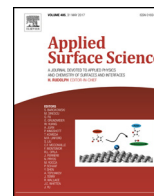




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Full Length Article

Ultrasound assisted catalytic degradation of textile dye under the presence of reduced Graphene Oxide enveloped Copper Phthalocyanine nanotube

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ABSTRACT

In this work, ultrasound assisted catalytic removal of Rhodamine B (RhB) dye has been carried out in the presence of reduced Graphene Oxide enveloped Copper Phthalocyanine nanotube (RGO-CuPc) for the first time. This RGO-CuPc nanocomposite has been synthesized by in situ chemical reduction of Graphene Oxide (GO) with CuPc tube. Then our as prepared composite and pristine CuPc tubes are well characterized by various spectroscopic techniques such as X-Ray Diffraction, UV-vis and microscopic techniques like FESEM, HRTEM etc. Electrochemical EIS measurement has also been carried out to investigate charge transfer mechanism. These results confirm the purity of the as prepared samples. Efficient sonocatalytic RhB dye removal upto ~92.22% is achieved by RGO-CuPc composite within 100 min as compared to pristine CuPc tube (~70%). A plausible reaction pathway towards dye removal is discussed in detail. Also degradation performance in the presence of enhancer and scavenger has been investigated.

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1. Introduction

With rapidly growing industrialization, water contamination by organic or synthetic pollutants has been a major environmental problem worldwide from last few decades. In case of textile industries, the dyeing process causes in the production of wastewater with intense coloration [1,2]. In the past few years, different kinds of advanced oxidation processes (AOPs) such as ozonation, photocatalysis, and Fenton process have been widely developed for the removal of organic dyes [3], but they cannot mineralize contaminants completely due to some technical limitations. Among other AOPs, sonocatalytic degradation is gaining interest towards the mineralization of dyes in aqueous medium. So, sonocatalysis has attracted more attention as a novel, fast and efficient method of degrading water contaminants. During ultrasonication (US), the formation, growth and collapse of microbubble in an extremely small interval of time occur due to the acoustic cavi-

tion effect from ultrasonic irradiation and huge energy is released. The effects of bubble collapse are the creation of hotspots, the release of free radicals, surface cleaning. The release of free radicals OH^{*} by the dissociation of H₂O molecules during pyrolysis is an important element for degradation mechanism [4,5]. There are different ways to attain better degradation is that the combination of ultrasonic cavitation with other advanced oxidation schemes such as ultrasonic/ozone, ultrasonic/H₂O₂, ultrasonic/Fenton process, ultrasonic/UV irradiation and ultrasonic/semiconductor catalysis [6–9]. When semiconductor catalyst materials are coupled with ultrasound cavitations, it can produce synergistic effect between the sonochemical and catalytic reactions, which remarkably speed up the degradation of organic pollutants by supplying the additional cavitation effect. The present work has been committed to study the synergistic effect of ultrasonication and semiconducting nanostructures for the degradation of toxic, hazardous dyes.

There are many reports on catalysis, gas sensing, and photoluminescence study using inorganic material [10–14]. But catalytic removal using organic semiconductor material is new area of research. Among these, organic metal phthalocyanine has been chosen as catalyst in our study. This is an aromatic macrocyclic compound having lots of π conjugated bonds and exhibit superior charge transfer capabilities. Now these have different

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potential applications in the field of non-volatile memory devices, field effect transistors and field emission display etc. [15–18]. In literature, there are some reports that explained that the introduction of carbon based nanostructures such as carbon nanotube (CNT), graphene, functionalized graphene within the phthalocyanine matrix can improve the photocatalytic activity [19–23]. Carbon/Graphene-based materials exhibit good electrical conductivity, high electron mobility and large theoretical specific surface areas, which are capable of accepting, transporting and storing electrons and thus slowing down the recombination of the electrons and holes. Due to the mutual electronic interaction between them helps to transfer photoinduced electron from porphyrins ring to CNT/Graphene. Graphene or RGO can be used as effective co-catalysts in sonocatalytic processes due to the electron-acceptor/transport and adsorption properties. Wang et al. reported the synthesis and visible light assisted photocatalytic activity of tetraamino zinc phthalocyanine covalently bound to benzoic acid-functionalized graphene and 82% degradation of RhB was achieved in 2.5 h [24]. Mukherjee et al. prepared graphene wrapped CuPc nanotube via in situ reduction method and they achieved maximum 96.2% RhB degradation within 3.5 h [25]. Apart from photocatalysis, for achieving more degradation within short duration, sonocatalysis plays important role towards dye degradation. In literature, there are several reports on sonocatalytic activity of different inorganic metal oxide (ZnO, TiO₂, Fe₂O₃ etc.) nanostructures, doped oxide nanoparticles and composites with RGO [26] for removal of different organic contaminants [27–30].

In our study, RGO wrapped CuPc tube has been prepared by chemical method and investigate their catalytic activity towards dye degradation under the presence of ultrasound. To the best of authors' knowledge and based on the literature review, there are no reports related to sonocatalytic degradation of RhB by using RGO enveloped CuPc nanotubes. In this work, authors report the enhanced sonocatalytic activity towards dye degradation by RGO-CuPc composite for the first time.

2. Experimental

CuPc nanotube has been synthesized by two step process. First, CuPc nanowire is prepared from CuPc powder by simple solution process. Then, CuPc tube is formed after hydrothermal treatment of CuPc nanowires at 180 °C as reported earlier [31].

Graphene Oxide (GO) has been synthesized by modified Hummer's method [32]. Briefly, a little amount of HOPG and NaNO₃ were mixed vigorously in concentrated H₂SO₄. Then KMnO₄ was added in this solution, keeping the beaker in ice bath. After the solution turned thicker, ice bath was removed and water has been added dropwise until the temperature reached at 90 °C. In the last step of preparing GO, 30 wt% H₂O₂ has been added and the solution turned yellow in color. The precipitate was then repeatedly washed by centrifugation and the supernatant was collected. After dried in vacuum oven for 12 h at 70 °C, the brown powder of GO was obtained. Now a small amount of GO and CuPc nanotube were mixed thoroughly in DMF and raise the temperature upto 90 °C. Hydrazine hydrate and ammonia solution have been added in this solution and after 1 h the color of solution turned black. The solution was then filtered and washed repeatedly with water. Finally, RGO-CuPc nanocomposite has been collected after drying for 6 h at 70 °C.

To investigate the Phase purity and crystal structure of as prepared RGO enveloped CuPc nanotubes, X-ray diffraction technique was used. The diffractometer was D8 Advance ECO, Bruker, Germany with Cu K α ($\lambda = 0.154$ nm) radiation, 40 kV accelerating voltage and 25 mA emission current. Raman spectroscopy of the as synthesized pristine CuPc as well as the RGO-CuPc composite is carried out at room temperature in the wavenumber

range of 700–3500 cm⁻¹ using a confocal Raman spectrometer (alpha 300, Witec, Germany, laser source of $\lambda = 532$ nm). The spectrograph is equipped with a Peltier cooled back illuminated CCD camera. To know the optical absorption and to evaluate the bandgap of the synthesized RGO enveloped CuPc nanotube, UV–vis absorbance spectra were carried out by UV–vis-NIR spectrophotometer (Shimadzu-3600). To investigate the surface morphology and elemental composition, Field Emission Scanning Electron Microscopy (FESEM) was performed by Hitachi (S-4800). To know more insight about the microstructure, High resolution Transmission Electron Microscopy (HRTEM) (JEOL JEM 2100) was employed.

Sonocatalytic degradation was investigated for RhB dye under the presence of as prepared pristine CuPc nanotube and RGO-CuPc composite nanostructures. In this experiment, 60 ml of aqueous pink colored RhB solution was kept in water cooled quartz jacket and then 83.33 mg/L catalyst was added. Initial dye concentration was chosen as 10⁻⁵ M. Prior to ultrasonic irradiation, solution was stirred for 1 h to establish good adsorption desorption equilibrium. Then it was irradiated with 20 KHz frequency advanced probe sonicator [PKS-750F] with 13 mm titanium probe which provides maximum 750 W output power. 15% of maximum output amplitude was used during the experiment. At regular interval of 10 min, 5 ml solution was collected and centrifuged for 20 min and then remnant RhB concentration was detected by UV–vis spectrophotometer at maximum wavelength, $\lambda = 554$ nm.

The control experiment was carried out to exactly determine the effectiveness of the catalyst separately and to prove the proposed mechanism accurately; sonocatalysis has been carried out under N₂ atmosphere. Prior to application of ultrasound, N₂ gas was purged for 30 min and constant purging was continued till to the end of the experiment. An addition to that, catalytic experiment was also carried out with visible light and same remaining experimental conditions for comparative study between conventional photocatalysis and sonocatalysis. To evaluate the effect of pH on sonocatalytic degradation, experiments were done in different pH medium. To make pH ~1 and pH ~10, 2 M HCl and 2 M NaOH were used respectively.

Electrochemical Impedance Spectroscopy (EIS) was carried out for our two samples in Autolab Potentiostat/Galvanostat (M-204) under three electrodes set up. Our samples behave as working electrode, Ag/AgCl as reference and Platinum wire was considered as counter electrode. Working electrode was prepared by mixing sample: carbon black: PVDF in 8:1:1 ratio. Then certain amount of NMP was added to make it slurry and kept at stirring for 3 h. Initially, nickel foam substrate was ultrasonicated by diluted HCl for 5 min and then washed repeatedly by de-ionized water and ethanol. Then prepared mixture was pasted on nickel foam and dried at 60 °C in vacuum oven. Here, 0.1 M KOH was taken as electrolyte. The Nyquist plots were acquired by applying 10 mV ac voltage in the frequency range from 10 mHz to 10⁵ Hz.

3. Results & discussion

3.1. Structural & optical properties

Fig. 1(a) shows the X-Ray diffraction pattern of RGO-CuPc composite where two intense peaks at $2\theta = 7.1^\circ$ and 9.3° of pure CuPc tube are present which corresponds to ($\bar{1}01$) and (101) planes. All other remaining small peaks are well suited with JCPDS data card no: 39-1881. A broad hump around $2\theta = 25^\circ$ is present that confirms the incorporation of RGO sheets within the Pristine CuPc system.

For analyzing the different vibrational modes, powder samples of CuPc and composites are considered. Here, the full range of the Raman spectra has been (700–3200 cm⁻¹) shown. For CuPc, vibrational modes at 744, 830, 950, 1036, 1140, 1334, 1444 and

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