Photodegradation of Indigo Dye Using TiO₂ and TiO₂/Zeolite System

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Photodegradation of indigo dye in aqueous solution using anatase TiO₂ and TiO₂/zeolite composite photocatalyst were studied. The composite photocatalysts were prepared by using sol-gel method. Calcination sol-gel was performed in a muffle furnace at 450 ºC for 4 h. The photocatalysts were characterized using SEM and XRD. 0.4 g of photocatalysts were used to degrade 500 mL of indigo dye giving a constant catalyst loading of 0.8 g/L in varying indigo dye concentration of between 10-20 mg/L. The results showed that the photocatalytic behaviour of TiO₂/zeolite composite sample was better as the degree of degradation for TiO₂/zeolite was higher compared to the neat TiO₂ sample. The percentage degradation achieved by using TiO₂/zeolite in 10 and 20 mg/L were 58.6 and 75.0 % respectively. In addition, the degradation process followed the first-order reaction kinetics where the rate constant, k, for the degradation of indigo dye solution was in the range of 0.1207-0.2669 h^{-1} (not presented). This work demonstrates that the sol-gel method was successful in preparing an effective TiO₂/zeolite composite photocatalyst.

Key Words: TiO₂/zeolite, Photodegradation, Indigo dye.

INTRODUCTION

In modern industrial society, dyes are widely used in textiles, printing, dyeing and food[1]. It is estimated that from 1 to 15 % of the dye is lost during dyeing processes and is released in wastewater[2]. The disposal of industrial waste is an important issue since the discharges of highly coloured wastewater into the ecosystem lead to environmental problems like aesthetic pollution (even a small amount of dye is clearly apparent) and perturbation of aquatic life[3]. In other word, dyes represent a serious danger for the aquatic environment. However, dye pollution do not only affect the water quality, but also affect health as some of these dyes are mutagenic, carcinogenic and teratogenic[4]. Therefore, research has been carried out over the last two decades to develop strategies for removing, destroying or recovering dyes present in water[5]. In this study, indigo dye is used as a target pollutant to undergo photodegradation. Indigo dye belongs to an ancient class of dyes called vat dyes. In modern times, it is synthetically produced in large quantities (20 million kg annually) and used mainly for dyeing cotton materials such as denim cloth or jeans. Indigo dye is an organic compound with a molecular formula, $C_{16}H_{10}N_2O_2$. This dye is a blue colorant obtained from the indigo plant (*Indigoferatinctoria*) and woad (*Isatistinctoria*). Photocatalysis, an advanced oxidation process, employing semiconductors

such as TiO₂ as photocatalysts, is a promising method for the *in situ* elimination of organic pollutants in water[6]. Photocatalysis is a heterogeneous catalytic reaction under the irradiation of ultraviolet light in the presence of a light activated photocatalyst[4]. Various studies have been published on the photocatalytic degradation of organic dyes in wastewater utilizing titanium dioxide[4,7,8]. Titanium dioxide exists in four mineral forms *i.e.*, anatase, rutile, brookite and titanium dioxide (B). Anatase type TiO₂ has a crystalline structure that corresponds to the tetragonal system which mainly used as photocatalyst under UV irradiation. Rutile type TiO₂ has a tetragonal crystal structure. It is normally used as white pigment in paint. On the other hand, Brookite type of TiO₂ has an orthorhombic crystalline structure. Titanium dioxide (B) is a monoclinic mineral and is a relatively a new form in titania family[7,8]. TiO₂ photocatalysis is attractive due to the possibility of utilizing solar source as a renewable energy. Besides, the stability of its chemical structure, biocompatibility, physical, optical and electrical properties it is also an easily obtainable material[7]. Titanium dioxide is an inexpensive material, because titanium is the world's 7th most abundant metal and 9th most abundant element[4]. Titanium dioxide can be used in form of a fine powder or crystals dispersed in water wastewater treatment applications[9]. Titanium dioxide is a semiconductor. This "semiconductor" can be activated by UVA light (near UV) of wavelength $\lambda \leq$

390 nm[4,10]. When TiO$_2$ is irradiated with UV light, electron (e$^-$)-hole (h$^+$) pairs are produced. The generated electron-hole pairs are capable of initiating oxidation and reduction reactions on the surface of TiO$_2$ particles. In aqueous solution, the holes are scavenged by surface hydroxyl groups to produce efficient oxidizing hydroxyl radicals (˙OH). Then, the reactive hydroxyl radicals will react rapidly with organic compounds leading to total mineralization of the organic substrate[2]. However, in order to enhance the properties of the TiO$_2$ such as to give it better adsorption properties or to enable fast separation of the photocatalyst from the treated solution, the TiO$_2$ is doped with other materials such as ferum, activated carbon or zeolite. Zeolites have a rigid, three-dimensional crystalline structure similar to a honeycomb which consists of a network of interconnected tunnels and cages. Water can move freely in and out of these pores but the zeolite framework remains rigid. The pore and channel sizes of zeolites are nearly uniform, thus allowing the zeolite to act as a molecular sieve. This unique porous property also allows zeolite to act as an adsorbent for separation work. Another ability of zeolite is in cation exchange. Zeolites offer a promising support for TiO$_2$ photocatalyst because of its regular pores and channel sizes and good adsorption ability. TiO$_2$ supported onto zeolite integrates the photocatalytic activity of TiO$_2$ with the adsorption properties of zeolite together, which induce a synergistic effect. This effect results in the enhancement of photocatalytic efficiency[11]. In other words, TiO$_2$ supported on zeolites have larger surface area and its light transparent nature offers improves in adsorption and uniform diffusion of pollutants towards TiO$_2$ for efficient degradation[6]. Besides, zeolites are considered ideal support for TiO$_2$ due to hydrophilicity and hydrophobicity properties, easily tunable chemical properties, high thermal stability and eco-friendly nature[12]. In addition, zeolite has been chosen as a support because zeolites can delocalize band gap excited electrons of TiO$_2$ and thereby minimizing electron-hole recombination. This will increase the photocatalytic efficiency[6].

EXPERIMENTAL

Methodology: The photocatalyst was prepared in three stages. The first stage was to prepare the TiO$_2$ sol-gel. This was followed by mixing the natural zeolite to the TiO$_2$ sol-gel to get TiO$_2$/zeolite mixture and then calcination to obtain the TiO$_2$/zeolite photocatalyst. To ensure the TiO$_2$/zeolite catalyst was successfully obtained, the photocatalyst was characterized using X-ray powder diffractometer (XRD), model EVO MA 10 and Scanning Electron Microscope (SEM) model EVO 50XPV. The prepared TiO$_2$/zeolite photo catalyst was compared with neat TiO$_2$ (P25 Degussa) under UV-A irradiation in the photodegradation of indigo dye. A 500 mL, 10 or 20 mg/L indigo dye solution (pH 6.3) was mixed with 0.4 g of photocatalyst in the all experimental solution. The solution was left stirring in the dark for 1 h to enable adsorption equilibrium to be established. Then, the collected samples were analyzed using UV-visible spectrometer (model Perkin Elmer Lamda 25) with a peak maxima of 725 nm and the graph of final concentration against time was plotted to evaluate the concentration of final dye after degradation. Percentage of degradation

efficiency for collected samples was also determined. All experiments were conducted in triplicate and the average data were plotted into graphs.

Preparation of TiO$_2$/zeolite photocatalyst: The chemicals used to prepare the photocatalyst in this experiment were listed in the Table-1. Anatase TiO$_2$ can be synthesized according to Huang *et al*.[11]. Anatase TiO$_2$ was prepared using sol gel method. 10 mL of tetrabutyl titanate was dissolved in 30 mL pure ethanol (1:3 ratio). The mixture was mechanically stirred vigorously. After stirring for 8 h, a weak yellow TiO$_2$ sol was obtained (Fig. 1). The pH of the solution mixture of tetrabutyl titanate and ethanol was 9.29. About 18 drops of nitric acid (1 M) was added to the solution in order to reduce the solution's pH to 4.

TABLE-1	
CHEMICALS USED IN THE EXPERIMENTS	
Chemicals	Brand and grade
Indigo dye	Hanawa
Tetrabutyltitanate	ALDRICH, reagent grade (RG)
Nitric acid	ORëC, analytical grade (AR)
Ethanol	GCE
Natural zeolite	Fluka
HCl	ORëC, Analytical grade (AR)
NaOH	ORëC, Analytical grade (AR)

Fig. 1. TiO₂ sol gel

After stirring for 0.5 h, 10.019 g of zeolite was added into the gel and the mixture is continuous (mechanically) stirred for 6 h (Fig. 2) with ethanol and deionized water (1:1 ratio) being added periodically. About 182 drops of ethanol/water solution were used in this process. After that, the mixture was dried in the oven at 80 ℃ for 6 h. The product was grinded into powder and further heated to 110 ℃. The powder was then calcined at 450 ℃ for 4 h. The final product is shown in Fig. 3.

Fig. 2. TiO₂/zeolite mixture

Fig. 3. TiO₂/zeolite powder

Batch photoreactor: A batch photoreactor was constructed as shown in Fig. 4. This design was employed due to the ease of experimental set-up and cleaning. This construction also maintains the temperature and avoids the intrusion of ambient light. The UV lamp used was a blacklight type with a maximum peak of 365 nm, (Sylvania LYNX S). The lamp was switched on for 1 h prior to the start of the experiment to bring the 9 Watt Hg low-pressure lamp up to working temperature. The lamp intensity was measure at 9 mW/cm². A 500 mL beaker was used during the degradation experimental process. During the process, the solution was stirred by a magnetic stirrer. Centrifugation was needed to separate the photocatalyst from the indigo dye solution as membrane syringe filtration resulted in the removal of the dye itself from the extracted sample. This removal of the photocatalyst's solid particles from the extracted samples is important to prevent interference during UV-visible spectrometer analysis.
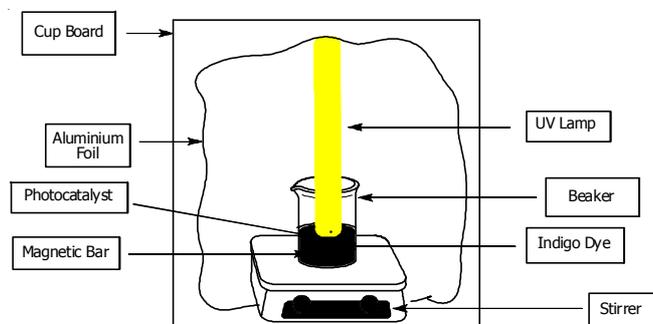
Fig. 4. Batchphotoreactor

RESULTS AND DISCUSSION

The degradation time (5 h) was chosen in evaluating the capacity of the prepared photo-catalytic degradation system. Samples were withdrawn at 1 h intervals throughout 5 h contact time. Table-2 shows the reaction scheme and parameter used in this study.

TABLE-2
EXPERIMENTAL LIST CONDUCTED IN THIS STUDY

Experiment	Process studied	Operational condition	Conc. (mg/L)
A	Photodegradation	TiO₂/UV system	10
B	Photodegradation	TiO₂/UV system	20
C	Photodegradation	TiO₂/zeolite/UV system	10
D	Photodegradation	TiO₂/zeolite/UV system	20

XRD characterization of the prepared TiO₂/zeolite photocatalyst: XRD analysis was performed to determine the crystallinity of TiO₂ on their respective supports[13,14]. The samples were scanned in 2θ ranged 5-67º. The peaks of the supported photocatalysts and TiO₂ were compared by the intensity of the parent zeolite and supported photocatalysts. The principal goal of carrying out XRD analysis was to identify the formation of anatase TiO₂. XRD analysis of neat TiO₂ and neat zeolite is shown in Figs. 5 and 6, respectively. X-Ray diffraction analysis was performed to determine the crystallinity of the TiO₂ on the zeolite support as well (Fig. 7)[15]. The main peak of anatase TiO₂ appeared at 2θ = 25.609º which was comparable with the spectra produce by the neat anatase TiO₂ (Fig. 5). In the range from 400-500 ºC, only anatase phase was obtained. Previous researchers determined that the formation of anatase TiO₂ begins from 400 ºC, indicating the start of the amorphous to anatase crystallization[16]. Other peaks corresponding to anatase TiO₂ also appeared at 2θ = 38, 48 and 54º. The natural zeolite shows a peak at 2θ = 27º[15]. Comparing the XRD pattern of natural zeolite, the intensities of some diffraction peaks of TiO₂/zeolite decreased or disappear, which was due to the surface of the zeolite being covered by crystallized TiO₂-anatase[12, 14].
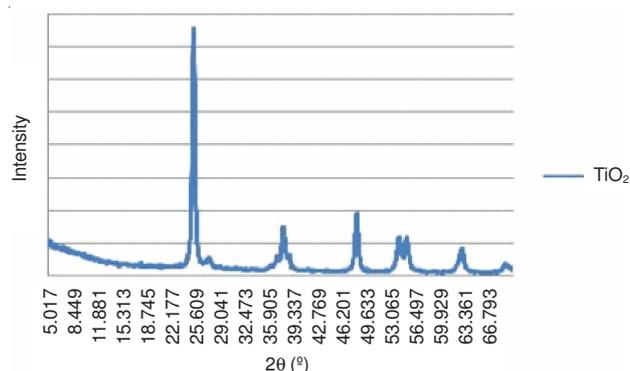
Fig. 5. TiO₂ (P25 Degussa)
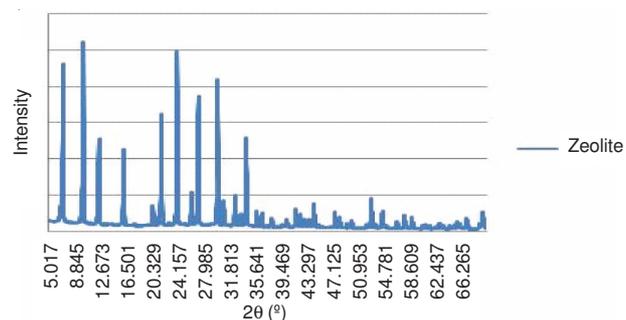
Fig. 6. Commercial zeolite

Surface morphology of the prepared TiO₂/zeolite photocatalyst: SEM was used to study the surface morphology of the prepared TiO₂/zeolite photocatalyst. Figs. 8 and 9 shows the morphology of neat TiO₂ and neat zeolite respectively at 5,000 times magnification. In comparisons, Fig. 10(a and b) shows that TiO₂ was successfully coated onto the commercial zeolite. However, the coating was not in a uniform manner. At higher magnification, it is clearly shown that agglomeration of titania occurred in some location of the zeolite particle.
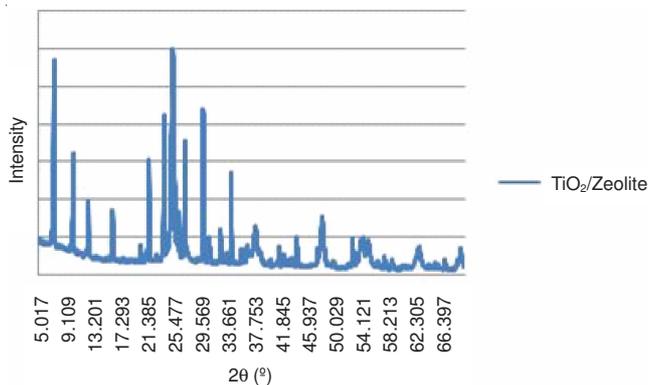
Fig. 7. TiO$_2$/zeolite
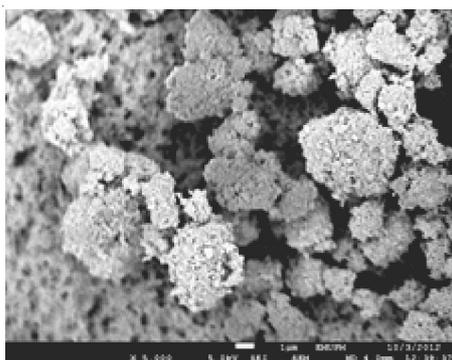
Fig. 8. SEM micrographs of neat TiO$_2$ at 5000X
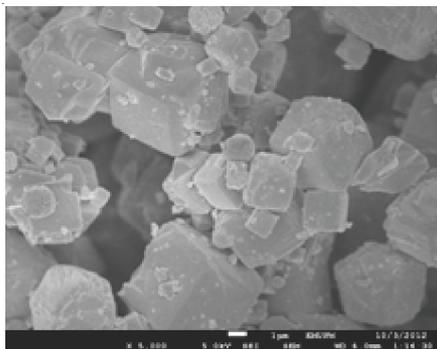
Fig. 9. SEM micrographs of neat zeolite at 5000X

       (a)   (b)
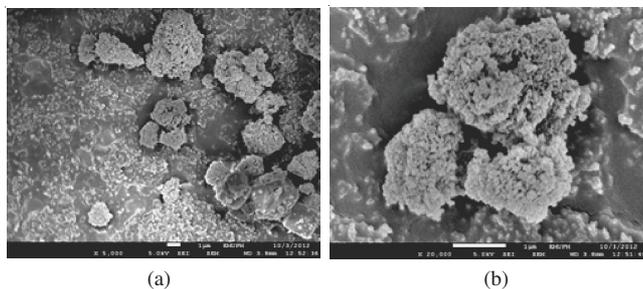
Fig. 10. SEM micrographs of the prepared TiO$_2$/zeolite photocatalyst at 5000X (a) and 20000X (b)

Photocatalytic degradation of indigo dye: TiO$_2$/UV system and TiO$_2$/zeolite/UV system were investigated under a heterogenous photocatalytic system during which UV irradiation that provides light energy greater than the semiconductor's band gap energy can photo-activate the TiO$_2$ to from electron-hole pairs[17]. 0.4 g of neat TiO$_2$ or TiO$_2$/zeolite powder (0.088-0.105

mm) were used in the heterogeneous photodegradation process using 10 and 20 mg/L concentration of indigo dye.

Photodegradation: Comparison between Figs. 11 and 12 indicated that the TiO$_2$/zeolite photodegradation system was more effective in degrading indigo dye in aqueous medium compare to neat TiO$_2$. However, due to pore blocking by the titania and pore trapping of the titania (as evidently shown in the SEM micrographs) during the sol-gel preparation method, the difference in degradation is somewhat less than expected.
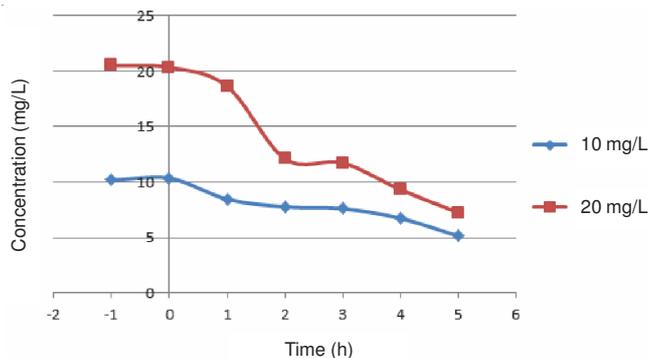
Fig. 11. Residual concentration of indigo dye after heterogeneous UV-A photodegradation using neat TiO$_2$
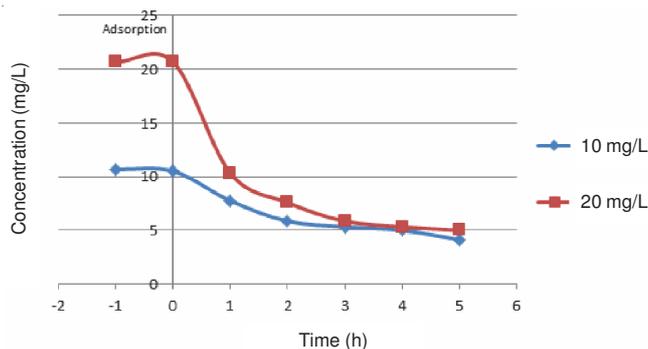
Fig. 12. Residual concentration of indigo dye after heterogeneous UV-A photodegradation using TiO$_2$/zeolite

Comparison of the percentage of photodegradation: The percentage of photodegradation efficiency of indigo dye solutions were shown in the Fig. 13. The photodegradation efficiency of indigo dye using of TiO$_2$/zeolite was better compared to anatase TiO$_2$. It shows higher photodegradation efficiency compared to TiO$_2$. This is due to the synergistic photodegradation effect by combining both adsorption (zeolite) with photodegrdation (TiO$_2$). Neat TiO$_2$ (A) successfully degraded 48.8 % of indigo dye while TiO$_2$/zeolite (C) degraded 58.6 % of indigo dye after 5 h of irradiation. When the concentration of indigo dye was increase to 20 mg/L, the neat TiO$_2$(B) had a 63.8 % of photodegradation efficiency while TiO$_2$/zeolite (D) gave a 75.0 % of photodegradation efficiency. There were several limitations while using TiO$_2$ in the photocatalytic reactor. TiO$_2$ particles aggregate rapidly in a suspension, resulting in smaller effective surface area. Thus, lower catalytic efficiency. The percentage of photodegradation efficiency using TiO$_2$/zeolite was higher than TiO$_2$. This could be due to the presence of zeolite possessing a larger surface area that widely enhanced the catalyst degradation efficiency[1]. TiO$_2$ was
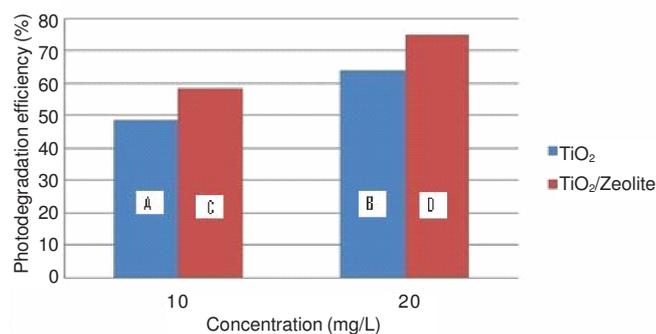
Fig. 13. Percentage photodegradation efficiency of indigo dye solution after 5 h

dispersed onto the zeolite's surfaces and the zeolite's pores were partially blocked with TiO_2. Since the pore size of zeolite was smaller than the size of TiO_2 particles. The TiO_2 particles might not be deposited within the pores of the zeolite. Moreover, at high TiO_2 loading, it is possible that the TiO_2 particles would likely aggregate at the surface of the zeolite. In order to avoid this aggregation from developing the percentage of TiO_2 added needs to be considered. The percentage of TiO_2 loaded onto the zeolite loaded was less than 50 % to avoid aggregation of TiO_2 particles[1]. In this experiment, 21.75 % of TiO_2 was used to prepare the TiO_2/zeolite photocatalyst.

The photodegradation of indigo dye occured according to the following mechanism. When TiO_2 was exposed to UV light at wavelength, $\lambda \approx 365$ nm, electrons are promoted from the valence band to the conduction band. As a result of this, an electron-hole pairwas produced[18].

$$TiO_2 + hv \longrightarrow e^-_{cb} + h^+_{vb}$$

where, e^-_{cb} and h^+_{vb} were the electrons in the conduction band and the holes in the valence band, respectively.

Both entities can migrate to the catalyst surface, where they could enter into a redox reaction with other species present on the surface. The valence band (h^+_{vb}) potential was positive enough to react with the surface bound H_2O to produce hydroxyl radicals ($^{\bullet}OH$) at the surface and the conduction band (e^-_{cb}) potential was negative enough to reduce molecular oxygen to form superoxide radical anion of oxygen ($O_2^{-\bullet}$)[9].

$$H_2O + h^+_{vb} \longrightarrow {}^{\bullet}OH + H^+$$

$$O_2 + e^-_{cb} \longrightarrow O_2^{-\bullet}$$
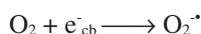
The resulting $^{\bullet}OH$ radical was a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO_2. It causes photooxidation of the dye according to the following reactions. The $^{\bullet}OH$ and $O_2^{-\bullet}$ produced can react with the dye to form other species and thus responsible for the discoloration of the dye[18].

$$Dye + {}^{\bullet}OH \longrightarrow degradation \ of \ dye$$

$$Dye + O_2^{-\bullet} \longrightarrow degradation \ of \ dye$$
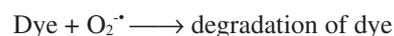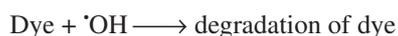
Conclusion

The preparation of TiO_2/zeolite was successfully performed using sol-gel method. Calcination of the sol-gel at 450 ºC gave anatase TiO_2 as shown the XRD analysis. The SEM showed that although the sol-gel method gave a reasonably good TiO_2 dispersion on the zeolite particle, some areas of the particle had no TiO_2 and others had TiO_2 agglomeration. In the photodegradation experiment, although the TiO_2/zeolite had only 21.75 % of TiO_2, it gave a much better photo degradation efficiency than the neat TiO_2. The final pH for solution (with TiO_2/zeolite photocatalyst) was 5.3 instead of 5.9 for the neat TiO_2), indicating that photodegradation was successful in breaking down the target pollutant. This also meant that the use of zeolite as a pollutant concentrator was successful in providing a synergistic collaboration between the TiO_2 and the zeolite matrix. In addition the ability of zeolite to photo-induced electron transfer reactions while retarding undesired back electron transfer was also favorable[19].

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