An efficient photocatalyst based on polyaniline decorated MWCNT/CeO₂ for degradation of Methylene Blue (MB) dye

Helena Moreira *

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This industrial waste contain organic dye was dropped without previous treatment which result a serious environmental pollution. Among many organic dye, Methylene Blue (MB) dye is an aromatic heterocyclic chemical compound and is harmful if swallowed or inhaled and also causes skin and eye irritation on contact. This study aims the degradation of this harmful dye by unique PANI-MWCNT/CeO₂ nanocomposite. The PANI decorated binary nanocomposite was synthesized by polymerization of aniline on the surface of MWCNT/CeO₂. The optical, structures, surface morphology and functional groups of the developed composites were studied using UV-V is diffuse reflectance, powdered X-Ray Diffraction (XRD), SEM and FT-IR spectroscopic techniques respectively. The synthesized nanocomposite shows effective degradation of MB. This is due to unique properties of PANI which is the delocalized π -conjugated structures is beneficial to rapid charge separation, thus the separation efficiency of photogenerated electron (e-)-

INTRODUCTION

Pollutant substances may be originated from different sources such as organic, inorganic or others. Among these, organic pollutants play great roles. Thus, hazardous organic waste that is widely spreading in water by industrial, military and domestic sources has become an emerging issue. Therefore, organic dyes are among the major groups of pollutants found in wastewater produced from different industries. This industrial waste contain organic dye was unloaded without previous treatment [1]. This dye is durable and stays in the environment for a long period without sufficient treatment. Methylene blue (MB) dye with molecular formula C16H18CIN3S is an aromatic heterocyclic chemical compound and is harmful if swallowed or inhaled and causes skin and eye irritation on contact [2]. Hence, the removal of organic pollutants in wastewater is an important measure in environmental protection. Several approaches have been employed for the treatment of waste water containing dyes, such as removal by adsorption [3], electrocoagulation [4] and photodecomposition [5].

Recently, photodecomposition of organic contaminants in the presence of photocatalyst (semiconductor particles) has stimulated much interest. Nanoparticles have emerged as sustainable alternatives to conventional bulk materials, as robust, high surface area heterogeneous photo-catalysts and catalyst supports [6]. The nano-sized particles have high surface to volume ratio which increase the exposed surface area of the active component of the catalyst [7]. It is also required for a contaminant molecule to be adsorbed on to the surface of photocatalyst for the redox reactions (oxidation and reduction) to occur for the complete degradation/mineralization of the contaminant [8].

Among many metals oxide, cerium dioxide (CeO_2) is an n-type semiconductor with a wide energy band gap of 3.2 eV, indicating that CeO_2 can only respond to ultraviolet light. It has some advantages such as chemical inertness, stability against photoirradiation, and non-toxicity. It is known that the photocatalytic properties of CeO₂ are strongly size/shape dependent at the nanometer scale.

hole (h+) pairs. The operational parameter is optimized, such as effects of pH, initial dye concentration, effect of irradiation time, effect of light and catalyst load were investigated using photocatalytic degradation of PANI-MWCNT/CeO2. The results obtained indicated the efficient degradation at pH=8 which extends to 92.5%, at 10 ppm extent to 90.93%, at 35 min interval extent to 95.01%, MB with PANI-MWCNT/CeO₂ on light extent to 89.52% and at 0.12 g/L extent to 97.48% respectively. Moreover, the mechanism of scavenger reaction was performed and it confirm the most important species in the degradation process would be (*O₂) and (*OH). The recyclability of PANI-MWCNT/CeO₂ for photocatalytic degradation MB was also evaluated for three consecutive cycles at optimum condition (10 ppm MB, 0.12 g/L of catalyst, at pH=8) and the results shows only a 14% decrement was observed after three cyclic run. The practical application was evaluated on a real sewage sample solution collected from Kombolcha Textile Industry, which shows a good performance about 71.74% degradation.

Key Words: Advance oxidation; Dye; Polymer; Semiconductor

In this regard, considerable effort has been made to design and synthesize CeO_2 nanomaterials with controllable morphology and large surface area [9]. In addition, the photocatalytic properties of CeO_2 are predominantly restricted by the rapid recombination of photo-induced electrons and holes. Therefore, it exhibits poor photocatalytic performance owing to its low charge-transfer rate, however, previous investigations indicated that CeO_2 is an excellent cocatalyst with other semiconductors such as MWNT, CdS, g-C3N4, and with supported such as polymers, because of the improved charge separation and oxygen reduction at the interfaces between the two coupled catalysts [10,11].

Consequently, the optical property of CeO₂ is improved when coupled/ hybrid with other semiconductor photocatalyst. In recent years, Carbon NanoTube (CNTs)/metal oxide nanocomposites are new generation with interesting properties that not only combine the properties CNTs and MOs but also hold new properties caused by the interaction between them. Therefore, Multi Walled Carbon NanoTubes (MWCNTs) have good catalytic properties, because of the unique internal structure, high surface area, low mass density, remarkable chemical stability, and electronic conductivity of MWCNTs. As a catalyst carrier, MWCNTs can not only act as photosensitizers for semiconductor, but also hinder the recombination of electrons and holes. Moreover, MWCNTs have a large surface area, and can act as a dispersing agent that prevents nanoparticles from agglomerating, resulting in higher active surface area for the resultant catalyst.

The present study focusses on modification of CeO_2 to get efficient catalytic property by coupled with suitable catalyst such as Multi Walled Carbon NanoTubes (MWCNTs). On the other hand, several attempts have also been made to improve the efficiency of photocatalysts using suitable supports. Among others, polyaniline has been successfully used to load various nanoparticles. It promotes the effective separation of photo excited electronhole pairs; this combination enhanced the photocatalytic activity for toxic pollutant degradation. In addition, PANI with delocalized π -conjugated

Department of Biotechnology, University of Coimbra, Portugal

Correspondence: Moreira H, Department of Biotechnology, University of Coimbra, Portugal, E-mail: helenamoreira@gmail.com

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This open-access article is distributed under the terms of the Creative Commons Attribution Non-Commercial License (CC BYNC) (http:// creativecommons.org/licenses/by-nc/4.0/), which permits reuse, distribution and reproduction of the article, provided that the original work is properly cited and the reuse is restricted to noncommercial purposes. For commercial reuse, contact reprints@pulsus.com structures is beneficial to rapid charge separation, thus the separation efficiency of photo generated electron (e-)⁻ hole (h⁺) pairs can be significantly improved [12]. In this work, the principal aim is to synthesize and characterize MWCNT using palm oil (methyl ester of *Elaeis Guineensis*) CNTs grown over silica impregnated Fe-Co bi-metallic catalyst by spray pyrolysis method and to synthesize PANI decorated MWCNT/CeO₂ and evaluates the photocatalytic activity for degradation Methylene Blue (MB) dye.

MATERIALS AND METHODS

Experimental section

Materials: Aniline (Aldrich) was purified by distillation under reduced pressure prior to use. The other reagents were of analytical grade or the highest commercially available purity and were used as received. Cerium nitrate hexahydrate, Iron nitrate hexahydrate, Cobalt nitrate trihydrate, sodium hydroxide, hydrochloric acid, hydrogen peroxide, ammonium hydroxide, ethanol, aniline and ammonium peroxysulphate were used without purification.

Synthesis of nanocomposites

Preparation of CeO₂ **nanoparticle:** The cerium oxide ultrafine nanoparticle was prepared by a precipitation method [13]. An aqueous solution of 0.1 M (4.334 g in 100 mL) of cerium nitrate hexahydrate Ce(NO₃)₃.6H₂O in deionized water was prepared and stirred for 30 min. The clear solution was precipitated by drop wise addition of aqueous NH3.H₂O solution with continuous stirring until precipitation gets completed. The stirring was continued another 2 h and the reaction condition then maintained at pH=10. The reaction mixture was then stirred for 12 h to complete the precipitation process. The mixture was aging for 12 h. The resulting yellow colored slurry was decanted; the precipitate was filtered and washed three times with deionized water and ethanol. The clean precipitate was oven dried at 140°C for 12 h and calcined at 500°C for 3 h to promote the crystallization.

Synthesis and purification of MWCNT: MWCNT was synthesized by spray pyrolysis method described as follow. The silica impregnated Fe-Co bi-metallic catalyst was placed on the quartz boat [14]. The boat was placed in the heating furnace. The carrier gas nitrogen (100 mL/min) was flushed out before switch on the reaction furnace to remove air and create nitrogen atmosphere. The temperature was raised from room temperature up to the desired growing temperature. Subsequently, methyl esters of Elaeis Guineensis were introduced into the quartz tube through spray nozzle and the flow was maintained using saline tube at the rate of 0.5 mL/min. The deposition time lasted for 45 minutes at temperature 650°C. The reactor was then allowed to cool to room temperature with nitrogen gas flowing. The carbon product on the silica support was then weighed to determine the carbon yield of the spray pyrolysis. The as-grown MWNTs were purified by the following procedure. 40 mg of raw material was added to 20 mL 1N HCl to form an acidic slurry. This slurry was heated to 60°C and stirred at 600 rpm. To this heated acidic slurry 20 mL H2O2 was added to form oxidative slurry that continued to be heated and stirred for 30 minutes. The addition of HCl, H₂O₂, subsequent heating and stirring was repeated three more times, each time allowing the heated oxidative slurry to stir for 30 minutes. Phase separation was allowed to proceed followed by filtering the carbon phase and washing with 1N HCl and distilled water. The collected sample was dried at 120°C in air for 2 hours [15].

Synthesis of MWCNT/CeO₂: A typical solgel method was adopted for the synthesis of MWCNT/CeO₂ nanocomposite with some modification [16]. Typically, 0.15 g of functionalized MWCNT was dispersed in a 100 mL of ethanol. The solution was allowed to continuous stirring for 3 h to achieve uniform dispersion. Then, in the above solution, 0.15 g (1:1) CeO₂ powder was added and the mixture was subjected for sonication for 2 h. Followed by, the solution was allowed for continuous stirring for 12 h at room temperature. After sonicating, the solution was centrifuged several times and washed with distilled water and ethanol. The precipitate was dried overnight at 60°C.

Synthesis of polyaniline decorated MWCNT/CeO₂: Polyaniline decorated MWCNT/CeO₂ was synthesized by situ polymerization method for the polymerization of aniline in the presence of MWCNT/CeO₂ nanocomposite. In brief, 0.5 g of MWCNT/CeO₂ powder was added into 30 mL aqueous solution of 0.01 mol aniline monomer and 0.01 mol hydrochloric acid. 0.01 mol ammonium peroxy-sulfate was dissolved in 15 mL distilled water and

added drop wise to the mixture of MWCNT/CeO₂ and aniline, with stirring on an ice bath. Polymerization proceeded for 5 h. The composite of PANI-decorated MWCNT/CeO₂ was obtained as a precipitate. The precipitate was isolated by filtration, washed with distilled water and ethanol several times, and then dried at 60°C for 5 h in an oven.

Characterization of the synthesized nanocomposites

To determine the characteristic maximum absorption of the as-synthesized samples and their band gaps, UV-Visible absorption spectrophotometer was used in the range of 200-900 nm wavelengths. The surface morphology was studied by Scanning Electron Microscopy (SEM) (Hitachi S-4700). The crystalline phases and the crystallite sizes were determined using powder X-ray Diffraction (XRD) with X'Pert Pro PANalytical with CuKII radiation (II=1.5405 Å). The data were registered with 2I steps of 0.02° and accumulation times of 20 s. FT-IR (Spectrum 65, PerkinElmer) in the range 4000-400 cm⁻¹ using KBr pellets was used to assign functional groups of as-synthesized PANI-MWCNT/CeO₂.

Photocatalytic degradation studies

Photocatalytic activities of the entire as-synthesized sample were tested for the degradation of aqueous solution of Methylene Blue (MB) dye. Typical photocatalytic experiment, 10 ppm of MB was mixed with 0.2 g/L of the photocatalyst. The mixture was magnetically stirred for 1 h in the dark to ensure adsorption/desorption equilibrium. Then the suspension was irradiated with visible light irradiation with continuous stirring using magnetic stirrer and the absorbance was measured in 20 min time interval to monitor the reaction of MB aqueous solution degradation. The distance between the light source and the dye solution is 20 cm. During the process air/oxygen was purged in to the solution using pipette. Then 10 mL suspension was withdrawn at 20 min time interval and centrifuged at 3000 rpm for 10 min. Dye absorbance was determined using UV/Visible spectrophotometer at the λ_{max} of MB solution. Percent degradation (%) was calculated using the following equation [17].

% Degradation = $\frac{C_0 - C_t}{C_0} \times 100$

Effect of operating parameter

Effects of operational parameters like initial pH, photocatalyst load, irradiation time, effect of light, initial concentration of methylene blue and scavenger effect was investigated for the PANI-MWCNT/CeO₂ photocatalyst in order to optimize the degradation efficiency.

Effect of pH: The effect of pH on photocatalytic degradation of MB was investigated in the pH range of 2-12 by keeping photocatalyst load (0.2 g/L) and initial dye concentration (10 ppm) constant. The pH was maintained each time by using 1M HCl or 1M of NaOH and measured using a pH meter.

Effect of initial concentration of MB: Methylene blue concentration is very important parameter in water treatment. Therefore, the effect of MB on the rates of photocatalytic degradation was studied by taking 10-35 ppm concentrations of MB solution and keeping other factors constant.

Effect of photocatalyst load: To avoid excess use of photocatalyst within the system and to ensure total absorption of efficient photons, the optimum mass of the photocatalyst has to be found [18]. To study this effect, the influence photocatalyst dose in degradation of methylene blue was carried out by varying the catalyst dose from 0.01 to 0.5 g/L keeping other parameters constant.

Effect of irradiation time: The aqueous solution of MB in the presence of as synthesized photocatalyst was irradiated with 5-35 min interval under UV light and keeping all other factor constant and the result were recorded.

Effect of light on the photocatalytic degradation: The effect of light on photocatalytic degradation of MB, experiments was examined both in the presence of light and catalyst and without light and photocatalyst with constant the other parameter. In each case during experiment, the photo reactor was kept maintained under magnetic stirring for 20 min achieving homogeneous suspension to promote the adsorption [19].

Effect of scavengers: The influences of active species in the photodegradation process were evaluated using initial concentration of MB at 10 ppm, 0.12 g/L of PANI-MWCNT/CeO, photocatalyst and pH at 8. The active species

were determined through the trapping experiments with different scavengers such as NaHCO₃ as h⁺ scavenger, AgNO₃ as •O₂ scavengers and methanol as •OH scavengers [20]. Hence, 0.12 g/L of the synthesized photocatalyst and 0.1 M of 10 mL of each scavenger were placed into 100 mL of 10 ppm of MB dye solution; then, the suspension was irradiated using visible irradiation for 160 min. The 10 mL suspension was withdrawn at 20 min interval and centrifuged at 3000 rpm for 10 min. Dye absorbance was determined using UV/Visible spectrophotometer at the λ_{max} of solution. Finally, the degradation efficiency of the photocatalyst over the dye can be calculated to determine the main role of active species.

Recyclability of the catalyst

The catalyst's life time is an important parameter of the photocatalytic degradation process, so it is essential to evaluate the stability of the photocatalyst for practical application. In order to determine the stability of the synthesized photocatalyst during the photocatalytic reaction, the composite was taken to investigate the number of cycles the catalyst could possibly be used with no pronounced drop in its catalytic efficiency. The recycle test was performed four times in three consecutive trials; recovering the catalyst in between runs by centrifuging and decanting. After a first photodegradation cycle of a 10 ppm solution of MB dye using 0.12 g/L of the synthesized photocatalyst and 180 min irradiation time, the treated solution of the dye was centrifuged for 10 min to settle the catalyst. The liquid phase was filtered and then the solid phase containing the photocatalyst was carefully separated for reuse. The recovered photocatalyst was washed by sufficient amount of deionized water and ethanol. Finally, the photocatalyst was dried in an oven at appropriate temperature before the use for next catalytic cycle and then reintroduced into fresh cycle. The process was repeated three times. The 10 mL suspension was withdrawn at 20 min time interval and centrifuged at 3000 rpm for 10 min. The MB degradation and photocatalytic stability of PANI-MWCNT/CeO, photocatalyst layer was measured at the end of each cycle.

Dye removal from wastewater using PANI-MWCNT/CeO,

The wastewater collected from Kombolcha Textile Industry was treated/ decolorized using polyaniline decorated MWCNT/CeO₂ nanocomposite under optimized conditions upon visible light irradiation. The experiment was conducted by taking 50 mL of sample of wastewater in 250 mL beaker and its pH was adjusted at 8. Then 0.12 g/L of the photocatalyst was added into the solution and the suspension was kept in the dark for 1 h with continuous stirring to make sure the establishment of adsorption/desorption equilibrium of MB solution. Finally, the suspension was irradiated with visible light upon continuous stirring and its absorbance was measured at 20 min interval by withdrawing 10 mL suspension for 180 min. Then the plot of Ct/Co versus irradiation time was plotted.

RESULTS AND DISCUSSION

Characterization of the photocatalyst

FTIR study of as-synthesized photocatalyst: The selected surface functional groups of the single, binary and polyaniline decorated nanocomposite materials were analyzed by FT-IR in the range from 400 to 4000 cm⁻¹ (Figure 1).

Pure MWCNT shows a peak at approximately 3500 cm⁻¹, characteristic of an H bonded O-H stretching of carboxyl or alcoholic group [21]. The peak at 1610 cm⁻¹ is also related to C=O vibration in carbonyl group and vibration due to C=C bond in the benzene ring. The formation of functional carboxylic, carbonylic and alcoholic groups as a result of the oxidation process of MWCNTs indicates that the functionalization process has been effectively taken place. In case of CeO₂, the band at 3450 cm⁻¹ corresponds to the O-H stretching vibration, 1625 cm⁻¹ due to O-H scissor bending mode which is originated from physical absorbed (H-bonded) water molecules or surface -OH groups [22]. The band at 1350 cm⁻¹ consists of the symmetrical stretching mode of N=O that is due to the precursor CeNO₃.6H₂O. It can be observed that the bands corresponding to Ce-O stretching vibrations are 1050 and 525 cm⁻¹; similar result has been reported in the other work [23].

The binary MWCNT/CeO₂ shows both the characteristics band of MWCNT and Ce , however there is a band shift. Peak observed at 3495 cm⁻¹ cans be attributed to O-H bond in alcoholic group. The peak at 1625 for O-H scissor bending shifted to 1595 cm⁻¹ and also the characteristic peak of Ce-O bond, in the case of pure CeO₂, appears at around 525 cm⁻¹ whereas, in the case of the nanocomposite it has been shifted to 515 cm⁻¹. This shift could be due to the formation of chemical bond between cerium dioxide and MWCNTs through oxygen containing groups such as carboxyl and carbonyl. Similar result has been observed elsewhere [24]. In fact, the formation of such strong interactions between the metal oxide and MWCNTs, during the synthesized nanocomposites. When compared with single nanoparticle the characteristics band is less intense with the MWCNT/CeO₂.

FT-IR spectrum of the PANI decorated MWCNT/CeO₂ nanomaterial shows a broad absorption band located at 3100 -3500 cm-1 corresponding to N-H stretching with hydrogen-bonded amino and imine site of polyaniline and also free O-H stretching vibration of water. The peak appeared at 1500 cm⁻¹ due to C=C stretching mode of benzenoid rings which indicated that, the presence of polyaniline. The peak at 1580 cm⁻¹ is also related to C=O vibration in carbonyl group due to the presence of MWCNT. It can be observed that the bands at 1250 cm⁻¹ corresponding to the characteristic of Ce-O stretching vibrations which confirm the presence of CeO₂. The band at 815 cm⁻¹ is corresponding to out-of-plane bending vibration of C-H bond which confirms the coupling of aniline units of PANI in the surface of MWCNT/CeO₂.

SEM analysis: The SEM analysis of the prepared MWCNT, CeO_2 , MWCNT/ CeO_2 and PANI-MWCNT/ CeO_2 photocatalyst presented in Figure 2a. It is clear from the Figure 2a that the pure MWCNTs are highly tangled tubes. The nanotubes formed are of multi-walled type composed of many walls. The SEM micrograph in Figure 2b of single CeO_2 indicate like a spherical shaped with some agglomeration. Figure 2c shows SEM images of the MWCNT/ CeO_2 that CeO_2 is wrapped up around MWCNT. Whereas, the surface morphologies of the as-synthesized PANI-MWCNT/ CeO_2 nanocomposite, as in Figure 2d described the MWCNT/ CeO_2 are deposited on the surface of polyaniline.



XRD analysis: X-ray diffraction was applied in order to investigate the change



in the crystalline structure of the synthesized photocatalyst. As Figure 3a presented, the pristine MWCNT exhibit two major characteristics peak at 25.5° is due to the reflection of (002) plane and at 44.3° is related to the reflection from the (100) planes. The diffraction peak for CeO₂ is described in Figure 3b. The analysis indicated that the peak at 2 θ values of 28.8°, 32.09°, 46.5°, 56.4°, 59.2°, 68.4°, 76.6°, 79.2° and 89.01° corresponding to the (111), (200), (220), (311), (222), (400), (313), (402) and (422) crystal lattice planes of cubic crystalline phases respectively (JCPDS: 96-434-3162) [25]. The general feature of the XRD patterns of CeO₂ shows the presence of strong peaks, which indicate that the produced nanoparticles are pure crystalline.

The XRD pattern for binary MWCNT/CeO₂ as described in Figure 3c, the characteristics peak of both single nanoparticles is present. However, there is peak shift and the peak at 25.5° of MWCNT is fully covered by CeO₂. This is may be due to this fact that the crystalline extent of MWCNTs is much lower than the crystalline extent of CeO₂, leading to the shielding of the peaks of MWCNTs by those of CeO₂ [21]. The XRD pattern of PANI decorated MWCNT/CeO₂ nanocomposite consist of the major characteristic's diffraction peak of PANI, MWCNT, and CeO₂, but the 2 θ values slightly shifted (Figure 3d). The diffraction signal observed at 2 θ values of 15.67° is attributed to the parallel repetition units of PANI, 47.43° are attributed to MWCNT and the ones from 30.01°, 33.9°, 57.47°, 69.46°, 77.2° and 77.86° are due to CeO₂. When compare with single and binary nanocomposite, PANI decorated material shows strong and sharp peak which confirms high crystallinity due to the presence of PANI polymer (Figure 3a).

UV/Vis diffuse absorption spectra: The optical absorption properties of each of the as-synthesized photocatalyst were investigated by using a UV/Vis diffuse reflectance spectrometer in the range of 200-900 nm. The band gap values of the photocatalysts were determined by analyzing the optical data with the expression for the optical absorbance α and the photon energy hv using Tauc's plot [26].

 $\alpha h\nu = A (h\nu - Eg)^{n/2}$

Where α is the absorption coefficient, which is proportional to the absorbance, h is the Planck's constant (J.s), v is the light frequency (s⁻¹), A is the absorption constant, Eg the band gap energy and n is a constant related to the electronic interband transition [27]. The band gaps of the photocatalyst were then determined by extrapolating the straight-line portion of the (ahv)2 versus (hv) graphs to the (hv) axis. It reveals that pure MWCNT exhibited a strong absorption peak at 442 nm. The pure CeO, also show a well-defined

absorption band at 310 nm, in the UV range, his may be originating from the charge transfer transition from $O_{7}(2p)$ to $Ce_{4}^{*}(4f)$ orbital in CeO₂.

The UV-visible spectra of binary system (MWCNT/CeO₂), that is after introducing wideband gap CeO, into MWCNT, the absorption edge is slightly red shift which is near to 467 nm. This is due to carbon containing materials like MWCNT affects the shape of the absorption curve. Red shift to higher wavelength was observed in the absorption edge of MWCNT/ CeO₂, which may be attributed to electronic interaction between MWCNT and CeO₂. This interaction resulted the delocalized of p-electrons of oxygen atoms and the formation of intermediate energy levels, which would have an influence on the band positions. For Polyaniline decorated MWCNT/ CeO₂, the absorption edge resulted in a slight red shift in compared with the binary nanocomposite. This red shift means a lower band gap, which may contribute to the electron transitions, leading to the light harvesting efficiency of the composite which is due to PANI in the visible light region and producing more photogenerated electron-hole pairs in the photodegradation process, which was favorable for the photocatalytic activity. Based on Tauc's plot as described in Figures 4a-4d, the band gaps for all the as-synthesized photocatalyst were displayed. The calculated band gaps of the MWCNT, CeO₂, MWCNT/CeO₂ and PANI-MWCNT/CeO₂ are found to be 2.8, 3.2, 2.65 and 2.4 eV respectively.

Photocatalytic studies

Comparison of the Photocatalytic Activities of the As-synthesized Photocatalysts: In this study, visible light serves as the irradiation source and Methylene Blue (MB), with a characteristic absorption at 664 nm as indicated in Figure 5, is chosen as a typical organic pollutant for testing the photocatalytic activity of the synthesized nanocomposite. The photocatalytic activities of all the developed sample were evaluated by testing their ability in the degradation of MB (initial dye concentration of 10 ppm and catalyst load of 0.02 g/L) under 160 min visible irradiation time. As described in Figure 6, the photocatalytic performance of CeO, demonstrated the lowest photocatalytic activity (17.41%) due to the photoinduced electrons and holes may recombine in the surface during the transfer process. This also due to its wide band gap that makes (B-type) it less sensitive to the visible portion of solar energy or that hinder the photocatalytic activity of CeO2. Pure MWCNT is degrading the MB about 32.78% which is greater than CeO₂. This is because of MWCNT has more active site on the surface to adsorb the MB dye.









The binary MWCNT/CeO, shows enhanced photocatalytic activity compared with the single nanoparticle that is 52.78%. The enhancement in photocatalytic activity of MWCNTs/CeO, nanocomposite can be explained based on electron transportation from nanoparticles to nanotubes and adsorption ability of nanotubes. In general, photons with sufficient energy are able to excite electrons (e-) from the Valance Band (VB) to the Conduction Band (CB) of CeO₂ creating a charge vacancy or hole (h⁺) in the valance band. However, the photogenerated electrons and holes in semiconductors have very short life time as they recombine within a short time. In order to enhance the photocatalytic activity of semiconductors, electron-hole recombination process has to be delayed [28]. Therefore, MWCNT act as a good electron acceptor and thereby facilitate the separation of the electron-hole to prevent their recombination. The mechanism of photocatalytic activity is valance band electrons (e⁻) of CeO₂, under the visible light irradiation are excited to CB, creating holes (h⁺) in the Valence Band (VB) which photogenerated electrons can transfer from CeO, to MWCNTs. Carbon nanotubes can adsorb oxygen as well as dye molecules, thus photogenerated electrons can reduce adsorbed oxygen molecule to superoxide anion radical (O, ·) which will increase the number of radicals that can react with the dye and produce hydroxyl radical (•OH) to oxidize the dye. Generally, when CeO2 was modified by the MWCNT, the photocatalytic activity was enhanced.

The photocatalyst activity of polyaniline decorated MWCNT/CeO, nanocomposite exhibited much higher percentage degradation (84.54%) as compared to the other pure and binary nanomaterial. This could be due to efficient charge separation of electron and hole pairs in the excited states that prevents recombination of charge pairs for a longer time under visible irradiation. This is due to their remarkable electroactive properties of PANI; they have lately proven to act as stable photosensitizers for semiconductors owing to their high electron-hole carrying efficiency [29]. The LUMO levels of the PANI polymer are also energetically higher than the conduction band of photocatalyst, electron transfer from the excited PANI polymer to the conduction band of photocatalyst is possible, leaving holes (PANI+) in HOMO of PANI. Additionally, PANI has an extended π -conjugated electron system acts as an excellent electron donor and a good hole acceptor when illuminated [30], which makes the PANI-MWCNT/CeO, highly efficient. These unique properties make PANI efficient photosensitizer for various semiconductors and provide more active sites for specific binding of dye molecules in order to enhance the separation efficiency of photogenerated electron-hole pairs and consequently better adsorption, photocatalytic activity and stability of the photocatalyst [31]. For the same irradiation time, the removal efficiency for target pollutants of unsupported and supported photocatalyst was 52.78 and 84.54% respectively. This result demonstrates that PANI can enhance the adsorption ability of photocatalyst and a large amount of MB can be adsorbed on the surface of photocatalyst. The general trend of catalytic performance becomes PANI-MWCNT/CeO_MWCNT/ CeO, MWCNTICeO,.

Effect of operating parameters

Effect of pH: The pH can affect the catalyst-pollutant interactions and generation of redox species during irradiation. pH is an important parameter to study the degradation of dyes. Therefore, the photocatalytic efficiency of PANLMWCNT/CeO₂ was determined at various pH values from 2-12. As shown from the Figure 7, the result indicates that the increase in pH of the solution, the gradual increase in the degradation of MB was observed, reaching a maximum degradation of 92.5% at pH=8. In the range of pH 6.2-8, an increase in OH radical formation and electrostatic interaction between MB (cationic dye) and the negatively charged PANLMWCNT/CeO₂ catalysts particles was suggested. These interactions supported the adsorption followed by photocatalytic degradation.



Figure 7) Effect of pH on the degradation of MB as a function of irradiation time (catalyst load at 0.12 g/L and initial concentration of MB at 10 ppm)

Below optimized pH (pH<8), the photocatalyst showed comparatively less degradation efficiency, since the photocatalysts are become cationic in acidic solution, so the degradation of cationic MB resulted lower below pH 7. This may be explained by the fact that the sorption of the MB on the catalyst surface will be prevented because of the increased positive charges on the catalyst surface, which persuades repulsion on the positive charged dye molecules (principle of ion-ion repulsion). However, when the pH further increases, the degradation efficiency also decreases because of OH- ions were repelled by negatively charged surface of the photocatalyst decreasing the photocatalytic degradation efficiency [32]. Generally, the PANI-MWCNT/CeO₂ surface is predominantly negatively charged when the pH is increased beyond isoelectric point (PZC=6.2) of photocatalyst. As the pH decreases, the functional groups are protonated, thus raising the positive charge of photocatalyst surface. The surface of photocatalyst will be charged negatively

at higher pH and results in the increased adsorption of cationic molecules like MB while in the reverse situation it would adsorb anionic molecules very easily.

Effect of initial concentration of MB dye: The effect of initial dye concentration on the photocatalytic degradation efficiency of PANI-MWCNT/CeO, was studied in the concentration range from 10 to 35 ppm of MB solution and the other parameters were kept constant. From Figure 8, the result indicated that the photocatalytic degradation of MB was decreased from 90.93 to 47.36% with increasing the initial MB concentration from 10 to 35 ppm after 180 min. The maximum degradation efficiency was obtained for the minimum MB dye concentration considered, which 10 ppm is. This is the reason that, when increased concentration of MB, it resulted in more adsorption of MB onto PANI-MWCNT/CeO, surface, which can cause inhibitive effect on the further photocatalytic degradation of MB due to decreased adsorption sites on the photocatalyst. Therefore, at high dye concentrations the generation of •OH radicals on the surface of catalyst are reduced since the active sites are covered by dye ions. However, the UV-screening effect of the dye itself was another effect. At a high dye concentration, a significant amount of UV may be absorbed by the dye molecules rather than the nanoparticles and that reduces the efficiency of the catalytic reaction because the concentrations of • OH and O₂ • -decrease [33].



function of irradiation time (catalyst load at 0.12 g/L, initial concentration of MB at 10 ppm and pH at 8). Note: (\blacksquare) 10 ppm, (\bigcirc) 15 ppm, (\bigcirc) 20 ppm, (\bigtriangledown) 25 ppm, (\bigcirc) 30 ppm, (\checkmark) 35 ppm

Effect of catalyst load: The amount of photocatalyst is one of the main parameters for the degradation of substrate from economical point of view. In order to avoid the use of excess photocatalyst, it is necessary to find out the optimum loading of photocatalyst for efficient removal of dye [33]. Accordingly, the influence photocatalyst dose in degradation MB dye was carried out by varying the catalyst dose from 0.02 to 0.5 g/L. The result indicated as displayed in Figure 9, initially the degradation of MB increases with increasing in photocatalyst load from 0.02 g/L to 0.12 g/L and further increase of catalyst loading from 0.12 g/L to 0.5 g/L results in decreasing degradation of MB.



Figure 9) The effect of PANI-MWCNT/CeO₂ photocatalyst load on MB dye degradation as a function of irradiation time (concentration of MB at 10 ppm and pH at 8). Note: (\Rightarrow) 0.02 mg/l, (\ddagger) 0.06 mg/l, (\Rightarrow) 0.12 mg/l, (\ddagger) 0.24 mg/l, (\Rightarrow) 0.5 mg/l

The maximum degradation of MB occurs at 0.12 g/L of PANI-MWCNT/ CeO_2 catalyst load. These is due to the fact that, the photocatalytic degradation rate initially increased with catalyst loading and then decreases at high values because of light scattering and screening effects. In brief, the tendency toward particle-particle interaction also increases at high solids concentration, resulting in a reduction in catalyst surface area available for light absorption and hence a decrease in the photocatalytic degradation rate. Even though the number of active sites in solution will increase with catalyst loading, a point appears to be reached where light penetration is to be compromised because of excessive particle concentration. The compromise between these two opposing phenomena results in an optimum catalyst loading for the photocatalytic reaction. Thus, 0.12 g/L of the photocatalyst load was selected as the optimal amount of photocatalyst for the subsequent experiments.

Effect of light: In order to investigate the effect of visible light irradiation on photocatalytic degradation (catalyst-methylene blue interaction), experiments were carried out for photolysis of MB under visible (blank), MB with PANI-MWCNT/CeO₂ on dark and MB with PANI-MWCNT/CeO₂ on light as depicted in Figure 10. The samples of dye solution for photolysis experiment under visible irradiation were conducted in the absence of the photocatalyst. The degradation of MB under these conditions provided degradation efficiency of 5.35%. This degradation was may be due to the solutions bubbled with O₂. The photocatalytic degradation efficiency of MB by PANI-MWCNT/CeO₂ composite under light is higher than PANI-MWCNT/CeO₂ under dark. The maximum degradation efficiency of 89.57% was PANI-MWCNT/CeO₂ under visible light.



Figure 10) Effect of UV light in photocatalytic degradation PMC (PANI-MWCNT/CeO₂) of MB as a function of irradiation time with (catalyst loading 0.12 g/L, MB conc.10 ppm and at pH 8). Note: ($\neg \Rightarrow \neg$) MB on dark, ($\neg \Rightarrow \neg$) MB with PMC on light

This due to the strong electrostatic field present in the polyaniline under visible light can effectively separate the e-and h⁺ produced during photo excitation of the MWCNT/CeO₂ and consequently resulted in lower recombination of them and higher photodegradation efficiency. The formation of electron-hole pair under light irradiation is fast for enhancing the redox reaction within MB. On the other hand, the percent adsorption of MB dyes without light irradiation over PANI-MWCNT/CeO₂ was 22.89 %. It is because of the electron in valence band did not get sufficient excitation energy from the conduction band in order to precede photocatalytic reaction. So, for the dark, no electron-hole pair could be generated in semiconducting material without light irradiation. Hence, the efficiency is low attributed only to adsorption of the dye on the photocatalyst surface.

Effect of irradiation time: The irradiation time interval also affects the efficiency of photocatalytic degradation. The effect of irradiation interval was carried out with 5, 15, 25 and 35 min and the other parameter is under constant. The result confirmed that when the irradiation time intervals increase the degradation efficiency also increases. It has been found that with the increasing in irradiation time interval from 5 min to 35 min, the degradation of MB was increased from 44 to 95.01%. The photodegradation was found maximum at 35 min irradiation of visible light. Figure 11 shows the effect of irradiation time on photocatalytic degradation of MB. This is

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due to the interaction of MB molecule with the surface of PANLMWCNT/ CeO₂ photocatalyst. The time of irradiation increase, the interaction of MB dye molecule increased with the surface of photocatalyst and form hydroxyl radicals which accelerate photocatalytic reaction. Hence, the photodegradation efficiency of photocatalyst was increased [34].



MB under UV light irradiation. Note: (-+-) 5 min interval, (-+-) 15 min interval, (-+-) 25 min interval, (-+-) 35 min interval.

Mechanism of scavenger reaction

The effect of active species on photocatalytic degradation of MB was examined by using superoxide radical (*O₂), hole (h⁺) and hydroxyl radical (*OH) and under the other parameter is constant. The source of the scavengers used in this reaction were NaHCO₃ for h⁺, CH3OH for *OH and AgNO₃ for superoxide radical *O₂. The result revealed that, the photocatalytic conversion of MB without scavenger was 92.77%. When NaHCO₃ was added, the photocatalytic degradation of MB decreased to 82.5% whereas when AgNO₃ and CH3OH were added, the photocatalytic conversion of MB become 63.43% and 74.55% respectively (Figure 12). The results indicated that all the scavengers considered have suppressed the photocatalytic degradation efficiency although the effect of AgNO₃ is more obvious. So, the main active species in this photodegradation reaction is superoxide radical *O₂ radicals who result the direct involvement of holes appeared to be restricted. In general, the main active species for PANI-MWCNT/CeO₂ follows the order: Hole >hydroxyl radical >superoxide radical.



Figure 12) Degradation rate of MB as function of irradiation time in the absence and presence of scavengers (catalyst load at 0.12 g/L, concentration of MB at 10 ppm and pH at 8). Note: (--) CH3OH Scavenger, (--) AgNO3 Scavenger, (--) MB without Scavenger, (--) NaHCO3

Recyclability of photocatalyst

The reusability of PANI-MWCNT/CeO, photocatalyst has performed in three consecutive repetitions by recovering the photocatalyst in between runs by centrifuging and decanting. For each new recycle the photocatalyst was reused for the degradation of a fresh MB solution under similar condition after photocatalyst sample was filtered and dried. The separation of the reaction mixtures and catalyst was done by decantation. The decolorating rates of MB solution catalyzed by the photocatalysts was slightly decreased (91.83-77.23%) from cycle 1 to cycle 3 as shown in Figure 13. This is due to a loss in the photocatalyst during recycling which eventually affect catalytic activity after each cycle. Additionally, agglomeration and sedimentation of the dye around PANI-MWCNT/CeO2 particles after each cycle of photocatalytic degradation is a possible cause of the observed decrease on the degradation rate, because each time the photocatalyst is reused new parts of the photocatalyst surface become unavailable for dye adsorption and thus photon absorption, reducing the efficiency of the catalytic reaction [35]. This experiment approves the potential recyclability of the as synthesized PANI-MWCNT/CeO2 photocatalyst for three subsequent cycles with slight losing its efficiency.



Figure 13) Recyclability for photocatalytic degradation of MB as a function of irradiation time, Where, C1, C2 and C3 are first, second and third cyclic run respectively. Note: $(-\oplus -)$ Cycle 1, $(-\oplus -)$ Cycle 2, $(-\oplus -)$ Cycle 3

Mechanism of photo catalytic degradation

The mechanism of photocatalytic degradation of methylene blue by PANI-MWCNT/CeO₂ photocatalyst explained as follow (Figure 14). Initially, the PANI can absorb visible light to induce the $\pi\pi^*$ transition, delivering the excited state electrons of the HOMO to LUMO. Then, the conducting PANI produces e-those transfers to the CB of MWCNT/CeO₂. In CB site, molecular oxygen (O₂) forms superoxide radical •O₂ in the presence of the photo excited CB e-and subsequently reacts with h⁺ to form HO₂ • radical species. Through the e-transfer from PANI to CB of MWCNT/CeO₂, the generated photoinduced h⁺ in VB might react with water (H₂O) and the adsorbed MB dye molecule to yield hydroxyl radical (•OH) and MB •-anions radical respectively. The formed MB •-radicals generally transforms to the oxidation and reduction products. On the other hand, electrons in the MWCNT/CeO₂ VB can also migrate to the HOMO of PANI and recombine with PANI holes, while the holes generated in the MWCNT/CeO₂ VB move to its surface.



 $PANI-MWCNT/CeO_{2}+hv \rightarrow h^{*}VB^{+}e^{*}CB$

Oxidative reaction

 $h^+VB+H_2O \rightarrow H^{++} \bullet OH$

• $OH^+MB \rightarrow (Intermediates) \rightarrow CO_2 + H_2O$

Reductive reaction

 $e^{-}CB+O_{2} \rightarrow \bullet O_{2}^{-}$

- $\bullet O_2^{+}H^{+} \rightarrow \bullet HO_2^{-}$
- $\bullet HO_2 \rightarrow \bullet O_2 + H_2O_2$
- O_2^+ +MB \rightarrow (Intermediates) \rightarrow CO_2^+ H₂O

Generally: $\bullet O_{2}(\bullet OH, h^{+}) + MB + O_{2}/H_{2}O \rightarrow Degradation products$

Application of PANI-MWCNT/CeO, for real sample analysis

The dye sample is collected from Kombolcha Textile Industry sewage tanker for degradation of color by PANL-MWCNT/CeO₂ photocatalyst. The degradation (decolorating) efficiency of the developed PANL-MWCNT/ CeO₂ photocatalyst for the degradation of the real sample under visible light irradiation was studied as a function of irradiation time and the results is described in Figure 15. The result shows that the percentage degradation (71.74%) of the real sample occurred at the PANL-MWCNT/ CeO₂ photocatalyst under 180 minute's visible light irradiation lower than the MB degradation (92.44%). These are due to the complexity of the wastewater which includes not only mixture of organic dyes but also other chemicals from the bleaching steps [34]. Therefore, PANL-MWCNT/CeO₂ photocatalyst is best material for degradation of MB and real sample due to special properties of polyaniline and MWCNT.



Figure 15) Photocatalytic degradation of MB and real textile wastewater using PMC (PANI-MWCNT/CeO₂). **Note:** (- - -) MB with PMC, (- - -) Real sample with MPC

The single, binary and decorated material, especially MWCNT was synthesized by spray pyrolysis method and the palm oil (Elaeis Guineensis) used as carbon source. The other nanomaterial like CeO,, MWCNT/ CeO, and PANI-MWCNT/CeO, were synthesized by precipitation, sol-gel and polymerization method respectively. The developed nanocomposite was characterized by modern spectroscopic technique like X-ray Diffraction (XRD), Uv-vis, FTIR and SEM. The characterization results specially, the XRD and FT-IR confirms there is strong interaction (chemical bond) b/n PANI and MWCNT/CeO2. The photocatalytic activities of the as synthesized single, binary and supported nanocomposites were investigated on the target pollutant methylene blue. The results revealed that the photocatalytic degradation of polyaniline decorated MWCNT/CeO, show higher degradation efficiency than the other single and binary nanomaterial. This study was also examined in detail the effect of key parameters, such as catalysts loading, pH and concentration of dye, irradiation time, recyclability and effect of light for the degradation of MB dye under UV-vis light irradiation. The photocatalytic degradation activities of the synthesized PANI decorated binary nanomaterial under visible light irradiation have been also evaluated for real sample treatment which is the sewage sample collected from Kombolcha Textile Industry and shows best performance.

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Competing interests statement

The authors declare no competing financial, professional and personal interests.

Consent for publication

We declare that we consented for the publication of this research work.

Consent to participate

Not Applicable

Consent for publication

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Availability of data and material

Authors are willing to share data and material according to the relevant needs.

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