Low power LED assisted effective photodegradation of cationic and anionic dyes by zinc phthalocyanine based 2D polyamide sensitized CuO photocatalyst

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Abstract

The present investigation details the synthesis and photocatalytic performance of an organic-inorganic hybrid system involving phthalocyanine-based 2D polyamide sensitized CuO photocatalyst in the presence of low-power LED visible light. Zinc phthalocyanine-based 2D polyamide (2D-ZnPcPA), CuO nanomaterial and their nanocomposites (2D-ZnPcPA@CuO) were successfully synthesized and characterized by Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) to understand the structure, size, morphology and optical properties. To examine the photodegradation capability of newly synthesized photocatalysts in the presence of the low-power white LED (16 W) as a source of visible light, cationic methylene blue (MB) and anionic congo red (CR) dyes were employed as modular pollutants.

The impact of different parameters on photocatalytic activity such as photocatalyst dosage, contact time, pH of dye solution and photocatalyst re-usage, is examined. The results indicate that photosensitizing CuO with 2D-ZnPcPA improved photocatalytic performance for the photodegradation of MB and CR dyes substantially. The removal effectiveness of MB and CR under optimised conditions was determined to be greater than 96 and 93% in 90 minutes respectively.

Keywords: Photodegradation, LED light source, Phthalocyanine, CuO, Cationic and anionic dyes.

Introduction

Organic dyes that are very hazardous and carcinogenic, are released into water bodies by the domestic and textile industries, endangering both human health and the environment as well as aquatic life. Hence, precautionary measures should be taken to remove pollutants from waste water and industrial effluent before discharging into water bodies to safeguard the environment and aquatic life.[8] There are numerous traditional techniques available for removing these hazardous contaminants from wastewater.[13] Techniques like membrane filtration, coagulation, chemical precipitation, sedimentation, flocculation, ion-exchange, flotation and adsorption are effective but not conclusive because they typically require expensive equipment and slower operation.

In addition, these methods transfer pollutants from one phase to another, thereby resulting in the production of secondary pollutants that need to be removed further. This in turn will increase the overall cost of the process.

The photocatalyst-mediated degradation of organic pollutants is a suitable choice of operation to remove harmful dye pollution in water because it generates highly reactive hydroxyl free radicals that can efficiently breakdown the organic pollutants including dye molecules.[3]

In addition, photocatalytic degradation of dyes is a simple, effective and environmentally friendly mode, since sunlight is renewable and this process results in minimal or no production of secondary pollutants.[12]

Transition metal oxides interact with UV or visible light and are found to be photoactive.[3] Copper oxide (CuO) is one of the highly stable visible-light active semiconductors with a narrow band gap.[4] It has been well documented that the optical and electrical properties of phthalocyanines can be tuned by peripheral substitution.[5,6] Highly stable, extensively conjugated, electroactive and photoactive metal phthalocyanines (MPc's) have been explored as active materials in sensing applications.[14-16] In addition, substituted metal phthalocyanines have demonstrated their applicability in energy conversion and storage applications.[1,2,9,10] It has been well documented that surface functionalization and composite formation of transition metal oxides with conjugated systems result in more efficient organic-inorganic photoactive hybrid systems.[12]

In this context, in the present work, zinc phthalocyanine-based 2D polyamide (2D-ZnPcPA) was synthesized and their composite with CuO was prepared to examine the photocatalytic effectiveness towards cationic methylene blue (MB) and anionic congo red (CR) dye degradation in the presence of eco-friendly low power white LED (16 W) as the source of visible light.

Material and Methods

Materials: The reagents utilized in this study were obtained from well-known commercial sources. Ammonium orthomolybdate, 4- nitrophthalophthalimide, $Na_2S.9H_2O$, zinc acetate, copper acetate and 1,3,5-benzenetricarbonyl trichloride were obtained from Sigma Aldrich. Additional reagents were bought from Merck (India). All solutions were prepared by using double distilled water.

Synthesis of Copper oxide nano particles (CuO): CuO nanoparticles were synthesized by employing a documented procedure in the literature with little modification. [11] 5 mmol of copper (II) acetate monohydrate [$Cu(CH_3COO)_2 \cdot H_2O$] was stirred into a 200 ml water:ethylene glycol (1:1 ratio) mixture, followed by the addition of 50 mmol of urea. The reaction mixture was stirred at room temperature for 10 minutes followed by microwave irradiation at 462 W in a domestic microwave oven for 10 minutes. The reaction mixture was cooled to room temperature and the precipitate was filtered and washed with water followed by ethanol and dried in a vacuum oven at 100 °C.

Synthesis of tetra amino zinc phthalocyanine (TAZnPc): TAZnPc was prepared by employing a process reported in our earlier study.[10,12] In brief, tetra nitro zinc phthalocyanine was first synthesized by reacting 4-nitro phthalimide with urea, zinc acetate, ammonium chloride and a catalytic amount of ammonium molybdate in nitrobenzene solvent at 180 °C for 8 h. The product obtained was purified and subjected to reduction by employing $Na_2S.9H_2O$ as a reducing agent in DMF solvent to obtain TAZnPc.

Synthesis of zinc phthalocyanine based 2D polyamide (2D-ZnPcPA): 1 m mole of TAZnPc was dissolved in 50 mL of N-methyl-2-pyrrolidone in a 250 mL round-bottomed flask followed by the addition of 1.3 m mole of 1,3,5-benzenetricarbonyl trichloride. The reaction mixture was stirred at room temperature for 24 hours. The resulting reaction mixture was treated with double distilled water and the product obtained was filtrated, washed with water, ethanol and acetone and dried in a vacuum oven at 100 °C to get 2D-ZnPcPA (72 % yield). A schematic representation for the synthesis of 2D-ZnPcPA is presented in figure 1.

Synthesis of zinc phthalocyanine based 2D polyamide sensitized CuO photo catalyst (2D-ZnPcPA@CuO): 20 weight percent of 2D-ZnPcPA was treated with CuO (100 mg) in 5 mL ethanol under sonication for 1 hour. The product obtained was centrifuged and dried at 100 °C to get 2D-ZnPcPA@CuO.

Photocatalysis experiments: The photocatalytic activity of CuO nanoparticles and 2D-ZnPcPA@CuO photocatalyst has been examined by exploiting MB (cationic dye) and CR (anionic) as model waste water pollutants in the presence of visible light source (16W LED) in a photo reactor equipped with a magnetic stirrer. By dissolving 10 mg of MB and CR dye in double-distilled water, 10 ppm of dye solutions was prepared. In this study, before the visible light irradiation, an appropriate quantity of photocatalyst was dispersed in 100 ml of 10 ppm MB and CR solution and the mixture was stirred under dark for 30 minutes to establish adsorption-desorption equilibrium.

During the photocatalytic investigation, 5 ml of the sample was withdrawn at specific intervals of time and analyzed using a UV-Visible spectrophotometer. The percentage of dye removal was calculated using the following equation:

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 and C_t are the concentrations of dye at 0^{th} time and at time t respectively.

Results and Discussion

Characterization of CuO nanoparticles, 2D-ZnPcPA and 2D-ZnPcPA@CuO: The FTIR spectra of CuO, TAZnPc, 2D-ZnPcPA and 2D-ZnPcPA@CuO are presented in figure 2(a). The peaks located between 500 to 600 cm^{-1} confirm the formation of CuO and the peak observed at 534 cm^{-1} is assigned to stretching vibrations of Cu-O.

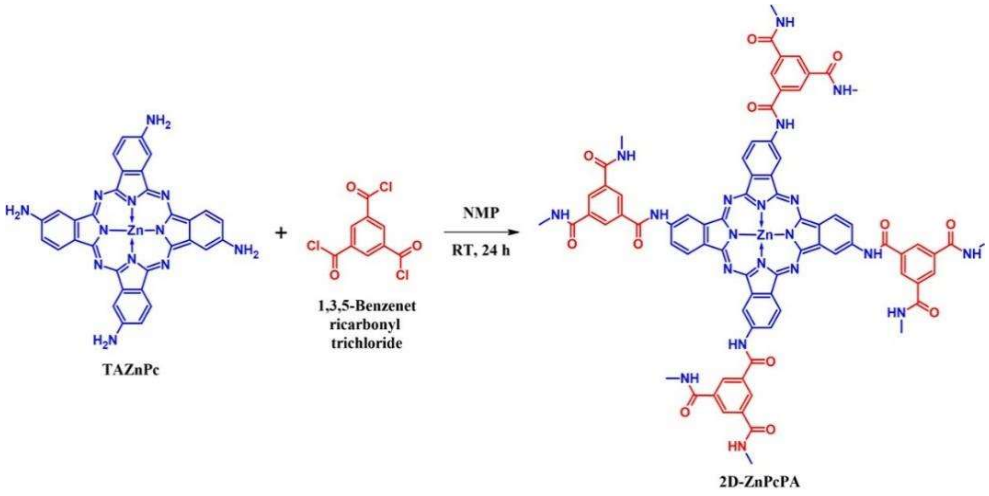

Figure 1: Schematic representation for the synthesis of Zinc phthalocyanine based 2D polyamide (2D-ZnPcPA)