Characterization and Application of Nanomaterials (2018) Volume1
doi:10.24294/can.v1i2.585

C-dots dispersed macro-mesoporous TiO_2 photocatalyst for effective waste water treatment

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ABSTRACT

Synthesis of macro-mesoporous Titania (titanium dioxide-TiO_2) nanospheres was successfully achieved using a modified template-free methodology to incorporate macroporous channels into a mesoporous TiO_2 framework to form mixed macro-mesoporous TiO_2 spheres (MMPT), which were doped with carbon dots (C-dots) to form improved nanocomposites (C-dots@MMPT). Elemental composition, surface bonding and optical properties of these nanocomposites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and ultraviolet-visible absorption spectroscopy (UV-VIS). Evaluation of photocatalytic activity for each (C-Dots@MMPT) sample was performed via degrading the Methylene Blue (MB) dye compared with bare samples (MMPT) under visible light irradiation using 300-Watt halogen lamp.

Keywords:*Photocatalysis; macro-mesoporous* TiO_2*; up-conversion photoluminescence; MB* degradation

1. Introduction

For many years, there has been a large interest in the synthesis of semiconductor nanostructures and the investigation of their properties due to their vital applications in electronic and optical devices. Among the transition metal oxide semiconductors, Titania possesses many outstanding features such as the strong oxidizing ability, cost-effectiveness, environmentally-benign and high chemical and thermal inertness [1], Titanium dioxide is also recognized as the most efficient, non-toxic, insoluble and stable photocatalyst. Titania has three crystalline phases such as: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). The anatase phase shows superior photocatalytic activity compared to other polymorphs of Titania [2].

Unfortunately, the technological usage of bare TiO_2 is hampered by two main limitations. First, it has a wide band gap (3.2, 3.02, 2.96 ev) for the anatase, rutile and brookite phases, respectively. Thereby it is only activated by ultraviolet (UV) light which represents 2-3% of the total solar spectrum. Second, the short time for recombination of photo generated electron-hole pairs (in the order of nanoseconds). These limitations deteriorate the quantum efficiency of TiO_2 [3].

Many authors reported different strategies to overcome such drawbacks and improve the photocatalytic performance by tailoring the semiconductor heterojunction [4], including the doping of noble metals such as Ag [5], Au and Pt [6] or modification of TiO_2 by means of doping with non-metal ions such as sulfur [7], chlorine [8]and nitrogen [9].

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Furthermore, “It was supposed that doping with metal-ions could improve the electronic energy band structure of TiO_2 and thus enhances the photocatalytic performance by effective charge transform from the doping metal ions to Ti^{4+} ions” [10]. In addition, the combination with carbon nanotubes [11,12] and graphene [13-16] has proven their efficiency to provide high electron mobility to extend electron-hole separation lifetime [17].

Carbon dots are a recent class of carbonaceous nanomaterials, discovered during the purification of Single-walled carbon nanotubes [18], which received remarkable attention as the most reliable and green approach to promoting effective energy conversion. It has been reported that C-dots doped photocatalyst significantly improving the photocatalytic reaction based on their ability to absorb long wavelength photons in the visible region and emit light of the shorter wavelength in the ultraviolet region and vice versa (Up-conversion - down-conversion photoluminescence) [19-23], this eventually leads to an efficient utilization of the solar spectrum. Furthermore, C-dots inhibited the recombination of the electron-hole pairs generated during photocatalysis [24].

The present work introduces an improved methodology to synthesize macro-mesoporous TiO_2 spheres (MMPT). All as-prepared samples were doped with C-dots, and their performance against degradation of an aqueous solution of Methylene blue (MB) dye under visible light irradiation was examined.

Schematic diagram of **Figure 1**(a-c) represents hierarchical C-Dots dispersed macro-mesoporous TiO_2 composites with (0.4 wt.%) of carbon explored an enhanced photocatalytic activity, while in the mechanism of TiO_2 photocatalytic activity for microorganism inactivation, water treatment and air purification dramatically presented in the **Figure 1**(d).

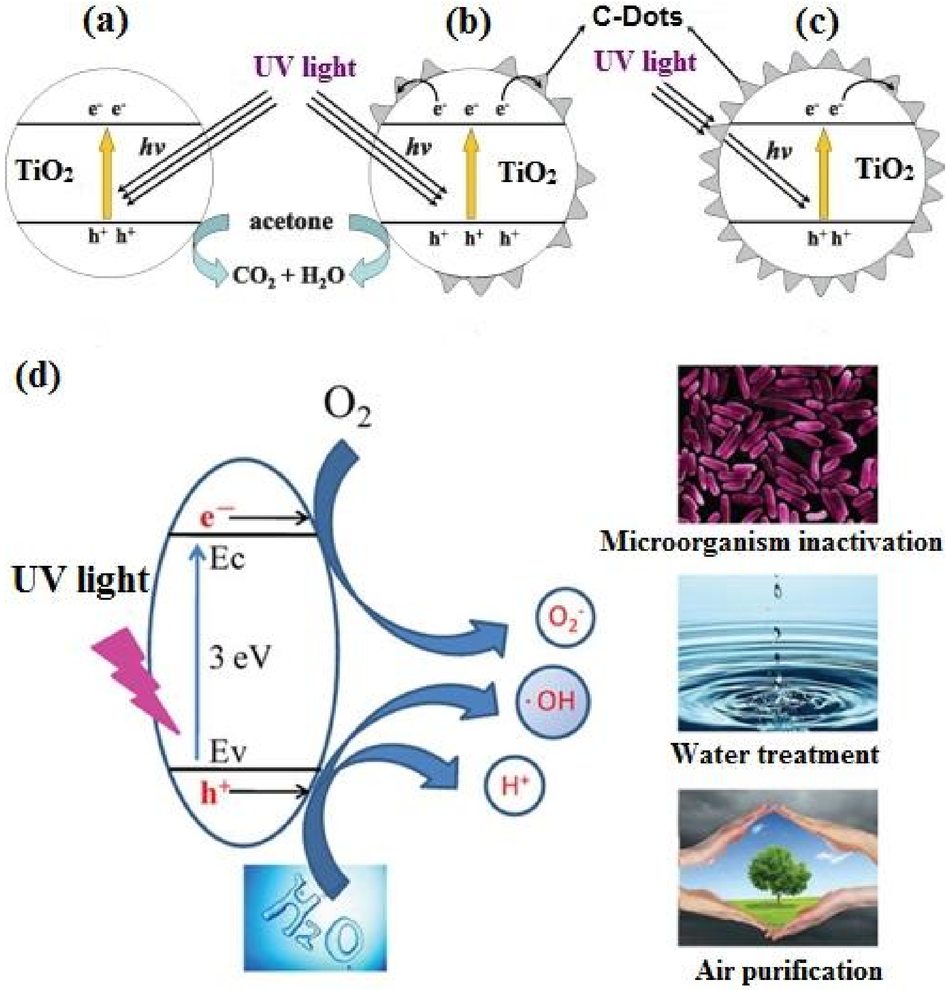

Figure 1, (a-c); The hierarchical C-dots dispersed macro-mesoporous TiO_2 composites with low loadings (0.4 wt.%) of carbon showed an enhanced photocatalytic activity in the photodegradation of acetone in air, and (d) the mechanism of TiO_2 photocatalytic activity for microorganism inactivation, water treatment and air purification

2. Experimental details

2.1 Materials

All chemicals used were of extra pure grade of 99.5%, purchased from Sigma Aldrich and were used as received without further purification.

2.2 Methods

2.2.1 Preparation of mixed macro-mesoporous TiO_2 nanospheres

MMPT spheres were prepared by a surfactant-free method, through assembly of TiO_2 nano-crystalline particles using ammonium citrate as a chemical linker [25]. In a typical procedure, (0.0015 mole) citric acid was mixed with (2 ml) deionized water DIW) and then (20 ml) Ammonia was added portion-wise to the mixture. Then the mixture was dipped directly into the ethanol solution of Titanium (IV) isopropoxide (6 ml of Titanium (IV) isopropoxide dissolved in (40 ml) of absolute ethanol). The mixed solution was stirred for 4 h and left to stand for overnight. The resulting white precipitate was then filtered, washed several times with DIW and ethanol and dried at 60 ° C for 8 h, Finally the powder was calcined at 500 ° C for 4 h to obtain pure anatase crystal structure. Four MMPT samples with different sizes were synthesized by controlling the concentration of ammonium hydroxide solution ($NH_3.H_2O$), 28%, 29%, 30% and 32%, the corresponding samples were named MMPT 28%, MMPT 29%, MMPT 30% and MMPT 32%, respectively.

2.2.2 Preparation of C-dots

C-dots were fabricated facilely by one-pot green method [26]. In a typical synthesis, (1.7 g) Ascorbic acid was dissolved in (100 ml) D.I. Water, followed by adding (0.2 g) copper (II) acetate. The mixture was then stirred for 10 min. at room temperature and then maintained at 90 ° C under stirring for 8 h. C-dots were obtained after centrifugation at 9000 rpm, then the precipitate was washed several times with DIW and dried at 80 ° C for 1 h.

2.2.3 Preparation of photocatalytic composites (C-dots@MMPT)

A typical amount of 0.8 g MMPT powder was dispersed in C-dots solution (0.6 g C-Dots dissolved in 50 ml DIW) with ultrasonic vibration for 45 min, the mixture was then dried in vacuum oven at 70 ° C for 6 h. The four composite samples were denoted C-Dots@MMPT 28%, C-dots@MMPT 29%, C-dots@MMPT 30% and C-Dots@MMPT 32%.

2.2.4 Photocatalytic degradation of MB dye

An aqueous suspension of MB dye (100 ml, with an initial concentration of 20 ppm) and photocatalyst prepared in the previous step (0.06 g) were placed in a beaker (250 ml). prior to irradiation, each suspension was magnetically stirred in dark for 2 h to get the adsorption-desorption equilibrium (between photocatalyst and dye), followed by visible light irradiation using 300 W halogen lamp fixed at a distance of about 10 cm. After a given time interval (20 min.) during the visible light irradiation, the suspension was filtered to separate the photocatalyst and the supernatant. The percentage of dye degradation was calculated as (C/C_0) where (C) was the concentration at each time interval and (C_0) was the initial concentration when the adsorption-desorption equilibrium is reached.

2.3 Spectroscopic characterization of materials

The crystal structure was verified by X-ray diffraction (XRD) on a Brucker axis D8 diffractometer with crystallographic data software Topas 2 utilizing Cu Kα (λ = 1.54060 Å) radiation operating at 40 kV and 40 mA. FTIR pattern was recorded using FTIR-4100 FT-IR Fourier-transform infrared Spectrometer. The UV-VIS absorption spectrum was recorded on a Perkin- Elmer lambda 950 UV-vis.-NIR spectrophotometer.

3. Results &Discussion

3.1 Morphology analysis by high resolution transmission electron microscopy (HR-TEM)

In **Figure 2** depicts the as-prepared photocomposite (C-dots decorated MMPT Nanosphere), and the chemical linkages between Titania nanosphere and the hydrophilic C-dots.

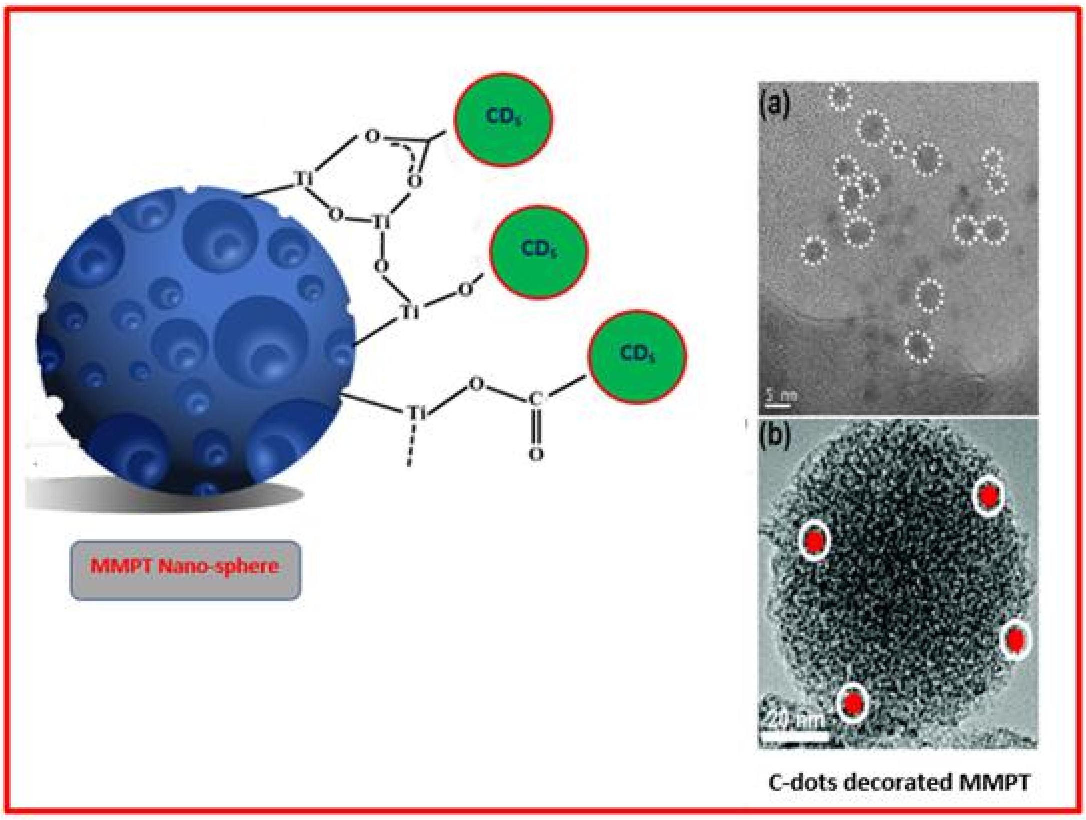

Figure 2; Schematic illustration of the as-prepared photocomposite (a) HR-TEM image of monodispersed C-dots with an average particle size ≈ 4 nm, and (b) C-dots decorated macro-mesoporous Titania nanosphere as displayed by 'white circle' in HR-TEM image

3.2 Purity and crystal structure

Nano-structure is examined by XRD analysis. **Figure 3** shows typical XRD patterns of MMPT 28% and MMPT 30% samples prepared via template-free method. The observed peaks of both samples are in good agreement with those of standard anatase TiO_2 (JCPDS card number 04-0477).

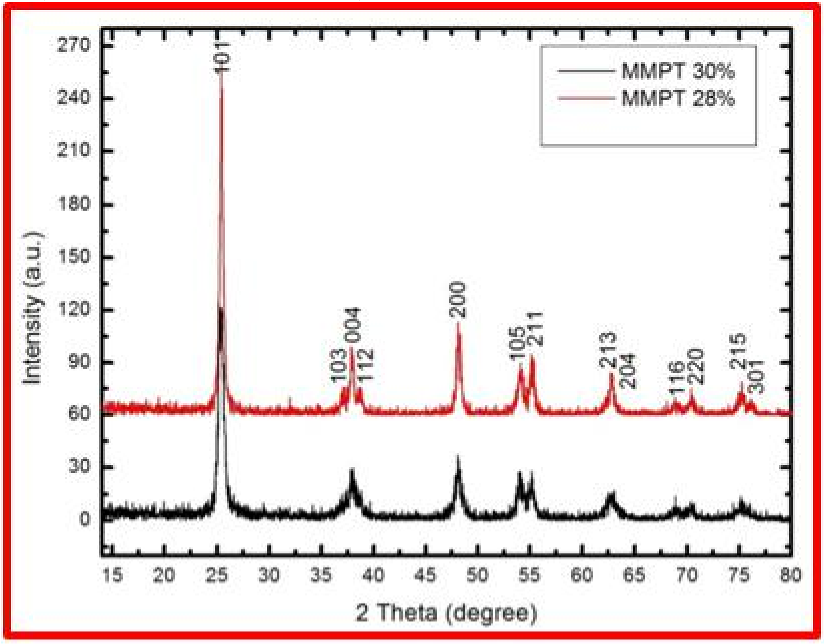

Figure 3; XRD pattern of MMPT 28% and MMPT 30% nanospheres calcined at 500 °C for 4 h

$$D = \frac{k\lambda}{\beta cos\theta}$$

Typical narrow peaks of Titania reveal the formation of TiO_2 nanospheres with relatively larger crystalline domain size compared with TiO_2 nanoparticles [27]. According to Debye-Scherrer equation (1), the particle size (D) based on the peak corresponding to (101 reflection) is found to be (41.3 nm for MMPT 28% and 51.7 nm for MMPT 30%) as shown in Table 1.

Where (D) is the particle size, (K) is the shape factor and has a value of about (0.9), (λ) is the wavelength of the x-ray radiation (1.54060 Ǻ for Cu-Kα), (β) is the full width at half maximum (FWHM) of the intensity and (θ) is the angle of diffraction.

Sample	2θ (degree)	Phase	FWHM (degree)	Particle size (nm)
MMPT 28%	25.4	Anatase	0.1968	41.3
MMPT 30%	25.4	Anatase	0.1574	51.7

Table 1. Particle size of both MMPT 28% and MMPT 30% nanoshperes

3.3 Optical properties of C-dots

UV-visible absorption spectrum of as-prepared C-dots are shown in the **Figure 4**, shows an absorption peak centered in the UV region nearly at 247 nm with a tail extending to the visible range revealing the formation of C-dots [28].

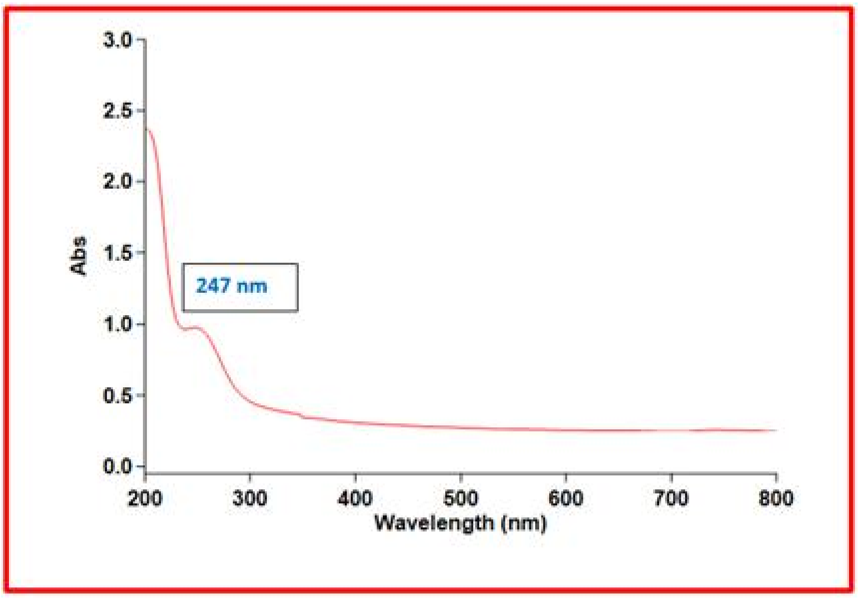

Figure 4; UV-Visible absorption spectrum of C-dots

To explore the optical properties of the as-prepared C-dots, Photoluminescence (PL) study was carried out at various excitation wavelengths. In agreement with previous literature reports, the as-prepared C-dots exhibit an excitation - dependent PL behavior. The as-prepared C-dots exhibit a clear up-converted and down-converted PL properties.

Figure 5, (a-b); reveals the up-conversion and down-conversion photoluminescence emission spectra of C-dots excited by short (270 nm) and long wavelength (600 nm) light and the excitation wavelengths were (540 nm) and (300 nm) respectively. This phenomenon could be attributed to a multiphoton active process [29].

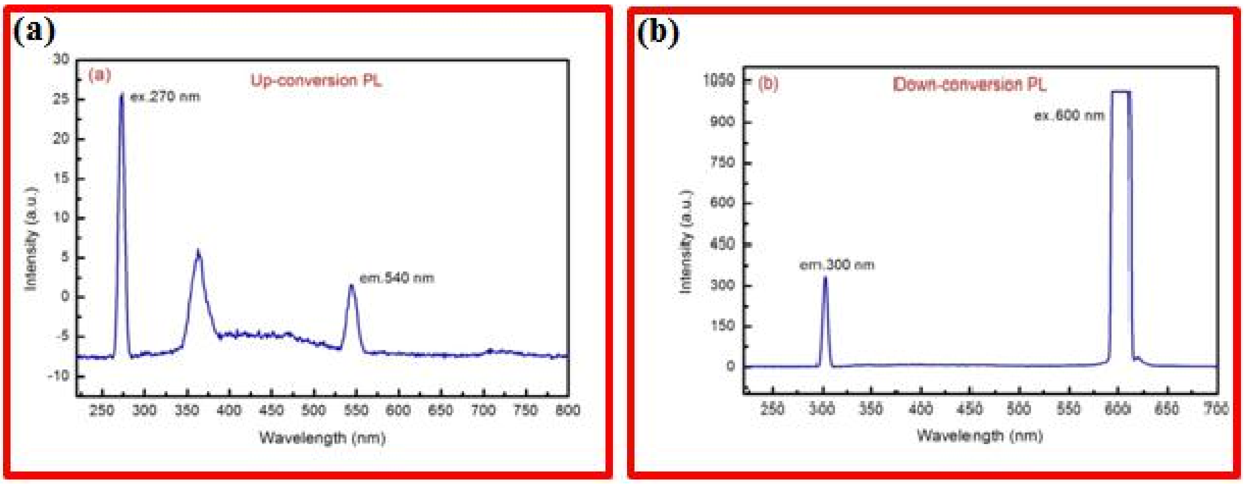

Figure 5; Photoluminescence (PL) properties of as- prepared C-dots, (a) Up-conversion PL spectrum of C-dots (λ_{ex} = 270 nm and λ_{em} = 540 nm), and (b) Down-conversion PL of as prepared c-dots (λ_{ex} = 600 nm and λ_{em} = 300 nm)

3.4 Surface bonding

FT-IR spectrum of as-prepared MMPT 28% and C-dots@MMPT 28% samples as shown in **Figure 6.** In fact, MMPT 28% the broad band centered at 550 cm^{-1} is likely due to Ti-O-Ti stretching vibrations within TiO_2 lattice, absorbance peak at 1630 cm^{-1} originates from -OH bending vibrations, while the peak at 2920 cm^{-1} reveals the presence of atmospheric CO_2 and finally the peak at 3439 cm^{-1} corresponds to -OH stretching vibrations [30].

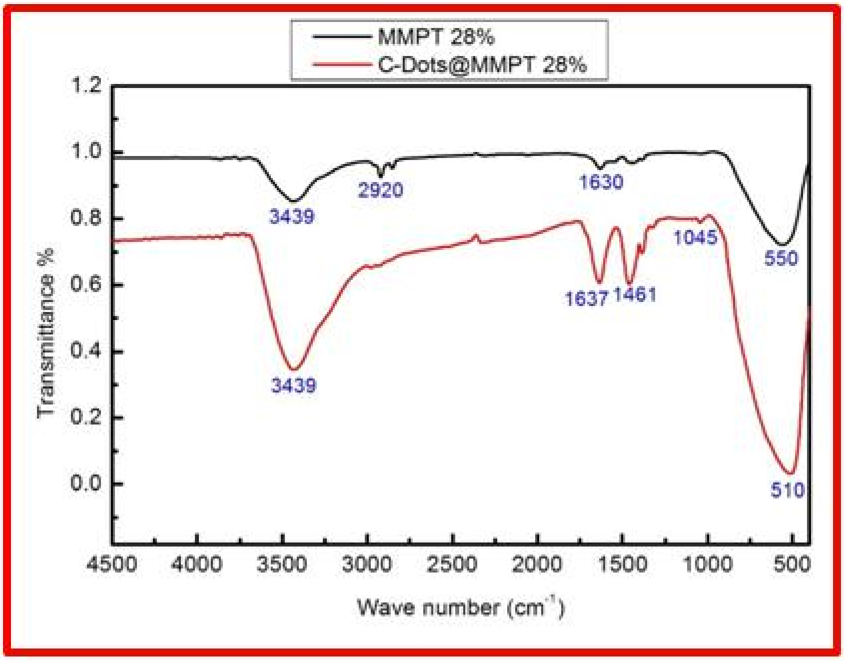

Figure 6; FT-IR spectrum of as-prepared MMPT 28% and C-dots@MMPT 28% samples

However, upon doping MMPT 28% with C-dots, another peak at 1045 cm^{-1} is observed and corresponds to Ti-O-C is bridging vibrations, indicating the physical adsorption of C-Dots on TiO_2 surface and the formation of C-dots@ MMPT 28% photocomposite.

3.5 Photocatalytic degradation of MB dye

A study of photocatalytic activity of as-prepared samples are performed by degrading fixed volume and concentration of MB dye under visible light irradiation using 300 W halogen lamp as a light source. Hence, in the **Figure 7** depicts the MB decomposition as a result of photocatalytic degradation under visible light illumination. During the reaction, the catalytic activity of C-dots@MMPT 28% sample deteriorated, such result revealed that the formation of the MMPT sample with very small particle sizes, decreased the number of pores and facilitated the formation of large aggregates. The photocatalytic activity of C-dots@MMPT 29% was slightly better than C-dots@MMPT 32%, which could be attributed to the relatively higher surface area of C-Dots@MMPT 29% sample.

While C-dots@MMPT 30% sample showed the highest photocatalytic activity among all samples due to the relatively higher surface area than C-dots@MMPT 32% sample and the better particle sizes than C-dots@MMPT 29% and C-dots@MMPT 28% samples, promoting the formation for the relatively increased number of pores (macropores and mesopores) which facilitated the diffusion of reactants , provided a large number of readily accessible active sites and fostered the light transfer into the inner surface of the photocatalyst.

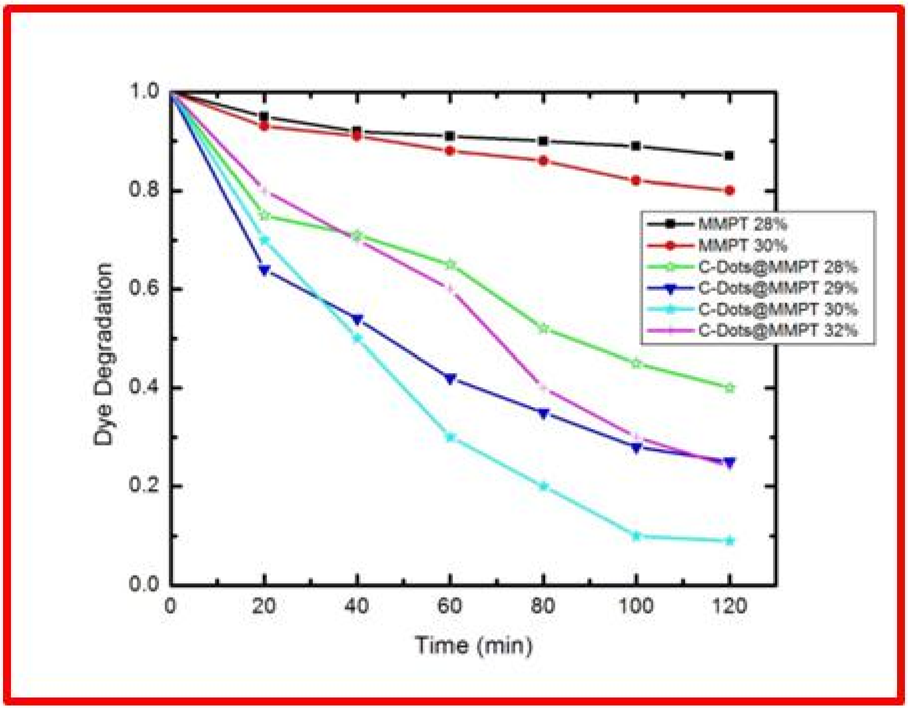

Figure 7; Photocatalytic efficiency of the as-prepared samples under visible light irradiation after adsorption-desorption equilibrium is reached

4. Conclusion

C-dots have been used to improve the photocatalytic efficacy of TiO_2 nanospheres prepared via a template-free methodology using Ammonium Citrate crystals as a chemical linker, in a trial to develop cost-effective technology for effective waste water recycling.

C-dots@MMPT 30% sample showed superior photocatalytic activity due to the combination and the benefits of a relatively high surface area of mesoporosity with the readily accessible diffusion pathways of microporous channels. Our novel findings could provide a new route to support current wastewater treatment modules, in terms of improving water quality and could complement ongoing efforts in developing treatment systems.

Acknowledgements

The authors acknowledge the financial support of Science and Technology Development Fund (STDF), researchers and operators form Nanotechnology department, Nile University, Egypt. Also, Dr. Kaushik Pal also grateful to Dean (Research) giving opportunity at Nanotechnology Department from Bharath Institute for Higher Education and Research (BIHER), Bharath University, Chennai (India).

Conflict of Interest

All the authors have declared that there is no competing financial interest in this contribution.

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Based on his outstanding research capabilities, experimental skills and knowledge, he was awarded many prestigious young fellowship awards like DAAD scholarship and Erasmus$^+$ Credit Mobility fellowship at Oviedo University in Spain for 6 Months to complete his Master thesis project entitled "Recyclable nanostructured composites for effective waste water treatment. Most recently he is coordinating International Conferences on materials science and nanotechnology with his Co-Supervisor Prof. Dr. Kaushik Pal.