Photodegradation of Indigo Dye Using TiO_2 and TiO_2 /Zeolite System

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Photodegradation of indigo dye in aqueous solution using anatase TiO_2 and TiO_2 /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°C 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 TiO_2 /zeolite composite sample was better as the degree of degradation for TiO_2 /zeolite was higher compared to the neat TiO_2 sample. The percentage degradation achieved by using TiO_2 /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 $0.1207\text{--}0.2669\text{ h}^{-1}$ (not presented). This work demonstrates that the sol-gel method was successful in preparing an effective TiO_2 /zeolite composite photocatalyst.

Key Words: TiO_2 /zeolite, Photodegradation, Indigo dye.

INTRODUCTION

In modern industrial society, dyes are widely used in textiles, printing, dyeing and food¹. It is estimated that from 1 to 15 % of the dye is lost during dyeing processes and is released in wastewater². 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 life³. 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 teratogenic⁴. Therefore, research has been carried out over the last two decades to develop strategies for removing, destroying or recovering dyes present in water⁵. 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, $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$. This dye is a blue colorant obtained from the indigo plant (*Indigoferatinctoria*) and woad (*Isatistinctoria*). Photocatalysis, an advanced oxidation process, employing semiconductors

such as TiO_2 as photocatalysts, is a promising method for the *in situ* elimination of organic pollutants in water⁶. Photocatalysis is a heterogeneous catalytic reaction under the irradiation of ultraviolet light in the presence of a light activated photocatalyst⁴. 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 TiO_2 has a crystalline structure that corresponds to the tetragonal system which mainly used as photocatalyst under UV irradiation. Rutile type TiO_2 has a tetragonal crystal structure. It is normally used as white pigment in paint. On the other hand, Brookite type of TiO_2 has an orthorhombic crystalline structure. Titanium dioxide (B) is a monoclinic mineral and is a relatively a new form in titania family^{7,8}. TiO_2 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 material⁷. Titanium dioxide is an inexpensive material, because titanium is the world's 7th most abundant metal and 9th most abundant element⁴. Titanium dioxide can be used in form of a fine powder or crystals dispersed in water wastewater treatment applications⁹. Titanium dioxide is a semiconductor. This "semiconductor" can be activated by UVA light (near UV) of wavelength $\lambda \leq$

390 nm^{4,10}. When TiO₂ 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 TiO₂ 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 substrate². However, in order to enhance the properties of the TiO₂ such as to give it better adsorption properties or to enable fast separation of the photocatalyst from the treated solution, the TiO₂ 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 TiO₂ photocatalyst because of its regular pores and channel sizes and good adsorption ability. TiO₂ supported onto zeolite integrates the photocatalytic activity of TiO₂ with the adsorption properties of zeolite together, which induce a synergistic effect. This effect results in the enhancement of photocatalytic efficiency¹¹. In other words, TiO₂ supported on zeolites have larger surface area and its light transparent nature offers improves in adsorption and uniform diffusion of pollutants towards TiO₂ for efficient degradation⁶. Besides, zeolites are considered ideal support for TiO₂ due to hydrophilicity and hydrophobicity properties, easily tunable chemical properties, high thermal stability and eco-friendly nature¹². In addition, zeolite has been chosen as a support because zeolites can delocalize band gap excited electrons of TiO₂ and thereby minimizing electron-hole recombination. This will increase the photocatalytic efficiency⁶.

EXPERIMENTAL

Methodology: The photocatalyst was prepared in three stages. The first stage was to prepare the TiO₂ sol-gel. This was followed by mixing the natural zeolite to the TiO₂ sol-gel to get TiO₂/zeolite mixture and then calcination to obtain the TiO₂/zeolite photocatalyst. To ensure the TiO₂/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 TiO₂/zeolite photocatalyst was compared with neat TiO₂ (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 Lambda 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 TiO₂/zeolite photocatalyst: The chemicals used to prepare the photocatalyst in this experiment were listed in the Table-1. Anatase TiO₂ can be synthesized according to Huang *et al.*¹¹. Anatase TiO₂ 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 TiO₂ 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 °C for 6 h. The product was grinded into powder and further heated to 110 °C. The powder was then calcined at 450 °C 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	TiO ₂ /UV system	10
B	Photodegradation	TiO ₂ /UV system	20
C	Photodegradation	TiO ₂ /zeolite/UV system	10
D	Photodegradation	TiO ₂ /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 5-67°. 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 = 25.609° which was comparable with the spectra produce by the neat anatase TiO₂ (Fig. 5). In the range from 400-500 °C, only anatase phase was obtained. Previous researchers determined that the formation of anatase TiO₂ begins from 400 °C, indicating the start of the amorphous to anatase crystallization¹⁶. Other peaks corresponding to anatase TiO₂ also appeared at 2θ = 38, 48 and 54°. The natural zeolite shows a peak at 2θ = 27°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. $\text{TiO}_2/\text{zeolite}$ Fig. 8. SEM micrographs of neat TiO_2 at 5000X

Fig. 9. SEM micrographs of neat zeolite at 5000X

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

Photocatalytic degradation of indigo dye: TiO_2/UV system and $\text{TiO}_2/\text{zeolite}/\text{UV}$ system were investigated under a heterogeneous 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 form electron-hole pairs¹⁷. 0.4 g of neat TiO_2 or $\text{TiO}_2/\text{zeolite}$ 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 $\text{TiO}_2/\text{zeolite}$ 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 $\text{TiO}_2/\text{zeolite}$

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 $\text{TiO}_2/\text{zeolite}$ 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 photodegradation (TiO_2). Neat TiO_2 (A) successfully degraded 48.8 % of indigo dye while $\text{TiO}_2/\text{zeolite}$ (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 $\text{TiO}_2/\text{zeolite}$ (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 $\text{TiO}_2/\text{zeolite}$ 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 efficiency¹. 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 TiO₂. Since the pore size of zeolite was smaller than the size of TiO₂ particles. The TiO₂ particles might not be deposited within the pores of the zeolite. Moreover, at high TiO₂ loading, it is possible that the TiO₂ particles would likely aggregate at the surface of the zeolite. In order to avoid this aggregation from developing the percentage of TiO₂ added needs to be considered. The percentage of TiO₂ loaded onto the zeolite loaded was less than 50 % to avoid aggregation of TiO₂ particles¹. In this experiment, 21.75 % of TiO₂ was used to prepare the TiO₂/zeolite photocatalyst.

The photodegradation of indigo dye occurred according to the following mechanism. When TiO₂ 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 pair was produced¹⁸.

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 H₂O to produce hydroxyl radicals ($\cdot\text{OH}$) 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^-)⁹.

The resulting $\cdot\text{OH}$ radical was a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO₂. It causes photooxidation of the dye according to the following reactions. The $\cdot\text{OH}$ and O_2^- produced can react with the dye to form other species and thus responsible for the discoloration of the dye¹⁸.

Conclusion

The preparation of TiO₂/zeolite was successfully performed using sol-gel method. Calcination of the sol-gel at 450 °C gave anatase TiO₂ as shown the XRD analysis. The SEM showed that although the sol-gel method gave a reasonably good TiO₂ dispersion on the zeolite particle, some areas of the particle had no TiO₂ and others had TiO₂ agglomeration. In the photodegradation experiment, although the TiO₂/zeolite had only 21.75 % of TiO₂, it gave a much better photo degradation efficiency than the neat TiO₂. The final pH for solution (with TiO₂/zeolite photocatalyst) was 5.3 instead of 5.9 for the neat TiO₂, 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 TiO₂ and the zeolite matrix. In addition the ability of zeolite to photo-induced electron transfer reactions while retarding undesired back electron transfer was also favorable¹⁹.

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