

# Photocatalytic degradation of Chromium (VI) from wastewater using nanomaterials like TiO<sub>2</sub>, ZnO, and CdS

K. M. Joshi · V. S. Shrivastava

Received: 21 May 2011 / Accepted: 8 August 2011 / Published online: 1 September 2011  
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**Abstract** The photocatalytic degradation of Cr(VI) from wastewater by using nanomaterials TiO<sub>2</sub>, ZnO, and CdS. All the experiments were carried out in the batch process. The wastewater obtained from various industries. The amount of chromium was removed using photocatalyst with UV light and in the dark at different pH range. The maximum removal of Cr(VI) was observed at pH 2; out of these photocatalyst TiO<sub>2</sub> showed highest capacity for Cr(VI) removal than TiO<sub>2</sub> thin film. The removal of chromium has been studied by considering influent concentration, loading of photocatalyst, pH, and contact time as operating variables. The degradation was characterized by FTIR, XRD, SEM, and EDX analysis before and after application of photocatalysts.

**Keywords** Photocatalysis · Sol–gel thin film · FTIR · XRD · SEM · EDX

## Introduction

The pollution of hazardous metals is increasing with extensive of industrial developments (Bhatkhande et al. 2001). Biological interest in chromium arises from its prominent role in industrial pollution and its toxicity to microbes, plants, and animals (Mills et al. 1996). Large amounts of chromium are introduced into the environment through various industries like dyeing and printing in

textile industries, chemical manufacture, leather tannery, metal plating, and processing industrial effluents affected living cells (Lozano et al. 1992; Suksabye et al. 2007). Chromium exists in two oxidation states, Cr(III) and Cr(VI). The hexavalent form is 500 times more toxic than the trivalent form (Kowalski 1994; Gimenez et al. 1996). Several studies have shown that the trace amount of chromium (VI) is considered to be essential for normal metabolic process (Barkat et al. 2004). Chromium discharged into the sewage system causes serious environmental impact. Chromium occurs mainly in Cr(III) form, which is oxidized into chromium (VI) due to the presence of organic compounds (Sarin and Pant 2006). The maximum level of Cr(VI) permitted in wastewater is 0.05 mg L<sup>-1</sup> (Acer and Malkoc 2004). However, higher levels of chromium metals have been found to be toxic mainly to the kidney and liver (Kajitvichyanukul et al. 2005; Shrivastava et al. 1996). World health organization (WHO) has determined that chromium (VI) is carcinogenic (Suksabye et al. 2009). The human toxicity includes lung cancer as well as liver and gastric damage (Acer and Malkoc 2004; Kabra et al. 2008). Nowadays, most of the industries are facing the difficult problem of disposal of chromium (VI) in wastewater produced in huge quantity.

Hexavalent chromium form chromate (CrO<sub>4</sub><sup>-2</sup>) is considerably more soluble in water than trivalent chromium Cr(III) (Butler and Davis 1993). The chromium removal treatment includes precipitation, ion exchange, photocatalysis, reverse osmosis, and adsorption process (Lin et al. 1993). Most of these methods require high capital and recurring expenditure and consequently they are not suitable for small-scale industries (Lee et al. 2006; Chenthamarakshan et al. 2000). Among all the aforementioned methods, photocatalysis is a highly effective and cheap process than the other methods. Photocatalysis is one of the potential techniques to either oxidize or reduce hazardous

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pollutants. In the present investigation, photocatalytic degradation method is used for the removal of chromium (VI) from industrial wastewater using  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{CdS}$  as photocatalysts. In addition, a comparative study using nanosized  $\text{TiO}_2$  powder and Sol–gel thin film of  $\text{TiO}_2$  was also studied under UV irradiation. Besides the above-detailed effect of pH, contact time, photocatalyst dosage, and kinetic study were also investigated.

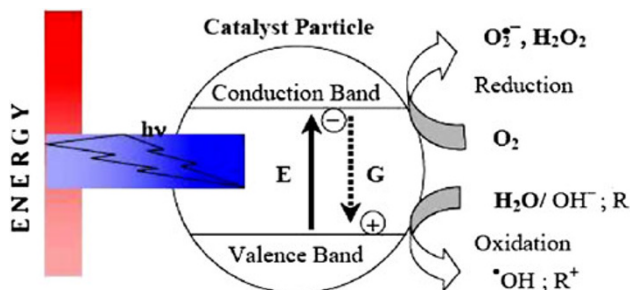
### Photocatalysis

The valence band hole is strongly oxidizing, and the conduction band electron is strongly reducing. At the external surface, the excited electron and the hole can take part in redox reactions with adsorbed species such as water, hydroxide ion ( $\text{OH}^-$ ), organic compounds, or oxygen. The charges can react directly with adsorbed pollutants, but reactions with water are far more likely since the water molecules are far more populous than contaminant molecules. Oxidation of water or  $\text{OH}^-$  by the hole produces the hydroxyl radical ( $\text{OH}^\bullet$ ), an extremely powerful and indiscriminant oxidant (Fig. 1).

## Experimental

### Materials and methods

All the chemicals used in this experiment were all of analytical grade. Accurately weighted potassium chromate treated with diphenyl carbazide (DPC) working as masking agent produces reddish purple colour in acid solution, and was neutralized by addition of  $\text{NaOH}$ . Nanocrystalline titanium dioxide was prepared via sol–gel hydrolysis and condensation of ethanol solutions (Merck Chemicals) of titanium isopropoxide ( $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ); diethyl glycol (DEG) was obtained from Merck Chemicals. Deionized water was used throughout the experiment. The absorbance was measured using a UV–Vis spectrophotometer obtained maximum at  $\lambda_{\text{max}} = 540 \text{ nm}$ . Batch experiments were



**Fig. 1** Simplified mechanism for the photocatalysis of a semiconductor catalyst

carried out with different doses (1–5 g/L) of with  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{CdS}$ .

### Preparation of nanosized photocatalysts

Nanosized semiconductors such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{CdS}$  are some of the most basic functional materials. The anatase  $\text{TiO}_2$  was prepared by using  $\text{TiCl}_4$  (20–30%  $\text{HCl}$ ) solution and ammonia. The pH was adjusted by  $\text{NH}_3$  between 10 and 12. The  $\text{TiO}_2$  particles are formed in the beaker, by the hydrolysis of  $\text{TiCl}_4$ . Surface morphology of  $\text{TiO}_2$  nano particles was analyzed using XRD. Nanosized  $\text{ZnO}$  semiconductor was prepared using Zinc sulfate and sodium hydroxide solution. During the reaction,  $\text{ZnO}$  was precipitated and it was annealed in the air at  $250^\circ$  for half an hour. After annealing  $\text{ZnO}$  nanosized particles are formed. Cadmium sulfide can be prepared by the precipitation from soluble cadmium(II) salts with sulfide ion by washing with  $\text{H}_2\text{SO}_4$  and precipitation of  $\text{CdS}$  is formed. After washing the precipitate, soluble cadmium salts were followed by calcinations at  $260^\circ\text{C}$  to convert it in to the hexagonal nanosized particles. These materials are used for photocatalysis for removal of  $\text{Cr(VI)}$ . After adsorption of  $\text{Cr(VI)}$  ions the size of the photocatalysts particles are increased (Table 1).

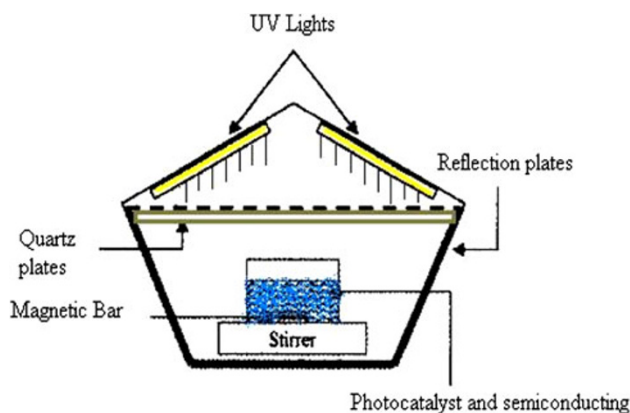
### Preparation of thin film

Titanium isopropoxide solution was added slowly to 0.1 M nitric acid solution dropwise under vigorous stirring; during the addition, a white precipitate was formed. The solution was then heated at  $70^\circ\text{C}$  for 6 h for peptization. In this way, white nanoparticles of  $\text{TiO}_2$  colloids were obtained as indicated by the appearance of turbidity. Finally, aqueous polyethylene glycol with molecular weight of 20,000 solution, with 40% by weight of  $\text{TiO}_2$  was added to get the viscous dispersion of  $\text{TiO}_2$  colloidal solution.

Microscopic glass slides were used as substrates. Prior to coating, the substrates were cleaned thoroughly. First, the substrates were cleaned in water with liquid detergent. Then, they were ultrasonically cleaned in acetone and ethanol for 10 min, respectively. Finally, they were thoroughly rinsed with deionized water.  $\text{TiO}_2$  thin films were

**Table 1** Nanosized photocatalyst before and after treatment using XRD

$\text{TiO}_2$		$\text{ZnO}$		$\text{CdS}$	
Before (nm)	After (nm)	Before (nm)	After (nm)	Before (nm)	After (nm)
0.458	0.576	0.401	0.458	0.421	0.435



**Fig. 2** Schematic diagram of the photocatalytic reactor

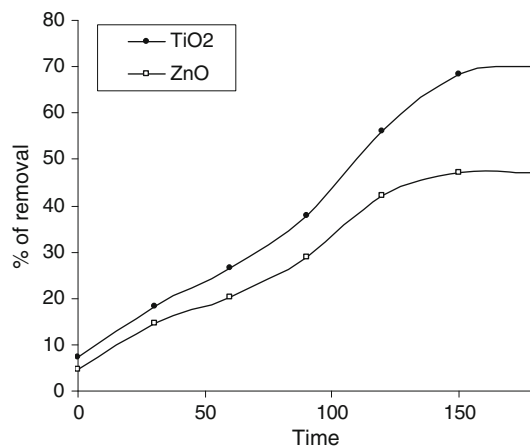
deposited on the substrates by a dip-coating method at room temperature with the withdrawing speed of a dip-coater about 6 cm/min, immediately wiped off an undesired side using isopropyl alcohol. The films were dried in air and then were calcined in air at 100–500°C for 2 h. The dip-coating technique is relatively cheap and easy. Another aspect of this technique is that one can deposit thin films layer by layer.

#### Instrumentation

The removal of Cr(VI) metal was observed by spectrophotometer (Systronic Model-2203). The solution was exposed to UV light (PHILIPS-400 Watt) by addition of TiO<sub>2</sub>, ZnO, and CdS. The distance of source and the reaction vessel is 30 cm (Fig. 2). UV-spectrophotometer in glass cuvette with path length 1.00 cm and the progress of photocatalytic reaction can be observed. The sample was separated from the photocatalysts by centrifuging. Samples were withdrawn at different time interval (15 min). Double-distilled water was used throughout the experiment. To study the effect of important parameters like pH, contact time, initial concentration, and photocatalyst dosage on the Cr(VI) concentration, a batch experiment was conducted for each experiment. The kinetics study was determined by removal of Cr(VI) from aqueous solution at different time intervals.

#### Photocatalytic study

The stock solution of 1,000 ppm of Cr(VI) was prepared by dissolving K<sub>2</sub>CrO<sub>4</sub> (A.R. grade), in the double-distilled water. All the batch studies were carried out using chromate stock solution to 1 L. The absorbance of chromate solution was measured. The calibration curve of Cr(VI) was obtained at  $\lambda_{\max} = 540$  nm. A uniform particle size of the photocatalysts were in between 120 to 500  $\mu$  size for photocatalytic degradation.



**Fig. 3** Photocatalysis of industrial wastewater

Kinetics study was determined by analyzing the metal removal from aqueous solution with constant time interval. In each experiment an accurately weighted amount of TiO<sub>2</sub>, ZnO and CdS was taken in 100 ml solution by adjusting pH of hexavalent chromium solution with addition of requisite volume of A.R. grade NaOH and HCl (E. Merck India) in the different flask at pH 2–7, the flask were placed under UV lamp, with constant shaking by magnetic stirrer. The photocatalyst was separated from the solution by centrifugation. The percentage of removal of Cr(VI) was increased with decrease in pH from 7 to 2. A maximum removal was found to be maximum at pH 2; therefore, pH was finalized at pH 2.

#### Photocatalysis of industrial wastewater

The tannery and dyeing wastewater containing Cr(VI) ions were extracted by using diphenyl carbazide as masking agent forms reddish purple colour of the solution is form. The absorbance of aqueous solution was measured by using spectrophotometer (systronics, model-2203). It was found maximum at  $\lambda_{\max} = 540$  nm. The wastewater sample solution was introduced with light source UV lamp (PHILIPS-400 Watt) at a distance 30 cm from the reaction vessel. In the experiment an accurately weighted amount of photocatalysts were added in the flask and adjusting a pH by using A.R. grade NaOH and HCl (E. Merck India) in the different flask at pH 2 to 7. The flask were placed under UV lamp, with constant shaking by magnetic stirrer. The percentage of removal of industrial wastewater was 68.4% on TiO<sub>2</sub> and 47.6% on ZnO respectively (Fig. 3).

#### Results and discussion

In the photocatalytic degradation of Cr(VI) batch experiments were carried out using different dosages of

photocatalysts TiO<sub>2</sub>, ZnO, and CdS (1–5 g/L). The influent chromium concentration varies from 10 to 50 mg/L.

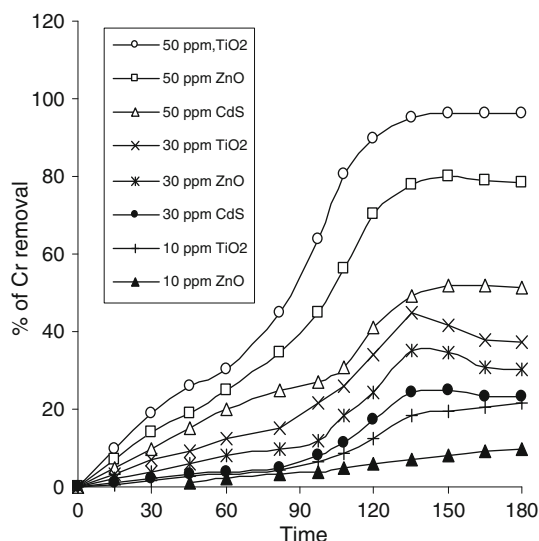
#### Effect of contact time

Effect of contact time and concentration for the removal of Cr(VI) from aqueous solution for TiO<sub>2</sub>, ZnO and CdS (5.0 g/L). The experiments were carried out at 200 rpm at room temperature, pH 2.0 and at initial concentrations of Cr(VI) (10 mg/L) for different time intervals up to 180 min. Percentage of Cr(VI) removal on TiO<sub>2</sub>, ZnO, and CdS increases with increasing in concentration of photocatalyst (Fig. 4).

Though the percentage of removal increases with photocatalysts concentration and it is constant after equilibrium time. The removal of Cr(VI) on TiO<sub>2</sub> was 96.4% for 50 mg/L, 45.4% for 30 mg/L and 21.5% for 10 mg/L. For ZnO the removal was 78.2%, 36.7% and 11.3% for 50, 30 and 10 mg/L respectively, with CdS it was 48.2% for 50 mg/L, 25% for 30 mg/L and it was just 6.3% for removal of Cr(VI) respectively. It was observed that as the amount of photocatalyst increases from 1.0 to 5.0 g/L, the degradation of Cr(VI) increases with increase the concentration of photocatalysts.

#### Effect of pH

The removal of chromium from wastewater using photocatalysts is highly dependent on the pH of the solution (Ku and Jung 2001). Degradation of typical inorganic pollutants from water is increased with decreasing pH. The effect of pH on the removal of chromium by different photocatalysts like TiO<sub>2</sub>, ZnO, and CdS on of different influent chromium

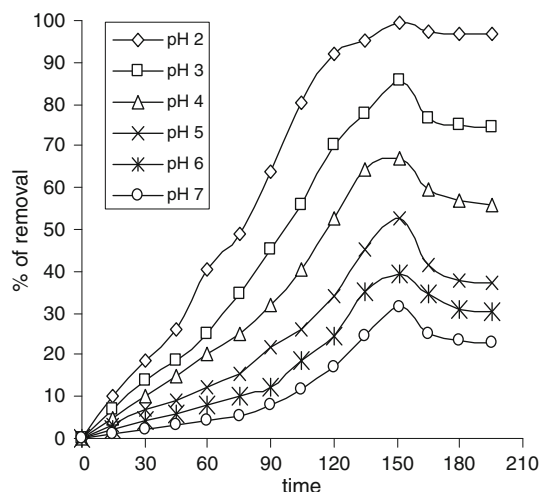


**Fig. 4** Effect of contact time on removal of Cr(VI), TiO<sub>2</sub>, ZnO and CdS at pH 2

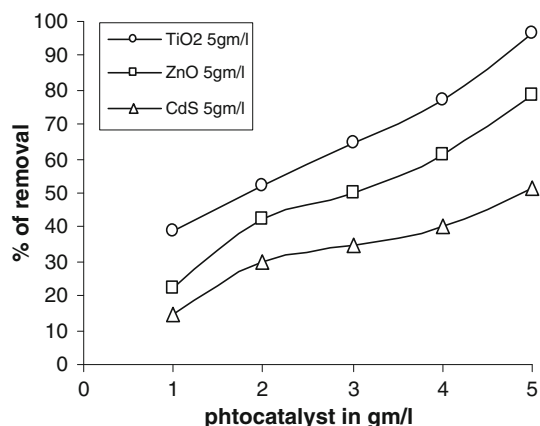
concentrations was studied (Senthilkumar et al. 2006). The Cr(VI) removed with different time interval at pH 2 shown in Fig. 5. The effect of pH 2 has highest removal of Cr(VI) at 96.8%; at pH 3 it was 85.6% and for pH 4 it was 67.2%, pH 2 was chosen for the further reaction.

#### Effect photocatalyst dosage

The effect of photocatalyst dosage on removal of chromium from aqueous solution is shown in Fig. 6. It is observed that, the percentage removal of chromium increases with increase in photocatalyst dosage. At highest photocatalyst loading the removal is more accessible and because of this, the removal per unit weight of photocatalysts is higher (Kelar et al. 2004). It is observed that the chromium removal rate increases with increase in photocatalyst dosage. It was observed that the chromium removal percentage is found to be 96.8% at photocatalyst loading of 5 g L<sup>-1</sup>. As the TiO<sub>2</sub> loading is increased from



**Fig. 5** Effect of pH on removal of Cr(VI) ion 5 g/L in the absence of photocatalyst



**Fig. 6** Effect of photocatalysts loading (5 g/L) Cr(VI) removal

1 to 5 g L<sup>-1</sup>, the chromium removal percentage also increases from 38.7 to 96.8%. As the photocatalyst dosage increases from 1 to 5 g L<sup>-1</sup>, the percentage increases from 22.6 to 78.5% for ZnO and 13.8 to 49.2% for CdS.

#### Dark adsorption and photodegradation of Cr(VI)

Dark adsorption of Cr(VI) was very low as compared to photodegradation under UV light. Maximum adsorption of 51.3% was obtained in absence of light. Rate of reduction was very low in spite of the presence of hole scavengers, due to less thermodynamic driving force. In the presence of UV light degradation was better Fig. 7.

#### Chemical oxygen demand

The chemical oxygen demand test is widely used as effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO<sub>2</sub> and water. In the present work result of COD were taken as one of the parameter to judge the feasibility of photocatalytic process for the degradation of Cr(VI) metal solution. In this experiment the Cr(VI) metal solution (100 ml) and the photocatalysts 0.05 g L<sup>-1</sup> were taken in the reactor and exposed to UV light for 120 min. Metal sample of about 10 mL was taken out at regular intervals from the test solution, centrifuged for 10–15 min and the absorbance was recorded at 540 nm. Comparison of the COD values of the initial dye concentration with ht irradiated solution indicates that the COD values are substantially reduced. It is observed that the COD values decreases from 875 to 116 mg L<sup>-1</sup>.

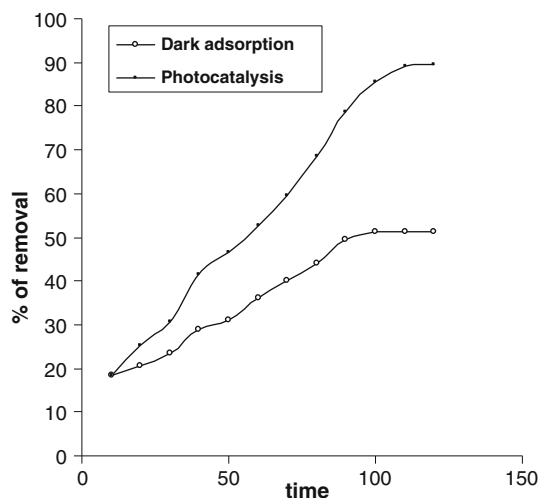


Fig. 7 Dark adsorption and photocatalytic deposition

The influence of Cr(VI) metal concentration on percentage of COD removal over photocatalyst TiO<sub>2</sub>, ZnO, and CdS is shown in Fig. 8. It is clearly understood that the percentage of COD reduction increases with increasing concentration of Cr(VI) ions for the same irradiation time. Thus, higher concentration of Cr(VI) may need longer illustration time.

#### Infrared spectra

The FT-IR spectra of before and after degradation nanomaterials TiO<sub>2</sub> were recorded with the help of Perkin\_Elmer, PE-RXI to study the functional group and binding sites. For FT-IR study, 1 g of fine powder was encapsulated in 20 mg of KBr in order to prepare translucent sample disks. The IR spectra of titanium dioxide exhibiting a stretching vibration at 752 cm<sup>-1</sup> is attributed to the presence of CH<sub>2</sub> group. A broadband at 1,205 cm<sup>-1</sup> is due to amine group. In addition with this, the IR spectrum shows the absorption band at 1,506, 1,510 cm<sup>-1</sup>, indicates the presence of aromatic ring. The sharp peak at 2,341 and 2,353 cm<sup>-1</sup> shows nitrile group. A stretchable vibration band at 2,931, 2,993 cm<sup>-1</sup> confirms the presence of C–H group and NH<sub>3</sub> residue present in the TiO<sub>2</sub>, the OH stretching vibrations at 3,410 and 3,419 cm<sup>-1</sup> and NH<sub>2</sub> stretching vibrations at 3,718, 3,724 cm<sup>-1</sup> (Fig. 9).

#### XRD analysis

The XRD pattern of TiO<sub>2</sub> and CdS shows the peak at 25.25°, 46.78° and 25.24°, 46.38° respectively. X ray diffraction of TiO<sub>2</sub> and CdS was recorded by Philips Holland. Xpert-MPD model using.

Cu-K $\alpha$  target. The *d* values obtained for TiO<sub>2</sub> and CdS were 0.5764, 0.4706 corresponding to 0.4583 and 0.4012, respectively, Table 1. It indicates that after photocatalytic

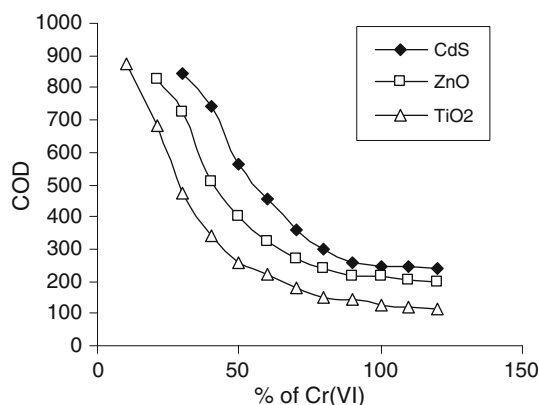
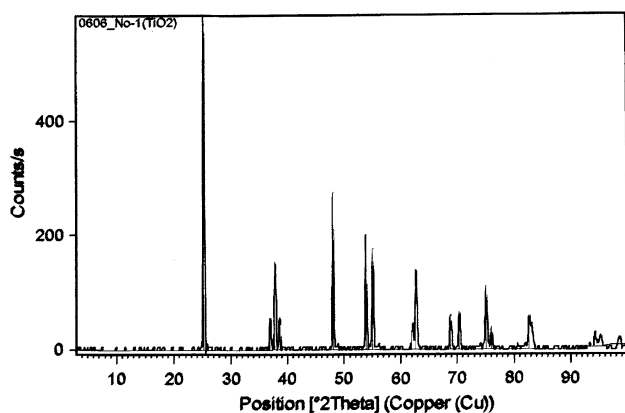
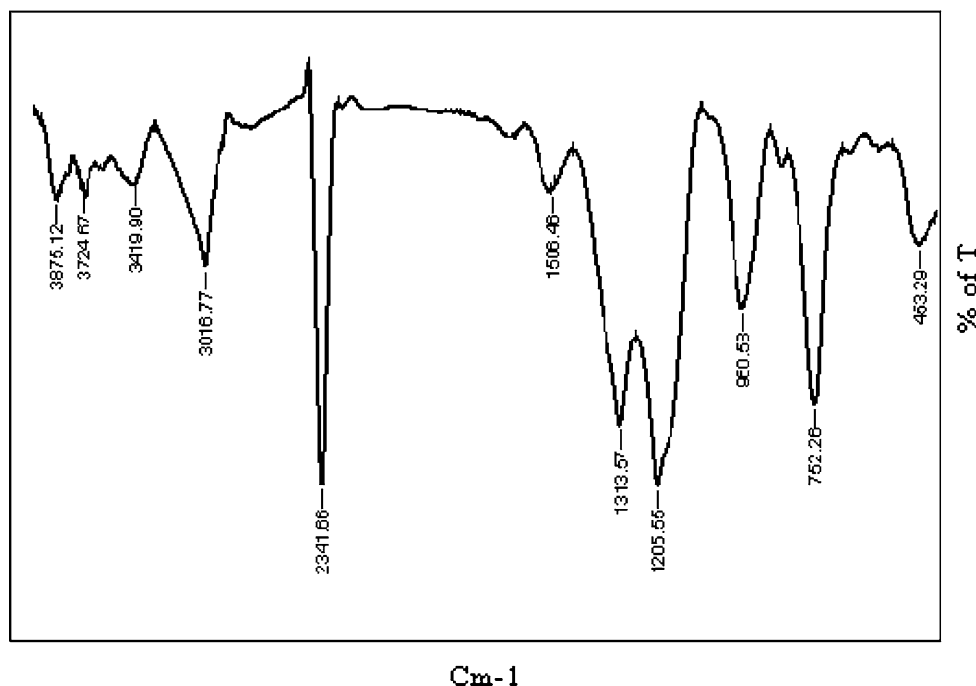


Fig. 8 COD reduction 2 h after

**Fig. 9** FT-IR spectra of TiO<sub>2</sub> before and after treatment

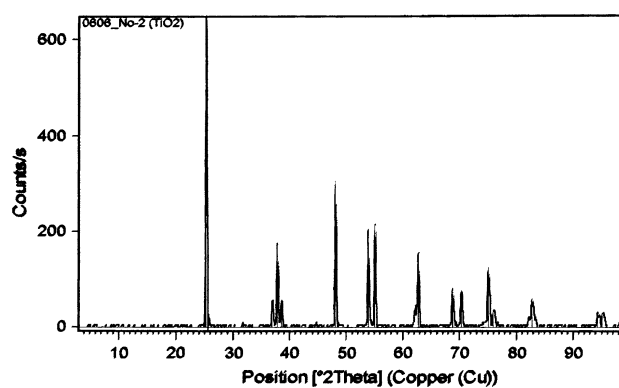


**Fig. 10** XRD diagram of TiO<sub>2</sub> semiconductor before the removal of metal

degradation the size of particles increases. The diffractogram of TiO<sub>2</sub> is shown before and after Fig. 10, 11 and 12 shows X ray diffraction of CdS.

### SEM

The scanning electron micrographs are recorded with Philips XL-30 SEM analyzer for characterization the surface morphology of TiO<sub>2</sub> and ZnO photocatalyst (Fig. 13 and 14) on the Cr(VI) before and after degradation. The SEM photographs depict the surface texture and porosity, before and after treatment of photocatalysts. It is clear that TiO<sub>2</sub> has rough surface with heterogeneous porous nature. It indicates that there is good possibility for adsorption Cr(VI) on TiO<sub>2</sub>.



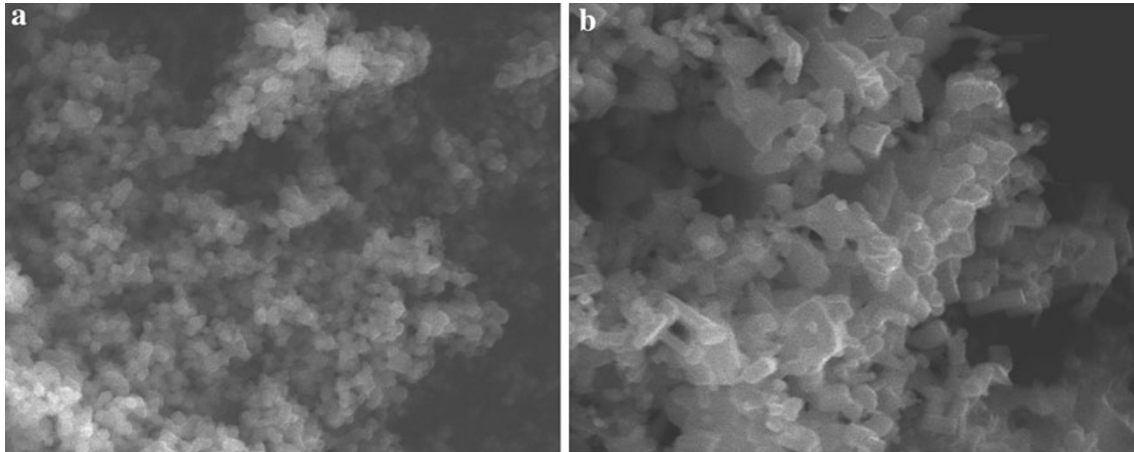
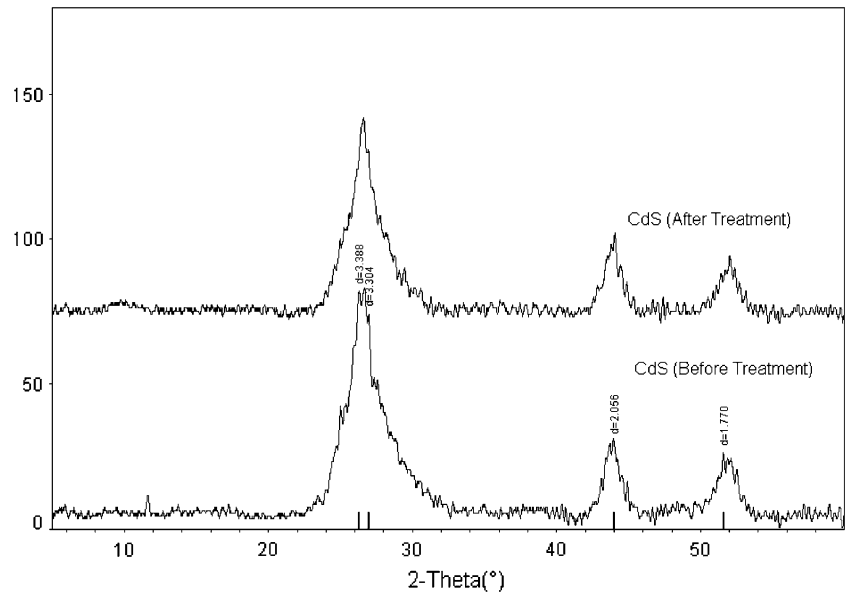
**Fig. 11** XRD diagram of TiO<sub>2</sub> semiconductor after the removal of metal

The SEM image of nano-TiO<sub>2</sub> film prepared by sol-gel method calcined at 300°C is shown in Fig. 15. The SEM micrograph is spherical and highly micro-porous in nature. The pore size ranges from 20 to 100 nm in diameter. The porosity occurs by using polyethylene glycol (PEG) which is used as binder leaves the surface of substrate at higher calcination temperature.

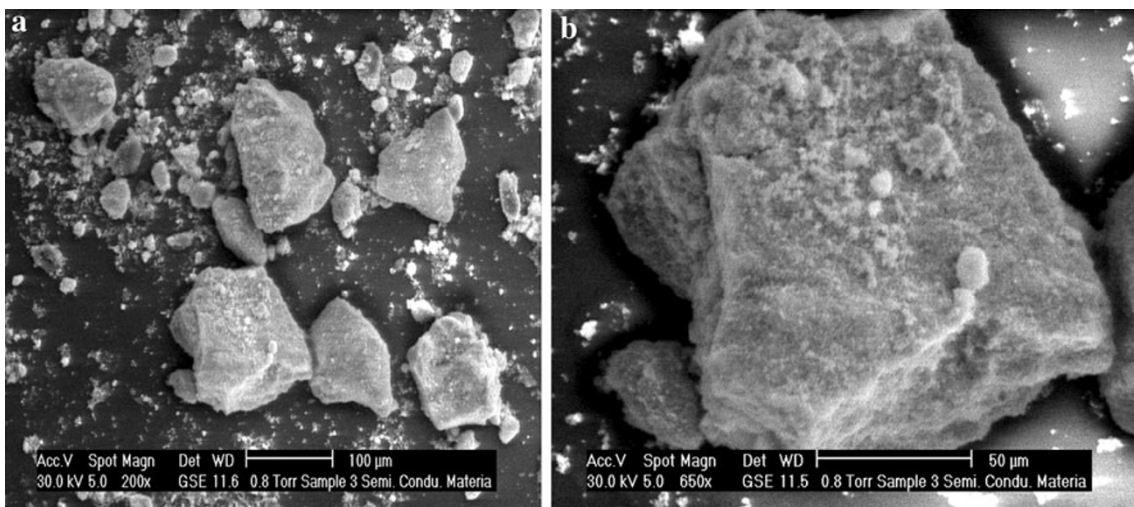
### EDX

Energy dispersive X ray spectroscopy (EDX) is chemical microanalysis technique is a co-junction with SEM, EDX analysis. It was characterized the element composition of the typical EDX pattern of TiO<sub>2</sub> as well as ZnO (Fig. 16 and 17).

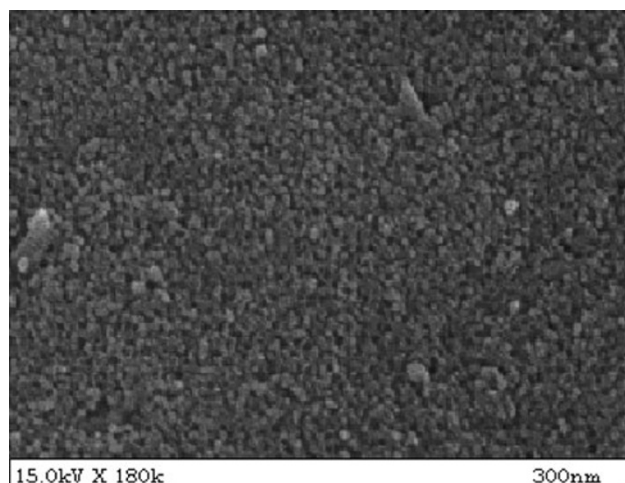
**Fig. 12** XRD diagram of CdS semiconductor before and after the removal of Cr(VI)



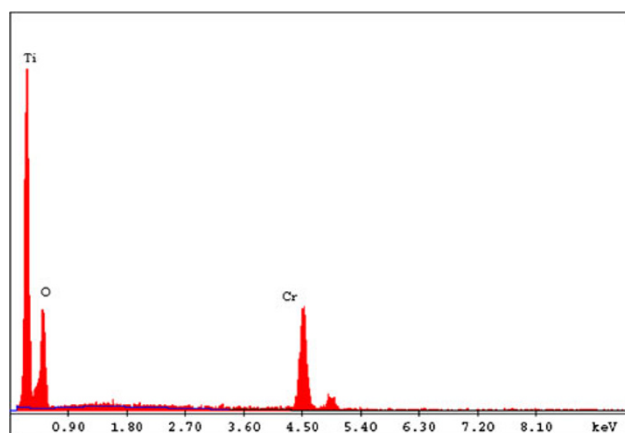
**Fig. 13** SEM images of TiO<sub>2</sub> **a** before treatment **b** after treatment



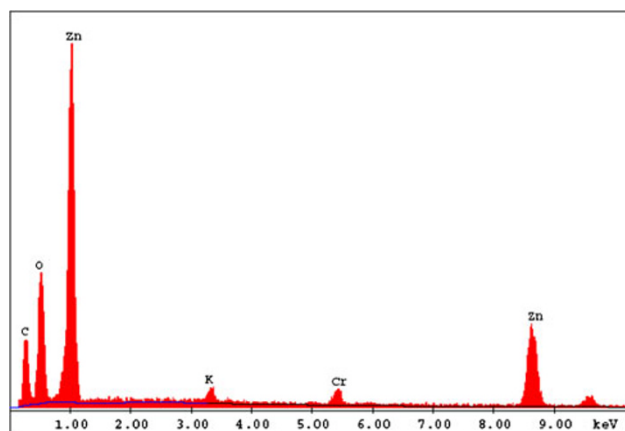
**Fig. 14** SEM images of ZnO **a** before treatment **b** after treatment



**Fig. 15** SEM micrograph from TiO<sub>2</sub> thin film deposited on glass substrate



**Fig. 16** EDX spectrum of TiO<sub>2</sub> photocatalyst



**Fig. 17** EDX spectrum of ZnO photocatalysts

The chemical composition of TiO<sub>2</sub> was found to be Ti = 69, O = 16, Cr = 12 and carbon = 3% confirmed the presence of Cr after degradation of Cr(VI) metal on TiO<sub>2</sub>. The EDX of

ZnO was C = 10, O = 15, Zn = 61, K = 6, and Cr = 8% found. It is also confirmed that Cr can be removed after degradation of Cr(VI) metal from waste water.

## Conclusion

Removal of toxic hexavalent form of Cr(VI) from wastewater was possible using selected photocatalysts like TiO<sub>2</sub>, ZnO, and CdS. Photocatalysis has been ascertained to be a promising technique for the removal of heavy metals from industrial effluents. The removal of chromium is maximum at pH 2 for different amount of photocatalysts. The removal of Cr(VI) at lower pH values may be attributed to the large number of the H<sup>+</sup> ions was neutralized the negatively charged or convert a neutral group. The chromium removal percentage increases as dosage of photocatalysts increases and mass removal rate increases with increase in photocatalyst loading. The highest photodegradation rate was found on TiO<sub>2</sub>; a nanocrystalline powder was the most effective for degradation of Cr(VI). than TiO<sub>2</sub> thin film prepared by by sol–gel method. It removed only 46.5% Cr(VI) with same time. More than 96% removal of Cr(VI) is possible at the 50-ppm concentration. With increase in the dose of photocatalysts, initial concentration of Cr(VI) and increase in contact time up to 180 min are favorable. TiO<sub>2</sub> was found to be the best photocatalyst. ZnO was a less effective photocatalyst than TiO<sub>2</sub> as it removes 80% Cr(VI), and CdS is very poor photocatalyst as it removes only 45% Cr(VI). The TiO<sub>2</sub> thin film prepared by sol–gel method removed only 46.5% Cr(VI) with same time. The removal of metals using thin film technique is less effective than that using the nanosized powder. By using XRD it is found that the size of the photocatalytic particles increases after the dye reacted with these particles. SEM photographs show that the TiO<sub>2</sub> and ZnO have heterogeneous pores in nature as well as the surface is rough in nature.

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