

Optical Photocatalytic Degradation of Methylene Blue Using Lignocellulose Modified TiO₂

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Abstract: This paper reports the photo-catalytic activity and stability of Lignocellulose/TiO₂ nanoparticles (NPs) was evaluated through using the decomposition of methylene blue (MB) as a testing model reaction under visible light irradiation ($\lambda_{max} > 420nm$). The modified (NPs) (pH = 6.94 - 6.97) photocatalyst material was dried for 24 hours at the temperature of 80°C and calcinated at 400°C for 2 hours through constant air flow. The degradation of MB was performed using 250 Watt xenon lamp within every 30 minute time interval followed by measuring the absorbance. The maximum characteristic absorption peak of MB solution was observed at ($\lambda_{max} \sim 664nm$) and the absorbance of this peak approaches to a minimum value and the degradation efficiency become effective after illumination for 150 minute. Optimized parametric conditions like pH \approx 6, initial concentration ($C_0 = 6$ ppm), time = 120 min and catalyst loading (160 mg) results were examined to improve the degradation efficiency (> 95%).

Keywords: Lignocellulose, Photo-Catalytic, Methylene Blue, Degradation

1. Introduction

Organic pollutant removal from waste water using electro-conducting nanomaterial's photocatalysts has an attracted attention towards issue on environmental protections [1, 2]. The photocatalytic activity of these nanoparticles under ultraviolet and visible lights has been found a considerable technique and academic interest throughout its property [3]. The degradation process is suitable for cleaning contaminant water with low to medium contaminants concentrations [4]. So, under the illumination of light that has energies higher than the photocatalyst band gap, electrons from valance band will be excited to the conduction band will cause creating of electron-hole pairs (e^-h^+) [5-7]. This pair will motivate a series of reactions and produce hydroxyl radicals, OH, and super oxide radical anions, O_2^- , when the photocatalyst is in contact with water. With the radicals and anions the electro-conducting photocatalyst surface, the organic contaminants like methylene blue are oxidized or degraded at or near to the photocatalyst surface [8].

Dyestuffs are materials extensively used in the textile and

other printing industries. The color and toxicity of dyes within water bodies are very undesirable and harmful to the water users especially for aesthetic and environmental reasons. Methylene blue (MB) is a cationic dye, used extensively for dying application in textile industry with the chemical name tetramethylthionine chloride. It has a characteristic deep blue color in the oxidized state. But the risk of the existence of this dye in waste water may be arisen from the burns effect of eye, nausea, vomiting and diarrhea. MB has a maximum absorption peak in the visible region at around 664 nm [9, 10].

Recently, photocatalytic reactions induced by illumination of electro-conducting nanomaterials in suspension have been shown to be one of the most promising techniques for waste water treatment [11]. Among various electro-conducting photo catalysts nanomaterial's, lignocellulose [12] and its modified with titanium oxide (TiO₂) conducting nanomaterial's exhibit promising photocatalytic activities due

to their especial environmental friendly behavior, low catalytic cost, unique degradable ability, and high crystalline property and therefore, could be an alternative nanomaterial for environmental application and wastewater treatment [13]. Likewise, lignocellulose modified titanium oxide is the most and selective nanomaterial under ambient condition and has special significant importance, due to their stability, particle size and for their better electron transfer mediator.

However, the photocatalytic activity of most transition metal oxide and their doped nano-sized materials are not always effective due to the agglomeration of nanomaterials in the aqueous solution, which causes lower efficiency in photocatalytic activity. So, to overcome this drawback is to apply innovative synthetic method of lignocellulose nanoparticles of the catalyst which can be easily dispersed in the organic medium and homogeneously loaded on to the supported materials. Many studies have continuously tried to improve their catalytic activity of titanium dioxide by coupling with different electro-conducting nanoparticles [14-19]. Therefore, in this work lignocellulose modified nanoelectromaterial was used as photocatalyst under visible radiation for methylene blue dye degradation in aqueous solution and investigates the effects of time, initial concentration, catalyst loading, and pH.

2. Experimental

2.1. Chemicals and Reagents

Commercial amorphous anatase titanium dioxide (titania: TiO_2 , > 99%) was purchased from Merck Analytical Reagent Co. Ltd. India. Methylene blue was obtained from Merck in the analytical grade and used without further purification. All chemicals and reagents used in this study were analytical grade.

2.2. Photocatalyst Preparation

Commercial available anatase titanium dioxide shows an

$$\text{Degradation efficiency} = \frac{C_0 - C}{C_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

Where C_0 and C concentration before and after degradation while A_0 and A absorbance before and after degradation, respectively.

3. Results and Discussions

3.1. Photocatalytic Activity of Lignocellulose - TiO_2 Nanoparticles

In this study photocatalytic of MB was used as the model organic pollutant to evaluate the activity of Lignocellulose modified TiO_2 nanomaterials. Figure 1(a) shows the UV-Vis diffuse reflectance spectra of methylene blue solution before and after visible light irradiation ($\lambda > 420 \text{ nm}$) for different contact time (minutes). The characteristic absorption bands of this organic pollutant solution at ($\lambda_{\text{max}} \sim 664 \text{ nm}$) were significantly decreased in intensity with increasing irradiation time. The absorbance of this peak approaches to a minimum

acidic reaction. So, the investigated material was washed with ammonia solution to neutralize the acidic solution. The solution was washed with distilled water to remove the excess ammonia and the final pH was recorded as (7.17-7.19). Subsequently, TiO_2 was dried at 80°C for a few hours and grounded with a mortar then after it was kept ready for further analysis [20].

Lignocellulose modified TiO_2 material was synthesized as follows: 6 g of amorphous TiO_2 and 5 g of lignocellulose extracted from cotton stalk dry biomass [21] were mixed with 25 mL of distilled water for 6 hours at 90°C using water bath and then air-cooled at room temperature. The resulting product was collected and washed thoroughly with distilled water, and finally dried at 60°C in an oven. The obtained powders (pH = 6.94- 6.97) were dried for 24 hours at the temperature of 80°C and calcinated in a muffle furnace at 400°C for 2 hours through constant air flow [22].

2.3. Degradation of Methylene Blue

The photocatalytic degradation of MB by lignocellulose- TiO_2 photocatalysts were performed under visible light irradiation. The photocatalytic degradation was monitored using UV-Vis light irradiation at $\lambda_{\text{max}} > 420 \text{ nm}$ as a light source using 250 Watt xenon lamp. In all experiments a 160 mg of catalyst was suspended in 100 mL of 6 ppm methylene blue solution in a conical flask. The flask was wrapped with aluminium foil then placed in the dark for an hour for adsorption to take place. The system was then irradiated with visible light from a lamp that was fixed in the middle of the system and 12 cm above the surface of the solution. To detect changes in concentration, aliquots of methylene blue solution (5 mL) were taken after every 30 minutes and centrifuged followed by measuring the absorbance of the clean solution by UV-Vis spectrometer [23]. The concentration of MB was proportional to its absorbance according to Beer-Lambert law, so the degradation efficiency of organic compound (MB) was calculated as formula [24]:

value and the removal (degradation) efficiency shown from Figure 1(b) become effective after illumination for 150 minute.

3.2. Effect of pH Solution

The role of pH on the efficiency of photocatalytic degradation of methylene blue (MB) was carried out in the range of 3-9; the results are plotted in Figure 2. At pH (3-5.5), molecules of MB are adsorbed on photocatalyst surface due to the undissociation nature of MB thereby producing higher photocatalytic efficiency (95%, at pH = 6), then decrease in efficiency due to negatively charged nature of photocatalyst surface at higher pH (higher alkalinity). Thus, lower degradation of MB is observed in the alkaline environments. Related results were reported in the unmodified TiO_2 photocatalyst with pH value from 4 to 8 efficiency 90% [25].

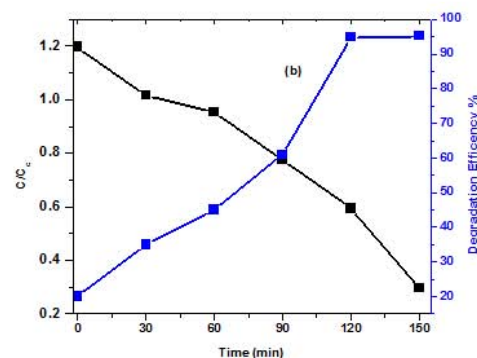
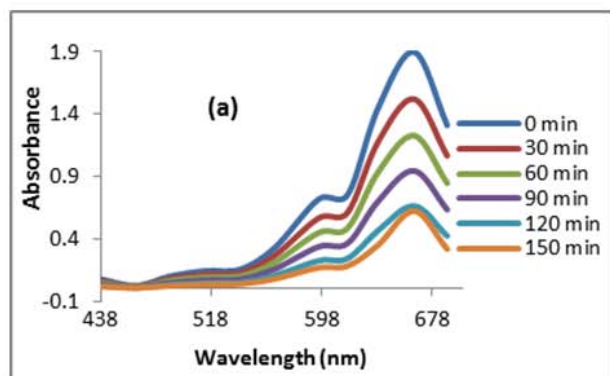


Figure 1. (a) Absorption spectral changes and photodegradation of Methylene Blue while and (b) degradation efficiency on titania loaded Lignocellulose under visible light irradiation ($\lambda > 420$ nm). Reaction conditions: $C_0 = 6$ ppm, catalyst loading: 160 mg, pH = 6, $T = 27 \pm 2^\circ\text{C}$.

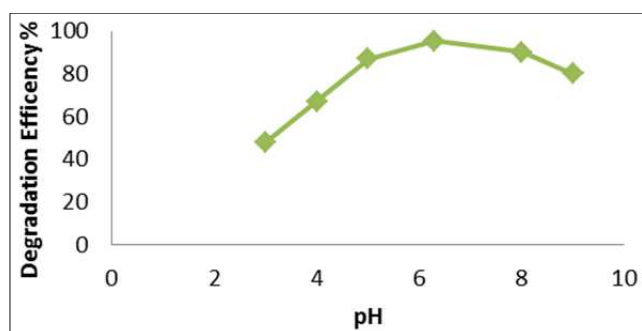


Figure 2. Effect of pH solution on degradation efficiency of methylene blue with concentration of 6 mg/L, 160 mg loading catalyst, time = 120 min, $T = 27 \pm 2^\circ\text{C}$.

3.3. Effect of Photocatalyst Loading

Figure 3 shows effect of catalyst loading at different amount of Lignocellulose, i.e., 57.14% Lignocellulose, 50% Lignocellulose and 44.44% Lignocellulose on the degradation of methylene blue in the range 140 mg to 180 mg by optimizing other conditions. The photodegradation efficiency was increased from 140 mg to 160 mg and reached at a maximum of 160 mg at around 2 hour irradiation time. Then decrease in efficiency was observed at maximum TiO₂ suspension due to increase in turbidity and low light penetration of a catalyst that is reported from earlier studies [26].

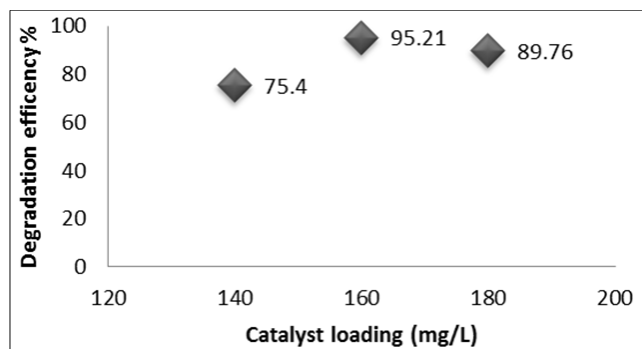


Figure 3. Effect of catalyst loading on degradation efficiency of methylene blue with concentration of 6 mg/L, pH = 6, time = 120 min, $T = 27 \pm 2^\circ\text{C}$.

4. Conclusions

A visible light active TiO₂ photocatalyst material was prepared by a surface chemical modification process with lignocellulose using sol-gel method in ethanol-water reaction system. The photo catalytic activity of lignocellulose modified TiO₂ exhibited a good photostability and high photocatalytic performance with > 95% degradation efficiency for the degradation of methylene blue under visible light irradiation as a model compound. Optimized parameters such as solution pH, catalyst amount and initial concentration were effectively studied. 120 min time, 6 pH, 160 mg catalyst load and 6 mg/L concentration were determined as optimum conditions for the experiment. Therefore, such photocatalysis was proved to be a good-looking method to remove such pollutants from its source.

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