Novel Green Photocatalysts Derived from Date Syrup-based biomass/TiO_2 for Photocatalytic Oxidation of Methylene Blue Dye in Aqueous Solutions

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ABSTRACT

This study reports for the first time, development of novel photocatalyst from date syrup-based biomass and TiO_2 for photocatalytic oxidation of methylene blue MB dye in wastewaters. The properties of the derived photocatalysts have been studied using Fourier Transform Infrared spectroscopy (FTIR). The performance for photocatalytic oxidation of MB dye was investigated in batch slurry reactor. The effects of operating conditions including, contact time, photocatalyst amount, pH, initial concentration, and temperature on photocatalytic oxidation behavior were investigated. The Langmuir-Hinshelwood kinetic model was applied to study the kinetics photocatalytic oxidation of MB dye. The results revealed that the derived photocatalysts exhibited an extremely high potential for photocatalytic oxidation of MB dye. A maximum ~88% conversion of MB dye was achieved at 50 ^oC and atmospheric pressure. The finding of this study may open a new avenue for not only improving the photocatalytic performance, but also for further research areas.

Keywords: Biomass; Wastewater treatment; Methylene blue dye; Photocatalytic oxidation; Langmuir-Hinshelwood kinetic model.

1. Introduction

Even though water covers about 70% of the Earth's surface, soft water is greatly limited. Therefore, the demand for water purification has been increased with modern life due to the increase of the pollution of water sources with an increase in world population and industrial revolution [1-3].

Water pollution is the main modern environmental problem, which is mainly is caused by variety activities such as domestic use, industry, and agricultural. Currently, there is growing concern throughout the world in reducing water pollution due to the fact that these

pollutants have significant environmental and health impacts for all living organisms. These various types of water pollutants can be classified into physical, biological, and chemical pollutants. However, organic pollutants are the most pollutants that available in water, including hydrocarbons and organic dyes. In addition, dyes are colored organic substances that capable of imparting their characteristic colors in water. Synthetic dye manufacturing started in 1856 by W.H. Perkin. Dyes are intensively used in many industries to color the products, including textiles, foods, pharmaceuticals, cosmetics, paints, pigments, and ceramics. The majority of dyes cause a potential health hazard to all forms of life. Among of them, allergic responses, skin dermatoses, and damages livers and lungs [2,4]. Therefore, it is very important to remove toxic dyes from water.

Separation processes based on fluid mechanics including sedimentation, centrifugation, filtration, flotation and membranes have been widely implied for wastewater treatment applications. Recently, the advanced oxidation techniques are considered the powerful methods for wastewater treatment, which are the processes of destruction of pollutants by agents that exhibit high oxidation potentials without secondary pollution.
Heterogeneous photocatalytic oxidation process was developed in the 1970s. In the past two decades, numerous studies have been carried out on the application of heterogeneous photocatalytic oxidation process for wastewater treatment [1]. Photocatalytic process has been gained much attention due to its significant efficiency for degradation of wide range of organic pollutants in aqueous solutions, such as organic solvents, hydrocarbons, and dyes [5]. Additionally, it is working by simple method, operating at wide range of conditions, low energy requirements, and it is environmentally friendly method.

Nowadays, heterogeneous photocatalytic oxidation technique has been considered as an unconventional technology in environmental remediation because it is capable of oxidation of the pollutants without production of any harmful by-products (see Figure 1) [7]. In addition, there is no second pollution associated with this method because no disposal problems [4,6].

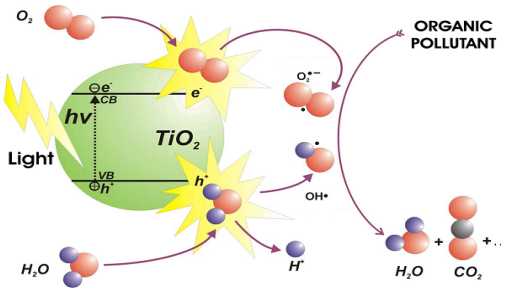

Figure 1 *Schematic diagram of photocatalytic excitation of TiO_2 as semiconductor by UV / solar irradiation* [7].

Photocatalytic oxidation technique possesses many heterogeneous photocatalytic process consists on utilizing the near UV radiation to photo excite a semiconductor catalyst

in the presence of oxygen. Photocatalytic reactions using semiconductors at the surface of the photocatalyst provide photo-induction of electron-hole pairs by band gap radiation. The most popular semiconductor is titanium dioxide (TiO_2) with a band gap width of 3.2 eV. A wide range of pollutants have been oxidized using UV/TiO_2 treatment. The objective of this research work has been proposed for development of a novel biomass-based photocatalyst with high performance for photocatalytic oxidation of MB dye.

2. Materials and Methods

2.1 Materials

Titanium dioxide (TiO_2) was purchased from BDH Laboratory Supplies, England with purity of 99.0%. Methylene blue (MB) dye was obtained from Sigma-Aldrich. NaOH and H_2SO_4 were purchased from Merck Chemical and these chemicals with analytical grade. All chemicals were used without further purification. The used date syrup (DS) was a homemade in Zliten city, Libya. The real water with pH ~7 was obtained from water tap at Faculty of Engineering, Elmergib University, Alkhoms, Libya.

2.2 Preparation of Date-Syrup/TiO_2 (DS-TiO_2) Photocatalyst

In this study, a novel photocatalyst has been developed using date syrup (DS) and titanium dioxide (TiO_2). A 0.5 g of titanium dioxide (TiO_2) was dispersed in 6 mL of homemade date syrup (DS) to make slurry. The mixture was stirred under heating at 70 ^oC for one hour (1 h) and then, the mixture was transferred into petri dish and dried in an oven at 60 °C for 24 h for drying. The dried DS-TiO_2 composites were carbonized to obtain DS-TiO_2 carbon monolith. The carbonized DS-TiO_2 monolith was ground to fine powders and then, it was used for photoxidation studies. The newly developed photocatalysts were abbreviated as DS-TiO_2-x, where x refers to the inclusion of TiO_2 semiconductor. In order to study the effect of important parameters like irradiation time, catalyst dosage, pH, and operating temperature, various batch experiments were run for each parameter.

2.3 Characterization

The structure of the DS-TiO_2 composites was confirmed by Fourier a Bruker Vertex infrared spectroscopy (FTIR), resolution 3 cm^{-1}, in the range of 4000-500 cm^{-1} using the KBr pellet technique. Dry and carbon DS-TiO_2-0.5 composites were crushed into powder in a mortar and an amount of 6-8 mg of the sample was used in each pellet.

2.4 Photocatalytic Oxidation of Methylene Blue Dye

The photocatalytic activity of the developed DS-TiO_2 photocatalyst was investigated by decomposition of the MB dye via photocatalytic oxidation technique. The photocatalytic oxidation experiments of MB dye were carried out by employing the obtained photocatalyst of date stone-titanium dioxide (DS-TiO_2) carbon powders under different experimental

conditions. For each run of photocatalytic oxidation of MB dye, a one-liter (1L) from the stock solution was placed into the reactor vessel. After the addition of the desired photocatalyst quantity, the solution was exposed to a UV light for a period of time. Because the UV lamp produces a heat, the temperature of irradiated solution was controlled using water flow heat exchanger. The performance of photocatalytic oxidation of MB dye was tested at different time intervals (10-20 min). The photocatalyst was removed from the samples using a centrifugation at 800 rpm for 30 min and then, the concentration of MB dye in the solution was analyzed using a UV-visible spectrophotometer at λ=664 nm. The unknown concentrations of the MB dye as function of time were calculated using the prepared calibration curve. Finally, according to the obtained MB dye concentration, the percentage conversion (x_A%) of photocatalytic oxidation was calculated using Eq. 1.

$$Conversion\ percentage, (x_A\%) = \frac{C_{Ao} - C_A}{C_{Ao}} * 100 \quad (1)$$

where, $x_{A\%}$ is oxidation percentage of MB dye, C_{Ao} and C_A are the initial concentration and the concentration of MB dye after irradiation time, t.

3. Results and Discussion

3.1 Analysis of FT-IR

The FT-IR spectra of DS-TiO_2-0.5 before used for photocatalytic oxidation of MB dye is shown in Figure 1. The absorption bands for prepared DS-TiO_2 show existence characteristics for both date syrup (DS) and titanium dioxide (TiO_2). The absorption band at 3402 cm^{-1} was due to the banding of hydroxyl groups (−OH) of DS. The FT-IR results also show significant peaks at about 2925 and 2887 cm^{-1}, which can be assigned to the C-H symmetrical and C-H asymmetrical stretching vibration from the organic-moiety. The band at 1634 cm^{-1} is ascribed to $-NH_2$ groups stretching vibrations and N−H for primary amine present in DS. Furthermore, appearance of bands at 920 and 876 cm^{-1} assigned to the existence of TiO_2 compound in the prepared photocatalyst. The apparent existence of amine and hydroxyl functional groups together with DS-TiO_2 photocatalyst helps to the removal of dyes through the photodegradation-adsorption process [8].

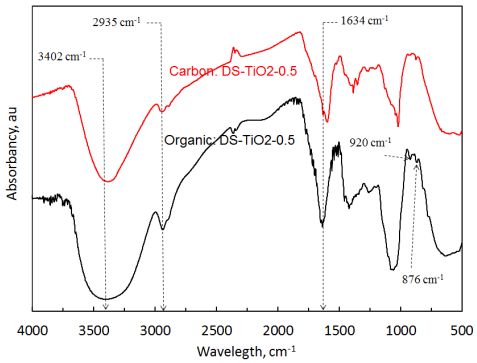

Figure 1 FT-IR spectra of DS-TiO_2-0.5 photocatalyst.

3.2 Effect of Irradiation Contact Time

The effect of irradiation time on photocatalytic oxidation efficiency of MB dye aqueous solution was investigated. The photocatalytic oxidation of 10 mg L^{-1} MB dye aqueous solution were performed in slurry batch reactor using neat TiO_2, DS-TiO_2-0.5, DS-TiO_2-1, and DS-TiO_2-2 photocatalysts at 50 °C and pH ~ 7 and the results are shown in Figure 2. The results showed that the photocatalytic oxidation efficiency of MB dye increases with an increase in the irradiation time until reaches an equilibrium. For example, the sample DS-TiO_2-0.5 showed an increased in the conversion of photocatalytic oxidation of MB dye from 25.9 % to 59.2 % with an increase of the irradiation time from 5 min to 60 min, respectively. The change in the photocatalytic oxidation conversion is ascribed to the fact that the oxidation conversion becomes slow after a certain time because most of MB dye molecules have been decomposed and a decrease in the MB dye concentration may occur [8,9].

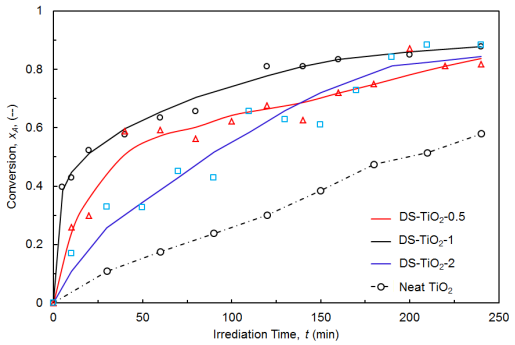

Figure 2: *Effect of irradiation time on photocatalytic oxidation of MB dye at 50 C°, initial concentration 10 mg L^{-1}, pH ~ 7.*

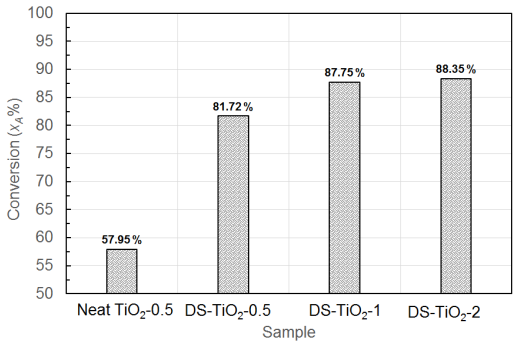

Figure 3: *Equilibrium conversion of photocatalytic oxidation of MB dye using the obtained photocatalysis.*

3.3 Effect of Sorbent Dosage

In photocatalytic processes, the amount of semiconductors has a large contribution for increasing the oxidation efficiency of MB dye up to a certain amount of catalyst. Therefore, because semiconductors are expensive materials, the used amount of catalyst should be optimized. Figures 2 and 3 demonstrate the effect of TiO_2 concentration on photocatalytic oxidation efficiency of MB dye. For example, when the irradiation time is 20 min the photocatalytic oxidation conversion of MB dye were 35.9 %, 52.2 %, and 18.3 %, for DS-TiO_2-0.5, DS-TiO_2-1 and DS-TiO_2-2, respectively. As seen in Figure 3, the results indicated that the maximum photocatalytic oxidation conversion of MB dye using neat-TiO_2 of 57.95% after 240 min. However, the photocatalytic oxidation efficiency increases after combination of date syrup (DS) with different amount of TiO_2 and significant photocatalytic oxidation efficiency was achieved. For example, the equilibrium conversions of 81.32 % to 87.75 % were obtained using DS-TiO_2-0.5 and DS-TiO_2-1, respectively. In addition, DS enhances the adsorption of MB dye to the catalyst surface due to presence of date syrup functional groups. The comparison of the results for DS-TiO_2-0.5 and DS-TiO_2-1, it clearly

that 0.5 TiO_2 in the sample DS-TiO_2-0.5 is the optimum amount of TiO_2 because a small increase in the oxidation conversion as compared to the amount of catalyst added. The increase of catalyst amount above the optimum value it causes a decrease in photocatalytic oxidation efficiency of MB dye due to the agglomeration of catalyst particles the interception of the light by the suspension [10-13].

3.4 Effect of Initial Concentration of MB dye

The effect of initial concentration of MB dye on the photoxidation efficiency have been also investigated using varying initial MB dye concentration, namely 10, 25, 50 mg L^{-1}. As seen in Figure 4, it is clearly that the results indicated that when the initial concentrations of MB dye increases, the photocatalytic oxidation efficacy decreases. For example, after 150 irradiation time, the photocatalytic oxidation efficiency was increased from 25.00 % to 56.62 % with a decrease in initial concentration from 50 mg L^{-1} to 10 mg L^{-1}, respectively. The decrease in the oxidation conversion is due to the fact that the quantity of light (quantum of photons) penetrating the MB dye aqueous solution to reach the photocatalyst surface is reduced owing to the hindrance in the path of light thus the formation of the hydroxyl radicals is simultaneously reduced [9].

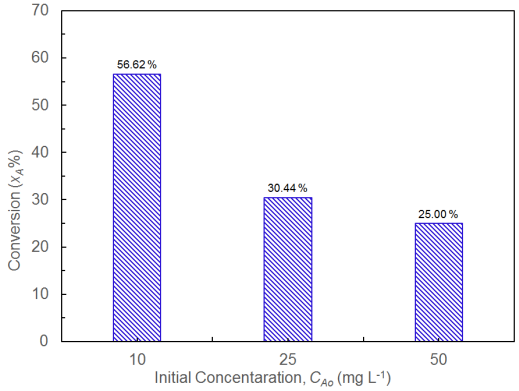

Figure 4: *Effect of initial concentration on photocatalytic oxidation of MB dye at 50 °C for 150 min of Irradiation time using DS-TiO_2-0.5 photocatalyst.*

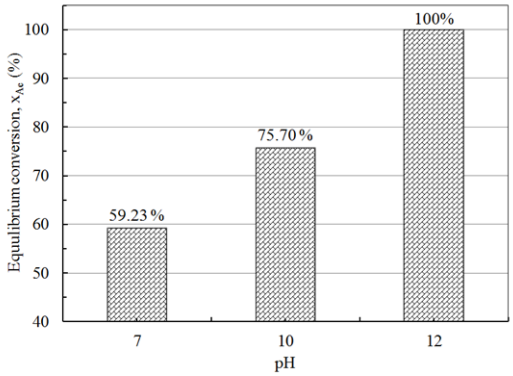

Figure 5: *Effect of initial pH of MB dye aqueous solution on the adsorption efficiency of MB dye.*

3.5 Effect of Initial pH

The initial pH of aqueous solution is an important parameter in the adsorption efficiency. The previous studies report that initial pH is the most important parameter that effects on the photocatalytic oxidation efficiency [8,10]. Therefore, in the present study, the effect of initial pH on conversion of photocatalytic oxidation of MB dye was evaluated for 10 mg L^{-1} initial concentration of MB dye at 45 °C using DS-TiO_2-0.5 photocatalyst for 60 min of irradiation time. The initial pH of the solutions were varied from 7 to 12, which were adjusted before exposure the solution to the UV light using acidic or basic solutions of H_2SO_4 or NaOH, respectively, and it was not controlled during the reaction process. The

photocatalytic oxidation of MB dye is found to be increase at alkaline pH due to its nature, cationic dye [8,11]. Therefore, the experiments were performed at neutral and alkaline conditions.

Figure 5 displays the effect of pH on the equilibrium photocatalytic oxidation of MB dye. The results showed that the oxidation conversion is proportional with the initial pH of the aqueous solution. For instance, the conversion of photocatalytic oxidation of MB dye was increased from 59% to 76% with an increase in pH value from 7 to 10, respectively. The pH influences the characteristics of the photocatalyst surface charge [10]. The increase in conversion of MB dye oxidation is attributed to the surface of photocatalyst gains negative charge, which is favorable to positively charged dye molecule such as MB dye. In addition, the increased efficiency in the alkaline pH range is due to the formation of OH^* radicals with an increase in pH [8]. This implies that high alkaline conditions significantly enhances the formation of the reactive intermediates that is hydroxyl radicals (OH^*), which further contribute in enhancing the reaction rate [9].

3.6 Effect of Temperature

To investigate the effect of operating temperature, the photoxidation efficiency of MB dye was evaluated at different temperatures. Two experiments were run for 10 mg L^{-1} initial concentration of MB dye using DS-TiO_2-0.5 for 180 min at operating temperature of 50 and 60 ^oC, respectively. Figure 6 represents the conversion of photocatalytic oxidation of MB dye as a function with operating temperatures. The results indicated that the oxidation conversion is increased proportionally with the operating temperature. For example, photocatalytic oxidation conversion is increased from 74.89 % to 86.94% with an increase in temperature from 50 ^oC to 60 ^oC, respectively. This increase is due to mass limitation of transport of reactants and reaction products to/from the catalyst surface, which increases with temperature. Therefore; the photocatalytic oxidation of MB dye is following an endothermic reaction [11].

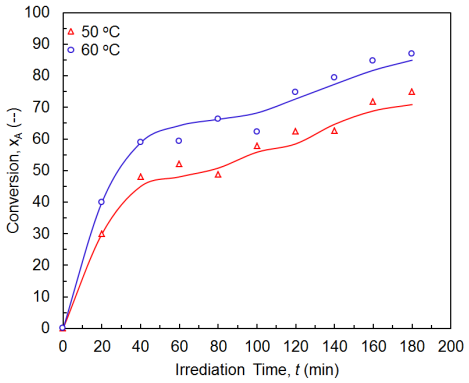

Figure 6 *Effect of operating temperature on photoxidation efficiency.*

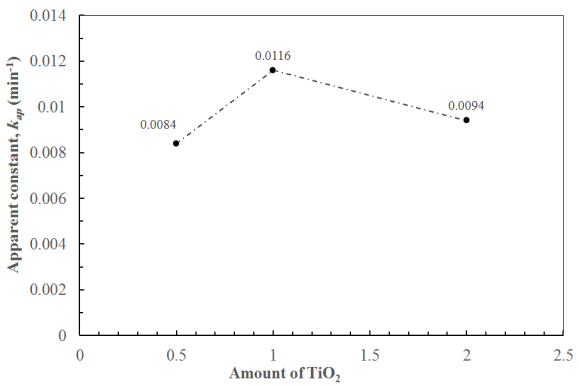

Figure 7 *Effect of TiO_2 content on apparent kinetic constant (k_{ap}) of MB dye.*

3.7 Kinetic Analysis

The kinetics of the photocatalytic oxidation of MB dye aqueous solution has been also investigated using the obtained photocatalysts. The experimental data for discoloration of the MB dye using various heterogeneous photocatalysts was used to investigate the kinetic parameters of the photocatalytic oxidation reaction. The obtained experimental data was fit the Eq. 2, a plot of $(-ln(1-x_A))$ versus irradiation time (t) (The Figure is not included). A straight line was fitted to the data for each sample and the correlation factors (R^2) were 0.93, 0.84, and 0.69 for DS-TiO_2-0.5, DS-TiO_2-1, and DS-TiO_2-2, respectively. These findings suggested that photocatalytic oxidation reaction (discoloration rate) followed pseudo first-order kinetics. Therefore, the oxidation rate depended on the MB dye concentration. The value of apparent rate constant (k_{ap}) has been also determined from the slope of the plot for each experiment. The k_{ap} values of the MB dye photocatalytic oxidation for the catalyst samples with varying TiO_2 concentrations of 0.5, 1.0, and 2.0 g were 8.10×10^{-3} min^{-1}, 10.06×10^{-3} min^{-1}, and 9.40×10^{-3} min^{-1}, respectively.

$$-ln(1-x_A) = k_{ap}\, t \qquad (2)$$

where x_A is the MB dye conversion, k_{ap} is the apparent reaction constant, and t is the reaction time.

Figure 7 displays the effect of TiO_2 content on apparent kinetic constant (k_{ap}) of MB dye. As seen in the Figure, the results indicated that the amount of TiO^2 has a small effect on the apparent constant (k_{ap}), which is in the range of from 8.10×10^{-3} min^{-1} to 10.06×10^{-3} min^{-1}. The apparent rate constant was found to be increased with increasing TiO_2 concentration up to 1 g and then it decreased, when other parameters are kept unchanged. According to the maximum apparent constant; the reaction rate expression for photocatalytic oxidation of MB dye in this study is given in Eq. 3.

$$-r_A = 10.06\times10^{-3} C_A \qquad (3)$$

Where $-r_A$ is the photocatalytic oxidation reaction rate in (mg L^{-1} min^{-1}) and C_A is the concentration of MB dye at time t in (mg L^{-1}).

The initial kinetic of photocatalytic oxidation of organics is often described by Langmuir-Hinshelwood (L-H) [8]. In this study, initial kinetics of photocatalytic oxidation of MB dye using L-H model was also investigated using a data collected for photocatalytic oxidation of MB dye in aqueous solutions at 50 ^oC, pH ~ 7 using DS-TiO_2-0.5. The experimental data of photocatalytic oxidation of MB dye at different three initial concentrations (10, 25, and 50 mg MB dye/L) were fitted to L-H model, and then the kinetic parameters were obtained. The apparent reaction constants (k_{ap}), were obtained according to Eq. 2. Figure 8 displays a plot of $(-ln(1-x_A))$ versus irradiation time at various initial MB dye

concentrations. The plot showed a lineal relationship; therefore, the photocatalytic oxidation of MB dye follows a first order kinetics. In addition, the results indicated that the value of apparent reaction constant (k_{ap}) were 6.5x10^{-3} min^{-1}, 2.5x10^{-3} min^{-1}, 2.1x10^{-3} min-1 at initial MB dye concentrations of 10, 25, and 50 mg L-1, respectively. The initial reaction rate (r_{Ao}) is a product of apparent reaction constant and the initial MB dye concentration ($r_{Ao} = k_{ap} \cdot C_{Ao}$) and the data was fitted with the L-H model (see Eq. 4) [8].

$$\frac{1}{-r_{Ao}} = \frac{1}{kK}\frac{1}{C_{Ao}} + \frac{1}{k} \qquad (4)$$

The intercept of the plot of $1/r_{Ao}$ against $1/C_{Ao}$ is inverse the kinetic constant (k) and the adsorption constant (K). Figure 9 demonstrates the relationship of inverse of the initial reaction rate ($1/r_{Ao}$) as a function of ($1/ C_{Ao}$). The obtained initial kinetic parameters of photocatalytic oxidation of MB dye the kinetic constant (k) and the adsorption constant (K) were found to be 0.9296 mg L^{-1} m^{-1} and 0.19925 L mg^{-1}, respectively.

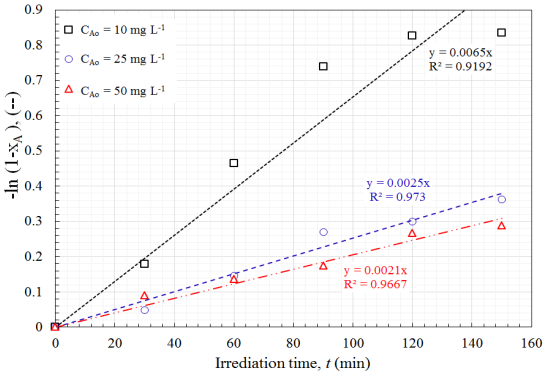

Figure 4.6 *The fit of the experimental data with the first-order kinetic model*

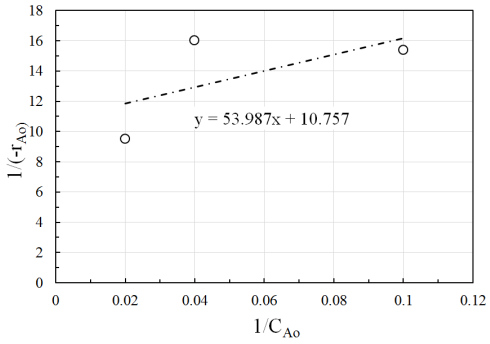

Figure 4.8 *The plot of Langmuir-Hinshelwood model: Inverse the initial reaction rate against inverse the initial concentration.*

4. Conclusions

The presence of methylene blue dye (MB) in water has negatively impacts to the humans and the environment. In this study, as a modern technology for wastewater treatment, photocatalytic oxidation technique was selected in this work because it is simple method for decomposition of organic pollutants to CO_2 and water without contribution of any secondary pollution. In addition, the present study provides a novel root for development new photocatalysts. Therefore, we report in the first time of using date syrup (DS) in synthesis of new environmentally friendly photocatalysts and investigate its application for removal of MB dye from aqueous systems. The interactions of DS with TiO_2 were confirmed using FT-IR. Date syrup (DS) was composed with different quantities of TiO_2 as a semiconductor material. The developed EY-TiO_2 photocatalysts exhibit an excellent performance of MB dye photocatalytic oxidation. A significant increase in the conversion of MB dye after composed DS TiO_2, and the sample of DS-TiO_2-0.5 showed the optimal TiO_2

content. This study also conducted the photocatalytic oxidation for removing MB dye from aqueous solutions under several parameters. The photocatalytic oxidation efficiency was promoted by increasing the amount of oxidizing agent (TiO_2), the initial pH of the solution, the irradiation time, and the operating temperature. The maximum conversion of 87.8 % for MB dye was achieved using the sample DS-TiO_2-1. In addition, the kinetics of photocatalytic oxidation of MB dye was also investigated. The kinetic analysis indicated that DS-TiO_2 photocatalysts exhibit fast kinetics of MB dye photocatalytic oxidation with a reaction constant in the range of $8.10x10^{-3}$ – $10.60x10^{-3}$ min^{-1}. Therefore, the obtained results may open a new opportunity for the rapid and large-scale industrial preparation of novel biomass-based photocatalysts with excellent conversion of MB dye at wide range of various operating conditions.

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