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# Photocatalytic Degradation of Methyl Red using $CeO_2$, $TiO_2$ and $CeO_2$-$TiO_2$ Nanocomposite

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## Abstract

Nanosized ceria ($CeO_2$), titania ($TiO_2$) and ceria- titania ($CeO_2$-$TiO_2$) have been synthesized by microwave method and studied its photocatalytic activity for methyl red degradation under UV-Visible type radiation. Phase formation study was carried out by using x-ray diffraction technique and it's reveals that ceria ($CeO_2$) properly supported on the surface of titania ($TiO_2$). Nano sized ceria, titania and ceria- titania nanocomposite were confirmed by transmission electron microscopy technique. The particle size of the $CeO_2$, $TiO_2$ and their nanocomposite is in the range of 10-15 nm. Photocatalytic activity of the $CeO_2$-$TiO_2$ composite was improved as compared to $CeO_2$ and $TiO_2$. The enhanced photocatalytic activity is attributed to the increased visible light absorption and improved adsorption of the dye on the surface of the composite catalyst.

**Keywords:** Ceria, titania, nanocomposite, photocatalytic degradation, methyl red

## INTRODUCTION

Photocatalytic reactions at the surface of titanium dioxide have been attracting much attention in view of their practical applications to environmental cleaning such as self cleaning of tiles, glasses and windows. Titanium dioxide represents an effective photocatalyst for water and air purification and for self-cleaning surfaces. Additionally, it can be used as antibacterial agent because of strong oxidation activity and superhydrophilicity [1]. Strong oxidation and reduction power of photoexcited titanium dioxide ($TiO_2$) was realized from the discovery of Honda-Fujishima effect [2]. Photocatalytic degradation using solar radiation is a potential technique for the removal of the organic contaminants from water. Photocatalysts like $TiO_2$, CdS, $WO_3$, $ZrO_2$ and $V_2O_5$ have been investigated for the treatment of these effluents with the aim of mineralizing the dyes completely [3, 4]. When photocatalysts are dispersed on other oxides, its surface area increases and it can lead to enhanced photocatalytic activity. The increased activity was attributed to the increased surface acidity of the mixed oxide.

$TiO_2$ is a high band gap semiconductor that is transparent to visible light and has excellent optical transmittance. The American Food and Drug Administration (FDA) has approved the use in human food, drugs and cosmetics and compounded in food contact materials such as cutting board and other surfaces in contact with unprotected food [5]. For photovoltaic applications, $TiO_2$ photo-catalyst is effective in solar light or light from visible region of the solar spectrum need to be developed as future generation photo-catalytic material [6]. $TiO_2$ has high refractive index and good insulating properties and as a result it is widely used as protective layer for very large scale integrated circuits and photovoltaic cells as well as antireflective coatings, gas sensors, electro-chromatic displays and planar waveguides. Similarly, $CeO_2$ is reported to be a predominantly ionic conductor, exhibits n-type conductivity under certain conditions. Cerium dioxide is an inexpensive and relatively harmless material that presents several characteristics that could be potentially advantageous for photocatalytic applications.

$TiO_2$ and $CeO_2$ nanomaterials reveal that they are promising materials for optoelectronic devices such as solar cells, conductive layers, and transistors due to its excellent electrical and optical properties. $CeO_2$ and $TiO_2$ are a well known photocatalyst having a suitable bandgap and works under UV illumination [7-8]. The observed photocatalytic activity of the composite was correlated with the proper microstructure of this composite and the isolation function of the supporting layer. In the present work, we report the synthesis, characterization and photocatalytic activity of $CeO_2$, $TiO_2$ and $CeO_2$-$TiO_2$ novel photocatalytic system. It is expected that a combination of $CeO_2$ and $TiO_2$ can show synergistic effect in improving the optical absorption property resulting in enhanced photocatalytic activity. With this aim, $CeO_2$, $TiO_2$ and $CeO_2$-$TiO_2$ nanocomposite has been synthesized and studied its photocatalytic activity for the degradation of methyl red dyes solution under UV-Visible light type irradiation.

## EXPERIMENTAL DETAILS

Ceria ($CeO_2$) and titania ($TiO_2$) has been synthesized by microwave method. All the chemicals are of analytical grade Cerium chloride is dissolved in Distilled water. After above solution is taken in 250 ml Beaker and 1M ammonia solution was added dropwise with constant stirring till precipitation completed and gel is formed. Then the solution was kept in (800 W EO-77 HORNO ELECTRICO, ORBIT) microwave oven at 353K for 30 min. The resulting gel was filtered through Whatmann filter paper No. 40 then it is dried at 353K for 24 Hrs in order to remove moisture or water molecule present in it. Then the precipitate obtained collected in silica crucible and calcination was carried out at 773K for 2 hrs finally ash colored tin oxide nanoparticles were formed. Similarly Titanium oxide has been synthesized. Also, titania-Ceria nanocomposite was prepared by sol–gel hydrolysis. X-ray diffractometer (Philips model PW-1710) was used to identify the crystalline nature of the samples using CuKα radiation. FT-IR spectra were recorded in a Perkin-Elmer spectrometer using KBr pellets. Average grain size was measured using a scanning electron microscope (SEM JSM-JEOL 6360). Particle size was measured using a transmission electron microscope (TEM) (Philips, CM200, operating voltages 20–200 kV). The diffuse reflectance UV–vis (DR-UV–vis) spectra of the powders were recorded using a Jasco (model V-670) spectrophotometer equipped with an integrating sphere accessory. Photocatalytic reaction was conducted in a 100 ml Pyrex glass vessel containing 50 ml of the aqueous methyl red dye solution (concentration: 50 ppm) having 50 mg of catalyst suspended in it. The UV-Visible type radiation was used. After every one hour of irradiation, 2 ml of the aliquot was withdrawn, centrifuged and quantitative determination was carried out using a spectrophotometer by measuring its absorbance at λ = 592, 411 and 330nm.

## RESULTS AND DISCUSSION

### XRD studies

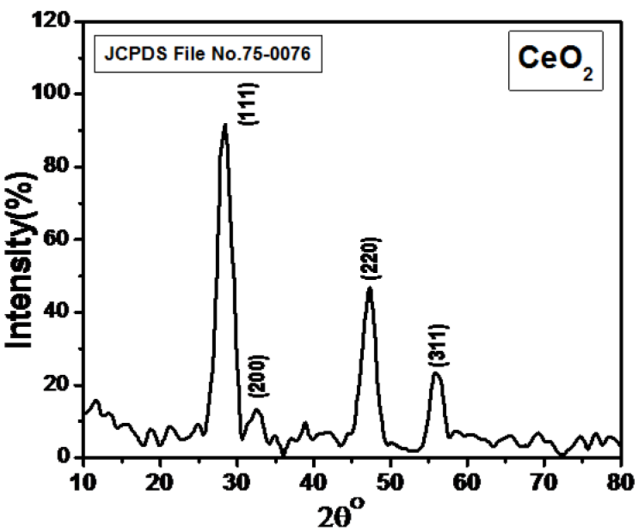


**Figure 1.** XRD Pattern of $CeO_2$

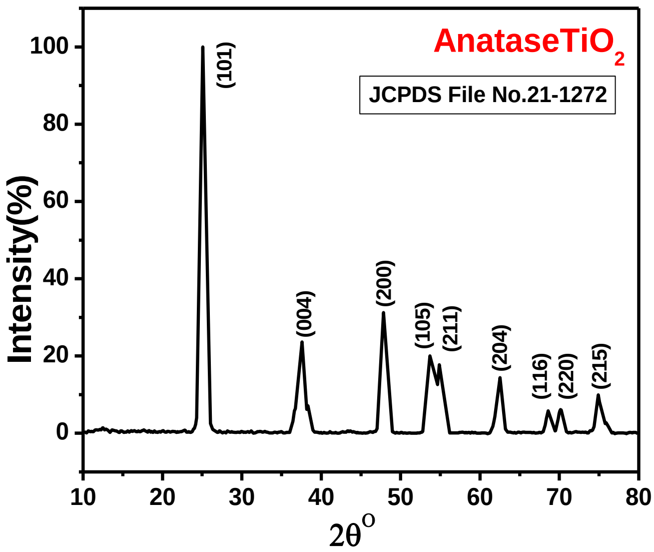


**Figure 2.** XRD Pattern of $TiO_2$

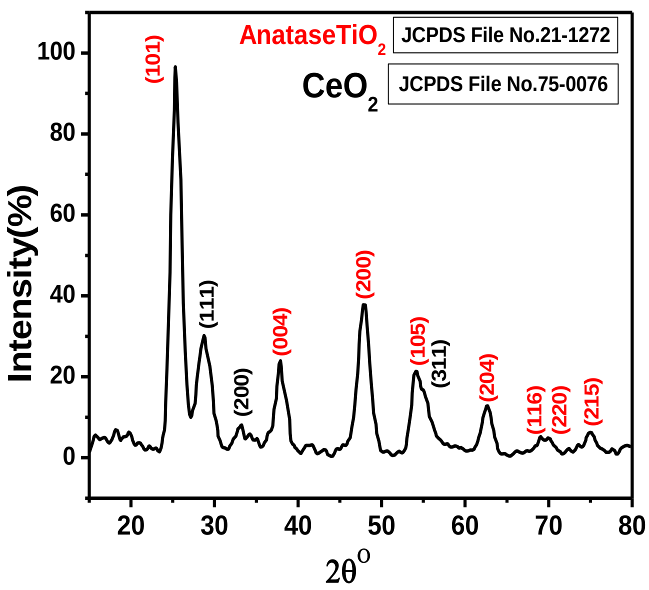


**Figure 3.** XRD Pattern of $CeO_2$-$TiO_2$

**Fig. 1-3** shows the powder X-ray diffraction (XRD) patterns of pure ceria, titania and the composites $CeO_2$ on $TiO_2$ nanoparticles. The diffraction pattern of anatase $TiO_2$ shows peaks corresponding to planes (111), (004), (200) (105), (211), (204), (116), (220) and (215) confirming the formation of anatase $TiO_2$ (JCPDS Patterns No. 21-1272). Diffraction peaks corresponding to planes (111), (200) (220) and (311) of $CeO_2$ (JCPDS Patterns No. 75-0076) besides that of $TiO_2$, are seen in the sample indicating the biphasic nature of the samples.

**FT-IR studies**

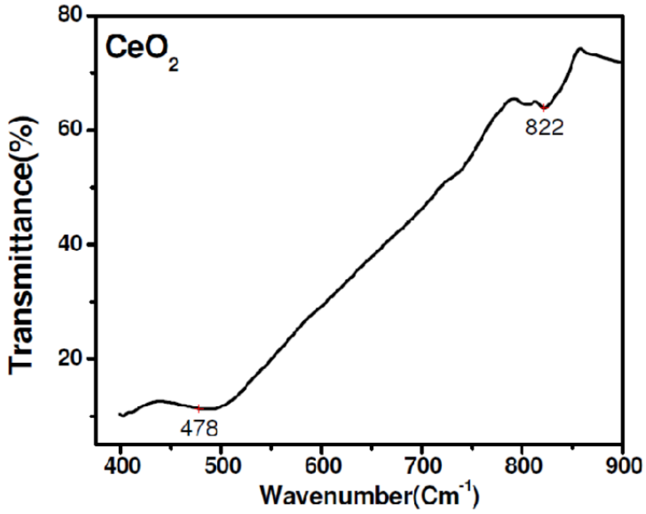


**Figure 4.** FT-IR Spectra of $CeO_2$

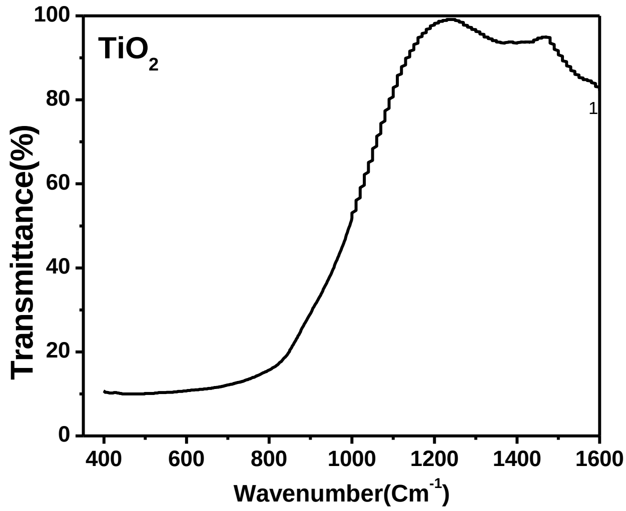


**Figure 5.** FT-IR Spectra of $TiO_2$

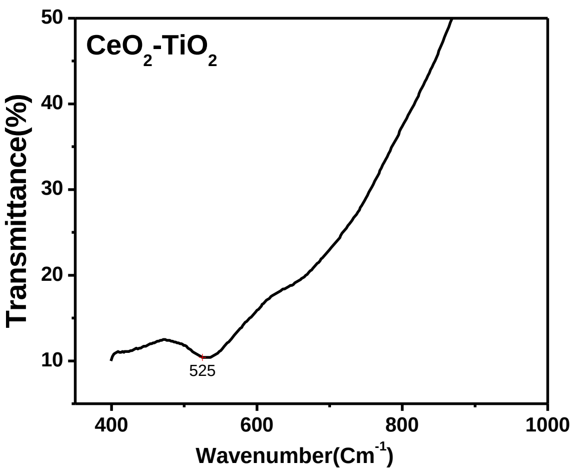


**Figure 6.** FT-IR Spectra of $CeO_2$-$TiO_2$

**Fig.4-6.** shows the typical FT-IR spectra of ceria ($CeO_2$), titania ($TiO_2$) and ceria- titania ($CeO_2$-$TiO_2$) in the spectral region 400-1000 $cm^{-1}$ sintered at 773K. The spectra have been used to locate the band positions. The lower frequency band is 478 $cm^{-1}$ in $CeO_2$. Also, the higher frequency band is 822 $cm^{-1}$ in $CeO_2$ and 609 $cm^{-1}$ in $TiO_2$. The absorption bands observed within this range is an indication of the formation of single phase metal oxides [9]. But ceria- titania nanocomposite lowers the 525 $cm^{-1}$ values of frequency band due to the different Ti-O and Ce-O starching frequencies in same samples and this is clearly observed in the figure.

**Scanning Electron Microscopy**

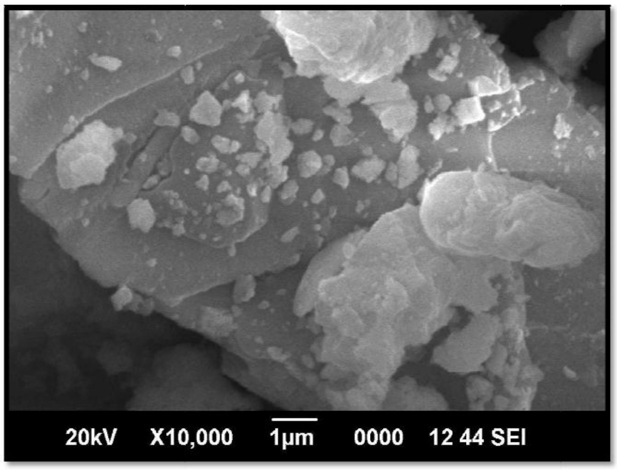


**Figure 7.** SEM Image of $CeO_2$

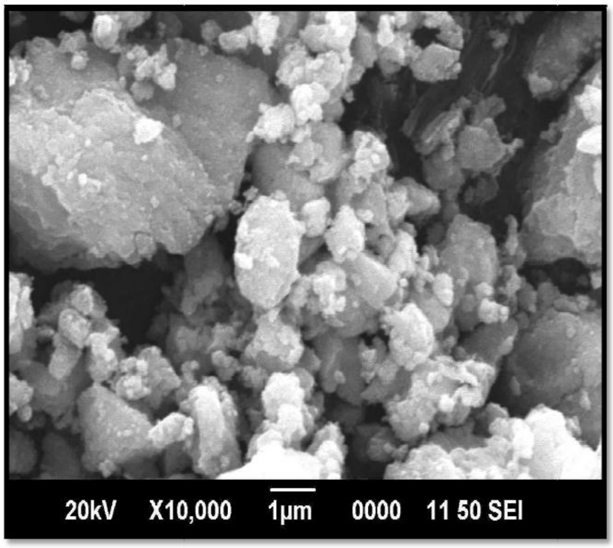


**Figure 8.** SEM Image of $TiO_2$

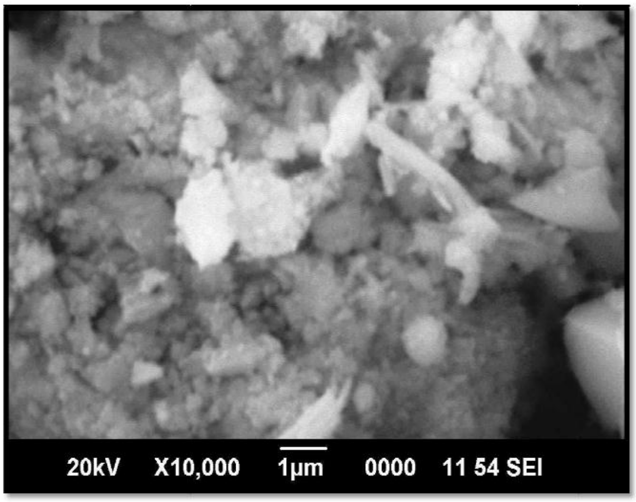


**Figure 9.** SEM Image of $CeO_2$-$TiO_2$

The SEM images of $CeO_2$, $TiO_2$ and $CeO_2$-$TiO_2$ are shown in the **Fig.7-9.** It is observed that the average grain size is smaller than 0.05μm for all the compositions. It can be seen that the grains and crystallinity both uniformly observed in ceria and titania. But SEM image of $CeO_2$-$TiO_2$ nanocomposite significantly indicates that the ceria is directly dispersed on the surface of titania.

**TEM analysis**

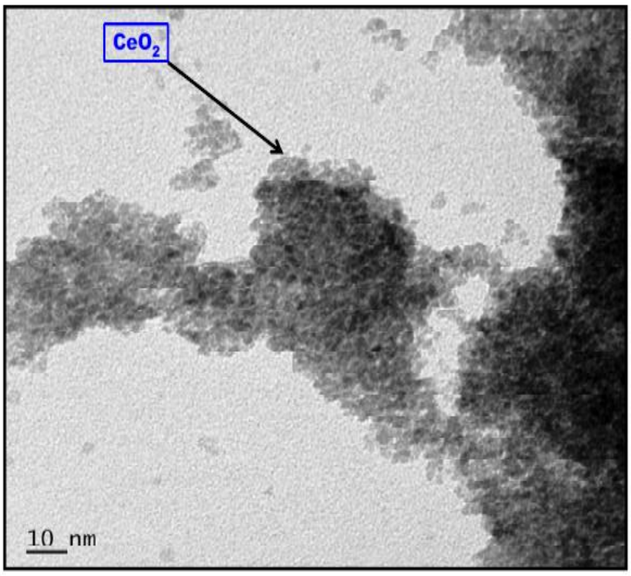


**Figure 10.** TEM Image of $CeO_2$

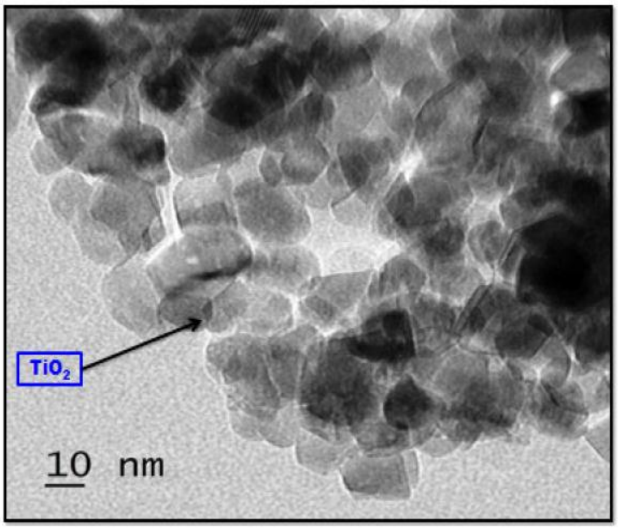


**Figure 11.** TEM Image of $TiO_2$

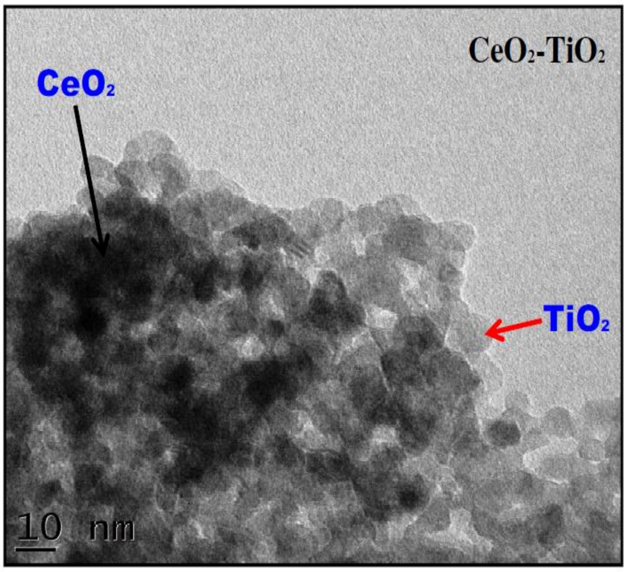


**Figure 12.** TEM Image of $CeO_2$-$TiO_2$

**Fig. 10-12** depicts the transmission electron micrographs of $CeO_2$, $TiO_2$ and $CeO_2$-$TiO_2$ nanocomposite samples. It is evident from **Fig. 10-11** that the average particle size of $CeO_2$ and $TiO_2$ is around 10-15 nm. **Fig. 12** clearly shows the presence of a dispersed phase of $CeO_2$ on $TiO_2$.

**UV–vis diffuse reflectance study**

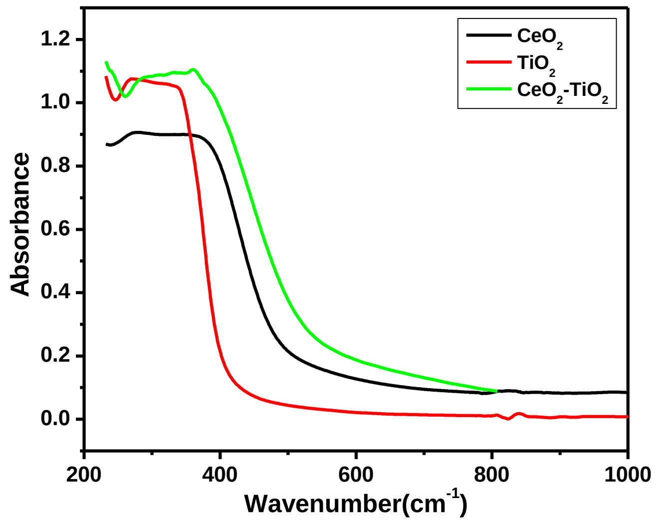


**Figure 13.** Absorption study of (A) $CeO_2$ (B) $TiO_2$ and (C) $CeO_2$-$TiO_2$

UV–vis diffuse reflectance spectra of $CeO_2$, $TiO_2$ and $CeO_2$-$TiO_2$ nanocomposite are presented in **Fig. 13.** It can be seen from the figure that there is hardly any shift for the absorption edges of the coated sample compared to that of single phase $CeO_2$ and $TiO_2$. But, when compared with single phase $TiO_2$, a large red shift of the absorption edge is seen for the composite sample. The large red shift observed for the $CeO_2$-$TiO_2$ powders can be due to the mixing effect of the band gaps of the two semiconductors in the composite sample and due to the interaction of the two semiconductors at the interface, introducing defect levels [10].

**Photocatalytic study**

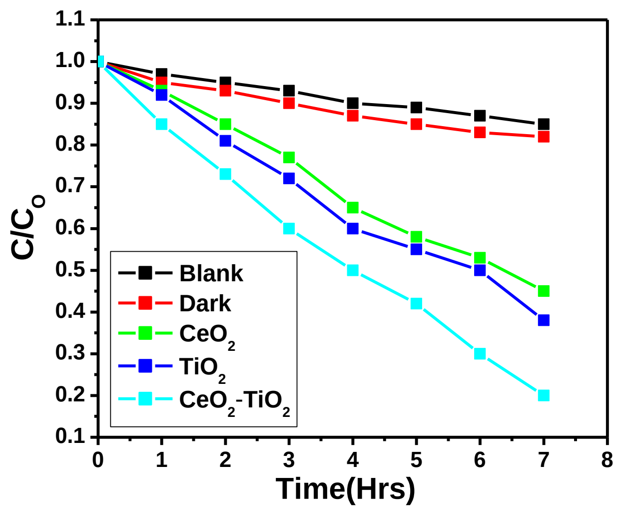


**Figure 14.** Photocatlytic study of (A) $CeO_2$ (B) $TiO_2$ and (C) $CeO_2$-$TiO_2$

Photocatalytic activity of $CeO_2$, $TiO_2$ and $CeO_2$-$TiO_2$ nanocomposite for the degradation of methyl red under UV-Visible type irradiation is shown in **Fig 14.** There is hardly any change in the concentration of the dye when the solution is irradiated in the absence of catalyst. Under dark conditions, a slight change in the concentration of the dye is observed over a period of 7 hours due to its adsorption on the catalyst's surface ($C/C_0=0.89$). It can be seen from the figure that the photocatalytic activity increases in $CeO_2$-$TiO_2$ nanocomposite as compared to $CeO_2$ and $TiO_2$ and the catalyst degrades the dye almost completely in 7 hours. The enhanced photocatalytic activity of the composites can be attributed to a combination of factors such as increased optical absorption and increased adsorption of the dyes on the surface of the catalyst. When the composite sample is exposed to UV-Visible type irradiation, both $CeO_2$ and $TiO_2$ can get excited leading to enhanced photocatalytic activity. The enhanced adsorption of the dye on the composite sample can be attributed to the increased surface acidity. As methyl red is a basic dye [11], an enhanced adsorption of the dyes takes place on the acidic surface of the composites [12]. Another reason for the UV-visible light activity of the composite catalyst can be due to the photobleaching process [13].

## CONCLUSIONS

Nanosized ceria ($CeO_2$), titania ($TiO_2$) and ceria-titania ($CeO_2$-$TiO_2$) nanocomposite was successful synthesize by using microwave method. This method is cost-effective and environmentally friendly because of no by-product effluents. X-ray diffraction technique reveals that ceria ($CeO_2$) properly supported on the surface of titania ($TiO_2$) and formation of single phase metal oxides. Nano sized ceria, titania and ceria-titania nanocomposite were confirmed by transmission electron microscopy technique. The particle size of the single oxide like $CeO_2$, $TiO_2$ and their nano composite is in the range of 10-15 nm. The photocatalytic activities of the prepared nanoparticles were measured by the photodegradation of methyl red under UV-Visible type irradiation. The results indicated that the composites exhibit a synergistic effect in enhancing the photodegradation of methyl red.

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