



# Photocatalytic treatment of dye wastewater and parametric study using a novel Z-scheme $\text{Ag}_2\text{CO}_3/\text{SiC}$ photocatalyst under natural sunlight

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## ARTICLE INFO

### Keywords:

Photocatalysis  
Solar light  
Methylene blue  
Hetero/nanojunction  
Quantum efficiency  
Parameter

## ABSTRACT

$\text{Ag}_2\text{CO}_3$  is a known photocatalyst active in the visible region of solar spectrum. In the present study, a series of novel hybrid  $\text{Ag}_2\text{CO}_3/\text{SiC}$  nanostructures have been successfully synthesised through a simple precipitation route. The photocatalytic performance was evaluated by the degradation of MB under natural solar irradiation. It was observed that heterojunction with SiC improves its photoactivity by inducing a charge transfer between SiC and  $\text{Ag}_2\text{CO}_3$  mimicking the Z-scheme in photosynthesis, proved by scavenger studies. The photocatalysts were characterized by XRD, SEM with EDX, TEM, TGA-DTG and UV-Vis/NIR. The best photocatalytic results and formal quantum efficiency (FQE) under natural sunlight were obtained with SCSC-12 nano-composite. The percentage photo-discolouration of MB over SCSC-12 was 98% against 90% with conventional  $\text{TiO}_2$ . Factors viz., photocatalyst dosage, solution pH, solar intensity, substrate and its initial concentration and speed of agitation were found to influence photo-treatment. Corresponding optimum parametric values have been found and reported in terms of FQE. As a case study, performance of the photocatalyst was investigated on a real industrial effluent and rate expression developed in terms of TOC and  $[\text{TOC}]_0$ . The present work, which includes a parametric study, has been carried out in direct solar light and is expected to be useful in real-time solar photocatalytic design of reactors and other solar applications for environmental remediation.

## 1. Introduction

Effluent from dye industries is usually coloured, toxic, carcinogenic and non-biodegradable. Conventional methods of effluent treatment possess major drawbacks such as sludge formation, secondary pollution and high electricity consumption. Energy required for the treatment generally comes by burning fossil fuels that are fast depleting and cause more pollution. Hence the use of alternative energy sources for the practice of effluent treatment is attracting a lot of attention. Solar energy, despite being abundantly and freely available, has found limited technical applications. Photocatalysis is a green technology that can treat liquid effluent with the help of sunlight. Excellent reviews on the same are available in literature [1,2].

$\text{TiO}_2$  has been a promising photocatalyst (bandgap  $\sim 3.2$  V) due to its many advantages but a major limitation of being able to utilise only the UV part of the solar spectrum, which amounts to  $\sim 4\%$  of the total spectrum. Efforts in the recent past have been made to extend the workability of photocatalysts to visible region that constitutes  $\sim 47\%$ . Such photocatalysts, in turn, have a limitation of narrow bandgap, leading to poor quantum efficiency and hence, low photocatalytic activity. Heterogeneous coupling of photocatalysts via Z-scheme

modulates the interfacial charge dynamics in such a way that the spatially separated electrons ( $e^-$ ) and holes ( $h^+$ ) are at a higher reduction and oxidation potential, while allowing the couples to be individually activated by visible light. For the application of degradation of organic dyes, the coupling members are so chosen that the reduction potential of the combination is higher than that of  $\text{O}_2/\text{O}_2^{\cdot-}$  ( $= -0.046$  V) and the oxidation potential is higher than that of  $\cdot\text{OH}$ ,  $\text{H}^+/\text{H}_2\text{O}$  ( $= 2.38$  V) [3–5]. Fig. S1 is a schematic of Z-scheme charge modulation process.

Silver carbonate has been proved to be working in the visible light region. It has found its application in wastewater degradation and disinfection [6,7]. Silver nanoparticles also have the property of exhibiting surface plasmon resonance wherein localised oscillations enhance the electromagnetic field that renders the reaction mass capable of generating more radicals. However, pristine  $\text{Ag}_2\text{CO}_3$  undergoes photo-corrosion and thus gets deactivated soon. Hence, coupling it with a suitable photocatalyst is essential. Silicon carbide has also been investigated for its photocatalytic activities for applications like water splitting,  $\text{CO}_2$  conversion and organic degradation and has been concluded to be acting satisfactorily [8,9]. Apart from favourable electronic properties, it also shows excellent thermal, mechanical and chemical stability. And most importantly, its conduction band potential

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