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# Cr Doped TiO2 Catalystin Photocatalytic Degradation of Jakofix Red Dye (HE7B)

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## ABSTRACT

Pigment / dye manufacturing industries are one of the highly polluting industries generating large volumes of high strength of waste water with disobedient properties. Different process covering anaerobic, aerobic as well as physico-chemical methods have been employed to treat this coloured effluent. The intense colour of the effluent leads to acute ecological problem when released untreated in to environment. Thedecolourisationor deterioration of effluent is known to be very challenging task. In this paper degradation of industrial dyein terms of colour, was studied by usingCr doped TiO2 photo catalyst. The Cr doped TiO2 nanoparticles were prepared by a using Chromium and titanium peroxide gel method with Titanium Isopropoxide as a precursor. The physico-chemical characteristics of the Chromium–titania catalysts of concentration range 0.5 to 5% (w/v) were determined using the methods of Brunauer-Emmett-Teller adsorption, X-ray diffraction, FE-SEM, FT-IR,and UV visible spectroscopy (DRS).The Cr-TiO2 catalystshowed a photo-degradation of dye for all concentration i.e. 0.5 to 5% (wt %).The maximum photocatalytic degradation (90%) ofwas observed for Jakofix red dye (HE 7B)at 0.5% Cr-TiO2sol gel catalyst, as compared to pure TiO2.

**Keywords:** BET, Colour, Dye, Effluent, Photocatalyst, and TiO2.

## I. INTRODUCTION

Effluent originating from any dye/ pigment manufacturing industries contain large amount of dark coloured wastewater called coloured effluent. This effluent is the unwanted residual liquid waste to dispose because of acidic / basic pH, dark colour, unpleasant odour and high percentage of organic and inorganic matter.Dark colour of effluent is due to the presence of dye / pigment content. It decreases sunlight penetration in rivers and lakes which in turn decrease both photosynthetic activity and dissolved oxygen concentration affecting aquatic life. So the disposal of this effluent is one of the critical environmental issues.

Photocatalytic degradation of organic contaminants using $TiO_2$ photocatalyst is being widely studied as a relatively new technique for pollution abatement due to its desirable properties, such as non-toxicity, wide band gap, and stability in acidic as well as basic media [1-3.] However, the wide band gap of $TiO_2$ only absorbs light of wavelength less than 400 nm in the UV region, which restricts its applications in the presence of UV irradiation. For widespread applications, a $TiO_2$-based catalyst effective in visible radiation or for solar light needs to be developed as a future generation photocatalytic material. $TiO_2$ absorbs only 5% energy of the solar spectrum and hence numerous studies have been performed to extend the photo-response and photo catalytic activity by modifying its surface structure, surface properties and composition to shift its absorption in visible region so as to improve its photocatalytic activity in visible/solar light [4-6]. The surface modification by doping with metal ions and organic polymers has been proven to be an efficient route to improve the photo catalytic activity of $TiO_2$ [7–10.]

Anpo et al. have studied the doping of $TiO_2$ with transition metals such as V, Cr and Fe by three different methods: sol–gel, co-precipitation and ion implantation techniques [11–14]. The higher photocatalytic activity of Chromium doped $TiO_2$ prepared by ion implantation was correlated to deep incorporation of Chromium into titanium oxide lattice due to bombardment of highly energetic vanadium ions on $TiO_2$ targets. Generally titania powder is used for photocatalytic degradation of pollutants in aqueous solution using a photocatalytic reactor. The used catalyst is recovered by filtration for its recycle; this is quite a cumbersome process because of the very fine nature of the powder.

Thin films of titania as an active photocatalyst would be an attractive alternative to overcome the catalysts separation problems. In an attempt to modify the optical properties of $TiO_2$, we were successful in improving the photocatalytic activity of $TiO_2$ in sunlight by doping titania thin films with Fe and Au, which shifted its absorption into visible region [15–17]. In continuation of our earlier efforts, thin films of Chromium doped titania were deposited by simple dip coating techniques using vanadium and titanium peroxide gel on various glass substrates. These films have been characterized by using various techniques to determine their structural properties. Most of the dyes and poisonous metals are used in the textile industries are stable to light and are non-biodegradable.[18] In order to reduce the risk of environmental pollution from such waste, it is necessary to treat them to before discharging it receiving in the environment [19]. Photocatalytic degradation Methylene blue dye by photochemical reactor was studied by Suryawanshi etal [20] and dye and removal of chromium from waste water was studied by Shrivastava [21]

Semiconductor photocatalysis is one technique that has great potential to control organic as well as inorganic contaminants. Hence, its degradation prior to discharge is essential for the environmental safety. Though, the various effective physical and chemical methods such as ozonation, flocculation and activated carbon adsorption etc. have been attempted for the removal of colour.

In this paper, the $Cr–TiO_2$ catalyst was prepared by the sol– gel method. The samples were characterized by XRD, FE-SEM, FT-IRand UV–Vis absorption spectrum. The photocatalytic activity of solgel Chromium doped $TiO_2$ for the degradation of Jakofix red dye (HE 7B) has been studied and results are reported here.

## II. Methods & Material

### 2.1 Catalyst Preparation:

A series of chromium–titania catalyst with Chromium content varying from 0.5,1,2,3,4 & 5 wt% were prepared by sol–gel technique using Chromium Nitrates and Titanium Isopropoxide astitanium precursors, respectively. In a typical synthesis of 1 wt% Chromium–titania catalyst, 4.028 g of Titanium Isopropoxide (Sigma-Aldrich make) was hydrolysed with 30 mL of MilliQ water (conductivity is <10 Ohm). To this, 20 mL of 30% aqueous hydrogen peroxide (Merck make) was added to get a transparent orange sol of titanium peroxide. Chromium Nitrate (76.9 mg, Merck make) was suspended in 20mL of MilliQ water; 3 mL of 30% aqueous hydrogen peroxide was added to it to get a clear green colored peroxochromic acid solution. This peroxochromic acid solution was added to the titanium peroxide solution and a transparent green yellow viscous gel was formed. To obtain the powder sample, we dried the Chromium–titania peroxide gel at ambient temperature and then heated it in ahot air oven at $110^0$C and further calcined it at $400^0$C under inert air flow using a muffle furnace. The heating / cooling rate was $5^0$C/min, with a5 hour dwell time at the selected temperature. Pure$TiO_2$ was also prepared similarly by the sol–gel technique using peroxide precursor for comparison.

### 2.2. Catalyst characterization:

**2.2.1** X-ray diffraction and UV–Visible Spectroscopy:
The powder X-ray diffraction analysis of the powdered samples was carried out using a Rigaku X-ray diffractometer (Model DMAX IIIVC). The data was collected in the 2 thetarange, 20–80 with a step size of 0.028 and counting time of 15 second at each step. The diffuse reflectance UV–vis spectra were recorded in the range 200–800 nm with 0.5 nm spectral bandwidth in air at ambient temperature by using a Shimadzu instrument (UV 3600) spectrophotometer.

### 2.2.2FE-SEM & BET:

The surface morphology of the samples was studied using FESEM (SEM, XL-20 Philips). The particle morphology of the Cr–TiO2 photo catalyst was tested using a Hitachi H-800 transmission electron microscope (TEM). The BET, Porosity was checkedbyMicromeritics Gemini VII 2140 instrument.

### 2.2.3Element analysis by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

The Cr concentration in prepared catalyst was measured by ICP-MS instrument. The catalyst was tested by using Agilent make 7700 model with Mass Hunter Software.

### 2.3. Photocatalytic activity

For photocatalytic degradation of Jakofix red dye (HE 7B), the powder sample of Cr-$TiO_2$ wereused as photocatalyst. The catalyst powder 15 mg were taken in to a 250 mL glass beaker containing solution of 50mL dyehaving concentration 250 ppm. For degradation of dye,all the beaker werekept in sunlight for four to five hr. The degradation of dyewas checked at different time interval by using UV–Visible spectrophotometer.

## III. Result & Discussion

### 3.1 Sol gel behaviour of Cr-$TiO_2$Sol:

When titanium Isopropoxide was hydrolysed and the resulting hydroxide was further reacted with hydrogen peroxide, a yellow solution was obtained after a vigorous exothermic reaction. The temperature of reaction was controlled by cooling the reaction mixture by jacketed cooled water or ice water till get transparent yellow solution. The Chromium nitrate solution was slowly added to this solution, a slightly greenish yellow solution was obtained. When this solution was kept for few hours, the thickness of solution was increased and transparent viscous gel was formed. The addition of Chromium concentration varies from 0.5%, 1%, 2%, 3%, 4% & 5% respectively. The non-gelatinous precipitate was obtained above the concentration of 4%. The sol gel behaviour of Cr-$TiO_2$ sol containing different concentrations of Chromium Nitrate (0.5-5 wt %) has been studied. The results showed similar behaviour, hence only sol containing 1% Cr-$TiO_2$ has been studied in detail as a characteristic example.

### 3.2 Optical Properties of Cr-$TiO_2$ powder.

The calibrated UV-3600 spectrophotometer was used in scanning mode at 200-400 nm range for measurement of absorbance of powder samples.The optical absorption of the powder sample calcined at $400^0$C in UV–Visible range is shown in Figure 3.

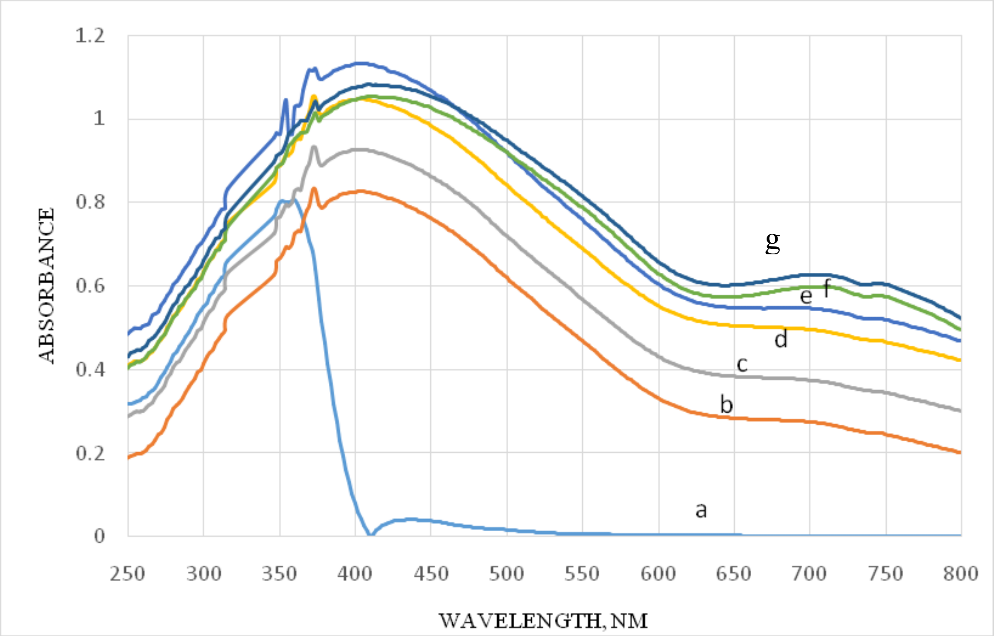
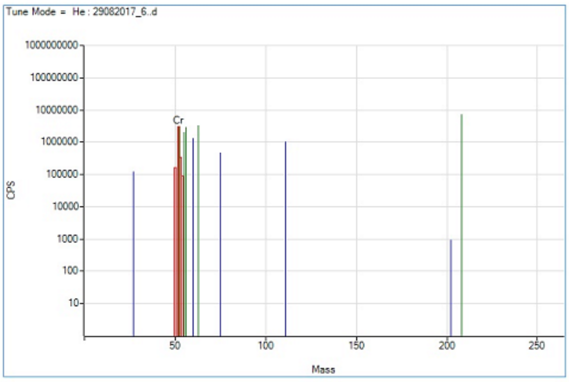


**Figure1.** DRS spectra of powder samples (a) $TiO_2$, (b) 0.5% Cr-$TiO_2$, (c)1.0% Cr-$TiO_2$, (d) 2% Cr-$TiO_2$, (e) 3.0% Cr-$TiO_2$, (f)4.0% Cr-$TiO_2$, (g) 5.0% Cr-$TiO_2$.

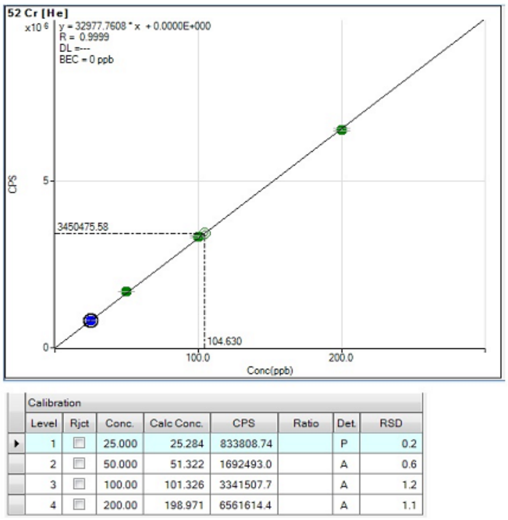
The pure $TiO_2$ curve (a) shows an absorption edge at around 360 nm, (the absorption edge is for bulk anatase $TiO_2$). It may be attributed to the smaller particle dimensions of $TiO_2$ (2–10 nm) in powder catalyst. The curve 'b' in figure represents the UV-Visible spectra of 0.5%Cr-$TiO_2$ which show absorption above 385 nm. In case of 1%, 2%, 3%, 4% and 5% Cr-$TiO_2$ (curves c, d, e, f and 'g') the absorption has been shifted further towards the visible side i.e. at 400 and 430 nm respectively. In all these samples, the wavelength shifting to visible regionmay be recognised to the incorporation of Chromium into the $TiO_{2,}$ since the extent of shift to visible region is dependent on the concentration of Crin $TiO_2$.

### Estimation of Cr by ICP-MS:

The calibrated ICP-MS (7700 model), Agilent make instrument was used for determination of chromium content.The catalyst powder sample were digested in Conc. Nitric acid (Merck make) solution for 1 hr. after cooling the solution dilute 250 ml with Milli Q water (conductivity is <10 Ohm). The linearity graph was plotted for 25 to 200 ppb concentration (Multistandard Element, Merck make)and resultant correlation coefficient of slope is 0.9999. The % RSD for this linear solution is not more than 1.2 indicate the less deviation in Cr estimation and performance of instrument (b)



a



Calibration

| Level | Rjct | Conc. | Calc Conc. | CPS | Ratio | Det. | RSD |
|---|---|---|---|---|---|---|---|
| 1 | ☐ | 25.000 | 25.284 | 833808.74 |  | P | 0.2 |
| 2 | ☐ | 50.000 | 51.322 | 1692493.0 |  | A | 0.6 |
| 3 | ☐ | 100.00 | 101.326 | 3341507.7 |  | A | 1.2 |
| 4 | ☐ | 200.00 | 198.971 | 6561614.4 |  | A | 1.1 |

b

**Table 1.** The concentration of Cr content in powder catalyst are mentioned.

| Catalyst | Conc. of Chromium, % |
|---|---|
| $TiO_2$ | ND |
| 0.5% Cr-$TiO_2$ | 0.4999 |
| 1.0% Cr-$TiO_2$ | 0.9998 |
| 2.0% Cr-$TiO_2$ | 1.9997 |
| 3.0% Cr-$TiO_2$ | 2.9989 |
| 4.0% Cr-$TiO_2$ | 3.9987 |
| 5.0% Cr-$TiO_2$ | 4.9985 |

### FT-IR spectra of Cr-$TiO_2$Catalyst:

The FT-IR of Perkin Elmer make with UATR technique instrument was used for measuring spectra of metal doped $TiO_2$ catalyst. The FT-IR spectra of pure $TiO_2$ and Cr-$TiO_2$ calcined at 400$^0$C are given in Figure 3.

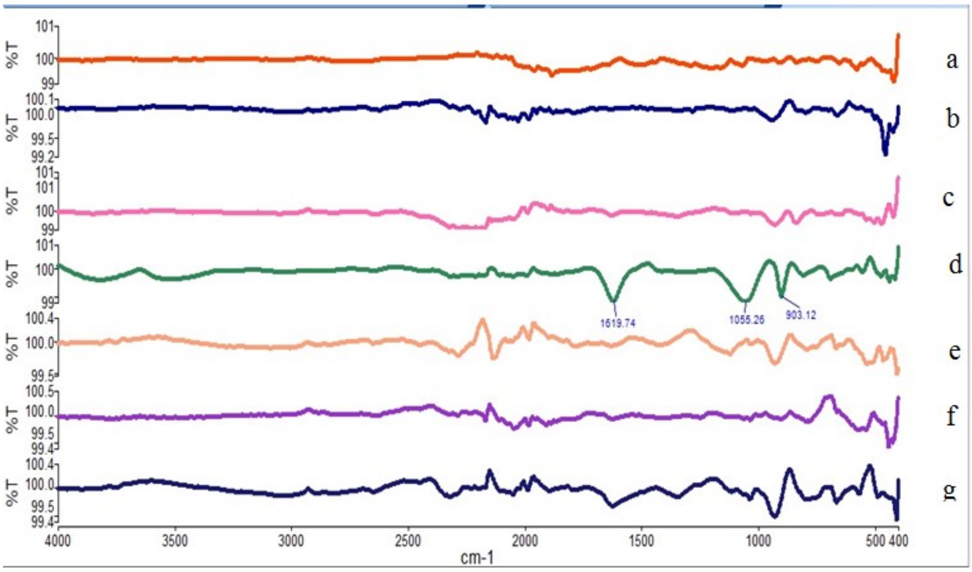


**Figure 3.** FT-IR spectra of (a) TiO2, (b) 0.5% Cr-$TiO_2$, (c) 1.0% Cr-$TiO_2$, (d) 2% Cr-$TiO_2$, (e) 3.0% Cr-$TiO_2$, (f) 4.0% Cr-$TiO_2$, (g) 5.0% Cr-$TiO_2$. Calcined at 400$^0$C

Each calcined catalyst sample was scan in the range of 4000 to 450cm-1. There are characteristic wide peaks in the region of 2000–500cm−1, which are related to the bending vibration of the Ti–O bonds. A new absorption at 1619, 1055 & 903cm−1 seen in the Cr–$TiO_2$sample but these peaks are absent in $TiO_2$ sample.

### 3.4 Crystallization behaviour of Cr-$TiO_2$ catalyst.

### XRD data information

The gel was allowed to dry in at ambient temperature and used for the XRD analysis. The dried gel was calcined at 400$^0$C; results showed good agreement with the calculated values based on the chromium and titanium weighed during the preparation. The XRD patterns of air dried 1 % Cr-$TiO_2$ gel and of the gels calcined at 200, 300, 400,500 and 600$^0$C for 5hr are shown in Figure 4 (curves (a–e). As expected, the XRD pattern of as prepared sample (curve (a) shows the amorphous nature of air dried Cr-$TiO_2$ gel.

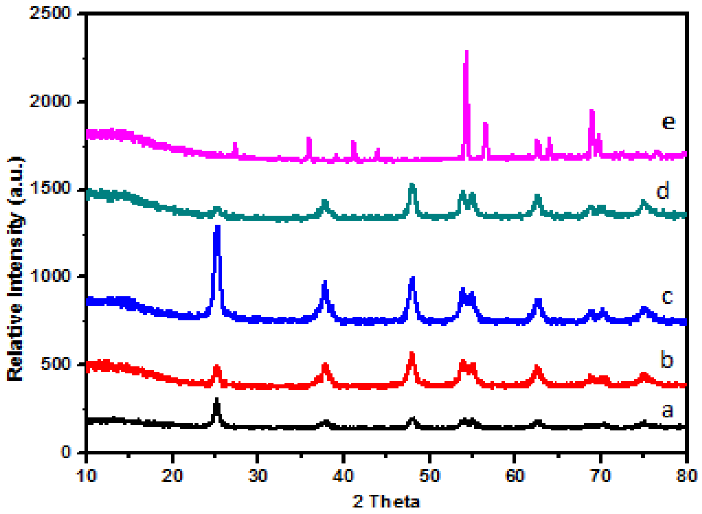


**Figure 4.** XRD pattern of 1% Cr-$TiO_2$ as prepared and calcined at (a) 200, (b) 300, (c) 400, (d) 500 and (e) $600^0$C.

The sample heated at $200^0$C (curve a) showed weak and broad peaks indicating the amorphous nature of the air dried gel. Curve (b) (sample calcined at $300^0$C) shows a slight increase in the intensity of peaks corresponding to anatase $TiO_2$, indicating the beginning of crystallization of Cr-$TiO_2$ at this temperature. Further increase in calcination temperature to $400^0$C curve (c) showed an increase in the intensity of the characteristic peaks of anatase phase, suggesting the further growth of anatase phase. The samples calcined at $400^0$C showed peaks of fully grown anatase phase. Conversion of anatase to rutile phase with sharp peak was observed at $500^0$C (d) & $600^0$C (e)

The surface area and porosity of Chromium content have been studied by measuring surface areas and porosity of Cr-$TiO_2$ samples containing 0.5–5% Chromium by Micromeritics Instrument. The results of BET surface area, porosity are summarized in Table 2.

| Catalyst | Surface Area, $m^2$/gm | Porosity, % |
|---|---|---|
| $TiO_2$ | 72.59 | 46.70 |
| 0.5% Cr.$TiO_2$ | 88.02 | 48.72 |
| 1.0% Cr.$TiO_2$ | 95.04 | 46.10 |
| 2.0% Cr.$TiO_2$ | 99.84 | 56.36 |
| 3.0% Cr.$TiO_2$ | 109.07 | 52.50 |
| 4.0% Cr.$TiO_2$ | 129.85 | 59.87 |
| 5.0% Cr.$TiO_2$ | 105.21 | 62.16 |

**Table 2.** BET, Porosity data of $TiO_2$ and Cr-$TiO_2$ catalyst.

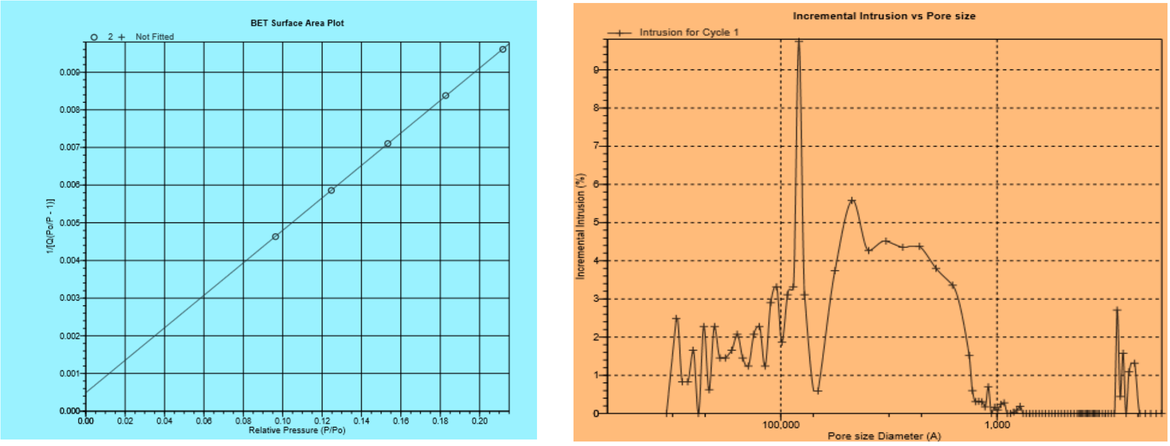


**Figure 5.** Graphical representation of 1% Cr-$TiO_2$ catalyst for Brunauer-Emmett-Teller (BET) & porosity

For BET surface area and Porosity measurement, sample was dried along with degassed with the help of UHP grade nitrogen gas at $110^0$C for 2 hr. BET surface area was measured by using liquid nitrogen. The porosity of sample was measured as per ASTM method (D2484-07) i.e. by Mercury Intrusion Porosimetry technique.

The surface are of pure $TiO_2$ gel was 72.59 $m^2$/g; this increased to 129.85 $m^2$/g when Chromium loading was increased from 0.5 to 4%. The increase of surface area may be ascribed to the formation of homogeneous gel with increase in Chromium content. In this Cr-$TiO_2$ system, when chromium peroxide sol is added to titanium peroxide solution, below 4% Crcontent it forms a homogeneous greenish gel but as the Chromium content was further increased beyond 4%, the gel characteristics change and a non-homogeneous gel with agglomerated flocks was formed leading to decrease in surface area.

### 3.5 Surface Morphology of powder.

The surface morphology/microstructure of the powder samples wasanalysed by FE-SEM showed that, the powder have sphere-shaped granules. A granular texture with spherical or spheroidal shaped particles and particle agglomerates were observed on the surface.

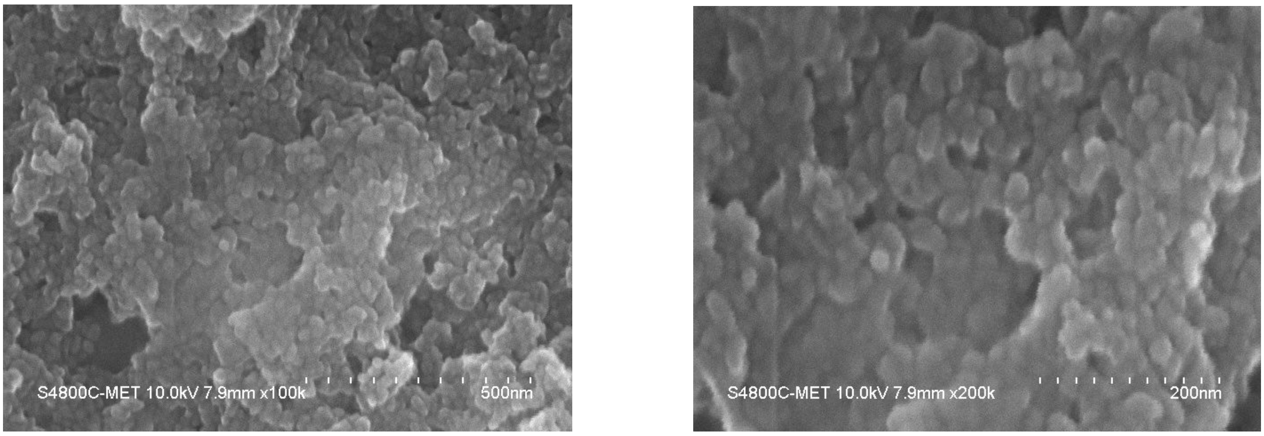
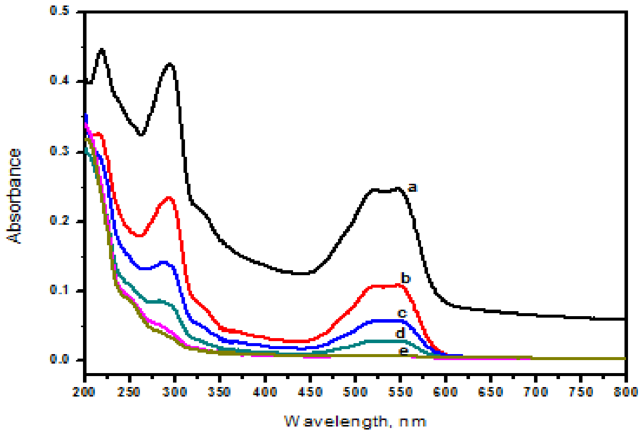


**Figure 6.** FE-SEM images of Cr-$TiO_2$.

### 3.6 Photo catalytic degradation of Jakofix red (HE 7B) dye.

Photocatalytic activity of Cr-$TiO_2$ thin film catalyst was tested for degradation of Jakofix red dye (HE 7B) (200 ppm solution) under solar radiation using Cr-$TiO_2$ powder. The change in the concentration of colour in the samples irradiated for different time intervals under solar radiation was monitored using UV–Visible spectrometer (200-800 nm) and compared with the blank which was kept in sunlight under identical experimental conditions. Typical UV spectra of the Jakofix red dye (HE 7B) solution in the presence of 0.5% Cr-$TiO_2$ catalysts, before and after solar light irradiation at different time intervals are presented in Figure 7.



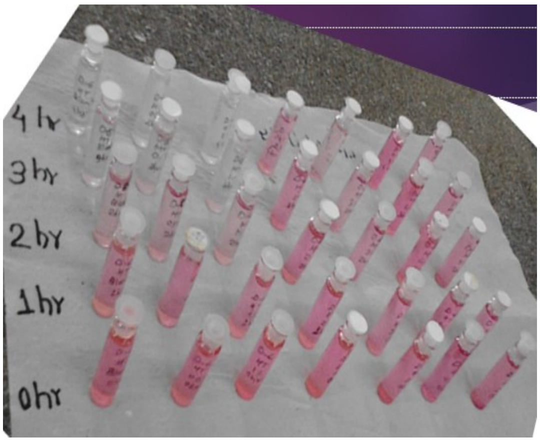


**Figure 7.** UV–vis spectra of Jakofix Red Dye (HE 7B) solution after irradiation with sunlight for (a) 0 h, (b) 1 h,(c) 2 h, (d) 3 h, (e) 4 h in presence of 0.5 % Cr-$TiO_2$ catalyst

The 99% degradation of Jakofix red dye (HE 7B) was observed in 3.5 hr. at 0.5 % Cr-$TiO_2$ catalyst. The degradation under sunlight was observed at UV & visible region.

## IV. Conclusion

Chromium doped Titania powder catalyst prepared by simple sol–geltechnique for photocatalytic degradation of Jakofix red dye (HE 7B) in sunlight. Among the catalysts investigated Cr-$TiO_2$ catalyst containing 0.5% Chromium was found to be the most active catalyst for degradation of dye colour. The Cr-$TiO_2$ catalyst was found to be quite active for the degradation of dye from aqueous solution, which shows the potential of this catalyst for the removal of organic contaminants from industrial polluted water.Semiconductor photocatalysis is one of very simple, economical technique that has great potential to reduce organic as well as inorganic contaminants. Hence, its degradation prior to discharge is essential for the environmental safety.

## V. Acknowledgement

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