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Nano-Magnetic Fe_3O_4/TiO_2 Composite : an Efficient Photocatalyst for 2,4 -Dichlorophenol Degradation Under Visible Light

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Abstract: In this work, pure TiO_2 and nano-magnetic of Fe_3O_4/TiO_2 were synthesized for degradation of 2,4-dichlorophenol (2, 4-DCP) as an organic pollutant. A range of analytical techniques including XRD, DRS, FESEM, and VSM were employed to reveal the crystal structure, morphology and property of the nanocomposite. The XRD results showed the prepared samples including 100% anatase phase. We obtained the band gap energy 2.9 and 2.8 eV for pure TiO_2 and Fe_3O_4/TiO_2 respectively. VSM results demonstrate that easy, fast separation and redispersion of Fe_3O_4/TiO_2 sample can be realized. We obtained 62% and 31% degradation of 2,4-DCP in the presence of Fe_3O_4/TiO_2 and pure TiO_2 under visible light respectively.

Keywords: Nano-Magnetic; TiO_2; Fe_3O_4; Degradation; 2,4-Dicholorophenol

Introduction

Titanium dioxide (TiO_2) is one of the photocatalysts that has been used to degrade organic pollutants. In practical application, there is a problem that needs to be resolved for the TiO_2 photocatalyst. However, when TiO_2 particles are dispersed into waste water, they are apt to be lost and difficult to be re-collected. To resolve this problem, photoactive TiO_2 particles are coated onto magnetic cores [1]. To enhance the re-collecting ability of the composite photocatalyst, a magnetic material with strong magnetization, such as Fe_3O_4, should be exploited as the magnetic core [2].

In this study, (TiO_2) and nano-magnetic (Fe_3O_4/TiO_2) composites were synthesized by sol-gel method. The synthesized samples were identified with various techniques such as XRD, DRS, FESEM and VSM, and eventually photocatalysts were used for photocatalytic degradation of 2,4-DCP as an organic pollutants under visible light.

Materials and Method

$FeCl_3{\bullet}6H_2O$ (Merck No. 103943), $FeSO_4{\bullet}7H_2O$ (Merck No. 103965) were used for synthesis of Fe_3O_4 nanoparticles (NPs). Titanium isopropoxide (TIP) (Merck No. 8.21895), anhydrous ethanol, ammonia, and High-purity 2, 4-DCP, 98%, (Merck No. 803774) were used as a probe molecule for photocatalytic tests were purchased from Merck Company.

We synthesized (Fe_3O_4) nanoparticles by chemical precipitation technique according to mentioned procedure in reference [3] and for synthesis of (TiO_2) and (Fe_3O_4/TiO_2), the method reported in reference [4] and reference [5], respectively was used with some modifications.

The XRD patterns were recorded on a Siemens, D5000 (Germany). The morphology of the prepared samples were characterized by using scanning electron microscope (FESEM) (Vegall-Tescan Company). The diffuse reflectance UV–Vis spectra (DRS) of the samples were recorded by an Ava Spec-2048TEC spectrometer. All the magnetic measurements have been done by VSM system which is made of Meghnatis Daghigh Kavir,(MDK), Company, Kashan I.R.Iran.

The photocatalytic activity of TiO_2 and Fe_3O_4/TiO_2 samples were evaluated by degradation of 2,4-DCP under visible-light which was used by (Halogen, ECO OSRAM, 500W) lamp. The degradation of 2,4-DCP was monitored by Rayleigh UV-2601 UV/VIS spectrophotometer (λ_{max}= 227nm).

Results and Discussion

X-RAY Diffraction Analyses

Fig. 1 shows the XRD patterns of the pure TiO_2 and nano-magnetic composite. All the observed diffractions are related to the anatase phase according to diffraction peaks at the reference[6], 2θ = 25.4◦, 38.0◦, 48.0◦, 54.7◦ and 63.1◦ were all designated to anatase crystal phase of TiO_2 [6], In addition peaks which showed with an asterisk (*) are related to diffractions of Fe_3O_4[7]. We also calculated the average crystal size of TiO_2 and Fe_3O_4/TiO_2 in the range of (7.12-8.89 nm), respectively.

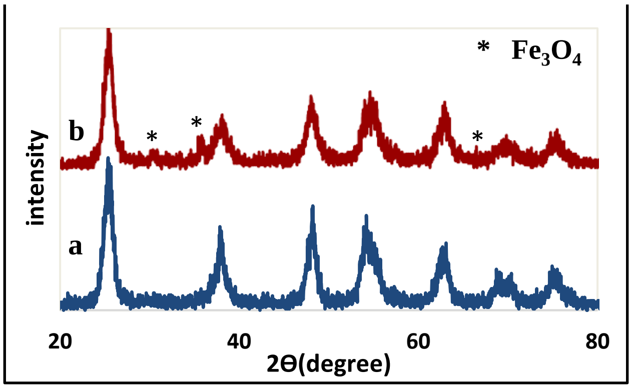


Fig.1: XRD patterns of a) TiO_2, b) Fe_3O_4/TiO_2

FESEM Analysis

Fig. 2 shows the FESEM images of TiO_2, and Fe_3O_4/TiO_2 nanocomposites. It is noteworthy that in the FESEM image of nano-magnetic composite, there are a number of particles dispersed on the outer surface of the Fe_3O_4 nanoparticles.

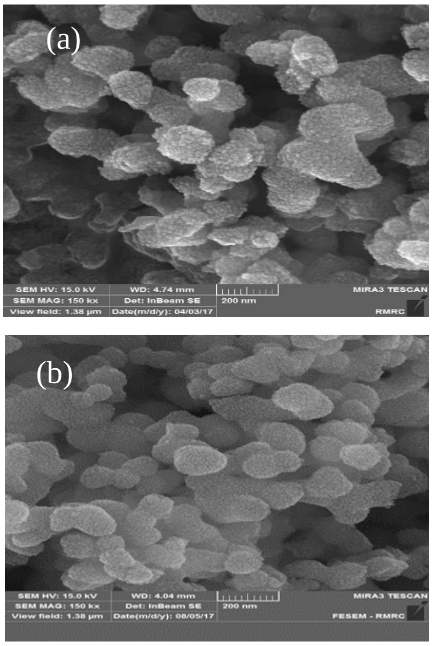


Fig.2: FESEM images of a) TiO_2 and b) Fe_3O_4/TiO_2.

DRS Analysis

Diffuse reflectance spectra of the prepared samples are shown in Fig.3 the DR spectra of TiO_2 consist of a broad intense absorption around 404 nm, due to 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[8]. The DR spectra of Fe_3O_4/TiO_2 exhibits an enhanced light absorption than TiO_2 in the range of 400-800 nm. This result suggests that presence of Fe_3O_4 can enhance the visible light absorption which may improve the photocatalytic activity.

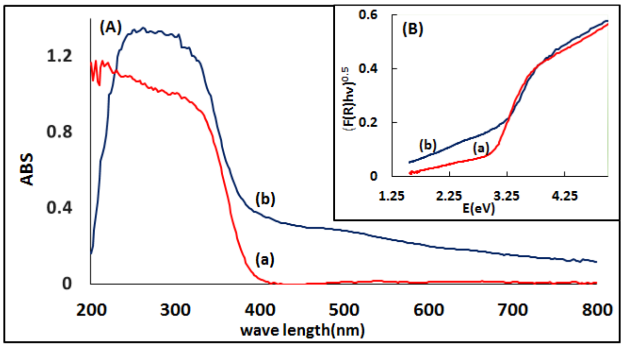


Fig.3: A) Diffuse reflectance spectra, B) Kubelka-Munk plots for the band gap energy calculation of a) TiO_2 and b) Fe_3O_4/TiO_2.

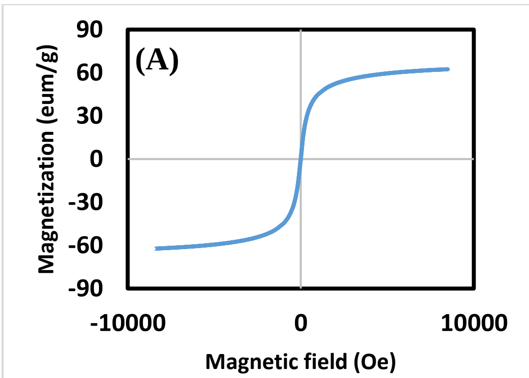
According to below equation, we calculated the band gap energy from the DR spectra for the prepared samples [9].

$$[F(R)h\nu]^{0.5} = A(h\nu - E_g) \qquad (1)$$

Where A is constant, F(R) is the Kubelka-Munk function and Eg is the band gap. The calculated band gap energy of pure TiO_2 and Fe_3O_4/TiO_2 were 2.90 and 2.80 respectively. The band gap of the binary nano-magnetic composites decreased slightly compared with TiO_2.

VSM Analysis

The magnetic properties of nano-magnetic composite was measured by VSM at room temperature. The hysteresis loops of the powered samples are shown in Fig. 4. It is worth nothing that the Ms value of the Fe_3O_4 nanoparticles is significantly higher than Fe_3O_4/TiO_2 sample, which is because the Fe_3O_4 nanoparticles are covered with an anatase TiO_2 layer in the Fe_3O_4/TiO_2 sample. [5]



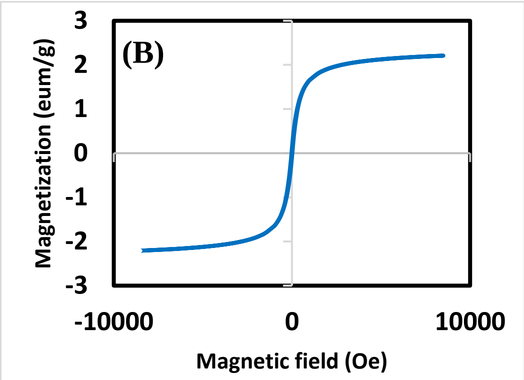


Fig.4: Comparison of hysteresis curves of A) Fe_3O_4 and B) Fe_3O_4/TiO_2.

Photocatalytic Degradation of 2,4-DCP

The performance of the synthesized samples was studied for photocatalytic treatment of synethic wastewater containing 2,4-DCP at room temperature, under visible light (Fig. 5). The experimental results demonstrated that nano-magnetic composite showed a higher activity for treatment of 2,4-DCP (62%) under visible light compared to pure TiO_2. It shows that Fe_3O_4 has been proved to be a good promoter to hybridize with TiO_2.

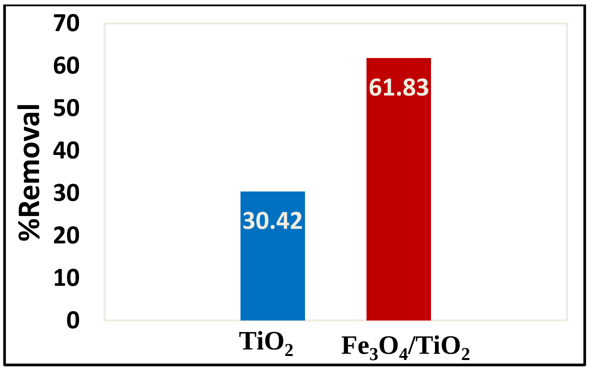


Fig.5: Photocatalytic degradation of 2, 4-DCP in the presence of the prepared samples under visible light. Initial concentration of 2, 4-DCP, 40 mg /L; volume, 100 mL; catalyst dosage: 10 mg.

Conclusion

Pure TiO_2 and nano-magnetic Fe_3O_4/TiO_2 composite were synthesized by 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. FESEM and DRS results confirmed Fe_3O_4 presence in the nano-magnetic sample by decreasing band gap. Furthermore VSM result confirmed magnetization of Fe_3O_4/TiO_2 sample. Nano-magnetic Fe_3O_4/TiO_2 composite exhibited the higher photocatalytic activity by 62% degradation compared with TiO_2 (31% degradation), under visible light after 180 min of irradiation.

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