Photocatalytic application of Cu_2O/PANI nanocomposites

K. Gopalakrishnan*, C. Ramesh, S.Sumathi

Department of Physics, SSM College of Engineering, Komarapalayam - 638 183,

Tamilnadu, India.

Dr. K. Gopalakrishnan

Department of Physics, SSM College of Engineering

Komarapalayam - 638 183

*E-mail: kgyaythish@yahoo.co.in

Abstract

The photocatalytic activities of Polyaniline encapsulated green copper oxide (Cu_2O/PANI) nanocomposites synthesized at room temperature through in-situ chemical polymerization method in acidic medium is investigated. The Cu_2O/PANI nanocomposites at the wt.% 25:75 of green Cu_2O NPs and PANI, respectively was estimated by the photocatalyticdecolorization of methylene blue dye solutions. The estimated weight of photo catalyst (0.04 gm) is introduced into the dye solution. Nanophoto-catalysts assisted dye solutions are exposed to solar irradiation for different time periods (0 to 150 min.). The spectrum was recorded for every 30 min. interval using UV visible absorption spectrophotometer at constant dye concentration (100 ppm) and dose level (0.04 g), for various irradiation time periods namely 0 to 150 min. From the recorded spectra, percentage of dye removal is calculated using the standard formula. The Cu_2O/PANI nanocomposites exhibit significantly enhanced photocatalytic activities for the degradation of dye.

Keywords: Nanocomposites, photocatalytic, methylene blue, UV spectrophotometer

1. Introduction

Over the past few decades, preparation of inorganic/organic nanocomposites materials has attracted many researchers, owing to their appreciable physical and chemical properties that have not occurred in the bulk state of the same (Alivisatos 1996). The physical properties ranged from conductivity to photocatalytic let the materials (nanoregime) to wide area of applications oriented with photocatalytic hydrogen production, industrial, medical, optoelectronic and so on (Sarkar et al 2008). Nanocomposites including oxides, chalcogenidesetc exhibit good absorption in the visible region due to their suitable band gap which can be done by altering the size of the nanomaterials (Zhang 2010). The size dependent optical properties of the nanocomposites allow them as photocatalytic agent. Hence, they can be used as photocatalysts in various processes (Miki Inada et al 2010, Hoffmann et al 1995), like degradation of industrial effluents, antimicrobial activity, splitting of water, H_2 production and so on.

Environmental problems associated with hazardous wastes and toxic water pollutants have gained much attention among the recent day researchers. Among them, organic dyes are one of the major groups of pollutants in wastewaters that are generated from textile and other industrial processes. Various physical, chemical, and biological techniques have been developed for alleviating the negative environmental impact of human activities at large. Traditional treatments such as coagulation, flocculation, absorption, and membrane technologies merely make the wastes concentrated or otherwise transported into other forms. Destructive techniques such as chemical and other advanced oxidation processes could overcome the above problem, but they suffered from high costs and incomplete degradation. Heterogeneous photocatalysis has been considered as a cost-effective alternative for waste water remediation (Hoffmann et al 1995).

As an important part of photocatalytic technology, heterogeneous photocatalysts with high activity have attracted considerable interest. From the viewpoint of energy efficiency and conservation, the development of efficient visible-light induced photocatalysts for the degradation of organic pollutants is an inevitable trend. The internal electric fields in layered materials are considered to favor charge separation, which can subsequently induce redox reactions on the semiconductor surface and contribute to the enhancement of the photocatalytic activity.

1.2. Classification of dyes

Dyes are mainly classified based on their structure, source, color and method of application in color index (C.I.), which has been continuously edited since 1924. Depending on the chromophores, dyes can be classified in various classes. These include the acridine dyes, azo dyes, arylmethane dyes, anthroqinone dyes, nitro dyes, xanthenes dyes and quinine–amine dyes etc. The investigation of radiation induced decomposition of dyes and their derivatives due to their environmental hazard is a rather popular subject and many papers have been published in this field.

1.2.1. Methylene Blue

Simple model of a series of thiazin dyes largely used in the industry. Methylene blue is a heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}C_lN_3S$. It has many uses in a range of different fields. At room temperature it appears as a solid and is odorless and a dark green powder, which yields a blue solution when dissolved in water. The absorption maxima wavelength of 663 nm of MB (λ_{max}) was used for the analysis during degradation and decolorization respectively. The natural pH of the aqueous dye solution is 6.5. This dye is stable, incompatible with bases, reducing agents and strong oxidizing agents. It is harmful if swallowed, inhaled and in contact with skin as well as causes severe eye irritation and investigated as a mutagen.

2. Experimental method

Photo catalysis is a process by which a semiconductor materials absorb light of energy more than or equal to its band-gap, thereby generating electrons and holes, which can further generate free-radicals in the system to oxidize the substrate. The resulting free-radicals are very efficient oxidizers of organic matter. The superiority of photocatalytic technique in wastewater treatment is due to its advantages over the traditional techniques, such as rapid oxidation, no formation of polycyclic products, oxidation of pollutants in the ppb range.

They drift into the nanocomposites/water interface to participate in redox reactions with surrounding species, results the degradation of pollutants in the medium. Obviously, the hydrophilic surface is mandatory for the photocatalytic degradation of aqueous pollutants. Nano-scale semiconductor particles possess higher surface area-to-volume ratio than their bulk counterparts, and thus allow greater photon absorption on the photocatalyst surface (Hoffmann et al 1995).

2.1. Catalyst test

The photocatalytic activities of the Cu_2O/PANI nanocomposites at the wt.% 25:75 of green Cu_2O NPs and PANI, respectively was estimated by the photocatalyticdecolorization of dye solutions. For that, the methylene blue dye is purchased from Merck and it is prepared as solution by dissolving it in an aqueous medium for degradation study. The estimated weight of photo catalyst (0.04 gm) is introduced into the dye solution. Nanophoto-catalysts assisted dye solutions are exposed to solar irradiation for different time periods (0 to 150 min.). The spectrum was recorded for every 30 min. interval using UV visible absorption spectrophotometer at constant dye concentration (100 ppm) and dose level (0.04 g), for various irradiation time periods namely 0 to 150 min. From the recorded spectra, percentage of dye removal is calculated using the standard formula (Equation 2.1).

$$C = \frac{A_0 - A}{A_0} \times 100\% \quad (2.1)$$

where'A_0' and 'A' are absorbance values of the dye before and after photo-irradiation.

3.Result and discussions

In order to study the effect of dye concentration on photocatalytic properties of green Cu_2O NPs embedded PANI nanocomposites, the dose and dye concentrations (0.04 gm& 100 ppm) are fixed by trial and error method for the photocatalysts and the spectra were recorded for every 30 min. interval (0 to 150 min.).

The photocatalytic activities of Cu_2O/PANI nanocomposites prepared at wt.% 25:75 is investigated by choosing the photodegradation of MB dye under solar irradiation. The target molecule MB is relatively stable in aqueous solutions upon solar irradiation. Furthermore, a photodegradation reaction cannot be observed in the presence of Cu_2O/PANI (wt.% 25:75) nanocomposites when the reaction mixture is maintained in darkness. Therefore, the light illumination is necessary for efficient degradation, and the degradation of MB is caused by the photocatalytic reactions on Cu_2O/PANI (wt.% 25:75) nanocomposites. The characteristic absorption of MB at λ=663 nm is used to monitor the photocatalytic degradation process.

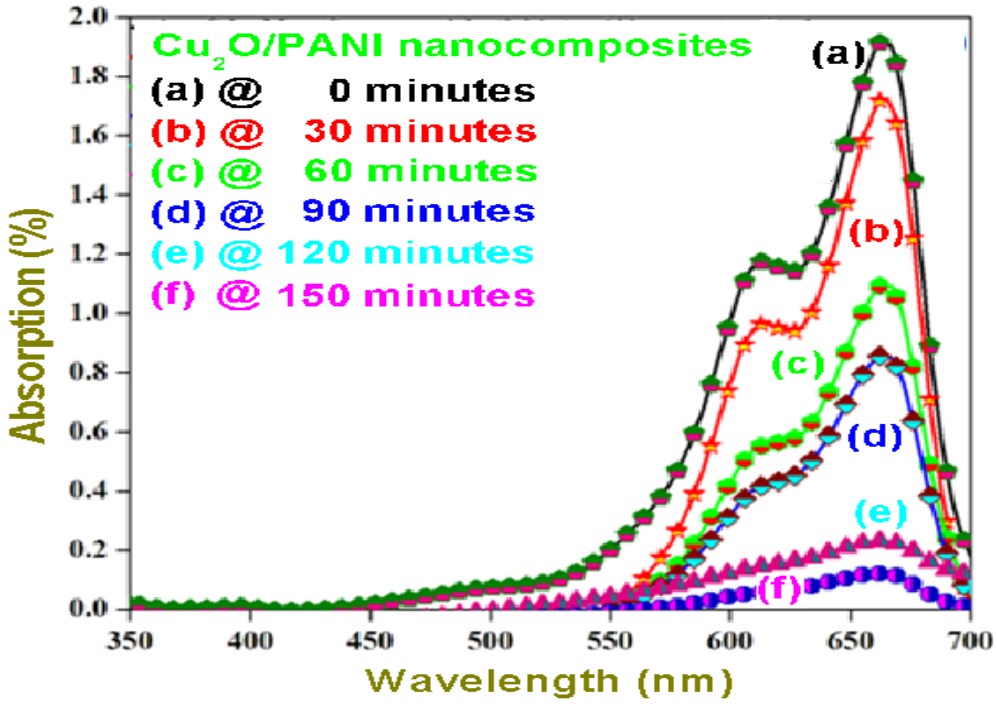

Figure 3.1 UV-visible absorption spectra of methylene blue degradation for Cu_2O/PANI nanocomposites

Figure 3.1 shows the UV-vis absorption spectra of the aqueous solution of MB with Cu_2O/PANI (wt.% 25:75) nanocomposites as photocatalyst for various durations. The absorption decreases rapidly with the extension of the exposure time, and completely disappears only after about 150 min. The intense blue color of the starting MB solution gradually fades during the process of photodegradation as the exposure time is extended. Thus, Cu_2O/PANI (wt.% 25:75) nanocomposites catalyst shows the excellent photocatalytic activity.

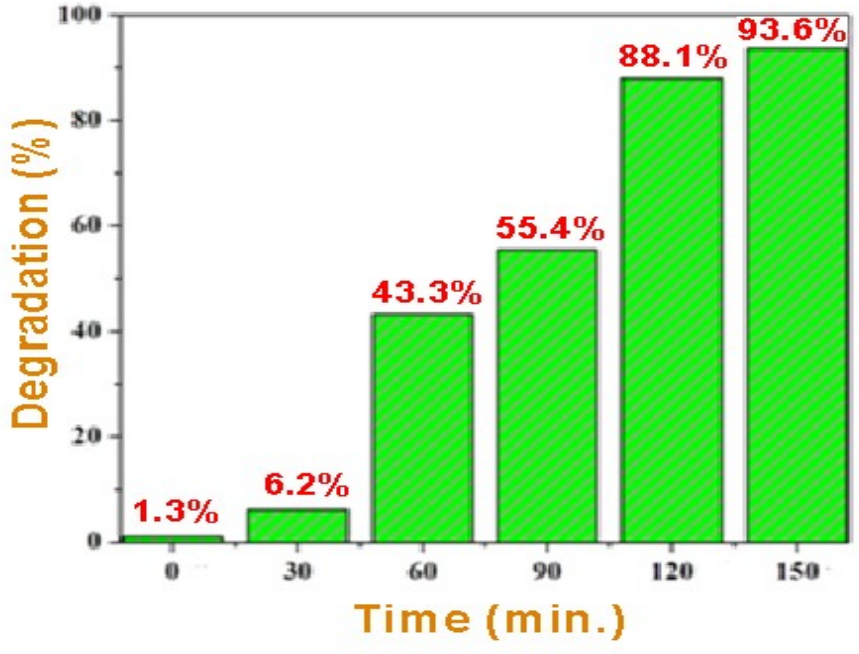

Figure 3.2 Dye degradations Vs irradiation time for Cu_2O/PANInanocomposites

The influence of irradiation period on the photocatalytic activated methylene blue dye degradation was carried out and the results are shown in the Figure 3.2. From study, it is identified that 0.04 gm Cu_2O/PANI nanocompositesphotocatalyst loaded 100 ppm dye concentration exhibit 93.61 % degradation for 150 min of solar irradiation, since the particle size of the Cu_2O and PANI is comparatively less, large number of surface charges involve in the photo absorption and emission processes. In addition, the excess number of Cu vacancy sites in the material enhances photocatalytic efficiency of the process.

Based on the results of structure characterizations and photocatalytic tests of the sample, a possible mechanism is proposed (Figure 3.3).

The significant enhancement of photocatalytic performance is attributed to synergistic effect between PANI and green Cu_2O NPs. The band gap of PANI is 1.57 eV and that of green Cu_2O NPs has 2.78 eV, which indicates that both PANI and green Cu_2O NPs can be

excited by visible light. The Cu_2O in the photocatalyst absorbs photons and excites electron and hole pairs when the system is irradiated with visible light.

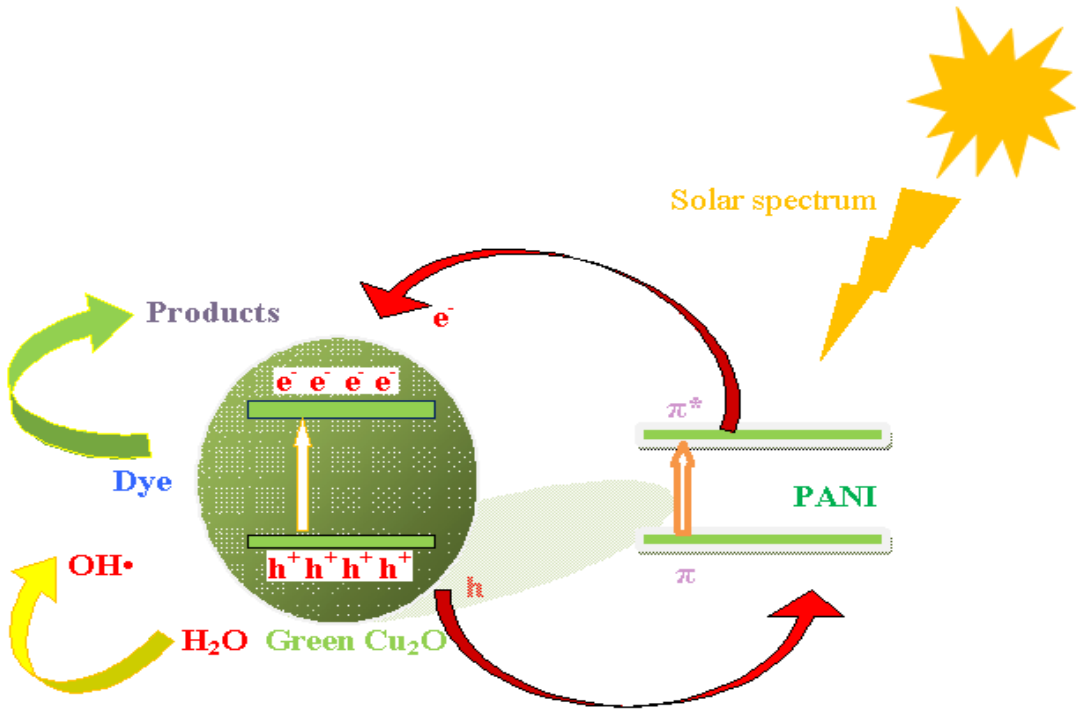

Figure 3.3 Schematic of the separation and transfer of photo-generated charge carriers in the Cu_2O/PANI system under solar light irradiation

The PANI also absorbs photons to induce π–π* transition, transporting the excited electrons to the π*-orbital. Thus the excited state electrons produced by PANI are injected into the conduction band of the green Cu_2O NPs. Subsequently, simultaneous holes on the valance band of green Cu_2O NPs migrate to the π-orbital of PANI because of the directed electric fields of the two materials. The photo-excited electrons are effectively collected by green Cu_2O NPs, and the holes by PANI. The recombination process of the electron–hole pairs is hindered, and charge separations as well as stabilization are achieved. Therefore, the efficient electron–hole separation leads to significant enhancement of photocatalytic dye degradation in the Cu_2O/PANI nanocomposites. With above understanding, the role played by PANI can be illustrated by injecting electrons into green Cu_2O NPs conduction band under visible light illumination and

triggering the formation of very reactive radical super-oxide radial ion O_2^- and hydroxyl radical $HO^{\cdot}$, which are responsible for the degradation of the organic compound. The possible photocatalytic reactions are proposed as hereunder:

$Cu_2O/PANI + hv \rightarrow Cu\text{-}PANI^+ + e^-$

$e^- + O_2 \rightarrow O_2^-$

$O_2^- + 2e^- + 2H^+ \rightarrow OH + OH^-$

$h^+ + (H_2O \leftrightarrow H^+ + OH^-) \rightarrow H^+ + OH\bullet$

Dye + $OH\bullet \rightarrow$ oxidation products

4. Conclusions

In order to investigate the application of obtained Cu_2O/PANI nanocomposites, the solar radiation assisted phocatalytic degradation of methylene blue was carried out and the degradation percentage was calculated. The Cu_2O/PANI nanocomposites exhibit significantly enhanced photocatalytic activities for the degradation of dye. Therefore, it is suggested that Cu_2O/PANI (25:75) nanocomposites system is the best candidate for good degradation of MB dye. A possible photocatalytic mechanism is proposed based on the experimental results.

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