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# CTAB Assisted Synthesis and Characterization of Cobalt Doped Titania Nano Material For Degradation of Orange II Under Visible Light Irradiation.

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**ABSTRACT:** The present research work describes about the synthesis of mesoporous Cobalt doped  $TiO_2$ nanocrystalline material assisted by Cetyltrimethyl ammonium bromide, a cationic conventional surfactant through solgel method: 0.5wt. % Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant). The synthesized catalysts were characterized by X-Ray Diffraction (XRD), Ultraviolet-visible Diffuse Reflectance Spectroscopy (UV-Vis DRS), X-ray Photoelectron Spectroscopy (XPS), Field Emission Scanning Electron Microscopy (FE-SEM), Fourier Transform Infrared Spectroscopic Studies (FT-IR), High Resolution Transmission Electron Microscopy (HR-TEM) and Brunauer-Emmett-Teller (BET) Analysis. XRD studies have shown that all catalysts were reported in anatase phase where the crystallite sizes were found to be 14.1 nm and the highest intensity peak was observed at  $2\theta=25.3^{\circ}$  for 0.5wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant). UV-DRS studies have shown that doping of cobalt ions lead to an increase in the absorption edge wavelength more towards visible light (red shift) and a decrease in the band gap energy of 0.5 eV was observed. From XPS studies the oxidation state of Cobalt was found to be in +2 oxidation state. FE SEM images have shown prominent change in the morphology of the particles where the nanoparticles were found to be irregular and without agglomeration. From FT-IR studies the stretching frequencies showed that the entry of  $Co^{2+}$  into TiO<sub>2</sub> lattice was substituitional. TEM images indicated particle size of  $Co^{2+}/TiO_2$ -(with CTAB surfactant) with 12.3-13.9 nm and 16.1 nm  $Co^{2+}/TiO_2$  catalyst (without surfactant). BET analysis for  $Co^{2+}/TiO_2$ -(with CTAB surfactant) confirmed the particle size with increase in surface area of 32 (m<sup>2</sup>/g). CTAB played a vital role during the synthesis and resulted in the formation of nanoparticles with reduced size. Evaluation of photocatalytic activity of the synthesized nanomaterials was performed with photo degradation of Orange II a model azo dye pollutant under visible light irradiation. The synthesized catalyst was proved to be effective and has shown higher photocatalytic activity under visible light irradiation. The optimum conditions for the degradation of Orange II dye solution with  $Co^{2+}/TiO_2$  (with CTAB surfactant) were found as 0.5 wt.% dopant concentration at (pH-5), (0.1g) catalyst dosage and for (10 mg  $\cdot$  L<sup>-1</sup>) initial dye concentration. Presence of CTAB during the synthesis of the catalyst played a significant role in the formation of nano particles with small grain size, high crystallinity, and high specific surface area. The catalysts to exhibit high photocatalytic activity could be attributed to the synergistic effect of decrease in the band gap energy due to doping of cobalt into titania matrix and by employing CTAB surfactant template method.

KEYWORDS: Cobalt doped titania nanomaterials, CTAB surfactant, Sol-gel method, Photocatalysis, Orange II.



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### **I.INTRODUCTION**

In recent years photocatalytic oxidation processes with titanium dioxide  $(TiO_2)$  as photocatalyst have gained immense research interest as an effective wastewater purification method because of its efficiency in decomposing and mineralizing the hazardous organic pollutants. Among several photoactive semiconductors, TiO<sub>2</sub> has proven to be most suitable in different media for wide spread environmental applications. It is more advantageous to consider  $TiO_2$  since it is stable with respect to photo and chemical corrosion; biologically and chemically inert, inexpensive, insoluble under any drastic conditions and non-toxic [1]. Although  $TiO_2$  is superior to other semiconductors for many practical uses, some defects limit its photo catalytic activity [2, 3] among which the important drawbacks are:  $TiO_2$  has a high band gap ( $E_{b\sigma}$  = 3.2 eV), and it can be excited only by UV light ( $\lambda < 387$  nm). It is known that only 4-5% of the overall solar spectrum reaching the surface of the earth is ultraviolet, which is not sufficient to achieve significant photo degradation in short time. The high rate of electron-hole recombination within nano seconds at  $TiO_2$  particles results in a low efficiency of Photocatalysis. The photocatalytic activity of titania can be improved by decrease in grain size, increasing surface area, sensitization using dye molecules and doping with metals and non-metals [4-7]. The advantage of doping the metal ions into TiO<sub>2</sub> is the temporary trapping of the photo generated charge carriers by the dopant and the inhibition of their recombination during migration from inside of the material to the surface. From the literature very few investigations were reported on doping of Cobalt into titania by adopting various methods [8]. We preferred doping of Co (II) into the titania matrix since it was a good electron trap and can be used as an efficient photocatalyst. It was also associated with ferromagnetism. Recently surfactants were also widely used in sol-gel reactions along with its wide spread applications in pharmaceutical industries etc. The properties of surfactants vary according to the functional groups that are attached. Hence very slight modification at the molecular structure of surfactants changes their morphology of structures [9-12]. Selecting a suitable surfactant was an important parameter to improve the photocatalytic activity of the catalyst. So far no one has reported on the synthesis of Cobalt doped titania nano material assisted by Cetyltrimethyl ammonium bromide surfactant through sol-gel method hence this work was carried out to synthesize  $Co^{2+}/TiO_2$  nanomaterial by using this surfactant template method. Our prime focus is to study the influence of the Cetyltrimethyl ammonium bromide on the synthesis of the Cobalt doped titania nanoparticles. Sol-gel method was one of the most versatile technique generally used for the synthesis of metal-doped nanocrystalline titania. We preferred Sol-gel process since it was more advantageous over other conventional methods. It possesses good homogeneity hence preferred for synthesizing nano materials. Surfactants are amphiphilic substances which exhibits a double affinity. Surfactants constitute two different components like polar hydrophilic and non-polar hydrophobic characteristics in the same molecule. Cetyltrimethyl ammonium bromide with chemical formula  $C_{19}H_{42}NBr$  and its molecular weight is 364.46 g/mol. It was a cationic conventional surfactant and abbreviated as CTAB. As a consequence, they are mostly used as bactericide, as positively charged substance which is able to adsorb on negatively charged substrates to produce antistatic and hydrophobant effect and of great commercial importance such as in corrosion inhibition. Among the azo dyes Orange II was considered as a model compound for oxidative degradation studies and it has been investigated extensively on different catalysts [13-15]. Orange II azo dye has been widely used in weaving, dying, tanning and paper industries and has wide environmental effects [16]. It possess high chemical stability, highly toxic in nature resists biodegradation and persists in environment for longer period. Jo Ho Kim et al., [17] studied the photocatalytic activity of the  $TiO_2$  catalyst samples by using Orange II under UV light irradiation. The photocatalytic efficiency of the catalyst was estimated by carrying out photocatalytic degradation with Orange II as a model dye azo pollutant under visible light irradiation. Optimum conditions of various parameters like dopant concentration, pH, catalytic dosage and initial dye pollutants concentration were studied thoroughly.

### **II. MATERIALS AND EXPERIMENTAL METHODS**

**II.I. Materials required:** Titanium tetra-n-butoxide (Ti (O-Bu)  $_4$ ) and Cobalt nitrate obtained from E.Merck (Germany) were considered as precursors for Titanium and Cobalt for synthesizing Co<sup>2+</sup>/TiO<sub>2</sub> photocatalysts. Orange II was used as model dye pollutant (India, analytical grade) for carrying out photocatalytic degradation studies. Cetyltrimethyl ammonium bromide obtained from Sigma Aldrich (Germany) and used as surfactant for synthesis of



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 $Co^{2+}/TiO_2$  (with CTAB surfactant) catalysts. All the chemicals used in this work were of analytical grade. De ionized water was used throughout.

**II.II. Synthesis of Cobalt doped TiO<sub>2</sub> by surfactant assisted sol-gel method:** For the synthesis of  $Co^{2+}/TiO_2$ -(with CTAB surfactant), Solution I was prepared by considering initially 21.0 mL of titanium tetra-butoxide was dissolved in 40.0 mL of absolute ethanol (100%) and stirred continuously for 10 min. To it 3.0 mL of Nitric acid was added drop wise and stirring was continued for 30 min. Solution II was prepared by considering 40.0 mL of absolute ethanol with 0.01475 g of cobalt nitrate (0.5wt. %) dissolved in 7.1 mL of water. To it (25mL of 0.05M) Cetyltrimethyl ammonium bromide (CTAB) surfactant solution was added and stirred vigorously for 30 min. Solution II was added to Solution I slowly with continuous stirring. Ammonium was added to maintain pH around 8. The resulting solution was vigorously stirred for 2 h until the formation of the gel was obtained. The gel was aged at 25°C for 48 h. Later gel formed was dried at 110°C in an oven for 24 h.

The catalyst was calcined at 450°C in a furnace for 4 h. The synthesis of the catalyst  $Co^{2+}/TiO_2$ -(with CTAB surfactant) procedure has been represented in Fig.1. Cobalt doped TiO<sub>2</sub> (without surfactant with required wt. % ranging from (0.25, 0. 5, 0.75 and 1.0) was also prepared by adopting the similar procedure but without adding the CTAB surfactant. The powdered catalysts were finely ground. The synthesized catalysts were characterized for XRD analysis, UV-vis. DRS, XPS, SEM, TEM and FT-IR studies. Later photocatalytic degradation studies were carried out by degradation of Orange II dye in the presence of visible light irradiation.



Fig.1. Schematic representation of synthesis of the catalyst: 0.5wt. % Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant).



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**II.III. Characterization of Cobalt doped titania nano materials by various techniques**: The synthesized  $Co^{2+}/TiO_2$  catalysts were characterized by the most advanced analytical techniques. XRD analysis was recorded with a Bruker AXS D8 advance diffractometer at room temperature with a copper (K $\alpha$ ) anode material of wavelength ( $\lambda$ ) 1.5406 A°, and carbon monochromator was used. Varian, carry 5000 UV–Vis spectrophotometer was used for the UV–Visible absorption spectroscopic analysis of the catalysts. For XPS analysis of the catalysts Auger Electron Spectroscopy (AES) module PHI 5000 Versa Prob II, was employed. JEOL Model JSM - 6390LV was used for carrying out SEM analysis of the samples. For the infrared spectra of the synthesized samples Thermo Nicolet Nexus 670 Spectrometer, with resolution of 4 cm<sup>-1</sup> in KBr pellets, was used. JEOL/JEM 2100, operated at 200 kV as accelerating was employed for TEM measurements. From the Brunauer-Emmett-Teller (BET) analysis surface area was determined from the N<sub>2</sub> adsorption-desorption isotherm at 77.3 K and surface area (A<sub>BET</sub>), pore volume (V<sub>p</sub>) was analyzed by using a Autosorb I; Quantachrome Corp. system. UV-Vis spectrophotometer, Milton Roy Spectronic 1201, was used for the quantitative determination of Orange II. Digital pH meter model 111E, EI was used for determining pH variations.

**II.IV. Photocatalytic activity of the catalyst - Degradation of Orange II:** In order to determine the photocatalytic efficiency of the  $Co^{2+}/TiO_2$  (with CTAB surfactant) experiments were carried with photocatalytic degradation of Orange II dye in the presence of visible light in the photo catalytic reactor. The description regarding the photocatalytic set up was given elsewhere [18]. Required amount (0.05-0.3g) of the catalyst was added to aqueous Orange II dye solution taken in 150 mL of Pyrex glass vessel where stirring was continued for 45 min in the dark. UV filtered Osram high pressure mercury vapour lamp with power 400W and 35000 lum with cut off filters were used for carrying out the degradation under visible light conditions. The  $\lambda$ max of Orange II dye solution was measured at 484 nm by using Milton –Roy Spectronic 1201 UV-visible spectrophotometer. The percentage degradation of the Orange II was calculated by measuring the absorbance of dye solution as =  $(A_0 - A_t) / A_0 \ge 100\%$ , Where  $A_0 =$  initial absorbance of Orange II dye solution at time t.

### **III. RESULTS AND DISCUSSION**

**III.I. X-Ray diffraction studies:** The crystal structure and phase characterization of all  $Co^{2+}/TiO_2$  catalysts were studied by X-Ray diffraction studies. The XRD patterns of (1) pure  $Co^{2+}/TiO_2$  (without surfactant) (2) 0.25wt. %  $Co^{2+}/TiO_2$  (with CTAB surfactant) (3) 0.75wt. %  $Co^{2+}/TiO_2$  (with CTAB surfactant) (4) 0.5wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant) were represented in Fig.2. From the XRD analysis all the catalysts were related to the anatase phase. The nano crystalline anatase structure for all the catalysts was confirmed by (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) diffraction peaks. The XRD patterns of anatase have a main peak at  $2\theta = 25.3^{\circ}$  correspond to the 101 plane (JCPDS 21-1272 [19]. The XRD patterns of  $Co^{2+}/TiO_2$  (with CTAB surfactant) catalysts almost coincide with that of pure TiO<sub>2</sub> and did not show any diffraction peaks related with cobalt indicating that Co ions were uniformly dispersed among the anatase crystallites which implies that crystal phase represented no changes in the cobalt doping process.

From the various levels of Cobalt doping the highest intensity peak for 0.5wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant) was observed at 20 =25.3<sup>0</sup>. Hence, further characterizations by using different techniques and studies were carried out only for 0.5 wt%  $Co^{2+}/TiO_2$  (with CTAB surfactant) catalyst and it also exhibited better photocatalytic activity which was confirmed from the later studies. The average crystallite sizes of the synthesized catalysts were calculated from (FWHM) peak by using Scherrer's equation [20] where the crystallite size was found to be 14.1 nm for  $Co^{2+}/TiO_2$  (with CTAB surfactant) and 16.7 nm for pure  $Co^{2+}/TiO_2$  (without surfactant). These values were represented in Table 2.



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**Fig.2.** XRD patterns of 1) pure Co<sup>2+</sup>/TiO<sub>2</sub> (without surfactant) (2) 0.25wt. % Co<sup>2+</sup>/TiO<sub>2</sub> (with CTAB surfactant) (3) 0.75wt. % Co<sup>2+</sup>/TiO<sub>2</sub> (with CTAB surfactant) (4) 0.5wt. % Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant).

**III.II. UV–Visible Diffuse Reflectance Spectroscopy:** Fig.3 shows the UV-Visible DRS of the synthesized (a) 0.5wt. %  $Co^{2+}/TiO_2$  (without surfactant) (b) 0.5wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant) nanophotocatalysts. From the spectrum there was shift observed in the absorbance peak more towards visible region (red shift) i.e. at around 500 to 700 nm. Decrease in the band gap energy was observed which was due to doping of cobalt into TiO<sub>2</sub> matrix. This resulted in increase in the number of photo generated electrons and holes and finally increased the photocatalytic efficiency of the catalysts in the visible region. Band gap energy was calculated by using the formula  $E_{g=}$  (1240/ $\lambda$ ), where  $E_g$  is band gap,  $\lambda$  is the wavelength. Values calculated were represented in Table 1. For  $Co^{2+}/TiO_2$  (without surfactant) the band gap of 0.5 eV. Thus these results confirm the lowering of band gap energy due to cobalt doping into titania matrix by using the CTAB surfactant Template method.



**Fig.3**. UV–Visible absorption spectra of (a) 0.5wt. % of  $\text{Co}^{2+}/\text{TiO}_2$  (without surfactant), (b) 0.5wt. % of  $\text{Co}^{2+}/\text{TiO}_2$ -(with CTAB surfactant), (c) 0.5wt. % of  $\text{Co}^{2+}/\text{TiO}_2$ -(with TX surfactant), (d) 0.5wt. % of  $\text{Co}^{2+}/\text{TiO}_2$ -(with SDS surfactant).



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Fable.1.Band	gap	Energy	of	the	synthesized	Co	<sup>2+</sup> /TiO <sub>2</sub>	cataly	ysts.
	<b>.</b>				•/		-		/

Catalyst	Band gap Energy (eV)
Pure TiO <sub>2</sub>	3.2
$Co^{2+}/TiO_2$ (without surfactant)	2.8
$Co^{2+}/TiO_2$ -(with CTAB surfactant)	2.7

**III.III. X-ray photoelectron spectroscopic study:** From XPS analysis chemical state information of Co 2p, O 1 s, and Ti 2p and their oxidation states can be found out. Fig.4. (a) & (b) indicates high resolution XPS Co 2p spectrum and the total survey spectrum of 0.5wt. % of  $Co^{2+}/TiO_2$ -(with CTAB surfactant). The binding Energies of Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  were found to be 458.0 eV and 463.7 eV and these correspond to the reported binding Energies values for Ti <sup>4+</sup> in TiO<sub>2</sub> [21, 22]. From Fig. 4(b) O 1S peak was located at 529 eV. From Fig. 4(a) Co  $2p_{3/2}$  and Co  $2p_{1/2}$  peaks were located at binding Energies of 780.1 eV and 781.15 eV respectively. These were characteristic for Co<sup>2+</sup> and the oxidation state of Co in +2 oxidation state was confirmed [23-26]. Thus from XPS analysis it was confirmed that the entry of  $Co^{2+}$  into TiO<sub>2</sub> lattice was substituitional [27] as the ionic radii were almost comparable. From this we can say that the doping of  $Co^{2+}$  into TiO<sub>2</sub> lattice as a substituitional dopant.







Fig.4. (b) Total Survey spectrum of 0.5wt. % of Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant)



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**III.IV.Scanning Electron Microscopic study:** Fig. 5 -7 shows the FE SEM-images of the pure TiO<sub>2</sub>, 0.5wt. %  $Co^{2+}/TiO_2$  (without surfactant), 0.5 wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant). From the micrographs it was clear that the morphology of the  $Co^{2+}/TiO_2$ -(with CTAB surfactant) was found to be different from that of pure TiO<sub>2</sub>. FE SEM-images of  $Co^{2+}/TiO_2$ -(without surfactant) show that the particles were irregular and bigger when compared to that of  $Co^{2+}/TiO_2$ -(with CTAB surfactant) nanoparticles. The change in morphology was due to the presence of CTAB surfactant during the synthesis of the catalyst. Agglomeration was totally minimized. This was due to the encapsulation of  $Co^{2+}/TiO_2$  formed due to the presence of CTAB surfactant. But this was not effective to larger extent which may be due to inter ionic repulsions and hence the particle size of the catalyst was observed to be ranging between 12.3-13.9 nm.



Fig.5. FE SEM micrograph of pure TiO<sub>2</sub>



Fig.6. FE SEM micrograph of 0.5wt. % Co<sup>2+</sup>/TiO<sub>2</sub>-(without surfactant)



Fig.7. FE SEM micrograph of 0.5wt. % Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant).



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**III.V. Fourier Transform Infrared spectroscopy:** Fig.8 (a-e) represents FT-IR images of pure TiO<sub>2</sub>, 0.5 wt. % Co<sup>2+/</sup> TiO<sub>2</sub> - (without surfactant) and 0.5 wt. % Co<sup>2+</sup>/ TiO<sub>2</sub>-(with CTAB surfactant) before and after calcinations while Fig.8(c). Corresponds to IR spectrum of CTAB surfactant. FT-IR spectra of pure TiO<sub>2</sub> and 0.5 wt. %  $Co^{2+/}$  TiO<sub>2</sub> (without surfactant) and 0.5wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant) have shown peaks corresponding to stretching vibrations of O-H and bending vibrations of adsorbed water molecules around 2910-3400 and 1620-1625 cm<sup>-</sup> respectively. Vibration spectral peaks observed between 581.69 - 745.81 cm<sup>-1</sup> for the catalyst were assigned due to the Ti-O-Ti bond and this is associated with the characteristic vibration modes of  $TiO_2$ . This small deviation may be due to Co doped substitutionally into the TiO<sub>2</sub> matrix. Hence the FT-IR spectral study along with XPS confirmed the substitution of  $Co^{2+}$  into  $TiO_2$  lattice. From the lit [28] peaks at 2918cm<sup>-1</sup>, 2850 cm<sup>-1</sup>, 2871 cm<sup>-1</sup>, 1473 cm<sup>-1</sup>, 1463 cm<sup>-1</sup>, 960 cm<sup>-1</sup>, 730 cm<sup>-1</sup>, 719 cm<sup>-1</sup> corresponds to the vibration peaks of which are characteristic peaks of CTAB surfactant similarly from the Fig.8 (c) the peaks located at 3129.08 cm<sup>-1</sup>, 2922.49 cm<sup>-1</sup>, 2375.03 cm<sup>-1</sup> 1871.83 cm<sup>-1</sup>, 1685.95 cm<sup>-1</sup>, 1475.78 cm<sup>-1</sup>, 1384 cm<sup>-1</sup>, 826.39 cm<sup>-1</sup> clearly indicated the existence of the CTAB surfactant during the synthesis of the catalyst. A peak at about 1456 cm<sup>-1</sup> can be ascribed as a bending vibration mode of the N-H band of the CTAB from the literature [29] whereas from the Fig 8(c) it was observed at 1459.86 cm<sup>-1</sup>. The slight shift in the peaks observed were due to the bond formed by the CTAB surfactant towards the cobalt doped titania during encapsulation. Whereas the N-H bending vibration is not marked on the calcined samples which indicated the absence of the surfactant after calcinations at  $450^{9}$ C. This restricted the grain growth and minimized agglomeration. From Fig.8 (d) absence of these peaks confirmed that there was no surfactant in the synthesized catalyst after calcinations at  $450^{\circ}$ C. This was clear evidence saying that CTAB surfactant had played an important role in the synthesis of nanoparticles with reduction. Hence the FT-IR spectral study along with XPS established clearly the substitution of  $Co^{2+}$  into  $TiO_2$ lattice.



Fig.8. (a) FT-IR images of pure TiO<sub>2</sub>



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Fig.8 (c) indicates FT-IR images of 0.5wt. %  $Co^{2+}/TiO_2$  - (with CTAB surfactant) before calcinations indicating the presence of surfactant.



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**Fig.8.** (d) indicates FT-IR images of 0.5wt. % Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant) after calcinations where the surfactant was eliminated.

**III.VI. Transmission electron microscopy:** TEM was used to further examine the particle size and crystallinity of the synthesized catalysts. Fig.9 & Fig.10 (a-d) represents HR TEM images of  $Co^{2+}/TiO_2$  (without surfactant) and 0.5wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant). CTAB played an important role resulting in encapsulation and this minimized further grain growth. From the figure, it was clear that all synthesized samples have shown tiny particles with average size of the nanoparticles in the range of 12-14 nm, and this was in good agreement with the value determined from XRD data. It was also observed that all synthesized samples were present in pure anatase phase. The lattice fringes were also shown in the Fig.10 (b) which indicated that the particles were in good crystalline nature which was also confirmed from XRD analysis. From the TEM analysis the particle size of the catalyst were found mostly to be in the range 12.3 to 13.9 nm, while that of pure  $Co^{2+}/TiO_2$  was reported to be 16.1 nm respectively. Due to the electrostatic interactions between cationic surfactant and positively charged titania surface, possibility for encapsulation on  $Co^{2+}/TiO_2$  may be occurred to a lesser extent. This minimized the further grain growth of the nanoparticles of the catalyst.



Fig.9. TEM images of 0.5wt. % Co<sup>2+</sup>/TiO<sub>2</sub>-(without surfactant).



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Fig.10 (a). The high resolution TEM images of 0.5wt. % Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant).





(d) Fig.10 (b),(c) & (d) The high resolution TEM images of 0.5wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant).



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III.VII. BET Analysis: From BET analysis of the nitrogen adsorption /desorption isotherms, surface area analysis and pore volume and pore size of nanoparticles of the catalyst were determined. The average crystallite size and Surface area  $A_{\text{BET}}$  (m<sup>2</sup>/g) of the catalysts calcined at 450°C were given in Table 2. Our findings clearly indicated that Cobalt doped  $TiO_2$  have a larger surface area and a greater adsorption capacity than pure  $TiO_2$ , which was due to the increase in the pore size. BET analysis indicated that the surface area of  $Co^{2+}/TiO_2$  (with CTAB surfactant) was reported to be-32 m<sup>2</sup>/g whereas 0.5 wt. %  $Co^{2+}/TiO_2$  (without surfactant) was reported with 23 m<sup>2</sup>/g. The increase in surface area was due to the presence of surfactant during the synthesis of  $Co^{2+}/TiO_2$  nano materials. Fig 11 shows nitrogen adsorption and desorption isotherms of  $Co^{2+}/TiO_2$  (with CTAB surfactant) as a function of calcinations temperatures. From the fig.11 at maximum & minimum relative pressure as 0.96 and 0.04 the curve exhibited hysteresis loop described as  $H_3$ type which indicates the presence of mesopores and were classified as mesoporous adsorbent [30-33] due to which enhanced photo catalytic activity was observed towards degradation of Orange II. The mesopores of the  $Co^{2+}/TiO_2$ (with CTAB surfactant) were reported with maximum average pore diameter as 5.31 nm. Pore volume of the mesopores were reported as  $V_{P=0.0625}$  cc/g, while the pore width as 5.43 nm. The mesopores of  $Co^{2+}/TiO_2$  (without surfactant) were reported with pore volume  $V_P = 0.019$  cc/g and pore diameter was Sp = 2.9 nm. Thus with increased surface area there was increase in the rate of photo degradation reactions observed [34, 35] and similar result was observed from the later studies.



Fig.11. Nitrogen adsorption and desorption isotherms of Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant).

Table 2. DET analysis Surface area $A_{\text{BET}}$ (in /g), crystante size of the synthesized catalyst						
Catalyst	$A_{BET} (m^2/g)$	Crystallite size(nm)	Vp (cc/g)	Sp (nm)		
Pure TiO <sub>2</sub>	18	19	0.009	1.9		
Co <sup>2+</sup> /TiO <sub>2</sub> (without surfactant)	23	16.7	0.019	2.9		
$Co^{2+}/TiO_2$ -(with CTAB surfactant)	32	14.1	0.0625	5.4		

Table 2. BET analysis Surface area A <sub>BET</sub> (n	<sup>2</sup> /g), crystallite size of the sy	nthesized catalyst
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**III.VIII. Evaluation of Photocatalytic activity of the Co^{2+}/TiO\_2-(with CTAB surfactant):** The photocatalytic efficiency of the synthesized nano catalyst,  $Co^{2+}/TiO_2$ -(with CTAB surfactant) was carried out by degradation of Orange II an azo dye pollutant under visible light irradiation. Experiments were performed in order to study regarding various parameters like dopant concentration, pH, catalytic dosage and initial dye pollutants concentration.

**III.VIII.I. Effect of dopant concentration:** A set of experiments were carried out using 0.25, 0.5, 0.75 and 1.0 wt. % of  $Co^{2+}/TiO_2$ -(with CTAB surfactant) for the degradation of Orange II solution under visible light irradiation by maintaining other conditions like pH maintained at 3 and dye concentration at 10 mg • L<sup>-1</sup> constant. Fig.12 shows the experimental results of degradation % of Orange II solution. From the results it was clear that doping of  $Co^{2+}$  ions into TiO<sub>2</sub> up to 0.5wt. % showed maximum photocatalytic activity. Hence 0.5 wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant) was found to be optimal dopant concentration and this result was also in agreement with XRD analysis. Fig.13 indicates rate of degradation of Orange II where rate was found to be 3.94 mg L<sup>-1</sup>min<sup>-1</sup>. Hence further photocatalytic experiments were carried out with 0.5 wt. %  $Co^{2+}/TiO_2$ -(with CTAB surfactant).



Fig.12. Degradation % of Orange II solution



Fig.13. Rate of degradation of Orange II

**III.VIII.II. Effect of pH:** In order to find the optimal pH of reaction mixture the experiments were carried out for decomposition of Orange II by varying the pH conditions from pH=3-9 with irradiation time at a 0.1 g of 0.5 wt. % of the catalyst and 10 mg •  $L^{-1}$  of Orange II dye concentration. The results were show in Fig.14 which indicates degradation % of Orange II solution. It was observed that the rate of degradation is higher in the acidic pH range (pH=5). pH changes can thus influence the adsorption of dye molecules onto the TiO<sub>2</sub> surface, an important step for the



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photo-oxidation to take place. For P25, the pH pzc is around 5.8–6.8. So, when pH<6 a strong adsorption of Orange II on the TiO<sub>2</sub> particles was observed as a result of the electrostatic attraction of the positively charged TiO<sub>2</sub> with the dye. In our case the highest degradation rate was achieved at pH=5.0. Thus due to Coulombic repulsion, substrate was scarcely adsorbed. Fig.15 indicates rate of degradation of Orange II. The rate of degradation for 0.5 wt. %  $Co^{2+}/TiO_2$  was found to be maximum at pH=5 is 6.2 mg L<sup>-1</sup>min<sup>-1</sup>.



Fig.14. Degradation % of Orange II solution.



Fig.15. Rate of degradation of Orange II.

**III.VIII.III: Effect of catalyst dosage:** In order to find out the optimum catalyst dosage experiments were carried on by varying the amount of the catalyst from 0.05 to 0.3 g in 100ml of Orange II dye solution while keeping the other conditions like 0.5 Wt. % of the catalyst at pH=5 and 10 mg • L<sup>-1</sup> constant. The experimental results were expressed in Fig.16. From the results it was clear that degradation of the dye was maximum at 0.1g and later with increase in catalyst dosage there was decrease in the rate of degradation. With increase in the amount of the catalyst more number of dye pollutants gets adsorbed to the catalyst surface which finally enhances the rate of degradation of Orange II. But beyond 0.1g of catalyst dosage the photocatalytic activity decreased. Fig.17 indicates rate of degradation of Orange II. The rate of degradation for Orange II dye solution at 0.1g of 0.5 wt. % Co<sup>2+</sup>/TiO<sub>2</sub> was found to be maximum at pH=5 was 7 mg L<sup>-1</sup>min<sup>-1</sup>.



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Fig.16. Degradation on % of Orange II solution.



Fig.17.Rate of degradation of Orange II

**III.VIII.IV. Effect of initial dye concentration:** For finding out the initial dye concentration experiments were carried out by varying the dye concentration from 5-20 mg • L<sup>-1</sup> while keeping the other conditions like 0.1 g of 0.5 Wt. % of the catalyst at pH=4 constant. The experimental results were given in Fig.18. From the results it was observed that the optimum initial dye concentration for maximum degradation of Orange II was observed at 10 mg • L<sup>-1</sup> and with further increase there was decrease in the degradation rate observed. But with increase in concentration of the Orange II dye solution, they start covering the surface of the catalyst from light intensity. Fig.19 indicates rate of degradation of Orange II. The rate of degradation of Orange II with 0.5 wt. % Co<sup>2+</sup>/TiO<sub>2</sub> was found to be maximum at 10 mg · L<sup>-1</sup> was 13.24 mg L<sup>-1</sup>min<sup>-1</sup>. Finally the optimum conditions for the degradation of Orange II dye solution was 0.5 wt. % of Co<sup>2+</sup>/TiO<sub>2</sub>-(with CTAB surfactant) dopant concentration, at 0.1 g catalyst dosage, and at pH 5 with 10 mg • L<sup>-1</sup> as the initial dye concentration. Under these conditions the rate of degradation of Orange II solution was found to be 13.24 mg L<sup>-1</sup>min<sup>-1</sup>.



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`Fig.18. Degradation % of Orange II solution.



Fig.19. Rate of degradation of Orange II.

**Overall mechanism**: Based on the above experimental results the following mechanism was proposed for the photocatalytic reactions  $\text{Co}^{2+}/\text{TiO}_2$ -(with CTAB surfactant). Formation of hydroxyl radicals was an important step in the photocatalytic degradation of Orange II azo dye pollutants. The synthesized photocatalyst  $\text{Co}^{2+}/\text{TiO}_2$ -(with CTAB surfactant) when illuminated with visible light electrons were ejected from the valence band to the conduction band and there by resulted in the formation of positive holes in the valence band. Due to doping of Cobalt into TiO<sub>2</sub> lattice, electrons were trapped by dopant ions there by eliminating the recombination process. With the generation of the superoxide radical, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), hydroperoxy (HO<sub>2</sub>) and hydroxyl (•OH) radicals formation takes place [36]. Due to the positive holes in the valence band and these acts as good oxidizing agents where degradation of Orange II azo dye pollutant was possible.

Thus, the Azo dye pollutant Orange II was attacked by the hydroxyl radicals formed both by trapped electrons and holes in the VB where degradation of Orange II takes place with generation of organic radicals and other intermediates.



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#### **IV. CONCLUSIONS**

In the present investigation, 0.5 wt. %  $Co^{2+}/TiO_2$  (with CTAB surfactant) catalyst has been successfully synthesized in presence of Cetyltrimethyl ammonium bromide surfactant by employing sol-gel technique. The photocatalytic degradation of Orange II, a model azo-dye pollutant has been studied in detail. From the XRD studies all the  $Co^{2+}/TiO_2$ (with CTAB surfactant) catalysts synthesized were reported in anatase phase. Surfactant influenced the formation of particles with much reduction. Agglomeration was totally minimized. Due to cobalt doping into TiO<sub>2</sub> matrix there was shift observed in the absorbance of  $TiO_2$  from UV to Visible region (red shift) i.e., above 400-800 nm with decrease in the band gap energy by 0.5 eV. XPS analysis confirmed that cobalt was in +2 oxidation state and it was substituitionally doped in the TiO<sub>2</sub> matrix. The BET surface analysis revealed that there was increase in the surface area of the catalyst for 0.5 wt. % Co<sup>2+</sup>/TiO<sub>2</sub> (with CTAB surfactant) i.e. 32 m<sup>2</sup>/g when compared with that 0.5 wt.%  $Co^{2+}/TiO_2$  (without surfactant) which was 23 m<sup>2</sup>/g. SEM micrographs have indicated irregular particles. Due to doping of Cobalt into TiO<sub>2</sub> matrix morphological change of the TiO<sub>2</sub> particles has been observed with decrease in particle size. From TEM analysis of 0.5 wt. % Co<sup>2+</sup>/TiO<sub>2</sub> (with CTAB surfactant) were reported with much reduction in particle size of 12.3 nm where as particle size of 0.5wt. %  $Co^{2+}/TiO_2$  (without surfactant) were reported with 16.1 nm respectively. This was due to encapsulation of cobalt doped titania by the surfactant which restricted the further growth of the particles and lead to the formation of reduced size nanoparticles. FT-IR studies revealed that Cobalt is doped substitutionally into the TiO<sub>2</sub> matrix. The photocatalytic studies were investigated by degradation of Orange II dye. The optimum conditions for the degradation of Orange II dye solution with  $Co^{2+}/TiO_2$  (with CTAB surfactant) were found as 0.5 wt.% dopant concentration at (pH-5), (0.1g) catalyst dosage and for  $(10 \text{ mg} \cdot \text{L}^{-1})$  initial dye concentration. The observed rate at optimum conditions for the degradation of Orange II was found to be 13.24 mg L<sup>-1</sup>min<sup>-1</sup>. Thus  $Co^{2+}/TiO_2$  (with CTAB surfactant) was successfully synthesized and proved to be an efficient photocatalyst by degradation of Orange II dye pollutant and can be used in waste water treatment.

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