A review on photocatalytic: Modification of material and the application to removal of dye in wastewater

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Abstract. Photocatalytic materials have become a field of expansion in research, as evidenced by the many publication in science. With the many variation of semiconductors being tested as photocatalytic, it is necessary it with other materials or different semiconductor materials. Dealing with such an amount of information requires updated and educated guidance to select the most significant realizations. The state of the art photocatalysis with regard to materials and systems, considering the well-established results, but also the emerging aspect, and the envisaged new directions of this technology in the near future. In simulation and optimization of the photocatalytic reaktor model offer the last design. In addition, the opportunity for light source to be increase durability, relatively low cost and increase flexibility in the design and operation of future photocatalytic reactors.

1. Introduction
In recent years, semiconductors (e.g. Ti, Zn, WO, Sn) have received much attention for new applications in catalysis, electronics, environmental and optics. In heterogeneous catalysis of semiconductor metals with other material (example: carbon, zeolite, clay, silica) as catalysts have been successfully used in the processing of dye wasted water, this process is urgently needed for prior treatment before being released into water streams in order to avoid serious environmental problems [1-3].

Various treatment techniques and process have been used to remove the dyes from dye-bearing effluents. Among them, adsorption has been shown to be a good method of colored contaminant removal. However, their process is non-destructive process due to transfer of pollutants from one phase to another, rather than being eliminated. Therefore regeneration of the absorbent is needed before its reuse. Another wastewater treatment is the photocatalytic process. Heterogeneous photocatalysis using semiconductor as a photocatalyst is a promising Advanced Oxidation Process (AOP) through mineralization of the toxic and after colored organic compounds under UV irradiation or visible light [4].
Degradation of discoloration occurs due to several factors, namely the type of catalyst, both concentration and amount of catalyst, temperature, duration of irradiation and pH. The purpose of this paper is to review the quality and effectiveness of the modified catalysts as photocatalyst.

2. Photocatalytic mechanism and factor influencing the degradation process
Photocatalytic mechanism is an n-type semiconductor when subjected to a light or photon that matches or exceeds the photocatalyst material band gap energy, so the electrons will be excited from the ground state to a higher energy level resulting in a hole (h+) [5, 6]. At this stage the band gap energy shows the wavelength of the light which is effectively absorbed in the photocatalyst material. After the electrons and holes are separated, most of the electrons and holes will interact again on the surface called the recombination effect. Each electron or hole will experience a process of reduction and oxidation to the substrate [7].

![Figure 1. Schematic representation of semiconductor photocatalytic mechanism [8].](image)

The catalysis process on the surface of the photocatalyst through the formation of holes and electrons from the reduction and oxidation mechanism (redox mechanism). Both of the electrons or holes can produce reactive ions which can be utilized in the process of deactivation and decomposition of contaminants or harmful microorganisms [7].

The efficiency of the photocatalysis was depending with several factor, such us concentration of dye, catalyst amount, pH, surface area, and particle size of catalyst. The photocatalysis processes depend on the adsorption of dye in catalyst. The higher concentration of dye in wastewater, the more of organic compound on the surface of catalyst, causing the less number of photons are available on surface catalyst, furthermore the production of •OH was less, and the last is reducing the percentage of degradation [9]. The higher amount of catalyst is equal with increasing number of active site of catalyst. Furthermore, the increasing amount of catalyst will affect the turbidity and viscosity of solution and the light/UV radiation was difficult to reach the catalyst and therefore the lowering in the degradation [4].

The other factor is pH of the solution, the surface of catalyst act as Lewis acid and the surface of anionic dye act as Lewis Base, this fact shown on the easily of dye to adsorb on surface of catalyst. Moreover, the photocatalysis reaction on zero charge (isoelectric point), the degradation was minimum. Because, the surface of catalyst was in positive charge below isoelectric point and carrier a negative charge above it [8].

The morphology and the agglomeration on surface of catalyst will affect the photocatalysis process because the contact and absorb on the surface of catalyst. The different form of metal oxide (example: TiO$_2$) or the metal modified on catalyst will decrease the percentage degradation. The surface area of catalyst is the important factor to be considered in the photocatalysis because the take place of
catalysis on the surface catalyst. The higher surface area will increase the photodegradation of dye because the active site more high than lower surface area [8].

3. Heterogeneous catalyst in photocatalyst process

The photo-degradation method can be done using a catalyst in the form of a semiconductor. Semiconductor catalysts that are often used are TiO$_2$, ZnO, CdS and Fe$_2$O$_3$ [10], but the photocatalyst material is not optimal if it is used in a pure state because it has a relatively low surface area so it is necessary to modify the catalyst. The following are some modifications to the catalysts that have been used in the research listed in table 1.

Table 1. The several of material in photocatalytic process.

| No | Material                  | Dye                    | Catalyst (mg) | Reaction Time (min) | Degradation (%) | Reference |
|----|--------------------------|------------------------|---------------|---------------------|-----------------|-----------|
| 1. | Fe$_2$O$_3$-Montmorillonite | Congo Red              | 50            | 60                  | 90.22           | [10]      |
| 2. | Clay-TiO$_2$             | Indigo Carmine, Metanil Yellow and Rhodamin | 100           | 90                  | 90.50 ; 31.75 ; 95.58 | [1]      |
| 3. | AgI/TiO$_2$              | Acid Orange 7          | 34            | 120                 | 99.25           | [14]      |
| 4. | Composite Kaolin-TiO$_2$ | Rhodamin B             | 150           | 60                  | 94.7            | [18]      |
| 5. | TiO$_2$-Bentonite        | Methylene Blue         | 50            | 60                  | 93.93           | [19]      |
| 6. | TiO$_2$-Zeolite          | Methylene Blue         | 50            | 50                  | 75.93           | [9]       |
| 7. | ZnO-Activated Carbon     | Methylene Blue         | 50            | 300                 | 99.97           | [2]       |
| 8. | TiO$_2$-N/Zeolite        | Methylene Blue         | 50            | 50                  | 96.81           | [31]      |
| 9. | WO$_3$/C-dots            | Methylene Blue         | 30            | 60                  | 76.22           | [3]       |
| 10. | TiO$_2$-DSBC             | Methylene Blue         | 1000          | 50                  | 90              | [33]      |
| 11. | ZnO/$\alpha$-Fe$_2$O$_3$/ATP | Methylene Orange | -             | 210                 | 85.3            | [39]      |

3.1. Modification of material and their application

3.1.1. Fe$_2$O$_3$-montmorillonite. The combination of Fe$_2$O$_3$ with montmorillonite using the iron polyhydroxy complex cation resulted in increased surface area, total pore volume, bandgap energy and increased iron content. This makes Fe$_2$O$_3$-montmorillonite more effective than Fe$_2$O$_3$ and montmorillonite as adsorbents in degrading colors on a waste with the help of UV light.

Fe$_2$O$_3$-montmorillonite is one type of adsorbent that can be used in the industrial world to cope with industrial waste that is discharged into the environment. With this combination it is able to degrade the color of congo red by 90.22% with the help of UV light. If it degrades the color of congo red with Fe$_2$O$_3$ only or montmorillonite alone the results are not maximal, so also if it is not helped with UV light the result is less than 85% [10].

3.1.2. Clay-TiO$_2$. Many studies have been conducted to maximize the work of TiO$_2$ by distributing it in supporting media, one of which is to impregnate it on activated carbon [11] and impregnate it on zeolite [12]. Another method used to maximize the work of TiO$_2$ is to make it a pillar in TiO$_2$ pillared clay, where TiO$_2$ acts as a pillar as well as a catalyst in photocatalytic reactions [13].

By synthesizing TiO$_2$ pillared clay using dodecylamine surfactant, the use of TiO$_2$ catalyst in degrading organic compounds that pollute the environment can be done so that environmental
pollution can be minimized. To determine the photocatalytic test, photo-degradation of indigo carmine compounds, methanlyl yellow, and rhodamine was carried out [1].

The photocatalyst process using clay-TiO$_2$ material can degrade indigo carmine, methanlyl yellow, and rhodamine dyes with the help of UV light. The result of indigo carmine dye degradation was 90.50%, methanlyl yellow was 31.75% and rhodamine was 95.58% [1].

3.1.3. AgI/TiO$_2$. TiO$_2$ is the most important titanium compound, which is a white powder, which is often used as a white dye on food, cosmetics and dyes. Based on the study of titanium dioxide it has been detected that titanium oxide is inert biologically. Iodide silver is more commonly known as photosensitive material and is often used in photographic films. The advantage of silver iodide is that its sensitivity to light is very good and during light exposure, silver iodide is relatively stable compared to other silver halide groups [14].

The addition of silver iodide to the TiO$_2$ photocatalyst is intended to increase the sensitivity of TiO$_2$ to light. In addition, the addition of silver iodide can increase electron-hole separation or what is often called an electron-hole joining reaction. In AgI/TiO$_2$ material with acid orange 7 through UV irradiation it can be used as an alternative photocatalyst because the percent value of degradation produced is quite large at 99.25% compared to degrade color with AgI/TiO$_2$, TiO$_2$ + UV and the resulting TiO$_2$ is 39.9%, 30.69% and 26.6% [14].

3.1.4. Composite kaolin-TiO$_2$. Embedded TiO$_2$ material in natural zeolite and clay has a dual function, namely as an adsorbent and as a photocatalyst [15], so that success in the synthesis of clay-TiO$_2$ composites is an alternative solution for processing wastewater, especially liquid wastes of dyes [16]. Photocatalytic oxidation of organic pollutants on the surface of TiO$_2$ has been extensively developed for air and also water remediation, because of its high effectiveness, capable of reducing toxicity and low costs [17]. The form of uptake that is owned by kaolin which is a leaner and sharper preparation shows a more homogeneous mineral composition than a kaolin sample without preparation.

Composite synthesis of kaolin-TiO$_2$ aims to obtain composites with better photo-degradation properties and capabilities. In this synthesis TiO$_2$ sol solution was obtained using the sol gel method. As a photocatalyst in this study, TiO$_2$ material that has a wide surface is needed, thus expanding the contact area. The choice of the sol gel method is done because the process is shorter and easier, the temperature used is lower, a homogeneous layer with a large area can be obtained [18].

Kaolin-TiO$_2$ is able to degrade Rhodamine B at 94.7% by UV irradiation and in the dark place only the adsorption process occurs, this also applies to the use of UV irradiation of kaolin. Kaolin-TiO$_2$ was formed from kaolin samples which were purified and made as carrier material for TiO$_2$ then calcined at 700°C for 3 hours and characterized using ultraviolet spectroscopy [18].

3.1.5. TiO$_2$-bentonite. Bentonite activation is done by using 0.4 M HCl which aims to exchange cations between H$^+$ ions with K$^+$, Na$^+$, and Ca$^{2+}$ ions in the interlayer area and aims to remove impurity metal ions such as Al$^{3+}$, Fe$^{3+}$, and Mg$^{2+}$ which cover the side active in the interlayer area. Impregnation of TiO$_2$ in activated bentonites to obtain photocatalysts with multiple capabilities between adsorption and catalysis in photochemical degradation of methylene blue dyes [19].

Whereas the TiO$_2$-bentonite using H$_2$O$_2$ oxidizer was able to degrade methylene blue dyes by 93.93%. H$_2$O$_2$ can produce OH • radicals which can oxidize methylene blue so that it is more effective at degrading methylene blue [19].

3.1.6. TiO$_2$-zeolite. Photocatalytic TiO$_2$ is not optimal if used in a pure state because it has a relatively low surface area. Thus, TiO$_2$ needs to be applied to an adsorbent. The usual adsorbent is zeolite because zeolite has a 3-dimensional structure with large pores so that it can adsorb other smaller compounds. In addition zeolite is abundant in nature at affordable prices [20].

Radiation time is the length of interaction between the photocatalyst of TiO$_2$ and UV light in producing OH radical (•OH). In addition, it also affects the length of contact between OH radicals.
(•OH) and degraded dyes, namely methylene blue. The longer the irradiation time will increase the energy of the photons produced.

Increasing the energy of the photons produced will produce more OH radicals (•OH). OH radical (•OH) here is a strong oxidizer that can be used to degrade methylene blue dyes. The amount of OH radicals is produced, the more methylene blue dyes are degraded [21].

Photocatalysis of TiO₂-zeolite degraded methylene blue by 75.93% by irradiation. The modification of TiO₂-zeolite is done because TiO₂ has a relatively low surface area so that it is not optimal if it is used in a pure state so TiO₂ needs to be applied to an adsorbent [9].

3.1.7. ZnO-activated carbon. Zinc oxide (ZnO) is one of the catalysts that can be used in photodegradation with a bandgap value of 3.17 eV [22]. Research conducted by Wawrzyniak et al. (2007) explained that ZnO catalyst can degrade methylene blue dye from 50 ppm to 94.67% [23].

The method used to make ZnO-activated charcoal composites is the sol-gel method because it is carried out at low temperatures and the time required for the formation of compounds is relatively short. The results of ZnO-activated charcoal composite synthesis will be characterized using X-RD (X-Ray Diffraction) and FT-IR (Fourier Transform Infra Red) [2].

ZnO-activated carbon material has hexagonal characteristics with a crystal size of 23.13 nm; 23.38 nm and 40.52 nm with X-RD similar to FT-IR, there is a strain vibration of Zn-O, C-O aliphatic group, C-H bending group, C-C aliphatic group and O-H group. In addition, activated charcoal functions to transfer methylene blue molecules to the surface of the catalyst so that the degradation will become more maximal. The percentage of degradation of methylene blue at optimum conditions is 99.97 ± 0.02% [2].

3.1.8. TiO₂-N/zeolite. The photocatalytic activity of TiO₂ can be increased by adding a dopant such as N dopant from urea which will cause the photocatalyst to be more active in the visible light region. The presence of N dopants in the TiO₂ matrix will reduce the band gap of TiO₂ so that there is a shift in absorption of the spectrum of light from UV light to visible light that is abundantly available in the sun. Based on the research of Hartoyo et al. (2013) [25], TiO₂ with dopant N showed an increase in photocatalytic activity of up to 40% in phenol degradation under visible light. In addition to the addition of dopants to the TiO₂ matrix, administration of carriers such as zeolite can also increase the photocatalytic activity of TiO₂. Based on the study of Lestari et al. (2015), the TiO₂ material embraced on zeolite has a dual function, namely as an adsorbent and photocatalyst which is able to absorb and decompose LAS surfactants with an effectiveness of 94.30% [26]. Another advantage with the presence of a stable photocatalyst on the carrier surface is that it can be used up to several times the photodegradation process (reusable) [26].

Color degradation of methylene blue with TiO₂-N/zeolite material with a long irradiation for 50 minutes resulted in 96.81% degradation using sunlight. Other factors that cause a decrease in the degradation of methylene blue are due to differences in temperature and intensity of sunlight when doing the photodegradation process, so the amount of radical OH produced is not the same for each use. The difference in the intensity of sunlight that reaches the earth is influenced by the season, geographical location and the presence of clouds. However, from the results of this study it can be seen that TiO₂-N/zeolite photocatalysts are effective enough to be used in photodegradation of methylene blue resulting in percentage of degradation above 50% [26].

3.1.9. WO3/C-dots. One of the semiconductor materials that has now been widely used in research on photocatalyst degradation processes is WO₃ where WO₃ is a substitute for TiO₂ material which has long been a catalyst for dye degradation. WO₃ material is the center of attention of researchers because it is considered as a material that is sensitive to visible light because it has a small band gap energy of about 2.7-2.8 eV [27]. According to the statement of Morales (2008), WO₃ has excellent photocatalytic ability [28]. WO₃ is also a material that is not harmful to the environment.
In the pure state of semiconductor powder WO₃ used in photocatalyst applications has a less than optimal performance, because according to Purwanto and Widiyandari (2010) stated that photoactivity carried out under visible light can be increased by adding a doping element or insertion of other atoms in semiconductors as efforts to increase optical properties in the range of visible light [29]. Therefore the doping compound used to stabilize electrons in WO₃ uses carbon nanodots (C-dots), this is based on the nature of C-dots as photoluminesens agents [30], has good optical properties, low toxicity, and have photoinduction properties [31]. C-dots also have the ability to be able to act as electron transfer intermediaries; this can significantly improve the efficiency of the photocatalyst process as did Li et al. (2012) [32].

At WO₃/C-dots photocatalysis it is more effective as a compound that can degrade methylene blue dyes by 76.22%. The photocatalytic degradation process with WO₃ material which is carried by C-dots begins by adsorbing the energy of photons sourced from UV-Vis by the WO₃/C-dots material which will then lead to the process of photoxitation or charge separation at WO₃ [3].

### 3.1.10. TiO₂–DSBC

In the present study, TiO₂ pillared DSBC were prepared from SBC and Titanium oxide in the presence of polymeric surfactant rarasaponin and the as prepared materials were characterized by X-Ray Diffraction (XRD), Fourier Transform Infra Red spectra (FTIR) and Scanning Electron Microscopy (SEM). The influence of optimum concentration and contact time of this material photocatalyst was investigated by evaluated methylene blue degradation. The fundamental information derived from this study is important in developing catalyst or adsorbent of pore structure from layered clays [33].

With TiO₂–DSBC catalyst, it is able to degrade methylene blue by 90%. TiO₂–DSBC material can be reused while maintaining 84% methylene blue degradation.

Modification of the catalyst material in the photocatalysis method is very diverse and serves to maximize the results of dyestuff degradation in the waste sample. With these modifications, it will be more efficient both in terms of time, process and cost in using materials as catalysts, so that industry can use the material as an effective catalyst [33].

### 3.1.11. Nanometer ZnO/α-Fe₂O₃/ATP

Nanometer ZnO hardly causes light scattering, and has large specific surface area and a wide band, so it is considered to be one of the promising photocatalysts for degradation of hazardous organic compounds [34]. α-Fe₂O₃ can absorb a wide spectrum of solar radiation. It’s the most stable iron oxide under ambient conditions and also is a resistive material towards photocorrosion in acidic and alkaline media [35]. Attapulgite (ATP) is a hydrated magnesium aluminum silicate presented in nature as fibrillar mineral [36-38], used in wastewater treatment with superior colloidal adsorption with a unique fibrous crystal structure

Nano ZnO/α-Fe₂O₃/ATP could degrade methyl orange efficiently. The composite materials had stable photocatalytic performance and excellent degradation rate. Furthermore, their degradation rate can achieve 85.3% within 3.5 h under natural sunlight. The degradation reaction of methyl orange was consistent with first-order kinetic equation. The adsorption property and photo-degradation performance of the composite materials ZnO/α-Fe₂O₃/ATP, nano-ZnO/ATP, and attapulgite were decreased in turn [39].

### 4. Conclusions

The research work involves the degradation and mineralization of synthetic dyestuffs present in industrial effluents by heterogeneous photocatalysis. UV or Visible (Solar) photocatalytic degradation proves to be economically cheap and simple method for the waste water treatment. The modification of material as composite was successfully synthesized and used as precursor material.

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