

DEGRADATION OF METHYLENE BLUE VIA GEOPOLYMER COMPOSITE PHOTOCATALYSIS

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ABSTRACT

A series of experiments were carried out to study the degradation of methylene blue (MB) by TiO₂ anatase (A), TiO₂ from titanyl sulfate (TS), geopolymer (GP), geopolymer with anatase (GPA) and geopolymer with titanyl sulfate (GPTS) in aqueous solution. Changes of UV-vis spectrum of MB with a prominent absorption peak occurred at around 660nm and 610nm. During the progress of 60min reaction time, the absorption intensity of MB component in solution became weaker along with the irradiation time. This phenomenon indicated that MB molecules were attacked and removed in the presence of other compound. Sample A had 89.22% MB component was residual in the solution, followed by TS 41.96%, GP 14.46%, GPA 8.65% and GPTS 5.7%. Without the geopolymer addition, the reaction of MB with the samples is very slow which can be resulted in the poor conversion of MB component. consequence and not surprisingly in this experiment it was observed that UV irradiation of MB ink on samples without geopolymer and with anatase produces very light blue and white colour accordingly as compared to other samples (GPTS, GPA and GP) that shows the colourless pattern.

Keywords: geopolymer composite; photocatalyst; UV Vis;

INTRODUCTION

Industrialization and agricultural development together with population growth, has drastically reduced clean water resources. Various kind of contaminants enter water, most of them in industrial wastewater. Wastewater from industries contains various dyestuffs, which are toxic to microorganism, aquatic life and human beings. To clean up these toxic chemical from water has been a complex problem. Thus several physico-chemical and biological methods have been proposed and are being developed for the destruction of organic contaminants. Decolourization of dye effluents has therefore acquired increasing attention. Photocatalytic degradation involving TiO₂ semiconductor particles under UV light illumination has become a promising technology for the removal of toxic organic and inorganic contaminants from wastewater.

Titania (TiO_2) photocatalysts have been used widely for various practical applications [1] due to its high photosensitivity and photostability. TiO_2 has attracted a great deal of attention because of its high activity, chemical stability, robustness against photocorrosion, low toxicity, low pollution load and availability at low cost [2]. However the shortcomings of conventional powder catalyst include low efficiency of light use, difficulty of stirring during reaction and separation after reaction and low-concentration contamination near TiO_2 due to its low surface. These disadvantages of TiO_2 result in low efficiency of photocatalytic activity in practical applications. Current efforts have been focused on their modification to extend the wavelength of photoabsorption towards the visible region that matches the solar spectrum or indoor illumination. However, it has been also clarified that its photocatalytic activity strongly depends on its physical properties of TiO_2 powder showed no appreciable activity but another powder was quite active. There have been many articles reporting the correlation of photocatalytic activity with the physical properties of TiO_2 powders, such as crystal structure [3], surface area [4], crystallite size [5], surface hydroxyl group and so on. Many finding believe that the crystal structure (anatase, rutile, brookite) is one of the most basic properties to predict the photocatalytic activity; e.g. anatase crystallites have relatively high photocatalytic activity than rutile crystallites [6]. Therefore, much recent work has focused on the preparation of composites such as $\text{TiO}_2/\text{SiO}_2$, $\text{TiO}_2/\text{zeolite}$, $\text{TiO}_2/\text{SnO}_2$ and $\text{TiO}_2/\text{polymer}$ [7-10]. Titania-silica system is considered a potential candidate as photocatalyst [2]. Further, the catalytic activity and anatase phase stability are closely related and silica addition has been reported in general to shift the anatase-rutile transformation to higher temperature range [2] in order to aid such catalyst to work at elevated temperatures. Typically, photocatalytic reaction is conducted in a suspension of submicrometer semiconductor materials, and therefore requires an additional separation step to remove the catalyst from the treated water. Removing such fine particles from large volumes of water involves further expense. This presents a major drawback to the application of the photocatalytic processes for treating wastewater. To minimize this problem, research has been carried out by immobilizing titania onto various substrates such as glass beads, sand, silica gel, quartz optical fibers and glass fibers in the form of mesh or on a glass reactor wall [10]. Geopolymer also called inorganic polymers composite materials based on these are prepared by reaction of a solid aluminosilicate such as dehydroxylated kaolinite clay (halloysite) with an alkali silicate solution under highly alkaline conditions. Alkali activated materials of this type have been known for a long time for the building materials. A most important practical property of these materials is that they are formed by condensing alumina and silica components under appropriate conditions at ambient temperatures and thus constitute a group of inorganic materials with the high-temperature properties of ceramics but which unlike ceramics, do not require high temperature to attain their properties of durability and hardness [11].

Our work is concerned with enhanced settling and reuse of suspended photocatalysts by using inorganic polymer (geopolymer) materials. This material had never been used with TiO_2 as a photocatalyst before.

MATERIALS AND METHODS

Methylene blue was supplied by HmbG Chemicals Ltd and used without further purification. Deionized water was used as solvent in this work to prepare MB solution. The solutions of MB were prepared with initial concentration of 100mg/L. 5 types of samples will be used for the photocatalytic experiment. There are commercial titania (American Elements Ltd.), titania sulphates from sol gel synthesis, geopolymer mixed with commercial titania and geopolymer mixed with titania sulphate from sol gel synthesis. Geopolymer were produce by mixing kaolin, deionized water, NaOH and sodium silicate with ratio 5:1:1:4 followed by drying overnight at 400°C. The measurements of photocatalytic activity of samples along 60 minutes were performed in UV-A photo chamber. After irradiation process, the solution was separated by centrifuge machine. The clear solution had been taken to analyze the absorption and degradation process by UV Vis spectrophotometer (Model Perkin-Elmer).

RESULTS AND DISCUSSIONS

Photocatalytic activity

Photoactivity for methylene blue (MB) in the dark and under UV irradiation in the presence of TiO₂ anatase (A), titania sulfate (TS), geopolymer (GP), geopolymer with anatase (GPA) and geopolymer with titanyl sulfate (GPTS) was evaluated. The UV–Vis absorption curves of methylene blue (MB) using all that samples as photocatalyst at different times i.e 0 minute (0M), 20 minutes (20M), 40 minutes (40M) and 60 minutes (60M) are illustrated in Figure. 1a-1e. Figure 1a-1e shows the spectral changes for the dye of MB, it was found that there was no degradation for the MB in the dark or without UV illumination (0M) for all the samples except adsorption of small amount of MB on the samples. Figure 1a-1e shows the change of UV–Vis spectrum of MB with a prominent absorption peak at around 660nm (monomer) and a hump at around 610nm (dimer). During the progress of 60min reaction time, the absorption intensity of MB component in solution became weaker along with the irradiation time. This phenomenon indicated that MB molecules were attacked and removed in the presence of other compound. The decrease of the absorption peak of MB solution at $\lambda_{\max} = 665\text{nm}$ (Figure.1a-1e) except for A sample indicated a degradation of MB component in the solution. Also the absorption of MB (Figure 1a) by A sample is higher than MB itself. Maybe only absorption process had occurred not degradation. For the case of GP, GPA and GPTS as shown in Figure. 1(b), (d) and (e), the peaks at 665nm were moving to the lower peak and become broader along with reaction time. For TS sample shows the sharp peaks which is mean only absorption occur rather than photodegradation and still continue absorbing after 60 minutes irradiation in the slow mode. Surprisingly, its shows better absorption without UV irradiation.

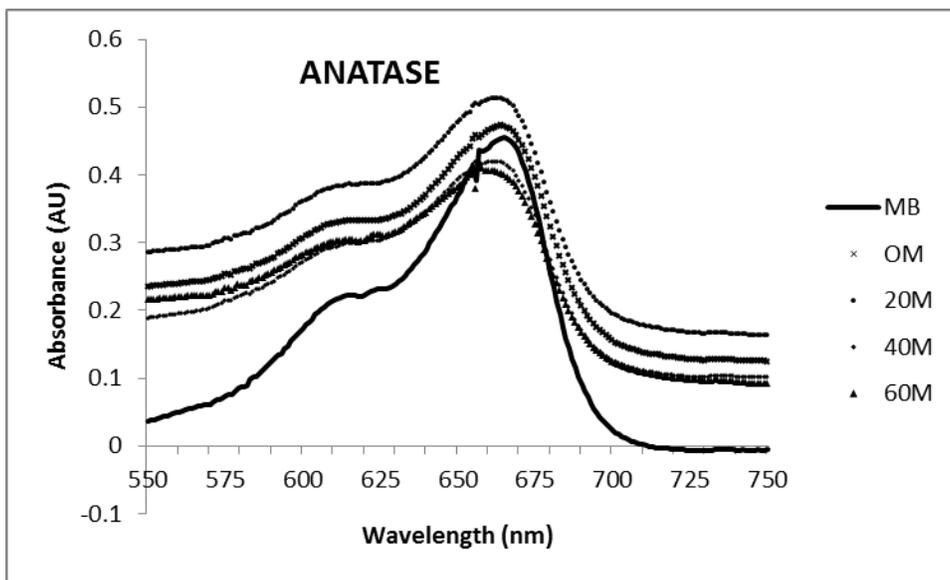


Figure 1 (a): UV Vis spectral changes of MB with anatase sample after different reaction time

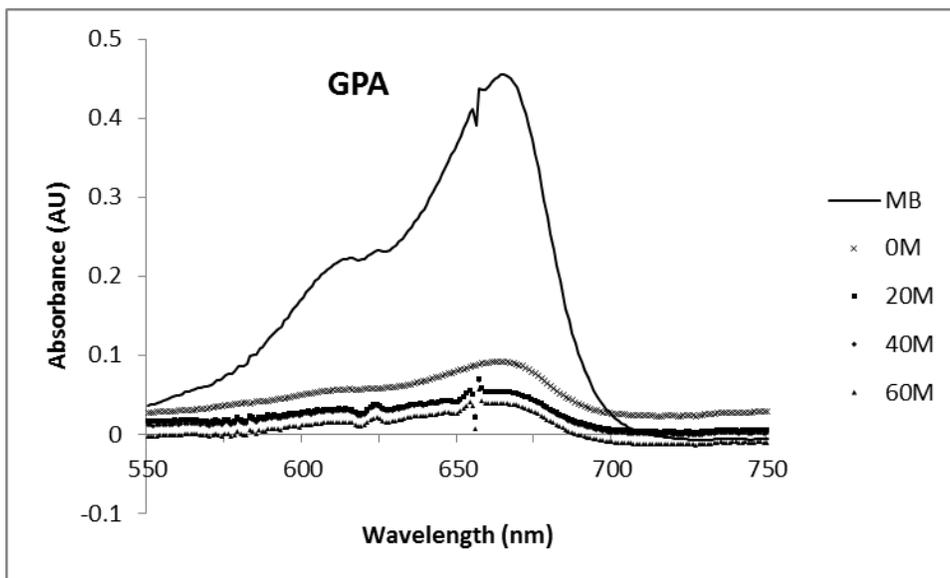


Figure 1(b): UV Vis spectral changes of MB with geopolymer/anatase sample after different reaction time

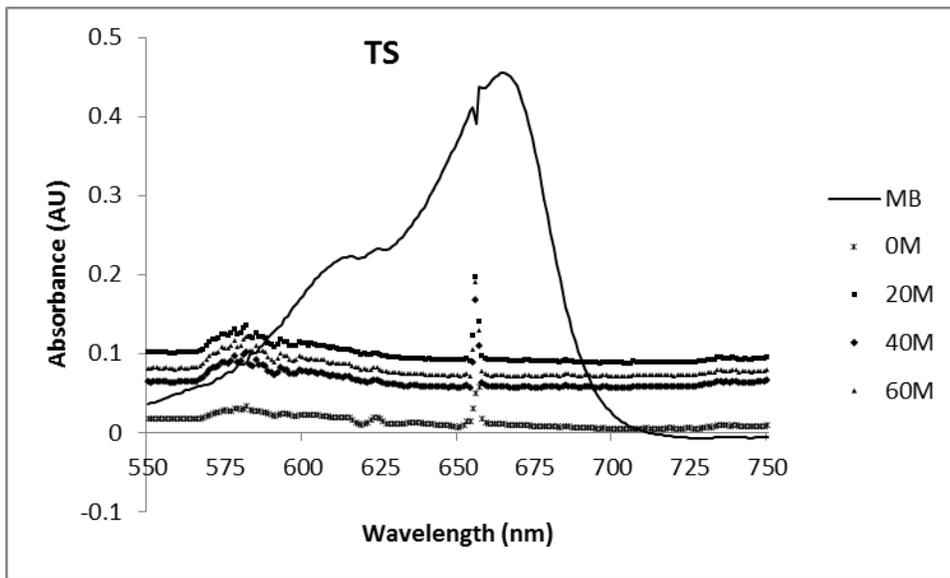


Figure 1(c): UV Vis spectral changes of MB with titania sulphate sample after different reaction time

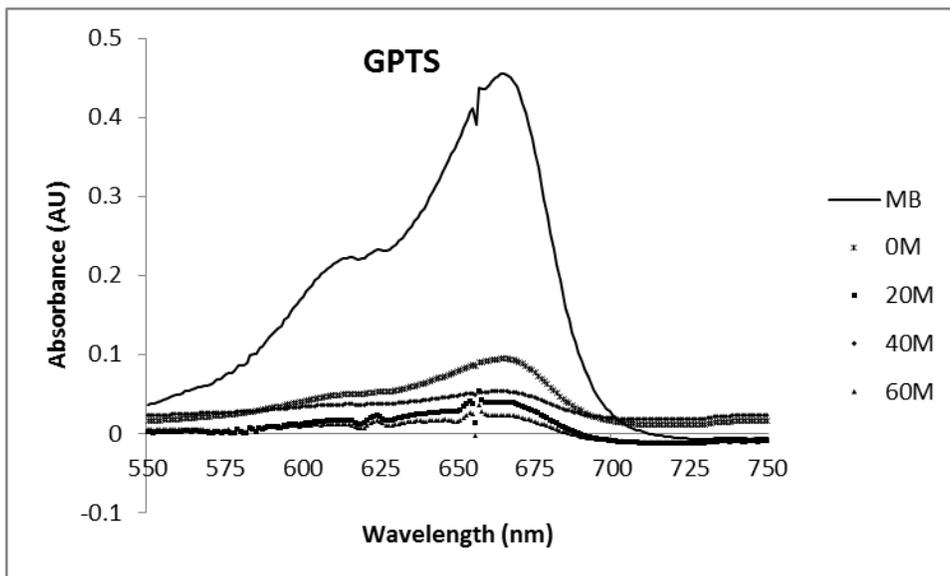


Figure 1(d): UV Vis spectral changes of MB with geopolymer/titania sulphate sample after different reaction time

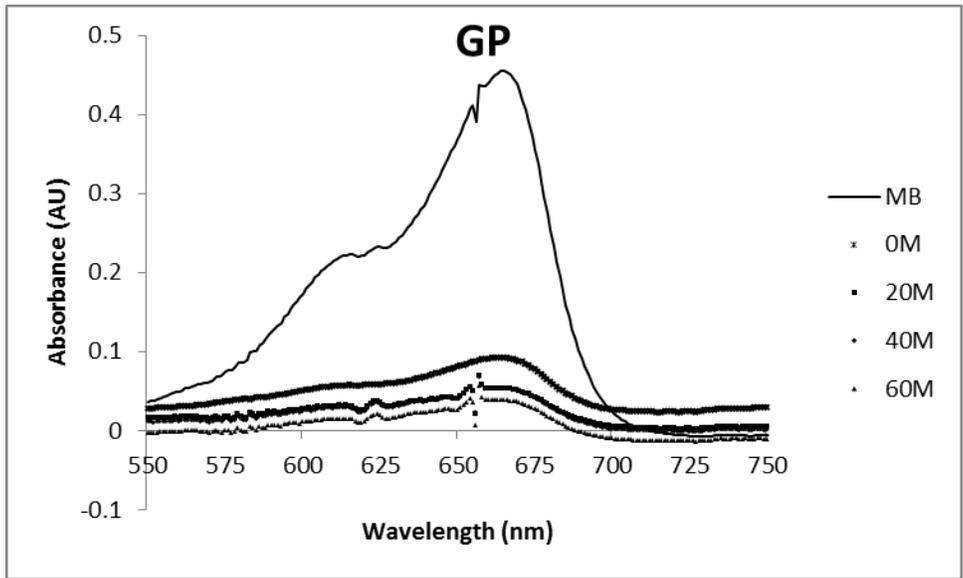


Figure 1(e): UV Vis spectral changes of MB with geopolymer sample after different reaction time

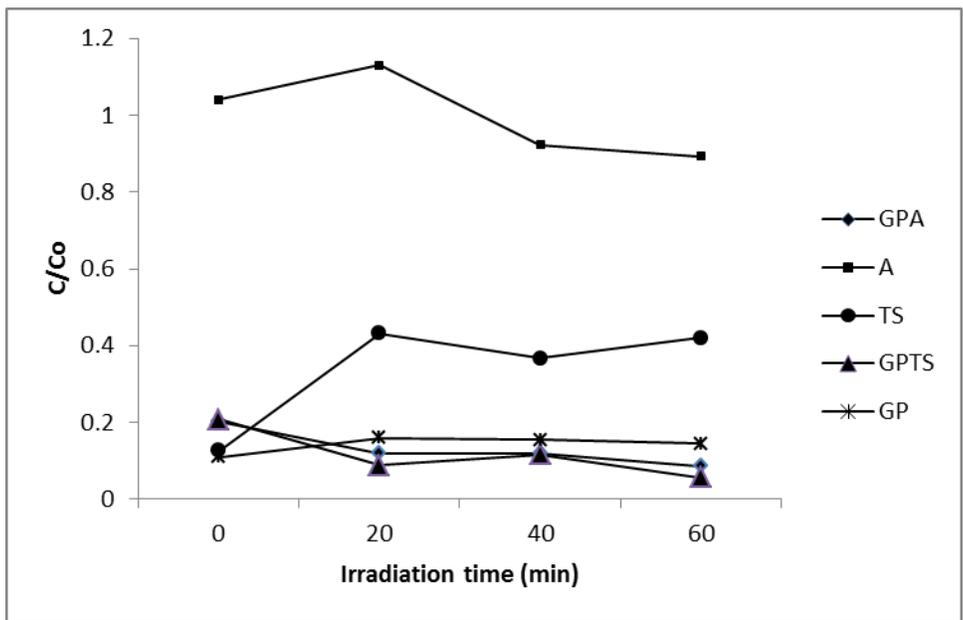


Figure 2: Photocatalytic activity of A, GPA, TS, GPTS and GP samples at different irradiation time

To investigate the degradation mechanisms of MB component, the UV-Vis absorption spectra of MB solution with all samples were compared, as shown in Figure 2. However, there were some differences by all samples in the MB photodegradation. On

the while, the degradation rate for A sample was relatively low. This is maybe due to mixture of some rutile that can be seen on XRD result. So, anatase cannot efficiently act as a photocatalyst in this experiment. Meanwhile, GPTS sample shows the highest photodegradation and prove that with the existence of geopolymer had enhanced the degradation capability. This is because the SiO₂ content in the geopolymer. SiO₂ had been reported gave influenced in photocatalytic activity [P. Cheng]. The same occurred to the GPA and GP themselves.

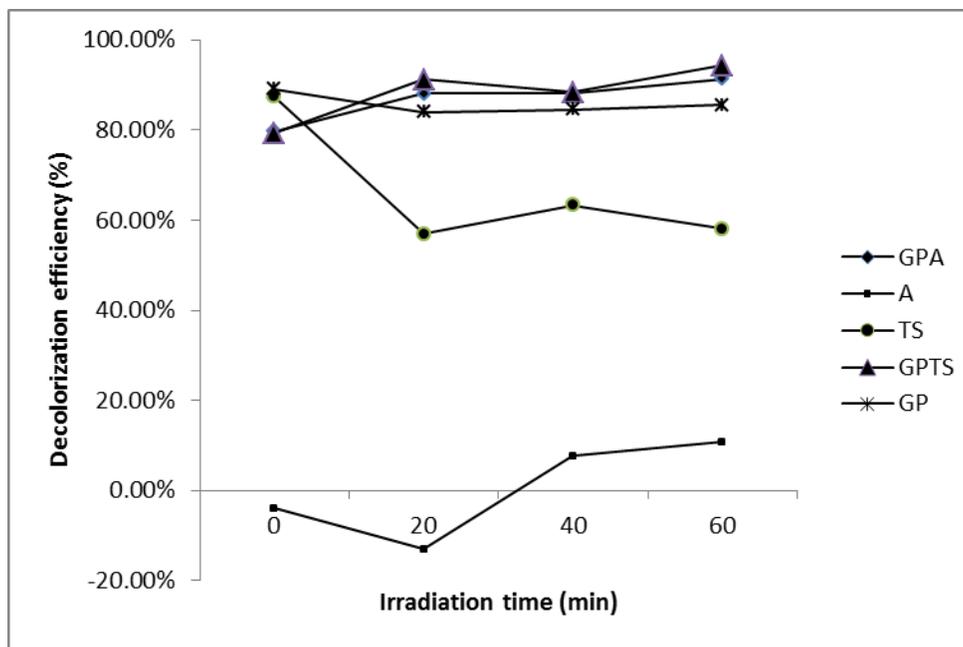


Figure 3: Decolourization efficiency of A, GPA, TS, GPTS and GP samples at different irradiation time

While after 60min reaction, for the A sample 89.22%MB component was residual in the solution, followed by TS 41.96%, GP 14.46%, GPA 8.65% and GPTS 5.7%. GPTS sample showed better results than other samples (as shown in Figure 3). Without the geopolymer addition, the reaction of MB with the samples is very slow which can be resulted in the poor conversion of MB component. The direct reaction between MB component in the solution and samples was demonstrated by the production of hydroxyl radical through formation of Si-O-Ti cross-linking bonds. These radicals are supposed to be responsible for the degradation of MB. In the presence of geopolymer during the irradiation of MB, it can be the initiator of the radical-type chain reaction that transforms O₂ into OH in the aqueous phase. Thus, when GP was applied in the degradation process, the high efficiency can be due to the combination of SiO₂, obviously accelerate the formation of OH.

CONCLUSIONS

The present study has indicated that the presence of geopolymer (contain of silica) in titanyl sulfate has been effective in enhance the photocatalyst properties of the sample. The geopolymer mix with titanyl sulfate show the most high photocatalyst activity compare to other sample.

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