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Photocatalytic treatment of dye wastewater and parametric study using a novel Z-scheme Ag_2CO_3/SiC photocatalyst under natural sunlight

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ABSTRACT

Ag_2CO_3 is a known photocatalyst active in the visible region of solar spectrum. In the present study, a series of novel hybrid Ag_2CO_3/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 Ag_2CO_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 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 $[TOC]_0$. 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].

TiO_2 has been a promising photocatalyst (bandgap ~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 ~4% of the total spectrum. Efforts in the recent past have been made to extend the workability of photocatalysts to visible region that constitutes ~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 $O_2/O_2^{*-}\cdot$ ($= -0.046$ V) and the oxidation potential is higher than that of $\cdot OH$, H^+/H_2O ($= 2.38$ 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 Ag_2CO_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, 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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is > O_2/O_2^{*-} (−0.046 V) hence it is one of the most suitable Z-scheme couples to Ag_2CO_3.

This work is based on a hypothesis of formation of Z-scheme mechanism between Ag_2CO_3 and SiC, which is expected to increase the photocatalytic activity. The composites have been prepared via a facile ion-exchange precipitation technique [10] and characterised with XRD, FESEM, TEM, TGA-DTG and UV–UV-Vis/NIR spectroscopy. The photocatalytic activity has been investigated in natural sunlight on Methylene Blue (MB) as a probe dye. MB ($C_{16}H_{18}ClN_3S$) is a basic cationic fast dye used extensively in textile industries.

Study of operational parameters and its influence is required to advance the research to a commercial level. Some of these parameters are type of photocatalyst, intensity of light, pollutant and its concentration, photocatalyst loading, pH, dopant, relative humidity, post thermal treatment, temperature, etc. [11]. Optimising the parameters increases the effectiveness and efficiency of the process. In this work, relevant parameters have been optimised to yield the highest possible thermodynamic efficiency.

The last section includes the treatment of a real dye-industry wastewater from a local factory. Since it is a mixture of colours and components, its organic content has been measured by determining the Total Organic Carbon content. A rate expression has also been proposed.

As compared to other treatment methods like ozonation, reverse osmosis, electrodialysis, freezing, etc. and other AOPs, the economic benefits gained from this research include:

1. Utilisation of naturally, freely and abundantly available solar light as a source of energy.
2. Extended utilisation of solar spectrum from just UV to visible light region. This enhances the efficiency and effectiveness of the process.
3. No generation of secondary pollutant hence no further treatment method is required.
4. Employment of Ag which also exhibits disinfection properties, hence, serving the dual purpose of organic treatment as well as disinfection, without necessitating any further treatment.

2. Experimental

2.1. Catalyst preparation

All chemicals were of analytical grade and used without further treatment. Ag_2CO_3 was prepared via a facile ion-exchange process. The composites were prepared via a simple *in-situ* precipitation reaction on SiC surface. The preparation method is depicted in Fig. 1.

2.1.1. Preparation of SiC and TiO_2

400 mesh silicon carbide (Mol. wt. 40.10) was used as-purchased. Similarly, anatase TiO_2 (Mol. wt. 79.87) was also used as-purchased and only for a comparative study.

2.1.2. Preparation of Ag_2CO_3

A measured quantity of $AgNO_3$ was dissolved in distilled water to prepare a 0.2 M solution. To this, stoichiometric amount of 0.1 M $NaHCO_3$ solution was added drop by drop, under ice-water bath conditions and vigorous stirring. The mixture was continuously stirred for another 24 h. The yellow-green precipitates formed were separated by filtration using cellulose nitrate membrane filters of 0.45 μm pore size. These precipitates were then washed several times with deionised water and absolute ethanol to dissolve any impurities. Finally, the Ag_2CO_3 obtained was dried in vacuum oven at 70 °C for 8 h. About 2 g of Ag_2CO_3 was prepared per batch.

2.1.3. Preparation of Ag_2CO_3/SiC composites

To prepare the composites, firstly, measured quantity of SiC was dispersed in deionised water and this mixture was ultrasonicated for 2 h. Stoichiometric amount of 0.2 M $AgNO_3$ was added slowly to this mixture under magnetic stirring and the mixture was further stirred for 1 h. Measured quantity of 0.1 M $NaHCO_3$ solution was added drop by drop under vigorous stirring. The total reaction mixture was stirred for the next 24 h at room temperature. The final product then was filtered with cellulose nitrate membrane of 0.45 μm pore size, thoroughly washed with deionised water and absolute ethanol and finally dried at 70 °C. Thus, five composites were prepared with SiC weight ratios 6%, 9%, 12%, 15% and 18% and these composites were denoted as SCSC-6, SCSC-9, SCSC-12, SCSC-15 and SCSC-18, respectively. About 2 g of SCSC composite was prepared per batch.

2.2. Characterisation

Phase analysis was carried out by X-ray diffraction using X'pert-MPD system (Philips) Cu-Kα radiation (λ = 1.5406 Å). The crystal phases were identified using JCPDS (Joint Committee on Powder Diffraction Standards) data bank. Lattice parameters were calculated from the reflections appearing in the 2θ = 2-99° range using a software. The crystal size of the catalysts (d_{XRD}) was calculated from XRD spectral data, using Scherrer equation

$$d_{XRD} = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

where, d_{XRD} is the crystal size, λ is the wavelength of Cu-Kα radiation, β is the effective line width of X-ray reflection and θ is Bragg diffraction angle. The morphology and elemental composition of the catalyst samples were obtained by scanning electron microscope (SEM) and energy dispersive of X-Ray (EDX) using a LEO 44 i (JEOL) instrument. Detailed structure and morphology was analysed by JEOL, JEM 2100 transmission electron microscope (TEM). Particle size distribution was carried by Malvern Mastersizer 2000 instrument. The thermal stability/behaviour of the samples was investigated by TGA-DTG using SF 752 (Metpler Toledo) with a heating rate of 5 °C/min in air with a flow of 50 ml/min, and ± 0.5% accuracy. The UV–vis/NIR spectra was analysed with Varian Cary 500, Shimadzu UV 3600.

2.3. Evaluation of degradation activity

The experimental setup for investigation of photo-performance of the photocatalysts is shown in Fig. S2. An indigenous reactor was configured using a closed quartz conical flask of capacity 1 l and containing exactly 800 ml of solution. Aqueous dye solution and definite amount of photocatalyst in suspension were provided a continuous magnetic stirring of 500 rpm. The pH of the solution was measured by Equip-tronics-EQ-614A pHmeter and adjusted by NaOH and HCl. All solutions were prepared in double-distilled water. Appropriate quantity of sample was withdrawn at regular intervals of time and centrifuged to remove suspended solid photocatalyst particles. All the experiments were performed at Ahmedabad, Gujarat, India, (Longitude: 72.5714° E, Latitude: 23.0225° N, 53 m above sea level). Decomposition of organic dye was carried out with 0.8 g of the as-prepared photocatalyst suspended in 78 μM of MB solution. Solar insolation was measured with a Vantage Pro2 Plus solar radiation sensor and recorded with a phase automation data logger.

2.3.1. Determination of point of zero charge (pH_{PZC})

The value of zero point of charge for SCSC-12 composite photocatalyst was determined using the procedure described in literature [12]. Thirteen different flasks were taken and filled with 50 ml of 0.01 M NaCl. pH of each solution was adjusted in the range 1–13 with the help of HCl or NaOH. To this was added 0.5 mg of synthesised photocatalyst and stirred well. The flasks were then kept in a shaker for 1 h and allowed to stand for 24 h for them to reach equilibrium. The final pH was measured and plotted against initial pH.