is higher than that of Ag metal. This results in the formation of a Schottky barrier at metal semiconductor contact region and improves the photocatalytic activity of TiO_2. The photocatalytic activity of Fe_3O_4/TiO_2 sample is lower than pure TiO_2 under UV irradiation implying that a stronger screen effect exists in our Fe_3O_4/TiO_2 sample as compared with pure TiO_2. The Fe_3O_4 NPs may be screened and weaken the UV irradiation needed to irradiate the TiO_2 NPs in the Fe_3O_4/TiO_2 sample [13] because, i) Fe_3O_4 particles blocked some of the TiO_2 active sites and ii) some UV irradiation was absorbed by Fe_3O_4 particles.

CONCLUSION

Pure TiO_2 and binary nanocomposites of Fe_3O_4/TiO_2 and Ag/TiO_2 were synthesized by the sol-gel method for degradation of 2, 4-dichlorophenol and characterized by several techniques successfully. From among all of the samples only anatase phase was confirmed from the XRD results. The presence of Ag, Fe, O, and Ti atoms in the synthesized nanocomposites was confirmed by SEM/EDX. Among all samples, Ag/TiO_2 catalyst exhibited the highest photocatalytic activity by 42.40 % degradation under visible light and 71.50 % degradation under UV irradiation after 180 min of irradiation.

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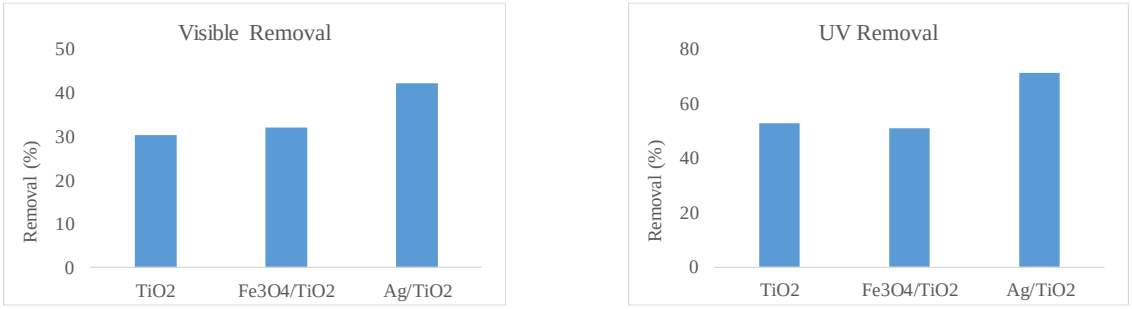

(A) (B)

FIGURE 6. Photocatalytic degradation of 2, 4-DCP in the presence of the prepared samples under (A) visible light and (B) UV irradiation. Initial concentration of 2, 4-DCP, 40 mg /L; volume, 100 mL; catalyst dosage: 10 mg.

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