Title: Photocatalytic degradation of sugarcane factory wastewater and methylene blue using TiO_2 photocatalyst under natural sunlight illumination.

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Introduction

Water is the most essential component on the earth for sustaining a life. It is necessary for health, absorption of food & helpful for maintaining muscle tone. About 97% of whole water is salty ocean water. Remaining 3% of water is fresh water from which two third is in frozen form. Only 1% is available for domestic use. In recent year, due to heavy industrialization large amount of organic waste such as dyes, acids, sugar factory effluent etc. are discharged into potable water sources hence, water gets polluted. Among these dyes are very toxic & carcinogenic and difficult to decolorize due to their complex structure and synthetic origin. Hence it is paramount importance to purify the wastewater.

Different Methods such as Distillation, sedimentation, Filtration, UV disinfection, activated sludge process, Advanced oxidation process (AOPs) used for the purification wastewater. The main aim is to develop a cost-effective solar photochemical process that can reduce the level of contaminants in wastewater to meet environmental regulations. Among these AOPs is effective for degradation of organic contaminants. The catalyst is the heart of the photocatalytic process because photocatalysis is based on the excitation of a photoelectrode with the irradiation of light energy. Photocatalysis is accelerated photoreaction in presence of catalyst. The overall photocatalytic process involves three major steps: **(i)** absorption of light by the semiconductor to the generate of electron-hole pairs, **(ii)** charge separation and migration to the surface of the semiconductor and **(iii)** surface reaction for the water reduction or oxidation reactions. TiO_2 is most important material as a catalyst for photochemical purification of wastewater because of its high oxidation potential, low cost, environmentally friendly. Therefore it is used for degradation of organic contaminants like dyes, acids, sugar factory effluent. Sugar factory waste contains carbonates, sulphates, nitrates, acids, bacteria, viruses.

Aim: Removal of organic contaminants from sugar factory wastewater and decolourization of dyes using TiO_2 as a photocatalyst under natural sunlight illumination.

Procedures details: The photocatalytic activity of the methyl blue (MB) and sugarcane factory wastewater was studied using UV–vis–NIR spectrophotometer. For each experiment, 300 ml of MB (0.5 mM) solution was taken in a beaker containing 0.3 g of TiO_2 catalyst suspended in it. During irradiation, the solution was stirred mechanically using a magnetic stirrer for the homogenization of suspension. For the photocatalytic activity measurement, a small volume (3-4 ml) of clear supernatant liquid was taken at regular time intervals (10 min) after sedimentation of powder and analysed with UV–vis–NIR spectrophotometer (Shimadzu 3600). The concentration of MB and sugarcane factory wastewater was monitored by taking its absorbance at max. = 662 and 270 nm respectively. The rate constants for different catalysts under sunlight irradiation were calculated by using the first order rate equation,

$$\ln \frac{C}{C_0} = -kt \qquad [1]$$

where t is the time, k can be taken as the apparent first order rate constant of the degradation reaction; C stands for the concentration of the solute or oxidizable atoms in the organic compound at time t; C_0 the initial concentration of solute (i.e. t = 0 min)

Result and Discussion

Fig.1 shows actual experimental setup for photocatalytic degradation of sugarcane factory wastewater and photograph of sugarcane wastewater samples collected at different time interval. From these photograph it is seen that recognisable change in colour has been observed i.e. its concentration decreases with reaction time.

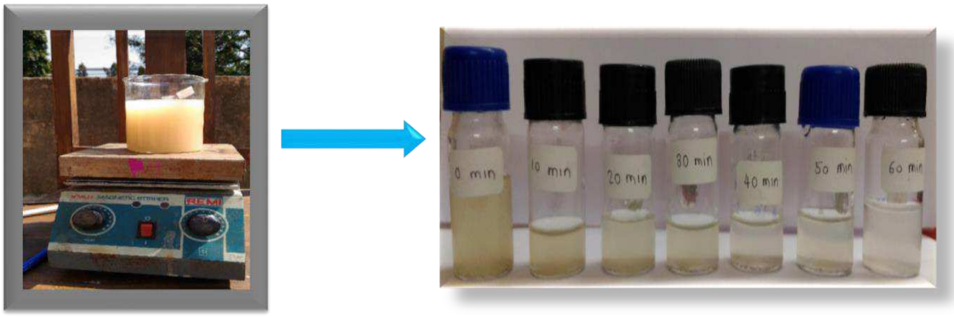

Fig.1 shows actual experimental setup for photocatalytic degradation experiment and photograph of sugarcane wastewater samples collected at different time intervals.

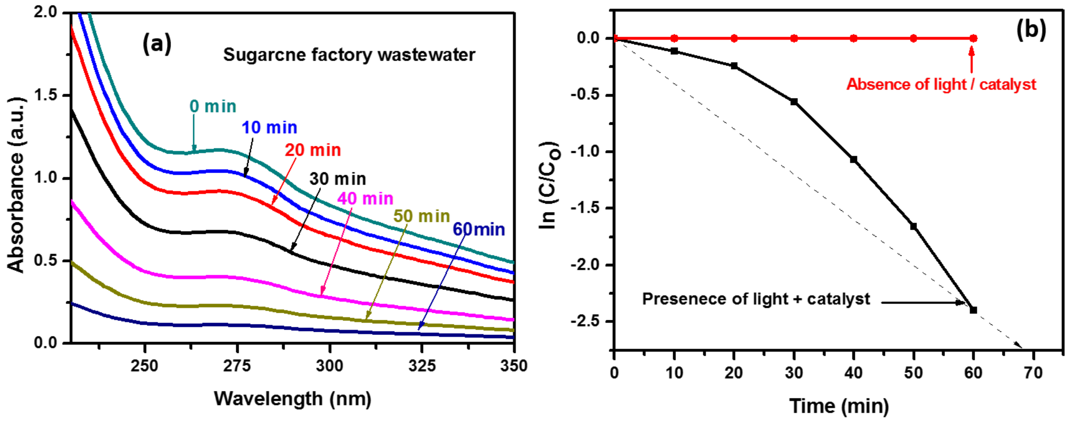

Fig. 2 Sugarcane factory wastewater degradation using TiO_2 photocatalyst under sunlight illumination: **(a)** absorbance spectra with illumination time **(b)** kinetics of degradation.

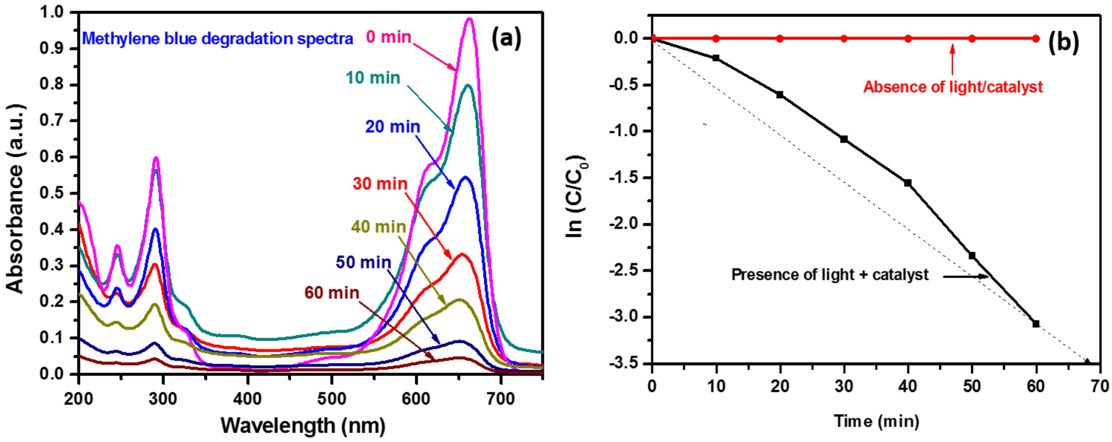

Fig. 3 Methylene blue degradation using TiO_2 photocatalyst under sunlight illumination: **(a)** absorbance spectra with illumination time **(b)** kinetics of degradation.

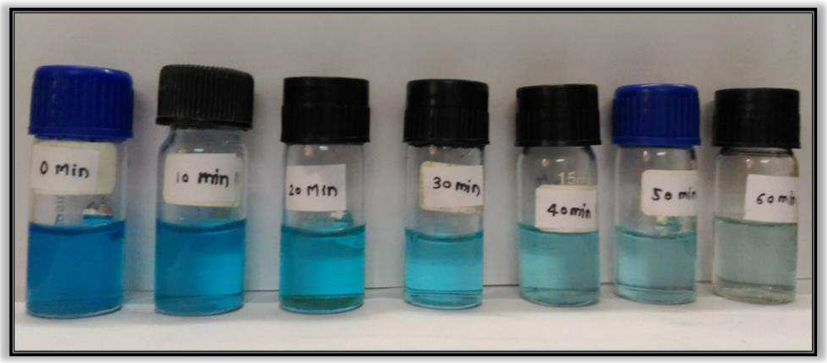

Fig.4 Shows photograph of samples of MB collected during photocatalytic degradation experiment.

Fig. 2 (a) shows the absorbance spectra of sugarcane factory wastewater collected at various intervals of time during its photocatalytic degradation experiment and is recorded in the wavelength range from 230 to 350 nm. During the course of the degradation experiment, frequent decrease of the absorbance peaks indicates decrease in sugarcane factory wastewater concentration and is also visually confirmed by the reaction solution decoloration. The degradation percentage is calculated using the equation

$$\text{Degradation percentage (\%)} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \qquad \textbf{[2]}$$

It is found that, the 90% degradation of sugarcane factory wastewater done in 60 min. under sunlight illumination. The absorbance is further used to plot variation in ln (C/C_0) as a function of reaction time as shown **fig 2 (b**). The photocatalytic degradation also follows a pseudo-first order reaction and its kinetics is expressed using Eq. (1). The slope of this plot gives a value of the rate constant and is found to be k = 3.31×10^{-5} s^{-1}. The same degradation experiment also performed in absence of photocatalyst without sunlight irradiation and it is found there is no degradation observed. This observations confirms that there is no redox reaction take place on the surface of semiconductor photocatalyst without light. However, in the presence of both, light and catalyst, shows the high efficient degradation of sugarcane factory waste, these observations indicated that presence of both catalyst and light are required for an effective degradation of organic pollutants.

Fig. 3 (a) shows the absorbance spectra of MB collected at various intervals of time during its photocatalytic degradation and is recorded in the wavelength range from 200 to 700 nm. The degradation percentage is calculated by using the Eq. (2). It is found that, the 95% degradation of MB done in 60 min. under sunlight illumination. The absorbance is further used to plot variation in ln (C/C_0) as a function of reaction time as shown **fig 3 (b).** The slope of this plot gives a value of the rate constant and is found to be k = 4.18×10^{-5} s^{-1}. **Fig. 4** shows the photograph of MB samples collected at different time intervals during photocatalytic degradation experiment. From these photograph it is observed that MB solution decolourization due to redox reaction.

Conclusions: Sugarcane factory wastewater (90%) and MB (95%) has been successfully degraded using TiO_2 photocatalyst. Thus TiO_2 powder is a promising photocatalyst with the potential practical application in polluted water treatment.

Note: Water quality testing results of sugarcane factory wastewater before and after the experiment is attached as a supplementary information for your reference.