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Enhanced photocatalytic activity for the destruction of monocrotophos pesticide by TiO_2/Hβ

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Abstract

The adsorption of monocrotophos (MCP) was carried out over HY, Hβ and H-ZSM-5 zeolites. The adsorption of MCP follows the order Hβ > HY > H-ZSM-5 and hence Hβ was chosen as the support for TiO_2. The photocatalytic degradation of MCP on TiO_2 and TiO_2/Hβ catalysts was studied using low-pressure mercury lamps ($\lambda = 254$ nm) in a slurry reactor. The Hβ supported TiO_2 showed higher degradation efficiency than bare TiO_2. This higher activity of the supported catalyst is due to the greater adsorption of MCP on the support and capability of support to delocalise the conduction band electrons of excited titania. Total organic carbon (TOC) analysis indicates complete mineralisation of MCP. The relative photonic efficiency was calculated for TiO_2 and TiO_2/Hβ.

Keywords: TiO_2 photocatalyst; Supported TiO_2; Relative photonic efficiency; Pesticides; Monocrotophos; Photocatalytic degradation

1. Introduction

In recent years, much attention has been focused on the complete mineralisation of toxic organic pollutants, especially pesticides, because they are identified as environmental endocrine disruptors. Photocatalysis is a clean and attractive, low-temperature, non-energy intensive approach for the treatment of pollutants in water and wastewater [1–3]. TiO_2 is one of the most investigated photocatalysts for this purpose, and it has been found to be capable of decomposing a wide variety of organic and inorganic pollutants in both liquid- and gas-phase systems. However, the photocatalytic activity of TiO_2 should be improved, and initial investment cost should be brought down for large-scale applications. The photocatalytic efficiency of TiO_2 is greatly influenced by crystal structure, particle size, surface area and porosity. One of the strategies to improve the photocatalytic efficiency is to increase the surface area of the catalyst. Thus, fixing TiO_2 particles of high surface area on inert support will simplify the recovery of TiO_2 from the treated effluent. The fixation of TiO_2 onto glass matrix, optical fibers and stainless steel plate were studied extensively [4–6]. Unfortunately, photocatalytic efficiency of immobilized TiO_2 is often less than the suspended TiO_2 particles.

Alternative route for supporting fine TiO_2 on porous materials of larger particle size has been investigated using silica gel, activated carbon, sand, clay and zeolite [7]. These studies have been attempted with a view to increase the adsorption of organic pollutants on the catalyst surface, thereby increasing the photocatalytic degradation rate. Among the various supports for TiO_2, zeolite seems to be the most suitable one [8]. Earlier investigations revealed that zeolite with low Si/Al ratio in the framework and relatively large pore size exhibited the highest photoactivity among the various zeolites. Taketa et al. [4] concluded that optimum adsorption strength of the co-adsorbent is needed to improve the photocatalytic activity of TiO_2. The results obtained previously in our laboratory clearly revealed the importance of adsorption characteristics of the supported system to obtain

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high degradation rate of pollutants. It has been observed that dye molecules are mainly adsorbed on the adsorbent sites to make high concentration environment around the loaded TiO_2, resulting in the enhanced photodegradation efficiency [9]. Yoneyama and Torimoto [10] observed lower degradation rate with TiO_2 loaded on carbon due to high adsorption constant of the activated carbon. This led to the slow diffusion of adsorbed pollutant. Takeda et al. [4] studied different adsorbents for the improvement of photodecomposition rate of pollutants. They concluded that the supports having moderate adsorbability form high concentration environment around the loaded titania and allow fairly easy supply from the support to the loaded titania. Hence an optimum adsorption strength of the co-adsorbent is needed to improve the photocatalytic activity of TiO_2. The present work is aimed at finding a suitable zeolite support for TiO_2 in order to enhance its photocatalytic activity for the degradation of MCP in aqueous solution.

2. Experimental

2.1. Preparation of supported TiO_2 photocatalysts

Sodium form of zeolite Y, β and ZSM-5 (Sud-Chemie India Ltd., Baroda) with Si/Al ratio 3, 15 and 53, respectively were converted into H-form by ion-exchange with 1M ammonium nitrate solution for 24 h at 80 °C (repeated three times) with subsequent calcination at 550 °C in air for 6 h. The resultant H-form of zeolites were denoted as HY, Hβ and HZSM-5. The commercially available TiO_2 (Degussa P-25 having 70% anatase and 30% rutile, surface area 50 m^2/g and particle size 30 nm) was obtained from Degussa Chemical, Germany and used as such without any further treatment. The technical grade of MCP was received from Sri Ramcides, India. Supported catalysts were prepared by stirring Hβ with requisite quantity of TiO_2 to give a loading in the range between 0.5 and 5 wt.%, for 8 h in acetone. After stirring, the samples were filtered, dried at 110 °C for 3 h and finally calcined at 400 °C for 6 h.

BET surface area analysis of HY, Hβ, HZSM-5, TiO_2 and Hβ supported TiO_2 was carried out using Quantochrome Autosorb 1 sorption analyser. X-ray diffraction patterns of Hβ, TiO_2 and Hβ supported TiO_2 were recorded on Siemens D5005 X-ray diffractometer.

2.2. Photocatalytic degradation of monocrotophos

Photocatalytic degradation was performed on an aqueous solution of monocrotophos (MCP) (Fig. 1) in a slurry batch reactor. The cylindrical photochemical reactor measuring 30 cm × 3 cm (height × diameter) provided with a water circulation arrangement to maintain the temperature in the range of 25–30 °C was used in all the experiments. Irradiation was carried out using 6 W × 8 W low-pressure mercury lamp built into a lamp housing with polished anodised aluminium reflectors and placed 6.5 cm away from the reactor. The lamps emit predominantly UV radiation at a wavelength of 254 nm. The reactor set up was covered with aluminium foil followed by a black cloth to prevent UV light leakage. A stock solution containing 500 ppm of MCP was prepared and diluted to the required concentrations (25–125 ppm). TiO_2 or Hβ supported TiO_2 (200 mg) was added to 100 ml of MCP solution (100 ppm) and the resultant slurry was stirred for 30 min to attain equilibrium followed by irradiation with UV lamps for degradation. Aliquots were withdrawn at specific time intervals and analysed after centrifugation followed by filtration with Gelman GHP acrodisc 0.45 μm to remove titania particles.

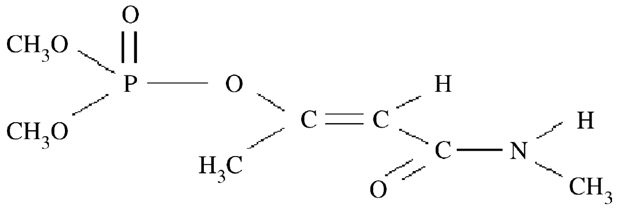
Fig. 1. Chemical structure of MCP.

The extent of degradation of MCP was determined by using a high-performance liquid chromatograph (HPLC), (Shimadzu, LC-10 AT VP series, CLS-ODS (M)) equipped with UV-visible detector adjusted to 230 nm. The mobile phase was acetonitrile and triple distilled water (60:40, v/v). The extent of mineralisation was determined using total organic carbon (TOC) analyser (Euroglas TOC 1200).

2.3. Determination of photocatalytic activity

2.3.1. Relative photonic efficiency (ξ_r)

The concept of relative photonic efficiency has been introduced to compare the efficiencies of different photocatalysts. The relative photonic efficiencies of the catalyst can be obtained by comparing them with a standard photocatalyst (Degussa P-25) and a test molecule (formic acid, FA) [11]. In the present study, relative photonic efficiencies for TiO_2 and supported TiO_2 were obtained by two ways. One way is correlating the initial rate of MCP degradation, R^{in} (MCP) to the initial rate of FA degradation, R^{in} (FA). The other way is correlating the initial rate of MCP mineralisation, R^{in} MCP (TOC) to the initial rate of FA mineralisation, R^{in} FA (TOC). Both the initial rates were obtained under identical conditions.

$$\xi_r = \frac{R^{in}(\mathrm{MCP})}{R^{in}(\mathrm{FA})}$$

$$\xi_{r\,\mathrm{TOC}} = \frac{R^{in}\,\mathrm{MCP\,(TOC)}}{R^{in}\,\mathrm{FA\,(TOC)}}$$

3. Results and discussion

3.1. Adsorption studies of monocrotophos

Adsorption studies were carried out initially over HY, Hβ, HZSM-5 zeolites and the adsorption capacity of MCP were found to be 19, 44 and 14%, respectively. The results revealed the greater adsorption of MCP on Hβ and hence it was chosen as the suitable support for further studies. The lower adsorption property of HY (19%) and HZSM-5 (14%) compared to Hβ (44%) is attributed to the higher hydrophilic nature of HY and lower surface area of HZSM-5 (BET surface area of the catalysts: HY = 648 m^2/g; Hβ = 575 m^2/g; HZSM-5 = 386 m^2/g). Apart from these facts, the presence of acid sites with good acid strength in Hβ [12] could also be yet another reason for the better adsorption of MCP. The anionic form of MCP can be efficiently adsorbed on the acid sites of Hβ.

3.2. X-Ray diffraction analysis

The XRD patterns of Hβ, TiO_2 and Hβ supported TiO_2 photocatalysts are shown in Fig. 2. The XRD peak of crystal plane 101 for anatase appeared at 25.4° (2θ) and crystal plane 110 for rutile appeared at 27.5° (2θ), which is in agreement with our previous report [13]. The representative peaks at 2θ = 5.4° and 22.4° correspond to Hβ, which is also consistent with earlier report [14]. The gradual increase in the intensity of the peak (2θ = 25.4°) of TiO_2 and decrease in the intensity of the representative peaks of Hβ clearly illustrates the increase in the loading of TiO_2.

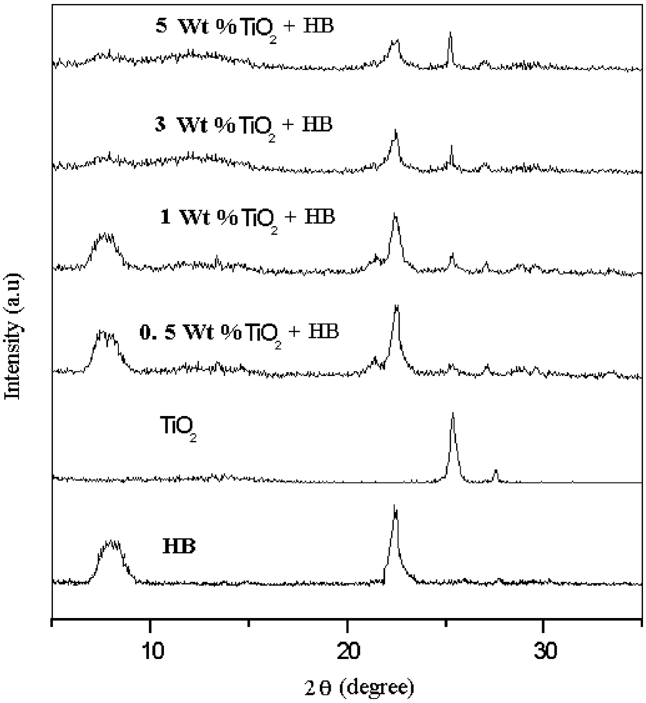

Fig. 2. X-ray diffraction patterns of Hβ, TiO_2 and Hβ-supported TiO_2.

3.3. Effect of initial monocrotophos concentration

The effect of initial MCP concentration on degradation rate was studied by varying the initial concentration from 25 to 125 ppm with constant catalyst loading of 200 mg, and the results are depicted in Fig. 3. It is clear that the degradation rate increases with an increase in initial concentration of the MCP from 25 to 100 ppm and then decreases. The rate of degradation is related to the formation of $^{\bullet}OH$ radical, which is the critical species in the degradation process [15]. The equilibrium adsorption of reactants on the catalyst surface and the reaction rate of $^{\bullet}OH$ radicals with other chemicals are also significant in the rate of degradation [16]. The hydroxyl radicals are formed through the reaction of holes with adsorbed OH^- and H_2O. If we assume that the adsorbed OH^- ions are replaced by MCP ions (MCP^-), which are generated from the dissociation of MCP molecules:

$$[\mathrm{MCP{-}H}] \rightarrow [\mathrm{MCP}^-] + \mathrm{H}^+ \tag{1}$$

then the generation of $^{\bullet}OH$ radicals will be reduced at higher MCP concentration since there are only a fewer active sites available for the generation of $^{\bullet}OH$ radicals. Further as the solution concentration increases above 100 ppm screening effect dominates preventing penetration of the light. This is accordance with literature report [17]. It also depends on the type of catalyst, reactor geomentry and irradiation source.

3.4. Effect of the amount of TiO_2

The reaction rate as a function of amount of catalyst is important [16–19]. Hence a series of experiments were carried out to find the optimum catalyst amount by varying TiO_2 from 50 to 250 mg (Fig. 4). The turbidity of the solution above 200 mg reduced the light transmission through the solution, while below this level the adsorption on TiO_2 surface and the

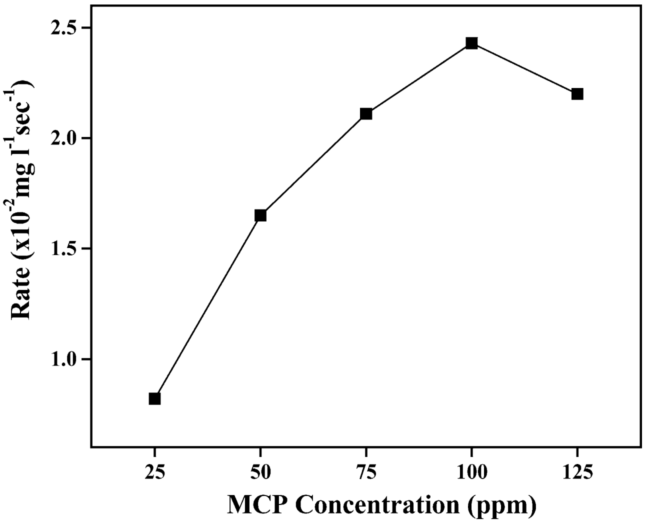

Fig. 3. Effect of initial concentration on degradation rate of MCP monocrotophos concentration = 25–125 ppm; catalyst amount = 200 mg/100 ml; pH = 5.5.

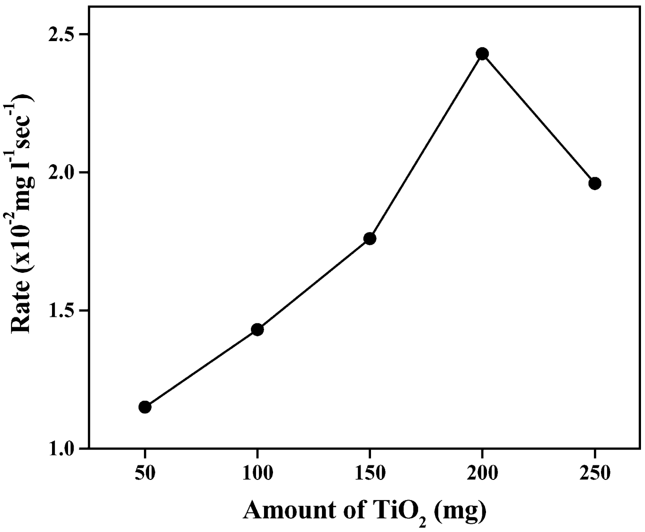

Fig. 4. Effect of amount of TiO_2 on degradation rate of MCP monocrotophos concentration = 100 ppm; catalyst amount = 50–250 mg/100 ml; pH = 5.5.

absorption of light by TiO_2 were the limiting factors. Wei and Wan [20] reported that the catalyst amount has both positive and negative impact on the photodecomposition rate. The increased amount of catalyst increases the quantity of photons absorbed and consequently the degradation rate. Further increase in catalyst amount beyond 200 mg may result in the deactivation of activated molecules due to collision with the ground state molecules as shown below [21].

$$TiO_2{}^* + TiO_2 \rightarrow TiO_2{}^{\#} + TiO_2 \qquad (2)$$

$TiO_2{}^*$ is the catalyst with active species adsorbed on its surface; $TiO_2{}^{\#}$ is the deactivated form of catalyst.

At concentrations higher than 0.2 mg, TiO_2/ml aggregation (particle–particle interactions) may commence and lower the effective surface area of the catalyst, and adsorption of the reactant.

3.5. Effect of pH

The amphoteric behaviour of titania influences the surface charge of the photocatalyst. The role of pH on the photocatalytic degradation rate was studied in the pH range 3–10 at constant MCP concentration of 100 ppm and 200 mg TiO_2. The results are shown in Fig. 5. It is observed that the rate of degradation increases with increase in pH exhibiting a maximum at pH 5 and then decreases. Pelizzetti et al. [22] reported that acid–base property of the metal oxide surfaces has considerable implications upon their photocatalytic activity. The effect of pH can be explained on the basis of zero point charge of titania. The adsorption of H_2O molecules at surface metal sites is followed by the dissociation of OH^- groups leading to a coverage with chemically equivalent metal hydroxyl groups (M–OH). The following two equilibria are significant for titania.

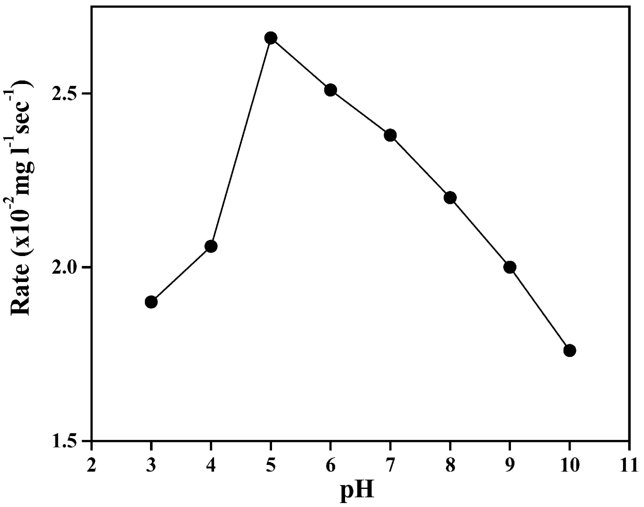

Fig. 5. Effect of pH on degradation rate of MCP monocrotophos concentration = 100 ppm; catalyst amount = 200 mg/100 ml; pH = 3–10.

$$Ti\text{–}OH_2 \rightleftharpoons Ti\text{–}OH + H^+ \qquad (3)$$

$$TiOH \rightleftharpoons Ti\text{–}O^- + H^+ \qquad (4)$$

The zero point charge (zpc) pH_{zpc} for TiO_2 (Degussa P-25) is 6.9, below this pH it is positively charged and above this pH it is negatively charged. The pKa value of MCP being 4.4, at the pH lower than this value, positively charged protonated MCP predominates and above the same, negatively charged MCP anion (MCP) predominates. Hence at pH 5, the electrostatic interaction between the positive TiO_2 surface and MCP lead to strong adsorption of the latter on the former and the formation of more number of OH. These combined effects results in maximum degradation rate.

3.6. Effect of TiO_2 loading on Hβ zeolite for photocatalytic activity

Experimental studies were performed with 0.5, 1, 3 and 5 wt.% TiO_2 loaded on Hβ to understand the effect of TiO_2 loading on the supported system, and to optimise the amount of TiO_2 loading for maximum degradation of MCP. The results are depicted in Fig. 6. The degradation rate increases with increase in TiO_2 loading on the support upto 3 wt.%. But above 3 wt.% loading, the degradation rate decreases. The decrease in degradation rate above 3 wt.% loading is attributed to scattering of light. Moreover, at higher percentage loading, the excited particles may not be close to the zeolite surface and hence its conduction band electron are not delocalised over zeolite. As a result, there could be much electron hole recombination giving low degradation rate. Hβ supported TiO_2 is more active towards degradation than other catalyst due to more adsorption of MCP on it. Hence, optimum loading of TiO_2 on zeolite surface alone can enhance the degradation rate.

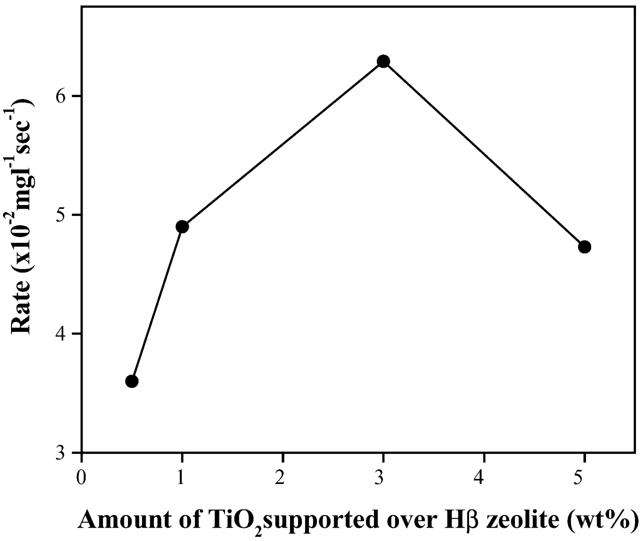

Fig. 6. Effect of TiO_2 loading on Hβ zeolite on degradation rate of MCP monocrotophos concentration = 100 ppm; wt.% of TiO_2 = 0.5, 1, 3 and 5; pH = 5.

3.7. *Effect of irradiation time on TiO_2 and supported TiO_2 photocatalysts*

The relationship between photodegradation efficiency of MCP and irradiation time on TiO_2 and supported TiO_2 is shown in Fig. 7. It is clearly seen that the extent of degradation increases with increase in irradiation time. The initial degradation is very high in supported TiO_2 due to higher adsorption of MCP on the support, and $^{\bullet}$OH generated is available for degradation. Whereas the degradation decreases after 1 h irradiation on TiO_2 as well as on supported TiO_2. The formation of intermediates and its competitiveness with MCP molecules in the photocatalytic degradation may be attributed for the slow degradation after one hour. Under the given experimental conditions TiO_2 requires 540 min and supported TiO_2 requires 420 min irradiation for complete degradation.

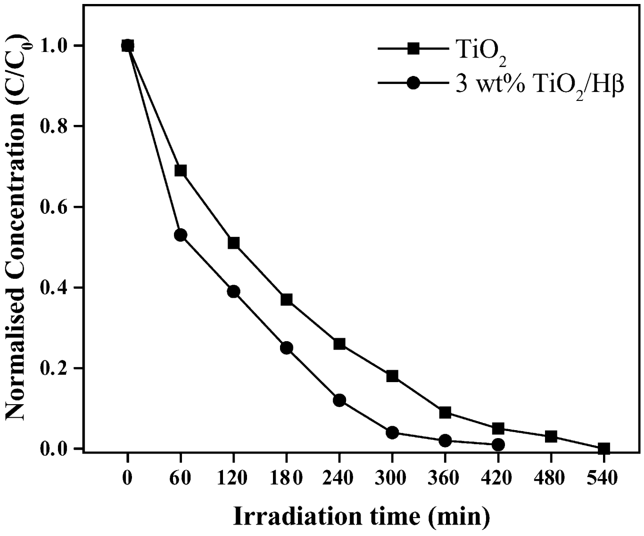

Fig. 7. Effect of irradiation time on MCP degradation monocrotophos concentration = 100 ppm; catalyst amount = 200 mg/100 ml; pH = 5.

3.8. *Mineralisation studies on TiO_2 and supported TiO_2 photocatalysts*

The extent of degradation and mineralisation of MCP were followed by high-performance liquid chromatography (HPLC) and total organic carbon (TOC) analyser. As irradiation time increases, MCP molecules degrade into fragments as evidenced by HPLC analysis and consequently mineralised completely. The decrease in degradation rate after one hour is due to the formation of less polar intermediates and their poor adsorption on the surface of titania. The experimental results revealed that MCP decomposed into harmless end products. The TOC results show that TiO_2 requires 540 min for complete mineralisation whereas supported TiO_2 requires only 420 min.

3.9. *Comparison of photocatalytic activity of TiO_2 and supported TiO_2 photocatalysts*

From the experimental results relative photonic efficiency was calculated for TiO_2 and TiO_2 supported on Hβ. The relative photonic efficiency in the MCP degradation employing TiO_2 and 3 wt.% TiO_2/Hβ is found to be 1.10 and 1.17, respectively. Similarly the relative photonic efficiency with respect to mineralisation for TiO_2 and 3 wt.% TiO_2/Hβ is found to be 1.07 and 1.10, respectively. It is evident that supported TiO_2 shows enhanced relative photonic efficiency. The higher adsorption capacity of supported TiO_2 results in higher MCP concentration around the TiO_2 particles, which enhances the possibility of attack of photogenerated active species on MCP molecules. Since TiO_2 is dispersed over Hβ zeolite this avoids particle–particle aggregation and light scattering by TiO_2. Further good dispersion leads to the presence of more number of active sites near the adsorbed MCP molecules resulting in its faster degradation. Apart from all, the strong electric field present in the zeolitic framework can effectively separate the electrons and holes produced during photo excitation of titania, a well known measure that can improve the photonic efficiency.

4. Conclusion

The results of the present investigation conclude that adsorption property of TiO_2 supported on Hβ zeolite enhances the photocatalytic degradation of MCP. Since MCP and its intermediates are adsorbed well over supported TiO_2 they are completely mineralised. Further 3 wt.% TiO_2 loading is sufficient to get higher degradation rate. It is also observed that zpc of TiO_2 and pK_a value for MCP has profound influence on the degradation rate. TOC results reveal that under optimal conditions TiO_2 requires 540 min and supported TiO_2 requires less than 420 min for complete mineralisation of MCP. Supported TiO_2 shows higher relative photonic efficiency for both degradation and mineralisation. Since supported system contains less amount of TiO_2 it reduces investment cost. Hence supported TiO_2 system has good potential for commercial applications.

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