

PHOTODEGRADATION OF TEXTILE WASTEWATER USING ULTRA VIOLET IRRADIATION AND TiO₂/ZEOLITE SYSTEM

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Abstract: The photodegradation of textile wastewater using UV irradiation and TiO₂/Zeolite system has been investigated. TiO₂/Zeolite was prepared by dispersing TiO₂ crystal into Zeolite. Zeolite and TiO₂/Zeolite were characterized by X-ray diffractometer (XRD), Fourier Transform Infra Red (FT-IR) spectrophotometer, X-ray fluorescence (XRF) analyzer and Gas Sorption Analyzer (GSA) to observe some physical and chemical properties. Photocatalytic activity of TiO₂/Zeolite was then tested. The filtrate was analyzed for Chemical Oxygen Demand (COD) by dichromate method. Analysis results showed that XRD and FTIR data did not indicate formation of TiO₂ in Zeolite. However, elemental analysis result with XRF indicated that the titanium concentration increased from 0.259% (w/w) in Zeolite to 1.597% (w/w) in TiO₂/Zeolite. GSA data showed the increase of specific surface area from 19.565 m² g⁻¹ for Zeolite to 21.530 m² g⁻¹ for TiO₂/Zeolite; total pore volume from 20.640 x 10⁻³ mL g⁻¹ for Zeolite to 21.755 x 10⁻³ mL g⁻¹ for TiO₂/Zeolite. Photocatalytic activity of TiO₂/Zeolite for degradation of textile wastewater showed that in 90 minutes UV radiation resulted in the decrease of wastewater COD up to 38.22% from its initial COD of 157 mg L⁻¹.

Keywords: Zeolite, TiO₂ photocatalyst, photodegradation, COD

INTRODUCTION

The interest in porous or layered materials as host structures for molecules with specific catalytic properties has increased over the years. A number of applications of such nanocomposites as photosensitive devices, photocatalyst and solar cells have been reported. A particularly successful system results by insertion of semiconductors, for examples CdS, Fe₂O₃ and TiO₂ into layered or pore system such as synthetic saponite, synthetic zeolite, MCM-41 which leads to photocatalytic properties of the nanocomposite materials [1-3]. In order to exploit the

photocatalytic properties of the semiconductor of TiO_2 in another porous material, we use natural zeolite as host materials for photocatalyst experiment because of its channel system. Formation of semiconductor in zeolite matrix depends on several factors, such as location of cations, migration of the cations, strength of the interactions between cations and guest molecules, dimensions of cavities and channels. The combination of the two properties will lead to distinct and different properties as compared to those with semiconductor alone. The combination can be carried out through three ways, namely: solid-solid, solid-liquid and solid-gas reactions [3-4]. Nowadays, so-called solid-solid reactions, which occur between powders in the solid-state, have attracted some considerable attention because of the possibility to prepare new compounds not accessible from solutions as well as the ease of operation. Solid-state reactions between inorganic species have been studied, however, solid-state reaction between TiO_2 powders with natural Zeolite has not yet been studied so far [5].

The present paper explores first the synthesis of TiO_2 /Zeolite by solid-solid reaction and its physicochemical properties. Secondly, we focus on a application of TiO_2 /Zeolite to decrease of Chemical Oxygen Demand (COD) concentration of Khangma Co. Ltd., Bhutan waste water by photodegradation method. The photodegradation was carried out by irradiating suspension of TiO_2 /Zeolite and waste water with UV light at certain wavelength for a few minutes. Due to the photodegradation, the harmful or toxic compounds in the wastewater will be decomposed into more environment-friendly compounds.

MATERIALS AND METHODS

Materials

Natural zeolite collected from Shajna village Bhutan was used as the host material (Fig. 1). As the guest semiconductor material, TiO_2 powder (mostly anatase type) was obtained from Merck and used without further purification.

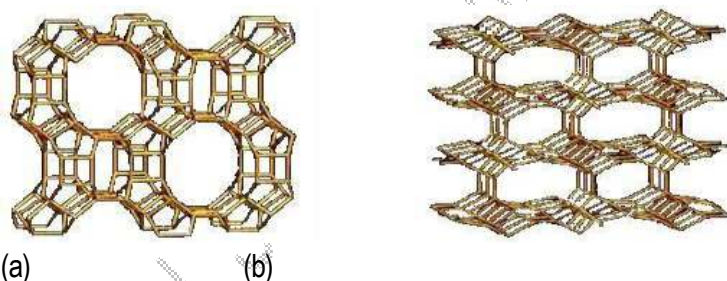


Fig. 1: The structure of common natural Zeolite found in Bhutan: (a) Mordenite, (b) Clinoptilolite.

Modification

TiO_2 /Zeolite was prepared by dispersing TiO_2 crystal into natural Zeolite and followed by grounding the mixture with a mortar and a pestle for a few minutes at ambient temperature. The mixture contained 2% (w/w) TiO_2 . The mixture then was heated using microwave oven of 800 watt for 5 minutes.

Characterization

Zeolite and photocatalyst TiO_2 /Zeolite were characterized by X-Ray Diffractometer (XRD), Shimadzu 6000, Fourier Transform Infra Red (FT-IR) spectrophotometer, FTIR-8201 PC, X-Ray Fluorescence (XRF) analyzer EG & G OTEG 7001 and Gas Sorption Analyzer (GSA) NOVA

1000 to observe some physical and chemical properties such as crystallinity, functional groups, titanium concentration, specific surface area, total pore volume, and isotherm adsorption.

Application of TiO₂/zeolite as photocatalyst to decrease COD number

Photocatalytic activity of TiO₂/Zeolite was tested by dispersing 100 mg photocatalyst into 100 mL wastewater and exposing the suspension by the UV light of 366 nm at room temperature for 15 – 90 minutes. The COD concentrations were determined in accordance to APHA [6].

RESULTS AND DISCUSSION

Synthesis of TiO₂/Zeolite

The X-ray powder diffractograms of pure TiO₂ (Merck), Zeolite and TiO₂/Zeolite are shown in Figure 2. The diffractogram indicated that the natural Zeolite was composed mostly by mordenite and some clinoptilolite. By grinding the mixture of natural Zeolite and TiO₂ powder for a few minutes, the obtained X-ray patterns exhibit no reflections characteristic of TiO₂ molecules on TiO₂/Zeolite. There is a possibility that the reflections of TiO₂ are overlapped with those of Zeolite. This fact implied that It does not mean that TiO₂ particles were not dispersed on Zeolite surfaces.

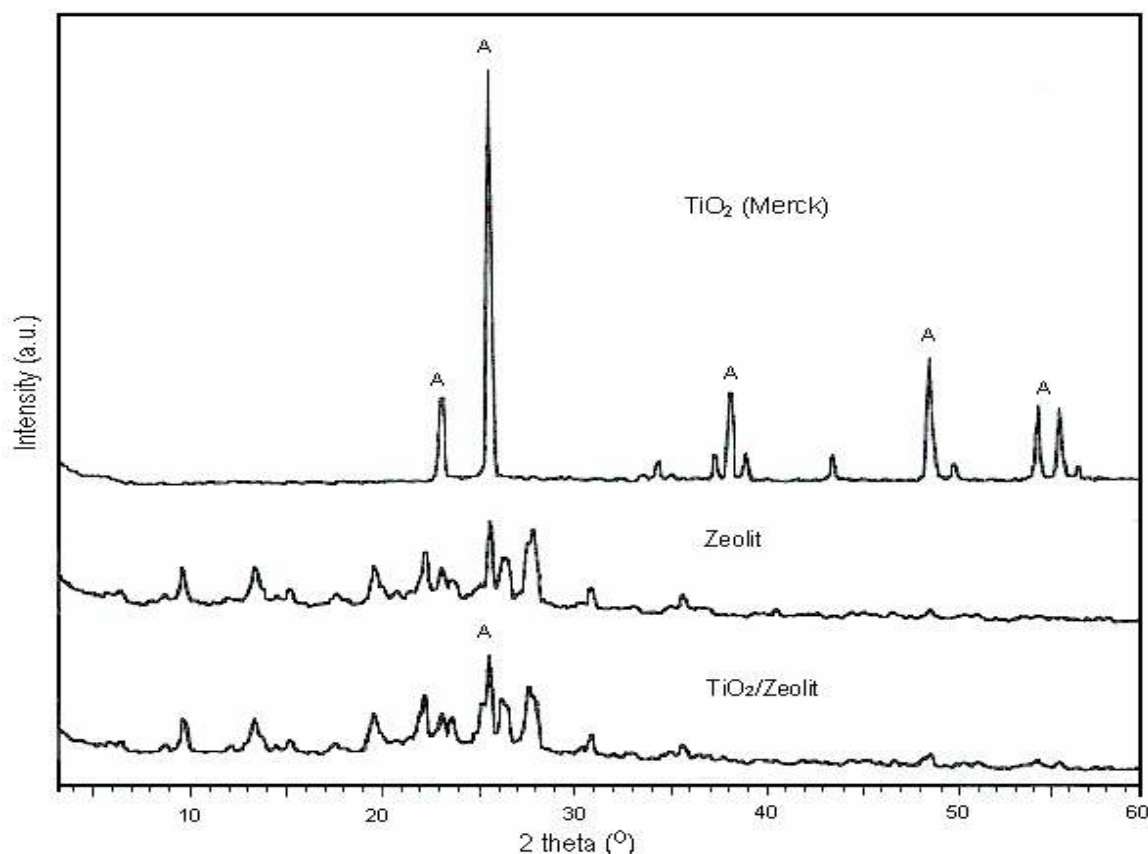


Fig. 2: Diffractograms of TiO₂ (Merck), Zeolite and TiO₂/Zeolite

Surface area and pore size distributions were calculated from the corresponding nitrogen adsorption isotherms at low temperature (Fig. 3 and Table 1). Figure 4 show the nitrogen adsorption of Zeolite and TiO₂/Zeolite. The shape of these samples corresponds with type IV of

the BDDT classification. These facts suggest that the samples are micro and mesoporous materials. The specific surface areas were calculated with the BET equation. Porosimetry analysis data showed that the dispersions of the TiO_2 resulted in the increase of specific surface area from $19.565 \text{ m}^2 \text{ g}^{-1}$ for Zeolite to $21.530 \text{ m}^2 \text{ g}^{-1}$ for $\text{TiO}_2/\text{Zeolite}$; total pore volume from $20.640 \times 10^{-3} \text{ mL g}^{-1}$ for Zeolite to $21.755 \times 10^{-3} \text{ mL g}^{-1}$ for $\text{TiO}_2/\text{Zeolite}$. Figure 3 showed that the incorporation of TiO_2 into Zeolite shift the pore distribution to the right side (meso and macro pore side). It is in agreement with the increasing of the specific surface area and total pore volume calculated by BET method. These results implied that TiO_2 particles have been distributed on the both external and internal surface of Zeolite.

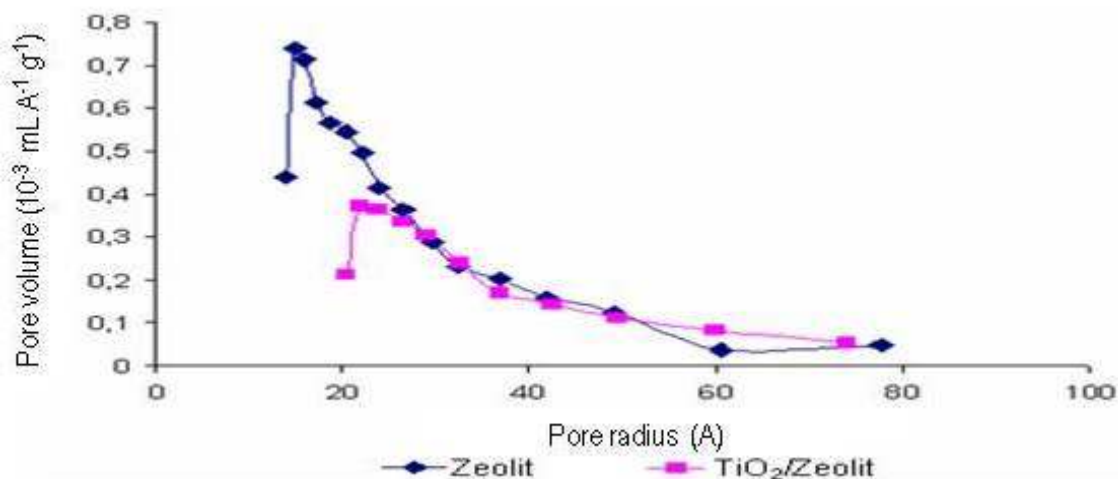


Fig. 3: Pore size distribution of $\text{TiO}_2/\text{Zeolite}$ and Zeolite

Table 1: Specific surface area and total pore volumes of natural Zeolite and $\text{TiO}_2/\text{Zeolite}$

Sample name	Specific Surface Area ($\text{m}^2 \text{ g}^{-1}$)	Total Pore Volume ($\times 10^{-3} \text{ mL g}^{-1}$)
Zeolite	19,565	20,64
$\text{TiO}_2/\text{Zeolite}$	21,530	21,755

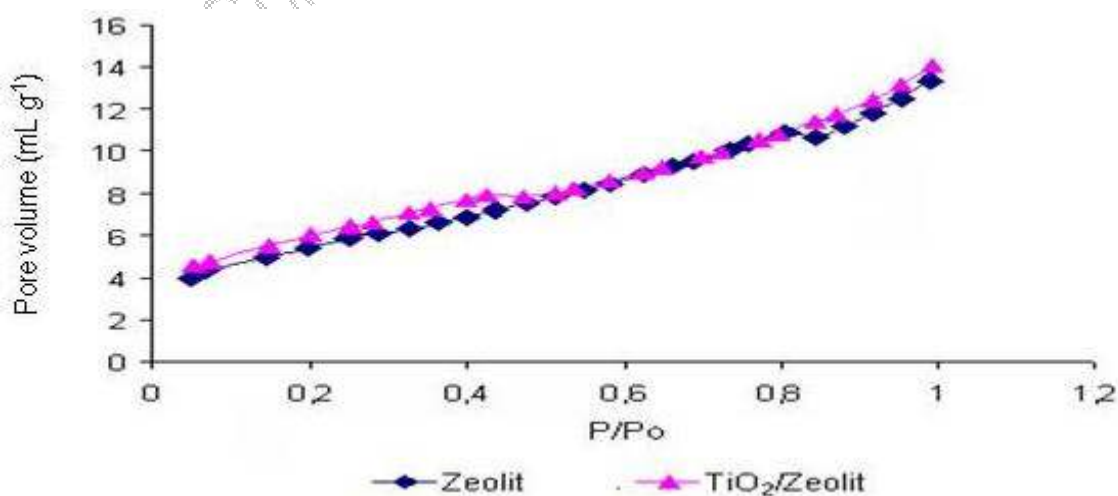


Fig. 4: N_2 -Adsorption isotherm curves of Zeolite and $\text{TiO}_2/\text{Zeolite}$

The FT-IR spectrum of TiO₂ loaded Zeolite is exhibited in Fig. 5. For comparison study the FT-IR spectra of pure TiO₂ (Merck) (middle curve in Fig. 5) and natural Zeolite (upper curve) are shown. The infrared spectra of the TiO₂/Zeolite at 424,3 cm⁻¹ showed the absorption bands due to TiO₂, confirming the existence of TiO₂ on TiO₂/Zeolite sample. Moreover, the dispersion of TiO₂ in Zeolite resulted in the broadening of absorption band between 900 cm⁻¹ up to 500 cm⁻¹ on TiO₂/Zeolite spectrum. Thus, it can be postulated that TiO₂ has been dispersed on the surface of Zeolite. The amount of the adsorbed TiO₂ (stated as titanium) on Zeolite and TiO₂/Zeolite were 0,259 and 1,597% (w/w) respectively. Even after the shocking and repeated washing with water, certain amounts of TiO₂ were involved in the product. These values indicated that the dispersion of TiO₂ on to natural Zeolite was successful.

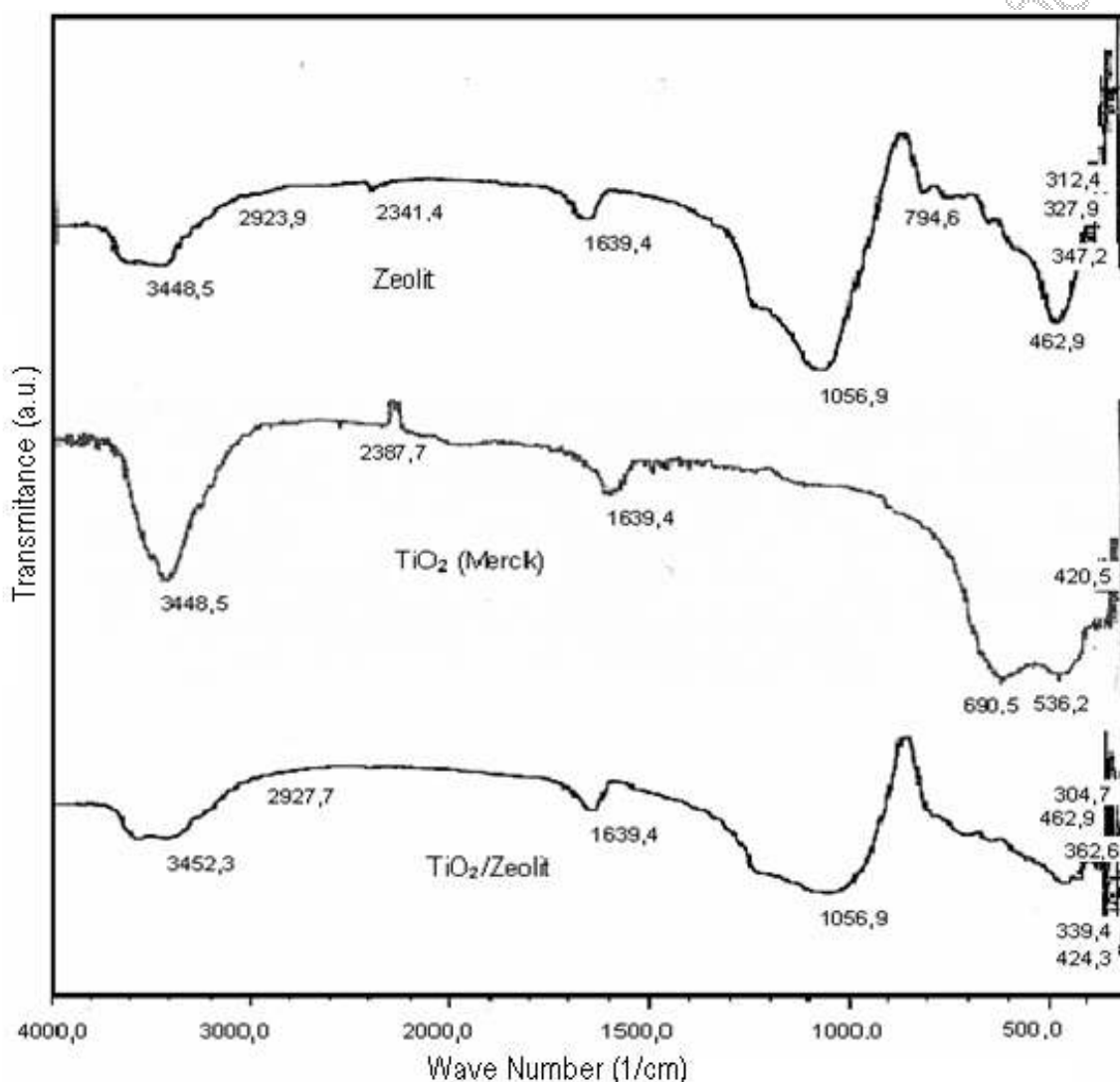


Fig. 5: Infra red spectra of Zeolite, TiO₂ (Merck) and TiO₂/Zeelite

From characterization results it can be concluded that the formation of TiO₂/Zeolite from its components may be represented as in Fig. 6. With mixing and grinding, TiO₂ particles would cover external and internal surface of zeolite. Calcination caused the particles partially sintered

and anchored to the surface of Zeolite. Finally, washing and shocking would remove some TiO_2 particles from the surface of Zeolite.

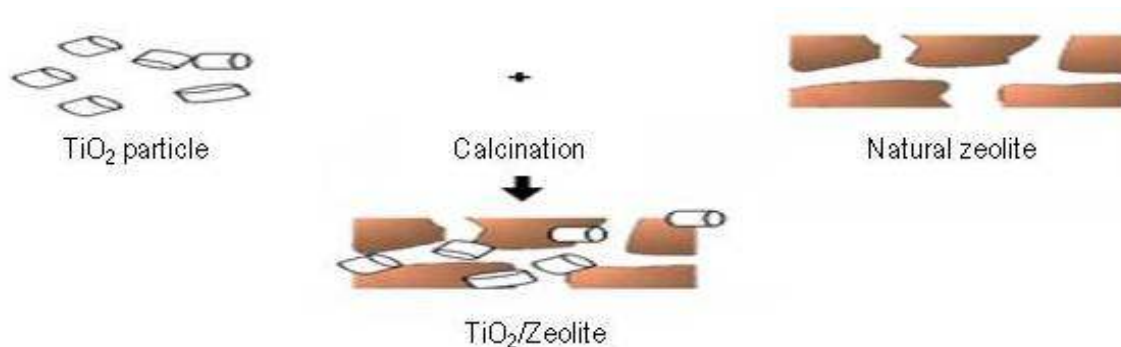


Fig. 6: The proposed model of TiO_2 dispersed natural Zeolite ($\text{TiO}_2/\text{Zeolite}$)

Application of $\text{TiO}_2/\text{Zeolite}$ as photocatalyst to decrease COD concentration

Table 2 lists the effect of time irradiation toward COD concentration of the test wastewater. The COD concentrations of sample in most right side of Table 3 do not change at all with irradiation time. This is primarily because the natural Zeolite do not contain TiO_2 particles as photocatalysts. The effect of both semiconductor, i.e TiO_2 as well as UV irradiation were demonstrated in the third and fourth columns of the table. In the third row it can be seen that the $\text{TiO}_2/\text{Zeolite}$ can decrease COD concentration with assisting UV irradiation, meanwhile without UV irradiation, COD concentration of the waste water sample were relatively constant with the increasing of the contact time.

Table 2: The effect of UV irradiation and $\text{TiO}_2/\text{Zeolite}$ toward the decreasing of COD of the textile wastewater

No	Time (minute)	COD concentration (mg L^{-1})		
		$\text{TiO}_2/\text{Zeolite}$ with UV	$\text{TiO}_2/\text{Zeolite}$ without UV	Zeolite with UV
1	15	121	113	97
2	30	113	105	97
3	45	105	97	-
4	60	97	113	97
5	75	105	97	97
6	90	97	113	97

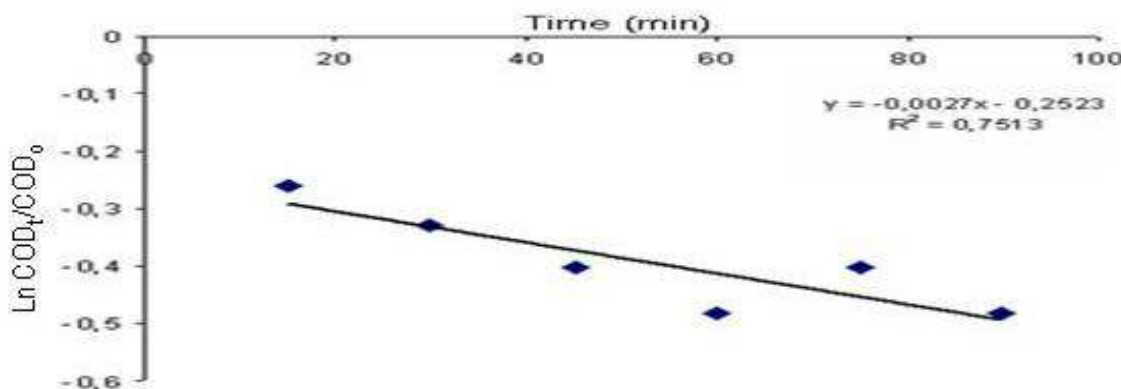


Fig. 7: The simple kinetics of the decrease of COD vs irradiation time

Figure 7 summarizes the effects of UV irradiation time and TiO₂ on the COD of the textile wastewater. The COD of the sample decreased with increasing irradiation time and the calculation results showed that the reaction followed probably pseudo first order reaction as stated by its low R² value which was relatively far from 1. From this curve it can be predicted that 90 minutes UV radiation on suspension of TiO₂/Zeolite and waste water resulted in the decrease of wastewater COD up to 38.22% from its initial COD number of 157 mg L⁻¹. This value exhibited that actually TiO₂/Zeolite was not an effective photocatalyst for degradation of toxic materials in the test wastewater.

CONCLUSION

In conclusion, XRD and FTIR analysis data did not indicate formation of TiO₂ in Zeolite. However, elemental analysis result with XRF indicated that the titanium concentration increased from 0.259% (w/w) in Zeolite to 1.597% (w/w) in TiO₂/Zeolite. Porosimetry analysis data showed the increase of specific surface area from 19.565 m² g⁻¹ for Zeolite to 21.530 m² g⁻¹ for TiO₂/Zeolite; total pore volume from 20.640 x 10⁻³ mL g⁻¹ for Zeolite to 21.755 x 10⁻³ mL g⁻¹ for TiO₂/Zeolite. Judging from observed physico-chemical properties of both Zeolite and TiO₂/Zeolite, TiO₂ particles were probably distributed randomly on internal as well as external surface of Zeolite. Photocatalytic activity of TiO₂/Zeolite for degradation of textile wastewater showed that in 90 minutes UV radiation resulted in the decrease of wastewater COD up to 38.22% from its initial COD of 157 mg L⁻¹. As a general conclusion, solid state reaction can be used as an alternative to prepare a TiO₂/Zeolite photocatalyst. Although this material was not an effective photocatalyst, it can be promoted as a photocatalyst for degradation of wastewater.

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