Photocatalytic activity of ZnO impregnated Hβ and mechanical mix of ZnO/Hβ in the degradation of monocrotophos in aqueous solution

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Abstract

Adsorption experiments were carried out with monocrotophos (MCP) over supports (Hβ, HY and HZSM-5), ZnO, supported ZnO (ZnO/Hβ(I), ZnO/Hβ(M), ZnO/HY(I), ZnO/HZSM-5(I)) and TiO$_2$/Hβ. The results revealed that Hβ has better adsorption than HY and HZSM-5. Among the supported catalysts, ZnO/Hβ(I) showed higher percentage of adsorption than others. A series of supported catalysts (impregnation and mechanical mix) were prepared with different ZnO loadings and characterised by X-ray diffraction (XRD), SEM and BET surface area analysis. The photocatalytic degradation of monocrotophos in aqueous solution was carried out by using ZnO, supports and supported ZnO with low pressure mercury lamps. The influence of various parameters such as initial concentration of MCP, pH, catalyst loading and light intensity on the degradation was optimised. It was found that degradation of MCP followed first order kinetics. The experimental results demonstrated that the presence of zeolite in ZnO could enhance adsorption as well as degradation of MCP in aqueous suspension. The optimum loading for impregnated catalysts is 5 wt% whereas 1 wt% for mechanical mix catalyst. The time required for complete mineralisation of MCP under optimal experimental conditions over ZnO, 1 wt% ZnO/Hβ(M) and 5 wt% ZnO/Hβ(I) was 600, 360 and 240 min, respectively. The higher activity of ZnO/Hβ(I) is mainly due to fine dispersion of ZnO and hydrophobicity of the support.
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1. Introduction

The photocatalytic degradation of organic pollutants in water, using semiconductors such as TiO$_2$ and ZnO, has attracted extensive attention during the last two decades [1].

Previous studies have proved that such semiconductors can degrade persistent organic pollutants such as pesticides, detergents, dyes and volatile organic compounds under UV light irradiation, leading to total mineralisation of these pollutants into CO$_2$ and water [2–5]. However, the fast recombination rate of photogenerated electron/hole pair hinders the commercialisation of this technique [4]. This has led to great interest in improving the photocatalytic activity by suitable modification of semiconductors for the degradation of organic compounds in water. There are a number of studies related to ZnO coupled with metal oxides such as SnO$_2$, WO$_3$, Fe$_2$O$_3$ [6,7] and a few rare earth

oxides [8] for the purpose of improving photocatalytic activity of ZnO. It is reported that coupled semiconductors increase the photocatalytic efficiency. Similarly supported semiconductors are also found to increase the photocatalytic efficiency [9,10].

ZnO, as a photocatalyst, has received much attention due to its low cost and high photo-activity in several photochemical and photo-electro-chemical processes [11–13]. ZnO is a II–IV compound semiconductor with a wide and direct band gap of 3.37 eV and a large excitation binding energy of 60 meV [14]. The salient advantage with ZnO is its large absorption of solar spectrum [15]. Akyol et al. [16] studied the photocatalytic decolorisation of Ramazol Red RR in aqueous ZnO suspension reporting that ZnO exhibited higher photocatalytic activity. Photocatalytic degradation of Reactive Blue 4 over ZnO in a slurry reactor was reported by Neppolian et al. [17]. The degradation of the dye was facilitated by alkaline pH, and the presence of persulfate and carbonate ions. Sakthivel et al. [18] reported photocatalytic degradation of Acid Green 16 using ZnO irradiated with sunlight. Poulios and Tsachpinis [19] investigated the photocatalytic degradation of Reactive Black
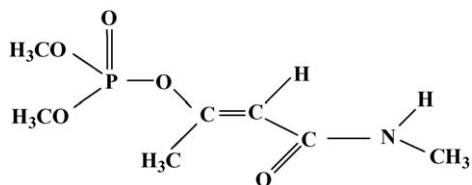
Fig. 1. Structure of monocrotophos.

5 using different semiconducting oxides viz., TiO$_2$ (Degussa P-25), UV-100 TiO$_2$, ZnO and TiO$_2$/WO$_3$ and observed that the decolorisation process was fastest with ZnO. Poulios et al. [20] conducted photocatalytic degradation of Auramine O in aqueous suspension using ZnO and TiO$_2$ separately in a batch reactor. They found that the rate of degradation of pollutants is faster with ZnO than with TiO$_2$ (Degussa P-25) [19,20]. Hoffman et al. [1] have also shown that ZnO produces H$_2$O$_2$ more efficiently than TiO$_2$. Thus, ZnO photo-assisted degradation may proceed in three different ways viz., photocatalytic oxidation or oxidation with photocatalytically generated H$_2$O$_2$, or simultaneous operation of both ways [21].

Despite the positive attributes of ZnO, poor adsorption properties lead to great limitation in exploiting this photocatalyst for its maximum efficiency. To circumvent this limitation, several attempts have been made to improve the efficiency of ZnO by using suitable supports such as glass, polymers, stainless steel, quartz, pyrex, paper, fabric, monoliths and zeolites [22–25]. Among the supports, zeolites have more advantageous owing to their special features such as high surface area, hydrophobic and hydrophilic properties, tunable chemical properties, high thermal stability and eco-friendly nature [26]. Reddy et al. [27] reported the photocatalytic degradation of salicylic acid using TiO$_2$/Hβ zeolite. They found that zeolite β increased the adsorption of pollutants as well as generation of large amount of hydroxyl ($^\bullet$OH) and peroxide radicals (HO$_2^\bullet$), which are the critical species in the photocatalytic degradation process. If the advantages of ZnO over TiO$_2$ are held, it is presumed that ZnO supported zeolite also exhibits better photocatalytic activity than TiO$_2$ supported zeolite. Further there is only limited literature available for the photocatalytic degradation of organic pollutants using ZnO supported zeolite. This prompted us to undertake an investigation featuring the preparation of ZnO supported catalysts by impregnation and mechanical mixing methods, and their photocatalytic activity towards degradation of monocrotophos (MCP) (Fig. 1), which is known as an insecticide. The influence of various parameters such as initial concentration of MCP, pH, amount of catalyst and light intensity on the degradation has been studied to achieve complete mineralisation of MCP. Finally, the relative photonic efficiency of ZnO supported catalysts and pure ZnO is compared and the results are presented in this manuscript.

2. Experimental

2.1. Materials

The technical grade sample of monocrotophos was received from Sree Ramcides Chemicals, India. Sodium form of zeolites

Y, β and ZSM-5 with Si/Al ratios 3, 15 and 53, respectively, was obtained from Sued-Chemie India Pvt. Ltd., India. Zinc oxide was obtained from Merck, India. HPLC grade acetonitrile was purchased from Merck, Darmstadt, Germany. All the chemicals were used without any further purification. Reaction mixtures and HPLC mobile phase were prepared in doubly distilled water.

2.2. Preparation of photocatalysts

The sodium form of zeolites Y, β and ZSM-5 was converted into the H-form by repeated ion exchange with 1 M ammonium nitrate solution at 80 °C, and subsequent calcination at 550 °C in air. The resultant H-form of zeolites was abbreviated as HY, Hβ and HZSM-5. ZnO supported catalyst was prepared by the impregnation method. HY, Hβ and HZSM-5 were used as the host material. The requisite volume of zinc nitrate solution was added into zeolite powder with continuous stirring. This mixture was kept in an oven at 120 °C overnight and then calcined at 550 °C for 5 h. Thus, ZnO impregnated catalysts were obtained and referred to as ZnO/Hβ(I). Different ZnO loadings (0.5, 1, 3, 5 and 7 wt%) were obtained by varying the concentration of zinc nitrate solution. The mechanical mixing method involved grinding of appropriate quantities of ZnO and Hβ in a pestle and mortar. The catalyst with ZnO of 0.5, 1, 3 and 5 wt% were prepared by the mechanical mixing method and referred to as ZnO/Hβ(M).

2.3. Characterisation of photocatalysts

X-ray diffraction patterns of Hβ, ZnO, ZnO impregnated Hβ catalysts were recorded by employing a PANalytical X-ray diffractometer with monochromated high intensity Cu Kα radiation in the scan range of 2θ between 5° and 70°. BET surface area analysis of Hβ, HY, HZSM-5, ZnO/Hβ(I) and ZnO/Hβ(M) was carried out using a Quantochrome Autosorb 1 sorption analyser. SEM analysis was performed using a Leo-Stereoscan 440 microscope.

2.4. Photocatalytic reactor set-up

Photocatalytic degradation was performed in a slurry batch reactor. The cylindrical photochemical reactor, measuring 30 cm × 3 cm (height × diameter) provided with a water circulation arrangement, was used in all the experiments. The irradiation was carried out using 8 × 8 W low pressure mercury lamps 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.

2.5. Adsorption studies

Prior to photocatalytic experiments, adsorption study of MCP on ZnO, support (Hβ, HY and HZSM-5) and ZnO supported catalysts was carried out by mixing 100 ml of aqueous solution of MCP with 100 mg of the catalyst. This slurry was equili-

brated for 30 min in a mechanical shaker. The aqueous MCP solution was then separated from the catalyst by centrifugation, and the change in MCP concentration was measured by HPLC. The extent of equilibrium adsorption was determined from the decrease in MCP concentration. From the adsorption experiments, the percentage of MCP adsorbed on the catalyst surface was determined from the following equation:

$$\text{adsorption}\,(\%) = \frac{C_0 - C_t}{C_0}$$

where C_0 is the initial concentration of MCP and C_t is the concentration of MCP at time 't' (min).

2.6. Photocatalytic degradation procedure

A stock solution containing $1000 \, \text{mg} \, \text{l}^{-1}$ of MCP was prepared in doubly distilled water and diluted to the required concentrations. Photocatalytic degradation was carried out with 100 ml MCP solution and 100 mg ZnO or supported ZnO. The experiments were performed at room temperature and the pH of reaction mixture was kept at solution pH (6.4–6.7). Prior to irradiation, the slurry consisting of MCP solution and ZnO or supported ZnO was stirred for 30 min to reach adsorption equilibrium followed by irradiation with UV lamps for degradation. Aliquots were withdrawn at specific time interval and analysed after centrifugation followed by filtration with Gelman GHP acrodisc of $0.2 \, \mu\text{m}$ to remove zinc oxide particles. The rate of degradation $(\text{mg} \, \text{l}^{-1} \, \text{min}^{-1})$ of MCP was calculated by multiplying the first order rate constant and initial concentration of MCP. The reusability of the catalyst was evaluated by retrieving the catalyst after degradation process followed by washing and drying in air at $110 \, ^\circ\text{C}$. Then the catalyst was reused for degradation of MCP under similar experimental conditions.

2.7. Analytical methods

The extent of degradation of MCP was determined by using a high performance liquid chromatograph (HPLC) (Shimadzu, LC-10 AT VP series, RP 18 CLS-ODS (M) column) equipped with a UV–vis detector. (Analysis conditions: eluent, acetonitrile:water (60:40); flow rate, $1 \, \text{ml} \, \text{min}^{-1}$; UV detector range, 230 nm.) The extent of mineralisation was determined by a total organic carbon (TOC) analyser (Euroglas TOC 1200).

2.8. Relative photonic efficiency (ξ_r)

The concept of relative photonic efficiency (ξ_r) has been introduced to compare the efficiencies of different photocatalysts. The relative photonic efficiency of the catalyst is obtained by comparing it with a standard photocatalyst (ZnO—Merck) and a standard test compound (formic acid, FA). In order to evaluate ξ_r, a solution of formic acid $(100 \, \text{mg} \, \text{l}^{-1})$ adjusted to pH 10 was irradiated for 30 min with 100 mg of ZnO or supported ZnO. From the degradation results, ξ_r was calculated as follows:

$$\varepsilon_r = \frac{\text{intial rate of formic acid degradation on supported ZnO}}{\text{intial rate of formic acid degradation on ZnO}}$$

where both initial rates were obtained under exactly identical conditions.

3. Results and discussion

3.1. Physiochemical characterisation of photocatalysts

3.1.1. X-ray diffraction

X-ray diffraction (XRD) patterns of Hβ, ZnO and ZnO/Hβ(I) catalysts are depicted in Fig. 2. It was observed that ZnO exhibited the hexagonal phase and the corresponding peaks were in good agreement with a previous report [18]. The intensity of peaks at $2\theta = 7.65^\circ$ and 22.4° corresponding to Hβ was also consistent with our earlier report [28]. The gradual increase in the intensity of ZnO peak $(2\theta = 37.5^\circ)$ and the decrease in the intensity of Hβ peak $(2\theta = 7.85^\circ$ and $22.4^\circ)$ clearly indicated increasing loading of ZnO. Similar observations were also made for ZnO/Hβ(M) catalysts.

3.1.2. Surface area measurements

The surface area of Hβ, HY and HZSM-5 are 575, 648 and $375 \, \text{m}^2 \, \text{g}^{-1}$. ZnO (0.5, 1, 3 and 5 wt%) was supported on zeolite by impregnation and mechanical mixing methods. The surface area of the impregnated ZnO/Hβ catalysts varied between 565 and $502 \, \text{m}^2 \, \text{g}^{-1}$ while that of mechanically mixed catalysts varied between 555 and $486 \, \text{m}^2 \, \text{g}^{-1}$. The surface area was gradually decreased for impregnated catalysts, but a rapid decrease was observed for mechanically mixed catalysts. The rapid decrease in the surface area for the latter would be due to blocking of zeolite pores by ZnO particles of large dimensions [29]. When zinc nitrate was used to produce ZnO/Hβ by the impregnation method, the ZnO particles were not as large as those in the com-
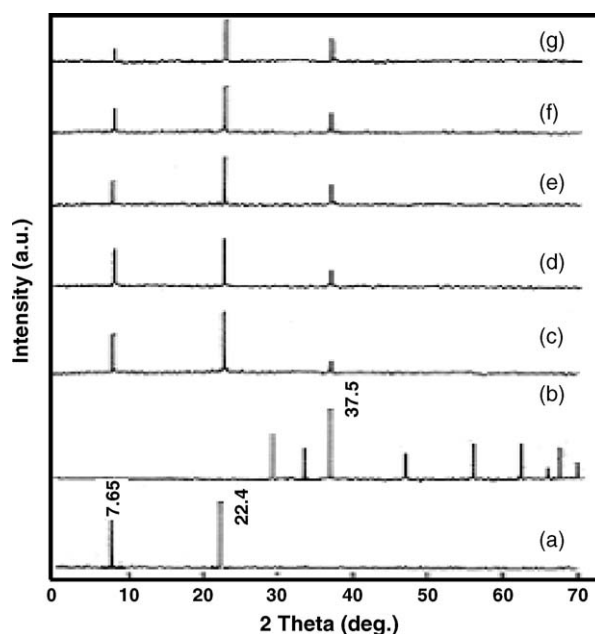
Fig. 2. XRD patterns of: (a) Hβ, (b) ZnO, (c) 0.5 wt% ZnO/Hβ, (d) 1 wt% ZnO/Hβ, (e) 3 wt% ZnO/Hβ, (f) 5 wt% ZnO/Hβ and (g) 7 wt% ZnO/Hβ.
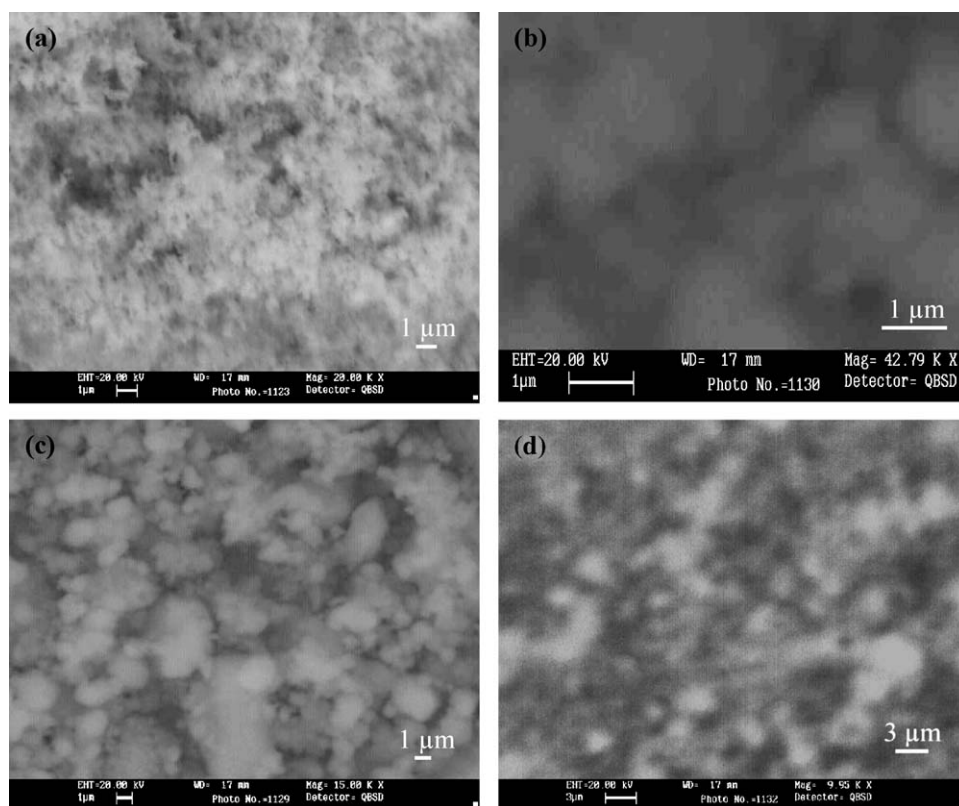
Fig. 3. SEM micrographs of ZnO and supported ZnO: (a) ZnO, (b) Hβ, (c) 1 wt% ZnO/Hβ(M) and (d) 5 wt% ZnO/Hβ(I).

mercial sample. Hence, the surface area was not much reduced. A similar decrease in surface area with ZnO loading on zeolite was reported earlier [30].

3.1.3. Scanning electron microscopy

SEM pictures of bulk ZnO, Hβ, ZnO/Hβ(M) and ZnO/Hβ(I) are shown in Fig. 3. The picture of ZnO/Hβ(I) clearly indicates the formation of tiny particles of ZnO (∼3 μm) on the surface of Hβ after impregnation followed by calcination (Fig. 3d). Bulk ZnO and ZnO/Hβ(M) (Fig. 3a and c) show particle size larger than about 5 μm.

3.2. Adsorption of MCP over zeolites

Prior to photocatalytic experiments, adsorption (dark) experiments were carried out with 100 ml MCP solution over zeolites (Hβ, HY and HZSM-5), pure ZnO, supported ZnO (ZnO/Hβ(I), ZnO/Hβ(M), ZnO/HY(I) and ZnO/HZSM-5(I)) and TiO$_2$/Hβ. As presented in Table 1, Hβ was found to adsorb more MCP than HY and HZSM-5. ZnO as such did not exhibit considerable adsorption capacity compared to zeolites. The large amount of MCP adsorbed over Hβ is due to hydrophobicity of Hβ zeolite. Furthermore, the presence of acid sites in Hβ could also be the reason for better adsorption of MCP [30]. The low adsorption capacity of HY and HZSM-5 is attributed to high hydrophilicity of HY and low surface area of HZSM-5. Among the supported catalysts, ZnO/Hβ(I) showed the highest percentage of adsorption. In addition, ZnO/Hβ(M) showed a similar adsorption

capacity to TiO$_2$/Hβ. The order of adsorption over supported catalysts was ZnO/Hβ(I) > TiO$_2$/Hβ ∼ ZnO/Hβ(M) > ZnO-HY(I) > ZnO-HZSM-5(I) > ZnO. This order closely follows the percentage of adsorption of MCP over parent zeolites: Hβ > HY > HZSM-5. These results are in accordance with a previous report [28]. The earlier study [31] revealed that about 40–50% adsorption on zeolite is ideal for differentiating adsorption from photocatalytic degradation. Therefore, it is necessary to optimise the amount of zeolite as well as ZnO for adjusting adsorption. Hence, adsorption of MCP was carried out by varying the amount of zeolites, and the results revealed that 45% of MCP was adsorbed over 100 mg of support containing 100 ml MCP solution within a period of 30 min. Hence, 100 mg of sample was used for further studies.

Table 1
Adsorption of MCP over zeolites and zeolite supported catalysts

Catalysts	Adsorption (%)
Hβ	45
HY	19
HZSM-5	15
ZnO	3.0
ZnO/Hβ(I)	40
ZnO/HY(I)	15
ZnO/HZSM-5(I)	11
ZnO/Hβ(M)	33
TiO$_2$/Hβ [28]	35

MCP = 100 mg l^{-1} (100 ml); pH 5; adsorption equilibrium time = 30 min.
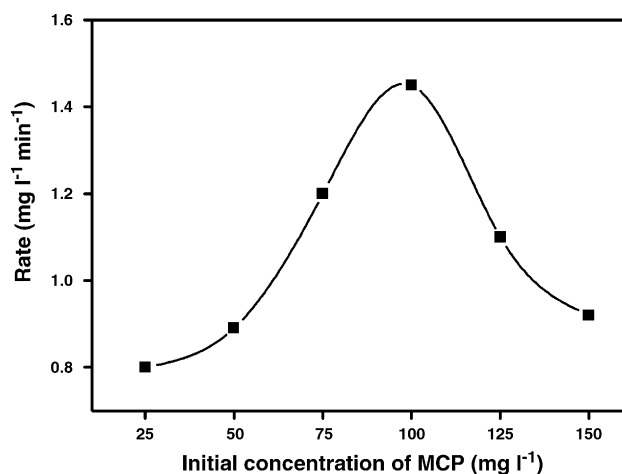
Fig. 4. Effect of initial MCP concentration on the rate of degradation (catalyst amount = 0.1 g/100 ml; pH 6.1).

3.3. Photocatalytic degradation of MCP

Photocatalytic degradation of MCP was carried out in a batch reactor and the reaction variables were optimised for maximum degradation efficiency. The essential reaction parameters viz., (i) initial MCP concentration, (ii) pH, (iii) light intensity and (iv) catalyst loading were varied and the results are delineated in the following sections.

3.3.1. Effect of initial concentration of MCP

The effect of initial MCP concentration on the degradation rate was evaluated by varying the initial concentration from 25 to $150 \, mg \, l^{-1}$ at a constant catalyst amount (0.1 g/100 ml) and at solution pH of 6.1. The plot of initial MCP concentration versus rate (Fig. 4) revealed that the degradation rate increased with increasing initial MCP concentration up to $100 \, mg \, l^{-1}$ and then decreased drastically. The degradation followed pseudo-first order kinetics at low MCP concentrations, which is also in accordance with our earlier reports [28]. The increase in degradation with increasing MCP concentration up to $100 \, mg \, l^{-1}$ was due to the increase in the adsorption of MCP on the catalyst surface. At higher concentrations, the absorption of UV light by MCP is supposed to be more than that by ZnO/Hβ, as the latter was completely blocked by the former and hence degradation efficiency decreased drastically at $150 \, mg \, l^{-1}$. This type of screening effect has been observed in the degradation of dyes [15,32]. Another reason for the decrease in degradation rate at higher concentration may be that major portion of degradation occurs in the region (termed as the reaction zone) close to the irradiated side since the irradiation intensity in this region was much higher than that on the other side [33]. Hence, at high concentrations degradation was hard to occur at sufficiently long distance from the light source or reaction zone due to retardation in the penetration of light [34]. It is concluded that as initial concentration of MCP increased, the requirement of catalyst surface needed for degradation also increased. Since illumination and amount of catalyst were constant, the $^{\bullet}OH$ and O_2^{2-} species attacking the MCP molecules presumably decreased with increasing MCP concentration [35].
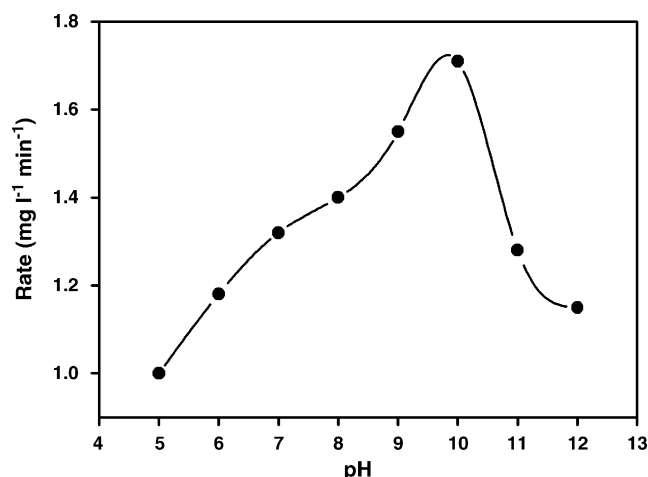

Fig. 5. Effect of solution pH on the rate of degradation (concentration of MCP = $100 \, mg \, l^{-1}$; catalyst amount = 0.1 g/100 ml).

3.3.2. Effect of pH

The solution pH exhibits profound influence on the ZnO oxidation potential and surface charge. The surface charge of ZnO has a significant effect on the adsorption and dissociation of MCP. Hence, the role of pH on the degradation rate was studied in the pH range 5–12 with $100 \, mg \, l^{-1}$ MCP concentration and 0.1 g/100 ml catalyst. The solution pH was adjusted only prior to irradiation and not controlled during the reaction. Fig. 5 shows that the rate of degradation increased with increasing pH and suddenly increased above pH 8, attaining a maximum value approximately at pH 10. The increase in the degradation rate with increasing pH up to 10 would be due to the increase in adsorption of MCP on the ZnO surface. Obviously photocatalytic degradation of MCP was strongly favored in alkaline pH. Sakthivel et al. [18] have observed a similar trend with ZnO, commenting that the acid–base property of the metal oxide surfaces have considerable implications upon their photocatalytic activity. The high degradation rate at pH 10 is accounted for by the zero point charge of ZnO 9.0 ± 0.3. Above this value, ZnO surface is negatively charged. The presence of large quantities of OH^- ions on the particle surfaces favors the formation of $^{\bullet}OH$ radical, which is accepted as the primary oxidizing species are responsible for degradation [36,37]. As the catalyst surface was covered by MCP molecules, absorption of UV radiation on the catalyst surface decreased. On the other hand, a noticeable decrease in the rate of degradation above pH 10 was observed as shown in Fig. 5. The decrease in the rate is not related to the partial solubilisation of amphoteric ZnO in alkaline media according to Eq. (1), which is negligible until pH 14 [38], as given in Eq. (2).

$$ZnO_{(s)} + 3H_2O_{(l)} \rightleftharpoons Zn(OH)_{4 \, (aq)}^{2-} + 2H_{(aq)}^+ \, (pK_{So} = 29.7)$$

$$(1)$$
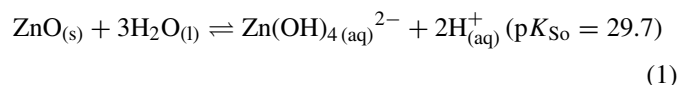
$$\log Zn(OH)_4^{2-} = -29.7 + 2 \, pH \tag{2}$$

At pH below the zero point charge of ZnO (9.0 ± 0.3), the surface is protonated. But MCP can also be protonated below pH 4.5 (pK_a value of MCP). Hence, below pH 4.5 MCP cannot be greatly adsorbed on the catalyst, giving low rates of

degradation. But above pH 4.5 MCP is deprotonated. Therefore, its adsorption on the surface will be favorable. When pH of the MCP solution increased there was an increase in the rate of degradation up to pH 10. Above pH 10, the catalyst surface may be covered by OH⁻ ions and hence it is negatively charged. Since MCP is not protonated above pH 10 it will be repelled by the negatively charged surface of ZnO. Hence, the degradation rate decreased above pH 10.

3.3.3. Optimisation of light intensity

The effect of light intensity was studied, keeping the wavelength (254 nm) unaltered. The influence of light intensity on the rate of MCP degradation has been examined at a constant MCP concentration ($100 \, mg \, l^{-1}$, pH 10) and a constant catalyst amount ($0.1 \, g/100 \, ml$). Two, four, six and eight UV lamps were turned on resulting in light intensities of 354, 600, 796 and 896 lx, respectively, as measured by a lux meter. The rate of degradation increased ($0.8–1.5 \, mg \, l^{-1} \, min^{-1}$) with increasing light intensity. Since the catalyst powder was suspended in a stirred solution, the light intensity would affect the degree of absorption of light by the catalyst surface. The catalyst powder could not promote oxidation of MCP without light. The degradation rate reached the maximum of $1.5 \, mg \, l^{-1} \, min^{-1}$ with light intensity of 896 lx ($8 \times 8 \, W$ lamps). The decrease in degradation at low light intensity is due to a decrease in the number of photons generated with a reduced intensity of light. Many researchers [15,39] previously observed similar linear relationship between the extent of degradation and light intensity.

3.3.4. Comparison of MCP degradation on ZnO and supported ZnO

The photocatalytic degradation of MCP over ZnO supported catalysts prepared by impregnation and mechanical mixing are presented in Table 2. In addition, the results obtained over TiO₂/Hβ [28], ZnO and Hβ are also given in Table 2. The rate obtained by photolysis is also given for comparison. It is evident that the photocatalytic method exhibited higher activity than the photolysis method. The parent ZnO catalyst and the supports (Hβ and HY) exhibited lower activity than the supported catalyst. Among the ZnO supported catalysts, ZnO/Hβ(I) showed the highest activity. The fine dispersion of ZnO (SEM pictures in

Table 2
Comparison of photocatalytic activity of various catalysts

Catalysts	Rate ($mg \, l^{-1} \, min^{-1}$)
ZnO	0.45
Hβ	0.30
HY	0.14
HZSM-5	0.11
ZnO/Hβ(I)	1.49
ZnO/HY(I)	0.80
ZnO/HZSM-5(I)	0.67
ZnO/Hβ(M)	1.18
Photolysis	0.10
TiO₂/Hβ [28]	1.09

MCP = $100 \, mg \, l^{-1}$ (100 ml); catalyst = 100 mg; pH 9; adsorption equilibrium time = 30 min; irradiation time = 30 min.
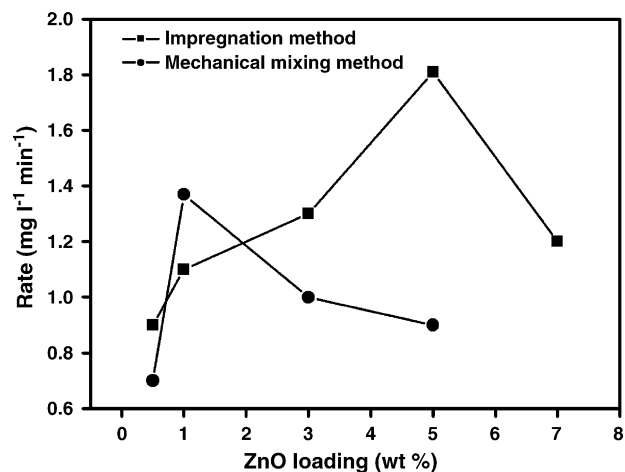

Fig. 6. Effect of ZnO loading on the rate of degradation (concentration of MCP = $100 \, mg \, l^{-1}$; catalyst amount = $0.1 \, g/100 \, ml$; pH 10).

Fig. 3d) and hydrophobicity of the support are the major factors for the high rate of degradation. ZnO/HY(I) showed lower activity than ZnO/Hβ(I). This is due to hydrophilicity of HY which reduces the adsorption of highly hydrophobic MCP. This observation clearly establishes the importance of support on the activity of degradation of MCP. ZnO/HZSM-5(I) is the least active among all the supported catalysts, although HZSM-5 is more hydrophobic. This observation reveals that adsorption of MCP on the surface of ZSM-5 is not the only necessary condition. The adsorption inside the pores becomes important for rapid degradation. Since HZSM-5 is a medium pore zeolite, it cannot permit the entry of all MCP. In addition it possesses the lowest surface area ($375 \, m^2 \, g^{-1}$) among all the supports. The catalyst ZnO/Hβ(M) showed activity close to that of TiO₂/Hβ but lower than that of ZnO/Hβ(I). ZnO/Hβ(M) catalysts (Fig. 3c) had particles of larger size, showing lower activity than ZnO/Hβ(I).

3.3.5. Optimisation of catalyst loading

Experiments were performed with ZnO/Hβ(I) and ZnO/Hβ(M) catalysts at various ZnO loadings to understand the influence of loading on degradation efficiency. The results depicted in Fig. 6 exhibit that increasing amount of ZnO on Hβ in the impregnation method increased the degradation up to 5 wt% and then decreased considerably. The higher degradation efficiency with 5 wt% might be due to •OH radicals produced by ZnO which is sufficient and readily accessible to nearby MCP. At higher loadings (>5 wt%) the degradation decreased due to less adsorption and light scattering. Free ZnO or growth of ZnO particle size may also be the reason for the decrease in the degradation rate at higher loadings. It is already reported that maximum photocatalytic activity in the degradation of MCP was achieved by supported catalysts with a low TiO₂ loading [28]. The results with mechanical mixing catalyst followed the same trend but it gives lower rate constant compared to those obtained by the impregnation method as this type of catalyst has free ZnO without resting on the support and ZnO of large dimensions. Among the four loadings of ZnO, 1 wt% is found to be the best. In the case of 0.5 wt% loading most ZnO can rest on the support but 3 and 5 wt% loading

Table 3
Comparison of relative photonic efficiencies in the photodegradation of formic acid by supported catalysts

Catalysts	Relative photonic efficiency (ξ_r)
ZnO	1.00 ± 0.03
ZnO/Hβ(I)	1.52 ± 0.01
ZnO/HY(I)	1.1 ± 0.01
ZnO/HZSM-5(I)	1.05 ± 0.01
ZnO/Hβ(M)	1.24 ± 0.01
TiO$_2$/Hβ [28]	1.17 ± 0.01

there will be free ZnO. Direct photolysis of MCP solution was conducted under identical experimental conditions led to very low degradation. In the impregnation method, with increasing ZnO loading from 0.5 to 5.0 wt%, there was an increase in the number of particles as well as their size. Hence, the degradation rate gradually increased. But in the mechanical mixing method, from 0.5 to 1.0 wt% loading, there was an increase in the degradation rate as more particles were present at 1 wt% loading, but above 1 wt% there was a decrease in the degradation rate due to agglomeration of particles. Hence, the optimum loading for impregnated catalysts was 5 wt% whereas 1 wt% for mechanically mixed catalysts.

3.4. Relative photonic efficiency (ξ_r)

Relative photonic efficiency is a useful quantitative parameter to compare the efficiency of different photocatalysts. In the present study, formic acid was chosen as the standard test compound and ZnO (Merck) as the standard photocatalyst [40]. The relative photonic efficiencies in the photocatalytic degradation of formic acid over ZnO, supported ZnO and TiO$_2$/Hβ are presented in Table 3. Pure ZnO without any support possessed lower photonic efficiency, thus illustrating the positive role of the support ZnO/Hβ(I) showed higher relative photonic efficiency than ZnO/HY(I) and ZnO/HZSM-5(I). ZnO/HY(I) showed low efficiency as this support was more hydrophilic which repels MCP and ZnO/HZSM-5(I) showed less efficiency as it did not permit the entry of MCP into its pore. Diffusion of MCP into the pores of the supports appears to be important to acquire high photonic efficiency. ZnO/Hβ(M) showed photonic efficiency close to that of TiO$_2$/Hβ, indicating a similar activity for TiO$_2$/Hβ and ZnO/Hβ(M) in MCP degradation.

3.5. Mineralisation studies

Complete mineralisation of pollutants with cost-effective process is important for industrial applications. The extent of degradation and mineralisation were followed by HPLC and TOC analysis, respectively. The HPLC chromatograms revealed that MCP molecules were degraded into smaller fragments of low molecular weight and subsequently mineralised completely. Figs. 7 and 8 illustrate that ZnO/Hβ(I) required shorter irradiation time for complete mineralisation of MCP than ZnO/Hβ(M) and ZnO alone. This would be due to good adsorption of MCP anions and its intermediates on zeolite surface where •OH radi-
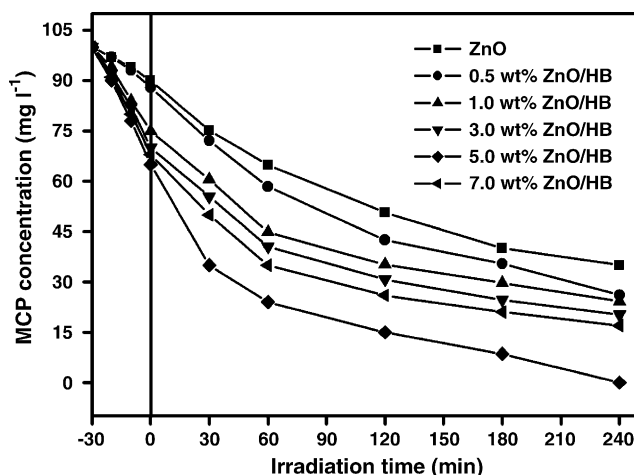

Fig. 7. Performance of ZnO/Hβ(I) on MCP adsorption and degradation (concentration of MCP = 100 mg l^{-1}; catalyst amount = 0.1 g/100 ml; pH 10).

cals are available for breaking MCP molecules. The high activity of ZnO/Hβ could be due to generation of large amount of hydroxyl (•OH) and peroxide (•HO$_2$) radicals by Hβ [27]. The •OH radical is strong enough to break different bonds in MCP adsorbed on the surface of ZnO thus leading to complete mineralisation of MCP [41,42]. The extent of MCP mineralisation increased with increasing irradiation time. The rate of mineralisation was high in the initial period followed by the slow rate. This slow rate indicates the formation of a few long-lived byproducts, which had a low rate of reaction with hydroxyl radicals [43,44]. This reveals the formation of intermediates and their competitiveness with MCP anions in the photocatalytic degradation process. A further increase in the degradation of MCP and release of phosphate and nitrate ions reduced the reaction rate more greatly as they get adsorbed on the catalyst surface. Carbonate, nitrate and perchlorate ions have a little effect on the rate of photo-oxidation. The inhibitory effects of chloride, sulfate and phosphate may be accounted for by the Langmuir–Hinshelwood kinetic model, in which inorganic ions compete with organic solutes for oxidizing sites on the catalyst surface. Abdullah et al. [45] reported that sulfate and phosphate ions inhibited the photocatalytic oxidation of organic solutes and reduced the rate
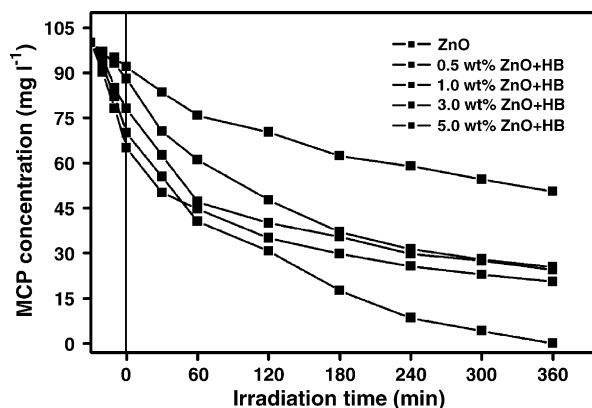

Fig. 8. Performance of ZnO/Hβ(M) on MCP adsorption and degradation (concentration of MCP = 100 mg l^{-1}; catalyst amount = 0.1 g/100 ml; pH 10).

up to 70%. The time required for complete degradation and mineralisation with 5 wt% ZnO/Hβ(I), 1 wt% ZnO/Hβ(M) and pure ZnO under optimised conditions was 240, 360 and 600 min, respectively.

3.6. Catalyst life

Catalyst life can be estimated by standard tests conducted with standard solution (formic acid) at specific intervals and determining the rate of reaction at each time. In the present study, $100 \, mg \, l^{-1}$ of formic acid was used as the standard reference. The reusability of ZnO/Hβ supported catalyst in the degradation of MCP was evaluated. After degradation, ZnO/Hβ in the quartz reactor was recovered by filtration, calcined and tested again for its activity under identical experimental conditions. ZnO/Hβ exhibited almost the same catalytic activity for four cycles of operation. The degradation rate before irradiation was found to be $1.49 \, mg \, l^{-1} \, min^{-1}$, but after four cycles it was equal to $1.2 \, mg \, l^{-1} \, min^{-1}$. There was not much change in the activity of these catalysts. Even if zinc hydroxide was formed during photocatalytic degradation, it could be converted into active ZnO during calcination. Thus, ZnO can be repeatedly used for photocatalytic degradation of organic pollutants. But the decrease in the efficiency of recycled catalyst after four cycles may be attributed to the deposition of photo-insensitive hydroxides (fouling) on the photocatalyst surface which block the active sites. When the experiment was done in the dark, the reproducibility was not obtained. This might be due to blocking of the surface of ZnO with components of MCP. Reutergardh and Iangphasuk [46] reported that TiO$_2$ could be used twice without significant change in the efficiency. In the present study, ZnO impregnated Hβ was readily recyclable for four cycles without significant loss of photocatalytic activity.

3.7. Comparison of MCP degradation over ZnO/Hβ and TiO₂/Hβ

Shankar et al. [28] reported the degradation of MCP over TiO$_2$/Hβ. They reported that complete mineralisation of MCP required 420 min over TiO$_2$/Hβ. But in the present study with ZnO/Hβ(I), complete mineralisation required only 240 min. In addition, the relative photonic efficiency for the degradation of MCP over TiO$_2$/Hβ was 1.17 whereas that for ZnO/Hβ(I) was 1.52. The results clearly reveal that ZnO supported Hβ exhibits higher photocatalytic activity than TiO$_2$ supported Hβ. The same trend was also reported in other studies [20,18]. The cause for higher photocatalytic activity over ZnO is due to greater quantum efficiency of ZnO than TiO$_2$. In addition, ZnO is stable in the pH range of 4–14 [37,47]. The solubility test involving ZnO with MCP solution at pH 10 and 13 revealed no solubility of ZnO. Based on these facts, it is concluded that ZnO/Hβ is a better photocatalyst than TiO$_2$/Hβ for the degradation of MCP.

4. Conclusion

The results of the present investigation concluded that zeolites play a key role in the adsorption of MCP. Hβ is found to adsorb more MCP than HY and HZSM-5. The rate of degradation over Hβ, ZnO and ZnO/Hβ supported catalysts revealed that neither the support nor the catalyst alone exhibits any influence independently, but there is a mutual synergistic influence on the degradation of MCP. The higher activity of supported ZnO is due to improved adsorption of MCP and efficient delocalisation of photogenerated electrons by the Hβ support. ZnO/Hβ catalyst prepared by the impregnation method exhibits higher photocatalytic efficiency than mechanically mixed ZnO/Hβ. Comparison of the photocatalytic activity of ZnO/Hβ and TiO$_2$/Hβ illustrates higher activity for the former than the latter. The recyclability test also reveals the stability of ZnO/Hβ catalysts. In addition, ZnO is cheaper than TiO$_2$ and hence can be exploited for the degradation of MCP and other pollutants at a low cost.

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