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Fe-Doped TiO₂ Supported on HY Zeolite for Solar Photocatalytic Treatment of Dye Pollutants

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Abstract: Zeolite-supported TiO₂ and Fe-doped TiO₂/zeolite photocatalysts were synthesized, aiming at improving the adsorption properties of the microporous support towards polluting dyes and the photocatalytic performance of TiO₂ in the treatment of the adsorbed organics. The TiO₂/HY zeolite catalyst exhibited the best performance in the photocatalytic degradation of methylene blue, MB, over 10 wt% TiO₂/HY under UV light at 254 nm. The addition of Fe species in the synthesis mixture led to Fe-TiO₂/HY catalyst. The combination of adequate zeolite, good titanium dioxide dispersion, and Fe doping led to a remarkable performance in the degradation of the model dye. Over a 10 wt% Fe-doped TiO₂/HY catalyst a total removal of MB (>98%) was achieved after 60 min under very mild conditions and simple visible light irradiation.

Keywords: titanium dioxide; zeolites; oxidation; photocatalysis; Fe doping; methylene blue; oxygen

1. Introduction

Dyes are extensively used in the manufacture of textiles, leather, printing, food, plastic, and cosmetics to give color to commercial products [1]. The presence of dyes in industrial waste water, even at low concentration, is highly visible and undesirable. They present mutagenic and carcinogenic properties and can cause significant damage to both aquatic life and human health, such as dysfunction of the kidneys, reproductive system, liver, brain, and central nervous system [2]. Methylene blue is one of the most widely used dyes. Although methylene blue is not highly hazardous in moderate doses (lethal dose LD₅₀ oral rat = 1180 mg kg⁻¹), it can cause some harmful effects [3]. Acute exposure to methylene blue causes increased heart rate, vomiting, diarrhea, nausea, shock, Heinz body formation, and tissue necrosis in humans [4,5].

With respect to the above critical negative effects, different strategies have been developed aiming at an efficient removal of this kind of pollutant from water and the human environment. In recent years, new processes based on the use of heterogeneous photocatalysts have attracted ever-increasing attention and titanium dioxide, TiO₂, proved to be one of the most appropriate semiconductor materials to be employed as a photocatalyst. However, two main fundamental disadvantages limit the application of “bare” TiO₂ alone in photocatalytic reactors: (i) the relatively wide band gap of TiO₂ (3.2 eV), which absorbs only 3–5% energy of the solar spectrum and restricts its applications to UV excitation sources [6]; and (ii), when used in slurry or suspension mode, a post-treatment recovery step for the TiO₂ catalyst is necessary, which is normally difficult, energy intensive, and expensive [7].

Moreover, TiO_2 powder is prone to form aggregates, especially at high concentrations, and this is a major limitation to the application in continuous flow systems [8]. This also leads to undesired scattering of incident UV light by the suspended particles [9,10].

Therefore, several approaches have been explored in order to extend the optical absorption of TiO_2 into the visible light region and, thus, to enhance its photocatalytic activity [11]. The doping with transition metals, such as Cr, Fe, Co, Mo, Mn, and V, or their ions [12–19], broadens the visible light absorption range by reducing the band gap or introducing additional intra-band gap energy states. Moreover, the immobilization of TiO_2 powder on solid supports, such as ceramic [20], silicates [21–24], activated carbon [25], clay [26–28], sands [29,30], or zeolites [31–34], is a good strategy to enhance the dispersion of the TiO_2 species and the light harvesting for an effective photodegradation. It is also a convenient method to solve the problem of the catalyst powder recovery after use, facilitating the recycling of the photocatalyst in long-term applications. Among them, zeolites have especially attracted an increasing interest, thanks to their high specific surface area, tunable hydrophobic/hydrophilic properties, tailored adsorption features, and environmentally friendly nature [35–37]. In addition, since zeolites possess relevant ionic exchange properties, they are, in principle, particularly suitable solids for the adsorption and subsequent catalytic degradation of positively-charged dye molecules [38].

Although many research teams have reported on the preparation of zeolite-supported or metal ion-doped TiO_2 catalysts separately, few studies have investigated the effect of the two above-mentioned modifications simultaneously. Miaoliang et al. have studied the photocatalytic degradation of methyl orange by platinum-modified TiO_2 on natural zeolite (Pt- TiO_2 /zeolites) [39]. It was found that the doping of Pt can improve significantly the degradation of methyl orange with 86.2% of the decolorization rate under 30 min irradiation time and the optimum Pt doping amount was 1.5 wt%. Lazau et al. [40] have compared the photodegradation of humic acid over undoped TiO_2 /natural zeolite (TiO_2 /zeolite) and the same TiO_2 /zeolite system doped with silver ions (Ag- TiO_2 /zeolite). The photocatalytic activity and the mineralization of humic acid under Ultraviolet-Visible (UV-VIS) irradiation was much more efficient in the presence of the Ag- TiO_2 /zeolite composite. The physical adsorption of humic acid by the composites could in addition accelerate its degradation rate. Khatamian et al. [41] evaluated the photocatalytic activity of supported Ni- TiO_2 and Fe- TiO_2 composites on the ZSM-5 (Zeolite Socony Mobil-5) zeolite during the transformation of Yellow GX pigment in aqueous solution under ambient conditions. The Fe- TiO_2 /ZSM-5 system showed to be a more efficient catalyst than Ni- TiO_2 /ZSM-5 and TiO_2 /ZSM-5 for the degradation of dye molecules. Its higher photocatalytic activity was attributed to the effective separation of charge carriers due to the fact that Fe^{3+} ions decrease the recombination process of electron-hole pairs. An Fe- TiO_2 system deposited on a natural clay was also used as a catalyst for the photo-treatment of wastewaters [26]. However, the solid was properly active only under UV-A irradiation and in the presence of peroxide-containing oxidants.

In the present work, we have followed two strategies: (i) supporting evenly-dispersed TiO_2 species onto a proton-containing microporous molecular sieve zeolite with variable oxide loadings, with the dual aim of avoiding the formation of TiO_2 aggregates, as well as of optimizing the amount of TiO_2 content for a maximal degradation of pollutants; and (ii) supporting Fe-doped TiO_2 species onto a HY zeolite in order to have a photocatalyst with high catalytic activity in the oxidation and degradation of pollutants under visible light. Thanks to a cooperative positive effect due to the presence of a zeolite support with enhanced adsorption features, a photocatalytically-active, highly-dispersed TiO_2 phase and a dopant (Fe species) with good properties in the catalytic degradation of pollutants, an improved performance of Fe + TiO_2 on zeolite systems is expected with respect to the current state of the art for similar photocatalysts. The metal ion-doped photocatalysts were synthesized by a simple and conventional sol-gel method. The photocatalytic performance of all of the prepared catalysts in decolorization reactions was then evaluated in the degradation of methylene blue, MB, as a model polluting dye. Throughout the work, a constant attention was paid to optimizing the reaction

under very mild conditions, with a simple experimental apparatus and under conventional visible light irradiation.

2. Results and Discussion

2.1. Adsorption Studies

Adsorption studies were initially carried out over a set of the most readily available zeolites, i.e., HY (H-faujasite), H β , HMOR (H-mordenite), and HZSM-5 zeolites in the presence of methylene blue, MB. The MB removal capability of the solids is shown in Figure 1. In all cases, after an initial rapid adsorption of MB within the first 10 min, the extent of MB removal attained a steady state in 30 min and no further significant decrease in MB concentration was detected even after 24 h, suggesting that adsorption equilibrium was reached. In order to be sure a steady situation is fully attained, 60 min was chosen as the optimum time for the adsorption equilibrium and all of the further photodegradation experiments were carried out after this time.

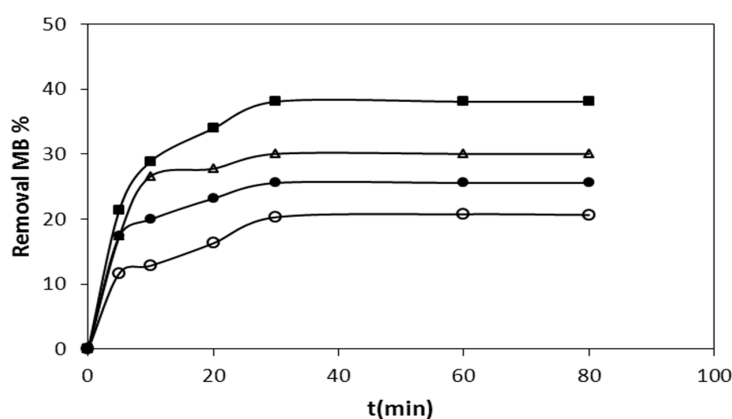


Figure 1. Adsorption of MB by different zeolites: HY (■), H β (Δ), HMOR (●), and HZSM-5 (○). Experimental conditions: dye concentration = 20 mg L⁻¹, zeolite amount = 1 g L⁻¹, T = 25 °C.

The lower adsorption property of H β (30%), HMOR (25%), and HZSM-5 (19%), compared to HY (38%), is attributed to the sterical constraints of the structure of zeolites. Actually, HY presents a network of interconnected cages with openings of 7.4 Å and a high specific surface area (880 m² g⁻¹). The faujasite structure of HY is, on the contrary, more accessible than the one of H β , which is composed of two straight pore channels (7.6 × 6.4 Å) together with a third zig-zag pore channel (5.6 × 5.6 Å), reducing the possibility of adsorption and diffusion of the adsorbate. Then, H-ZSM-5, which has a low specific surface area (411 m² g⁻¹) and the smallest pore size (5.1 × 5.5 Å), was the solid where the entry of MB was most difficult. Thus, the adsorption trend followed the order: HY > H β > HMOR > HZSM-5 (Figure 1).

In conclusion, HY zeolite showed the highest adsorption property for MB and, hence, it was chosen as the most suitable support for the rest of the MB photodegradation studies.

2.2. Effect of TiO₂ Loading on HY Zeolite

2.2.1. Characterization of the Photocatalysts

Starting from HY zeolite as a support, a series of TiO₂/HY catalysts was prepared with a TiO₂ content spanning from 3 wt% to 15 wt%. In order to confirm the crystalline structure of the solids, the samples were studied by XRD method. Figure 2 shows the XRD patterns of the TiO₂/HY catalysts, after calcination at 450 °C. The diffraction peaks at 2 θ = 25°, 38°, 48°, 55°, 63°, 68°, 70°, and 75° were matched to the spectrum of the anatase TiO₂ phase. The measurements showed that the thermal treatment at 450 °C had successfully transformed the amorphous TiO₂ phase into a 100% crystalline

TiO₂ anatase phase. The gradual increase in the intensity of the anatase peaks ($2\theta = 25^\circ$, 38° , and 48°) of TiO₂ and the corresponding relative decrease in the intensity of the peak ($2\theta = 16^\circ$) of HY indicates that the presence of anatase increased with the amount of TiO₂ loaded onto the HY support [42]. On the other hand, no peaks assigned to the rutile or brookite phase were observed in the XRD patterns in any of the TiO₂/HY catalysts. This result indicates that, for the TiO₂/HY catalysts, the anatase was the kinetically metastable phase under the synthesis conditions tested here [43]. As there is no significant shift in the peaks for TiO₂/HY in comparison with those of the pristine HY zeolite, it could be concluded that no change occurred in the zeolite crystal structure during the synthesis of TiO₂/HY [44].

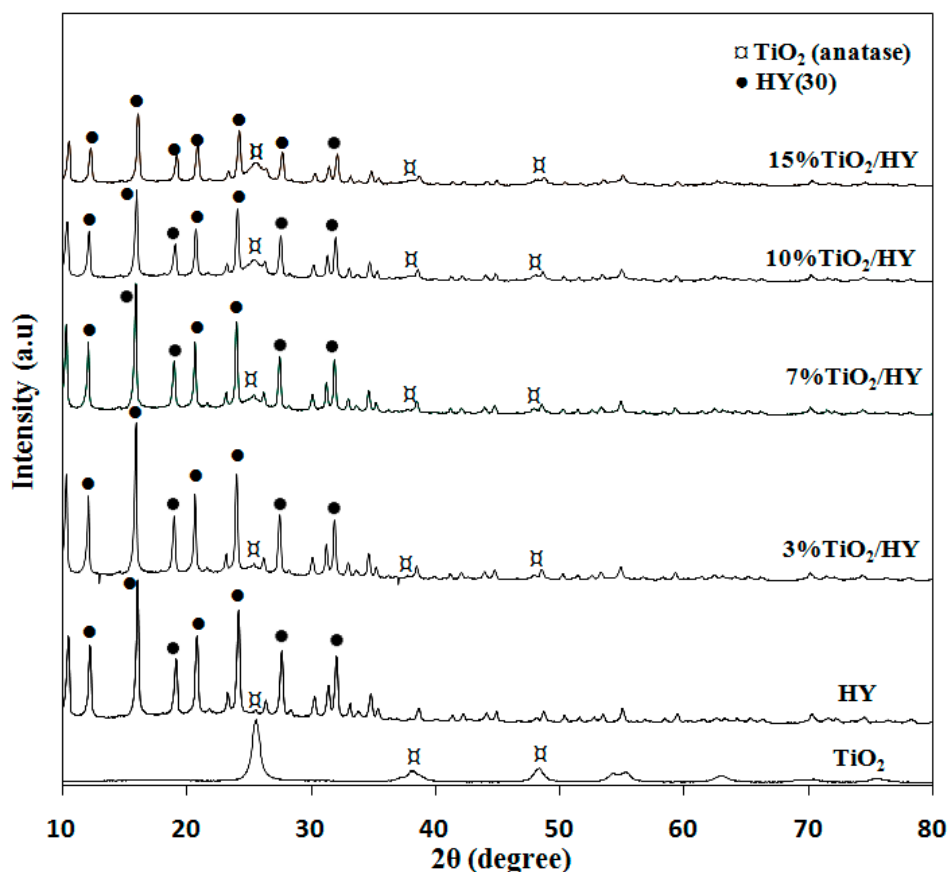


Figure 2. XRD patterns of TiO₂, HY and 3, 7, 10, and 15 wt% TiO₂/HY, from bottom to top, respectively.

Figure 3 shows the FTIR spectra of TiO₂ and supported TiO₂. For all of these samples, the region from 1600 cm^{−1} to 3700 cm^{−1} indicates the presence of water molecules and OH group in the zeolite [45]. The strongest absorption peak at 1047 cm^{−1} is assigned to the framework stretching vibration band of Si (Al)–O in the tetrahedral Si (Al) O₄ units of the zeolite, indicating that the zeolite structure was kept. The structural bands at 450–900 cm^{−1} are attributed to the stretching vibrations of T–O, T–O–T, and O–T–O bonds in tetrahedral SiO₄ and AlO₄ units (T = Si or Al atoms). At the same time, no evident bands were observed in the region of 950–960 cm^{−1}, commonly assigned to the antisymmetric stretching vibration of the Ti–O–Si bond [42,46]. As it is suggested that no strong chemical interaction takes place between the TiO₂ species and the zeolite, TiO₂ is likely dispersed on the surface of the zeolite or partially encapsulated within the zeolite cavities [47,48]. Furthermore, the peaks at 920, 895, and 860 cm^{−1} that are characteristic of Ti–O, Ti=O, and Ti–O–Ti, respectively, from bulk TiO₂ are not evident in these samples. This is a further clue that the Ti species are small and homogeneously dispersed within the zeolite framework [49,50].

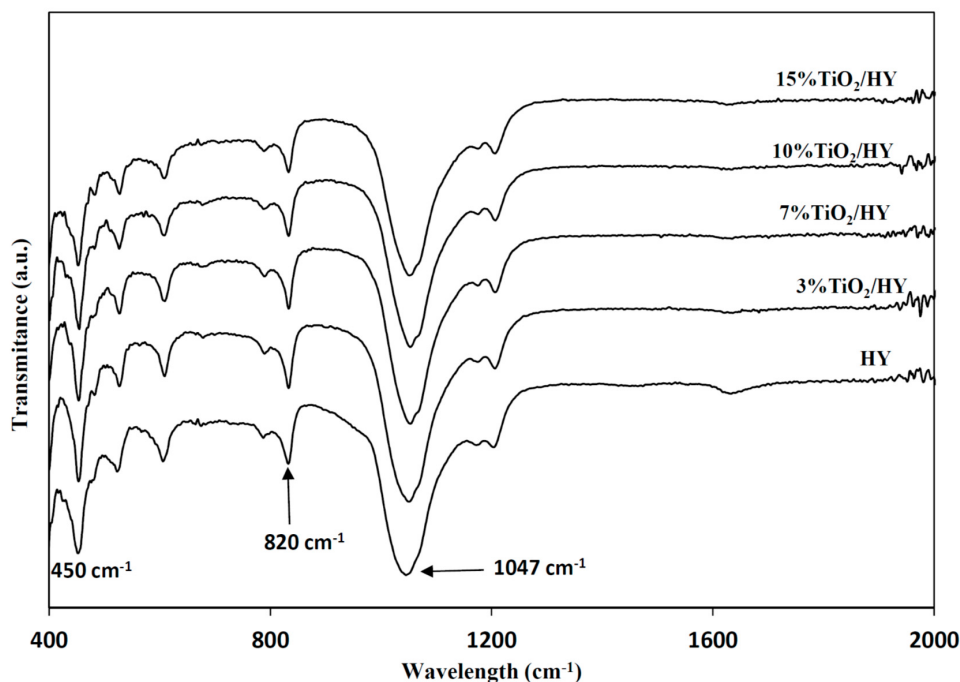


Figure 3. FTIR spectra of HY, 3, 7, 10, and 15 wt% TiO_2 /HY from bottom to top, respectively.

The values for the BET specific surface area of the HY zeolite and TiO_2 containing zeolite photocatalysts are reported in Figure 4. The BET area of the HY samples gradually decreased when the loading of TiO_2 increased. These diminutions in the surface area of the TiO_2 -containing zeolite solids, in comparison to the corresponding parent zeolite, are consistent with a gradual hindering and partial blocking of the pores of the zeolite by the TiO_2 particles [51]. It is, however, worth highlighting that the BET surface area decreases linearly, with a small negative constant slope. This is a further clue that the TiO_2 species are evenly and properly dispersed inside the support, as a function of the oxide loading.

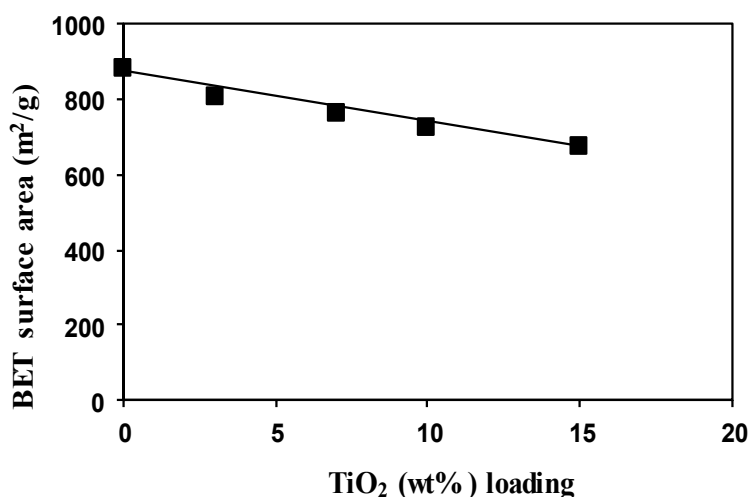


Figure 4. BET specific surface area vs. TiO_2 loading (wt%) on TiO_2 /HY zeolite solids.

The UV-VIS diffuse reflectance spectra of TiO_2 /HY and TiO_2 catalysts are shown in Figure 5 and provide an insight about the interaction of the TiO_2 species with the zeolite. The position of the absorption edge for pure anatase is around 400 nm. On the contrary, for the TiO_2 /HY systems, the edge is red-shifted and the shift increases as the TiO_2 loading increases. This is likely due to the high degree of dispersion of the anatase aggregates within the zeolite [52–54].

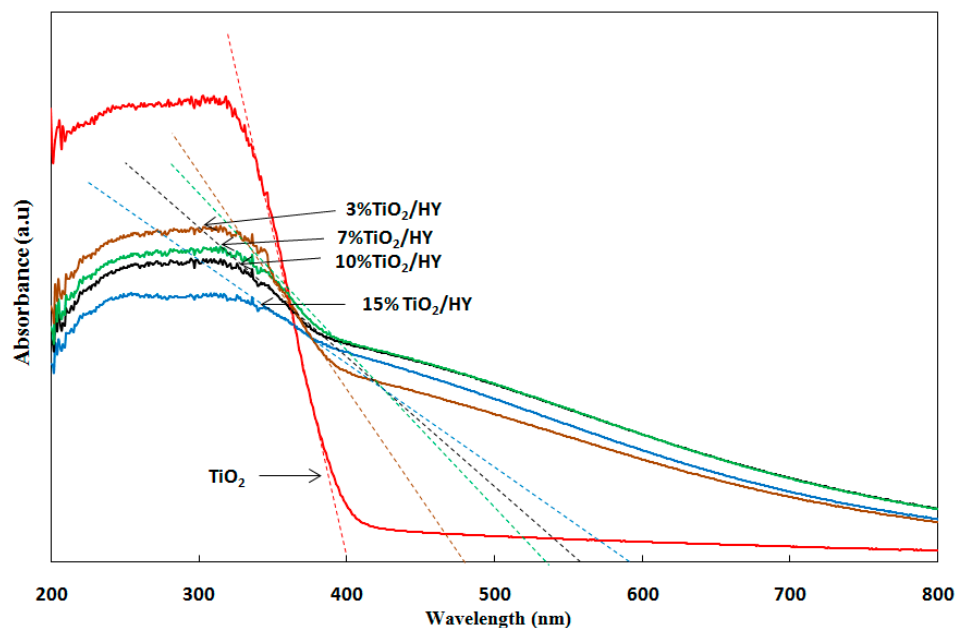


Figure 5. UV-VIS spectra of HY, TiO₂, and the series of 3, 7, 10, and 15 wt% TiO₂/HY systems.

2.2.2. Evaluation of the Photocatalytic Activity

The photocatalysis tests were performed over the series of 3, 7, 10, and 15 wt% TiO₂-loaded HY solids in order to understand their influence on the degradation efficiency, and to optimize the amount of TiO₂ loading for a maximal degradation of MB under UV irradiation (Figure 6). The results revealed that the use of the HY zeolite as a support in the TiO₂/HY system played a key role in increasing and improving the degradation rate. First, the deposition of TiO₂ onto the surface of HY zeolite enhances the electron transfer from the photo-excited semiconductor to the guest molecules of HY, as an electron acceptor and, consequently, the zeolite prevents the electron-hole recombination [55]. In addition, the presence of the zeolitic molecular sieve improves the photodegradation efficiency of TiO₂ particles thanks to the synergistic presence of various positive factors: its high specific surface area, its good adsorption properties, and its capability to keep TiO₂ moieties as dispersed as possible. For these reasons, the degradation efficiency increased by increasing the TiO₂ loading on the support up to 10 wt%. However, above 10 wt%, the maximum degradation percentage was lower and such behavior can be attributed to a more extensive pore blocking of HY zeolite by titania species. The incipient pore blocking not only negatively affected the adsorption capacity, but also increased the shielding of the incident light by TiO₂ particles, since an increased turbidity of the suspension reduces the solar light penetration [56]. Moreover, at higher TiO₂ loading, the excited particles may not be in close proximity to the zeolite surface and, hence, the conduction band electrons of the TiO₂ are less prone to be delocalized over the zeolite. As a result, there is a higher occurrence of the electron-hole recombination, giving rise to a lower degradation efficiency. Only an optimal tuning of the TiO₂ loading on the zeolite surface could, therefore, lead to a more efficient degradation.

Taking into account these observations, in the present study, the optimum loading of TiO₂ on HY was found to be 10 wt% and this value was chosen as a starting point for the further doping of the solids by iron species, in order to obtain Fe-doped TiO₂/HY systems.

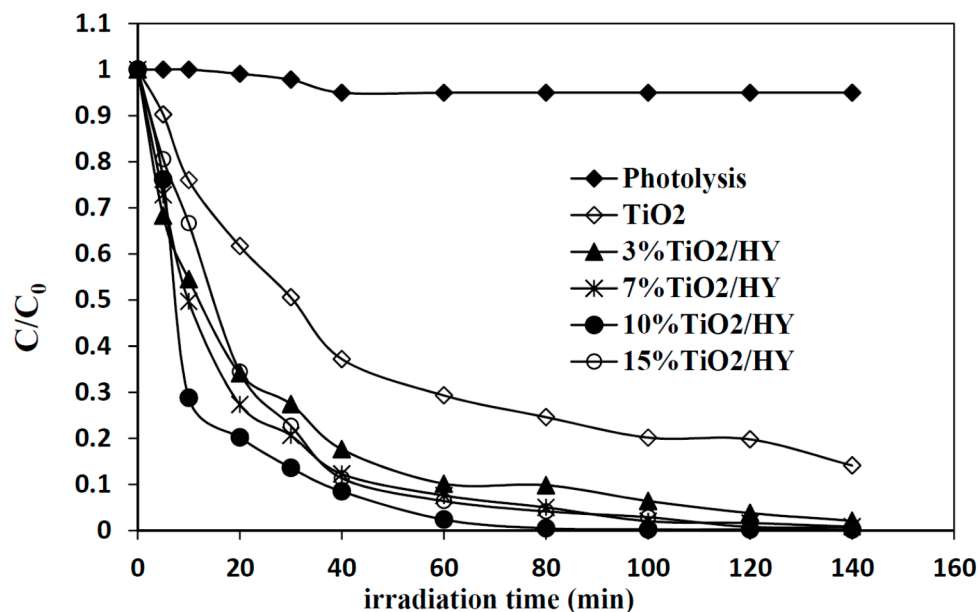


Figure 6. Photocatalytic degradation of MB over TiO₂ supported HY zeolite at different TiO₂ loadings under UV irradiation ($\lambda_{\text{max}} = 254 \text{ nm}$, dye concentration = 20 mg L^{-1} , zeolite amount = 1 g L^{-1} , $T = 25^\circ \text{C}$).

2.3. Effect of Fe Doping onto TiO₂/HY Zeolite

2.3.1. Characterization of the Photocatalysts

The diffuse reflectance spectroscopy shows the changes in the optical properties of the supported titania after Fe doping by iron species, also revealed by the adjusted Kubelka-Munk transformation (see the Experimental Details section) aimed at determining the band-gap energy of the doped oxide (Figure 7). The wavelength of the spectral onset increased by increasing the dopant amount (Figure 7a). Therefore, the band diminution in band gap with the increase in Fe doping is to be attributed to the overlap of Fe 3d, Ti 3d, and O 2p states, which eventually induces the absorption of higher wavelength photons in titania [57]. Figure 7b shows the indirect transition Kubelka-Munk plot as a function of the photon energy allowing the estimation at the intercept of the threshold energies, namely, 3.12, 2.81, and 2.55 eV for TiO₂, 3% Fe-TiO₂/HY, and 10% Fe-TiO₂/HY, respectively. The gradual decrease in the overall band gap energy with the amount of iron doping testifies to a shift towards the visible region.

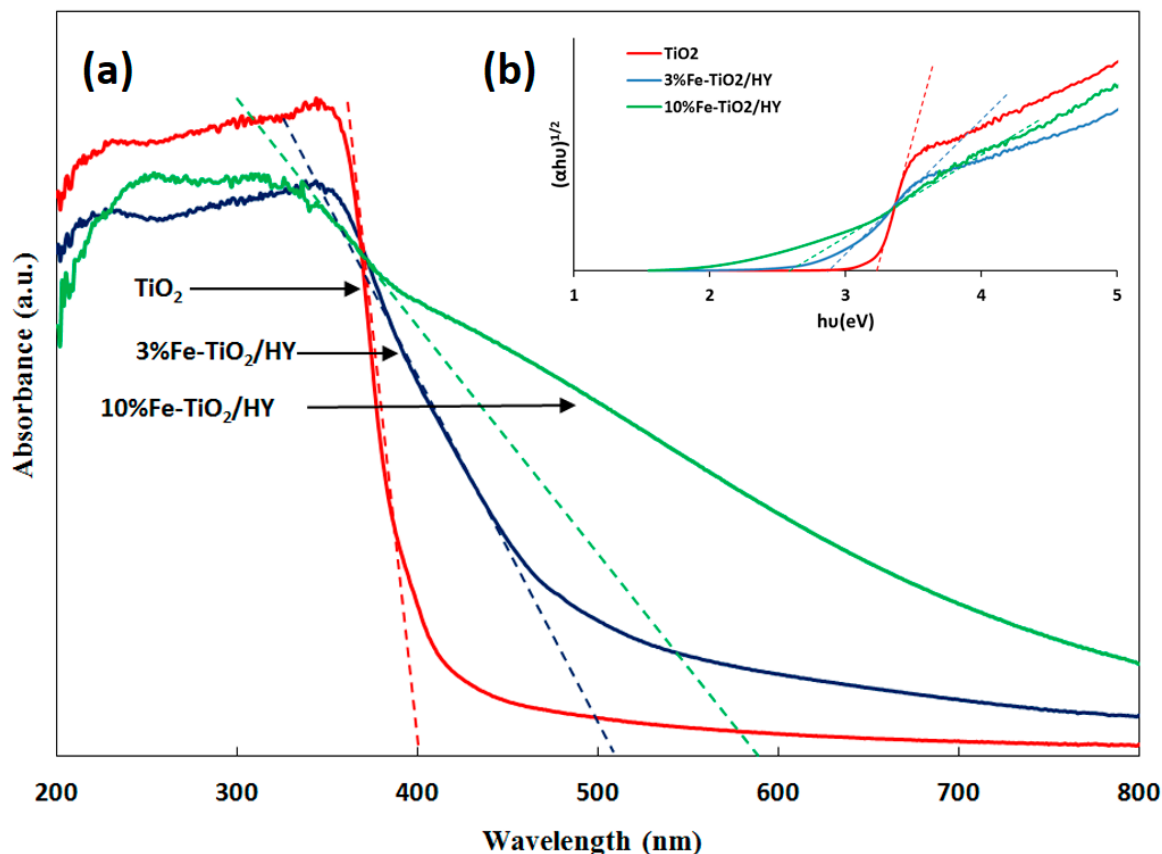


Figure 7. (a) UV-VIS diffuse reflectance spectra before and after doping with Fe; and (b) the corresponding Kubelka-Munk-transformed diffuse reflectance, as a function of $h\nu$.

Thanks to these modified absorption properties, it was possible to test the Fe-doped TiO₂/HY catalysts under visible light irradiation. The UV fraction of the emission of the lamp used in the experimental apparatus was cut by means of a UV filter in order to allow only the visible fraction to reach the photoreactor.

2.3.2. Photocatalytic Studies

Figure 8a shows the degradation curves of MB solutions catalyzed by Fe-doped TiO₂/HY photocatalysts at different Fe(III) dosages under visible light irradiation. It can be observed that the decolorization rate of MB solutions over these systems was higher than that one obtained in the presence of the undoped TiO₂/HY systems. The degradation rate increased as the iron concentration grew from 3 wt% to 10 wt%. Then it decreased back at Fe(III) concentrations higher than 10 wt% (Figure 8b). This result is fully consistent with some previous observations [58,59]. An appropriate concentration of iron ions can introduce trapping species in the transfer between for photo-generated holes and electrons, thus inhibiting the recombination of electron-hole pairs [60]. Indeed, the recombination rate decreases as the dopant concentration grows, because the distance between trapping sites in a particle decreases with a higher number of dopants. However, if the concentration of trapping species is too high (>12 wt%), the overall process is slowed down and a lower MB removal is obtained (Figure 8). On the contrary, if the iron concentration is very low, there are fewer trapping sites available, and this leads to an overall diminution of the photocatalytic activity [61].

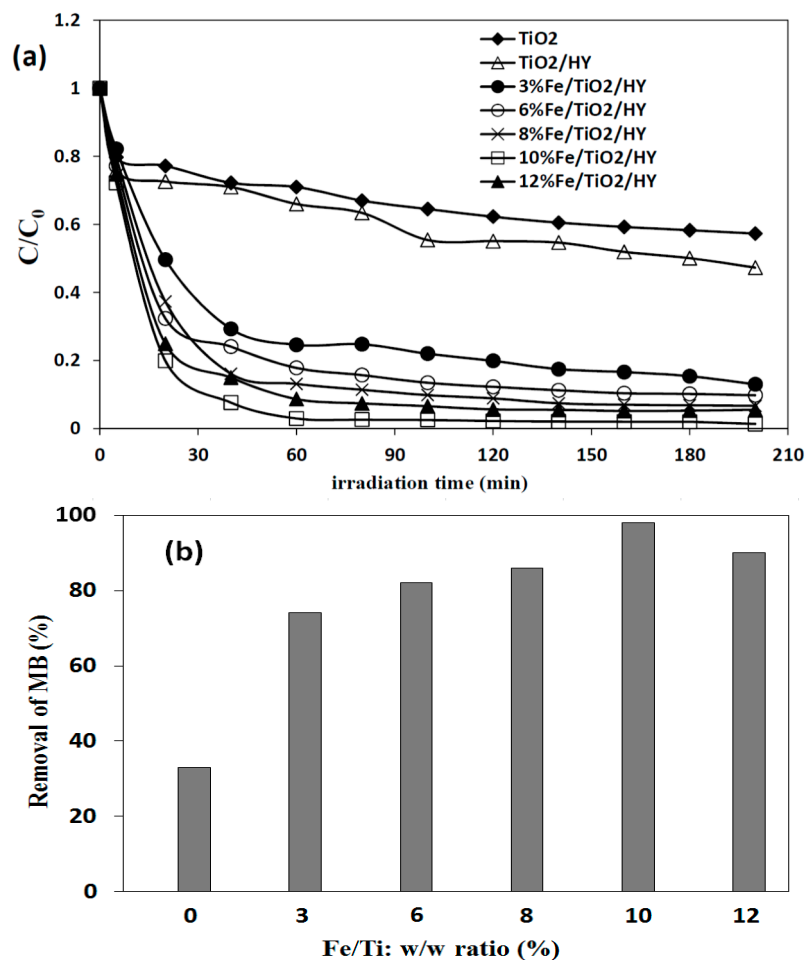


Figure 8. Photocatalytic degradation of MB solution catalyzed by undoped TiO₂/HY and doped TiO₂/HY with different amounts of iron dopant. Tests were run under visible light irradiation. (a) Photocatalytic degradation rate vs. irradiation time; and (b) the influence of the iron dopant on dye removal (time = 60 min). Experimental conditions: dye concentration = 20 mg L⁻¹, catalyst amount = 1 g L⁻¹, T = 25 °C.

The removal capacity of Fe-TiO₂/HY with 10 wt% of Fe content has been compared to the one of other similar catalytic systems reported in the literature and summarized in Table S1 (Supplementary Materials). The degradation performance is reported as percentage of dye removal (%). It should be noted that the comparison has a relative meaning only, because of different testing conditions (concentration and nature of dye, catalyst amount, concentration, and the nature of dopant, experimental setup, etc.) and the type of TiO₂ support [25,38,39,41,62–67]. Nevertheless, if we look closely at the degradation of the dye pollutants, the present photocatalyst based on Fe-TiO₂/HY attained very high decolorization percentages (>98%) at shorter times (60 min) and under milder conditions, avoiding the use of UV radiation or additional oxidizing reactants. The conceptually simple and reliable Fe-TiO₂/HY system can, therefore, be considered as a promising catalyst for a potential application in the elimination of organic dye pollutants from wastewater.

3. Materials and Experimental Details

3.1. Materials

The commercial zeolites used in this study were obtained from Zeolyst International (Delfzijl, The Netherlands): HY (Si/Al = 30), HMOR (Si/Al = 20), NH₄-β (Si/Al = 13.5), and NH₄-ZSM-5 (Si/Al = 17).

In order to obtain the protonic form (H β and HZSM-5), the ammonium form of the zeolite was calcined under dry air at 100 °C for 2 h and at 550 °C for 5 h using a heating rate of 1 °C min⁻¹. Methylene blue (MB: basic blue 9, C₁₆H₁₈N₃SCl; MW, 319.85 g mol⁻¹) was used as the model pollutant and obtained from Merck Eurolab S.A. (Figure 9). MB has a maximum visible absorbance at a wavelength of 666 nm. Solutions were prepared by dissolving an appropriate amount of the dye in doubly-distilled water.

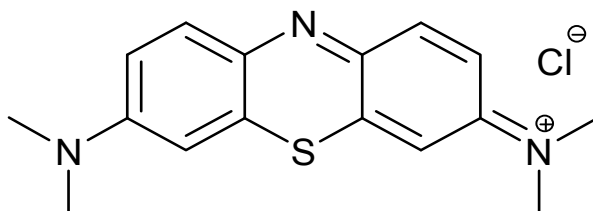


Figure 9. Methylene blue.

3.2. Photocatalyst Preparation

The zeolite-supported TiO₂ and Fe-doped TiO₂ catalysts (designated as TiO₂/zeolite and Fe-TiO₂/zeolite) were prepared according to a sol-gel method as described hereafter [68,69].

- (1) TiO₂/zeolite: titanium(IV) tetraisopropoxide, TIPT (Aldrich, 97%, Darmstadt, Germany), was added to the zeolite-suspended isopropanol solution and the mixture was stirred for 2 h. Water was added to the resulting slurry to hydrolyze titanium(IV) tetraisopropoxide adsorbed on zeolite particles and then the resulting slurry was left under continuous magnetic stirring until a gel was obtained. The gel was dried at 90 °C for 12 h and calcinated at 450 °C for 3 h to give rise to TiO₂ supported on zeolites. Finally, the catalysts were ground into a fine powder and stored in the dark. The amount of TiO₂ loaded on zeolite was in the range from 0 to 15 wt%, namely, 3, 7, 10 and 15 wt% TiO₂ on HY.
- (2) Fe-doped TiO₂/zeolite: HY zeolite powders (specific surface area = 880 m² g⁻¹) were dispersed in 10-fold distilled water and heated up to 70 °C. Subsequently, TIPT solution and Fe (NO₃)₃·9H₂O solution (the nominal weight ratios of Fe/Ti were 3.0, 6.0, 8.0, 10, 12% *w/w*, respectively) were added dropwise into the beaker and the pH of the suspension solution was adjusted to a value of about 3. The system was vigorously stirred at 70 °C for 4 h. After ageing for 12 h, the products were repeatedly washed with deionized water and then dried at 80 °C for 2 h. These samples were finally calcined at 450 °C for 3 h in a muffle furnace and then the photocatalysts were obtained. For the purpose of comparative photocatalysis study, a reference sample of titanium (IV) dioxide, TiO₂ was also prepared using the same procedure except for the addition of zeolite.

3.3. Characterization of Photocatalyst

The crystalline structure of the photocatalyst was measured using X-ray diffraction (XRD, X Pert Pro Panalytical, Almelo, The Netherlands) with a Cu K α source. The samples were analyzed in a 2 θ range of 10–80° to identify the crystalline phase. IR spectra of the samples were recorded using a Shimadzu (Kyoto, Japan) FTIR spectrometer with KBr pellets. The samples were analyzed in the wave number range of 400–4000 cm⁻¹. The BET specific surface area was measured by N₂ adsorption at low temperature on a surface area analyzer (ASAP 2000, Micromeritics, Norcross, GA, USA). The diffuse reflectance spectra of dry powders were measured using a Varian CARY 4000 (Mulgrave, Australia) UV-VIS) equipped with a DRA900 integrated sphere. The values of band gap energy (E_g) were calculated using Equation (1):

$$\frac{1}{(\alpha h\nu)^2} = a (h\nu - E_g) \quad (1)$$

where α , ν , E_g , and a represent the absorption coefficient, frequency vibration, band gap, and proportional constant, respectively.

3.4. Adsorption Study

Prior to photocatalytic experiments, an adsorption study of MB onto the catalyst surface was carried out by mixing 100 mL of aqueous solution of MB with a fixed weight of the catalyst (100 mg). Aliquots were withdrawn at specific time intervals and the change in MB concentration was measured by using a UV-160A UV-VIS spectrophotometer (ThermoFisher, Shanghai, China) at 666 nm, the $\lambda_{\max}$ of MB. The extent of equilibrium adsorption was determined from the decrease in MB concentration.

3.5. Photocatalysis Experiments

The experimental setup (Figure 10) was based on a rectangular photocatalytic reactor with a workable area of 9 cm $\times$ 45 cm, made out of Plexiglass[®] (Decoplast, Blida, Algeria). The wastewater stream to be treated entered the top of the chamber as a thin film onto the photocatalyst nanoparticles immobilized on the glass plate (8 cm $\times$ 44 cm). The sample to be treated (1000 mL of dye solution) was stored in a reservoir and continuously circulated in the system by a peristaltic pump at an adjustable flow rate. The reservoir was open to the air to ensure sufficient oxygenation. The solution in the reservoir was continuously stirred to keep the solution as homogeneous as possible. The whole reactor was thermostated at 25 °C.

Artificial irradiation was provided by a 15 W UV lamp with a maximum peak intensity at 254 nm, positioned above the reactor at a distance of 15 cm. The lamp was switched on at the beginning of each experiment. The immobilized photocatalyst was cleaned after every experiment by circulating deionized water with a few drops of aqueous hydrogen peroxide (30 wt%) under UV irradiation for regenerating the photocatalyst.

For visible light measurements, all the experimental parameters were the same except for the fact that the UV part of the light spectrum was cut by means of a 3 mm thick GG420 filter (Schott, Suzhou, China) placed on the photoreactor. The distance between the UV-VIS source and the solution was adjusted according to the experimental conditions. At different reaction times obtained with the experimental design, 2.5 mL samples were taken and the remaining BM was determined via spectrophotometer evaluation at $\lambda_{\max}$ = 665 nm and a calibration curve. The dye removal efficiency (in percentage) was calculated by Equation (2):

$$\text{degradation efficiency (\%)} = 100\% * \frac{(C_0 - C_t)}{C_0} \quad (2)$$

where C_0 is the initial concentration of the dye and C_t is its concentration at the time t .

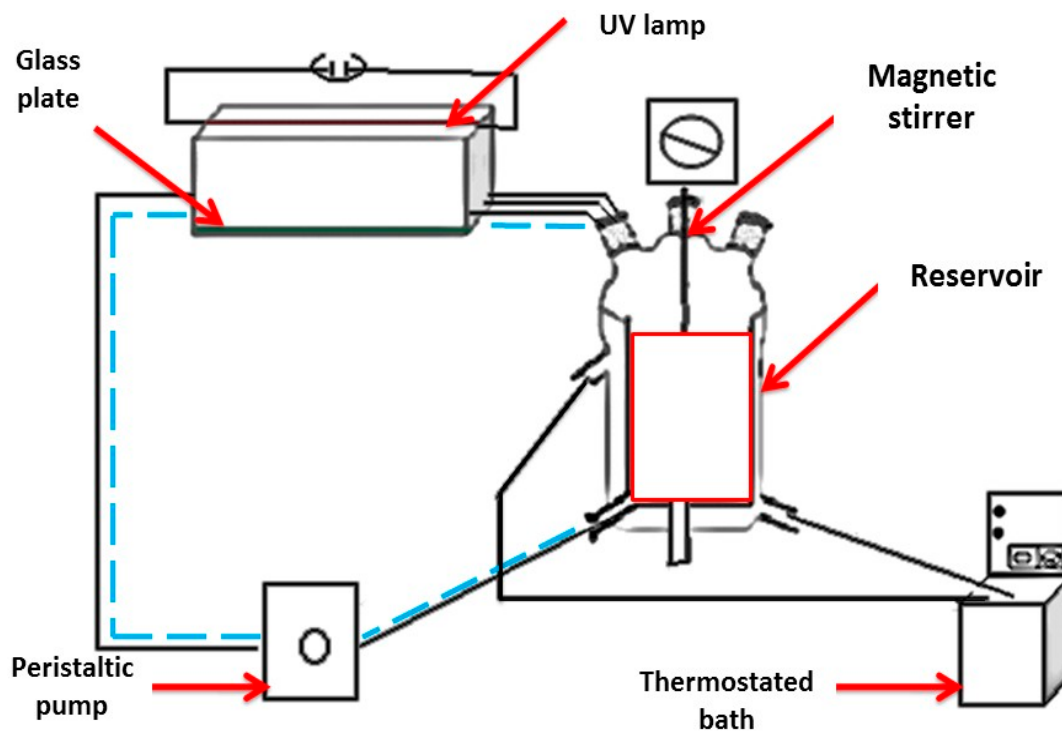


Figure 10. The experimental setup of the photocatalytic reactor.

4. Conclusions

The photocatalytic degradation of methylene blue, MB, was investigated using TiO_2 species supported onto HY zeolite either in the presence or in the absence of Fe(III) doping species. XRD and UV-VIS results showed that the TiO_2 species deposited on HY zeolite were in the anatase form and were mainly located on the outer surface of zeolite. The synergetic co-presence of the zeolite support, as an adsorbent, and TiO_2 species, as catalytically-active sites, led to an improved light harvesting capability and to increased adsorption of the polluting substrate. This resulted in an enhanced degradation of the MB dye. Under UV irradiation, the best photocatalytic degradation performance was achieved for TiO_2/HY at 10 wt% of TiO_2 loading.

The further addition of Fe(III) species, as a dopant, led to an improved photocatalyst that could be simply used under visible light irradiation. Over this system, the Fe-doped TiO_2/HY sample, with 10 wt% of Fe content, showed the best photocatalytic performance. A photo-assisted degradation of MB close to 100% was achieved after 60 min, under very mild conditions and visible light. Thanks to an appropriate tuning of the Fe(III) dopant concentration (10 wt%) within the TiO_2 species, the unproductive recombination of photogenerated electron and hole pairs could be successfully inhibited, giving rise to an efficient visible-light responsive photocatalyst for abatement of polluting dyes.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/11/344/s1, Table S1: Comparison of the efficiency in the removal of pollutant dyes from aqueous media catalyzed by different photocatalytic systems.

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Author Contributions: A.S. conceived and designed experiments; G.F. and N.C. performed the experiments; K.K. and D.R. analyzed the data; and A.S. and M.G. analyzed the data and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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