



## Photocatalytic Degradation of Pb(II) By Using Different Semiconducting Materials

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### ABSTRACT

A various processes are used for removal of metals from industrial wastewaters. The relatively newest technology of which is photocatalysis. The removal of hazardous metals Pb (II) by using semiconducting materials as Titanium dioxide, Zinc oxide as well as Cadmium sulphide from wastewater. In this study, photocatalysis processes had been employed for the removal of lead at different pH from 2 to 11, the detention time was kept constant (180 min). Results indicated that the removal were 98.8% for Pb (II) at pH 6 and shows optimum efficiencies. These results

were all obtained best in the use of UV irradiation and 0.6 g/L TiO<sub>2</sub>. These results are considered for all industrial treatment plants which have experienced the problem of this hazardous metal in their effluents. The kinetic studies were used to interpret the data of this investigated system. The semiconducting materials TiO<sub>2</sub> had higher degradation capacity than the ZnO and CdS. Results indicate that Lagergrin second order fits better for the removal of Pb (II).

**Keywords:** Pb(II), Photocatalysis, Adsorption isotherm, Kinetic study, XRD, SEM

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### INTRODUCTION

Due to rapid development and industrialization all over the world, the levels of industrial pollution have been steadily rising. The pollution problem of industrial wastewater is becoming more and more serious in the world. Consequently, the treatment of polluted industrial wastewater remains a topic of global concern<sup>1,2</sup>. Wastewater containing heavy metals are considered to be hazardous to both human life and the environment due to their acute toxicity and non-biodegradability, even when heavy metals are present in trace concentration<sup>3</sup>. Several mishaps due to heavy metals contamination in aquatic environment increased the awareness about heavy metal toxicity<sup>4</sup>.

The Important toxic metals which include Cr, Cd, Zn, Ni, Cu, Pb, etc. are used in the form of catalysts, additives or reagents<sup>5</sup>. The initial anthropogenic pathways through which lead enter in to aquatic environment is via waste from industrial process<sup>6</sup>. The industries like metal coating , Electroplating, fertilizer industries, tannery, dyes and pigments manufacturing, chemical industries, Petroleum refineries, Lead smelting, mining, dyeing and printing industries, petroleum refinery, ammunition, ceramic and glass industries, Mine drainage, Battery manufacturing etc. release hazardous wastewater disposal containing metal ions added in the water<sup>7,8</sup>.

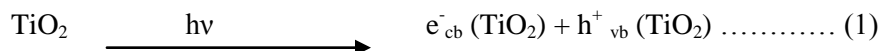
Industrial wastewater containing Pb (II) in the range of 120-250 ppm and in drinking water above the permissible level (0.05mg/L)<sup>9</sup>. A number of heavy metals such as Pb(II) have adverse effects on human health, particularly in children causes kidney failure, nervous system damage and bone softening as well as other serious illnesses<sup>10,11</sup>. Very low levels of exposure to young children under the age of six can result in reduced IQ, learning disabilities, attention deficit disorders, behavioral problems, stunted growth, and impaired hearing<sup>12</sup>. At high levels of exposure of Pb (II) a child may become mentally retarded, fall into coma and even die from lead

poisoning<sup>13</sup>. In adults, lead can increase blood pressure and cause fertility problems, muscle and joint pain, irritability and memory and concentration problems<sup>14</sup>. The presence of lead causes various types of diseases, anemia, encephalopathy, hepatitis and nephritic syndrome<sup>15</sup>.

A number of technologies have been developed over the year for the removal of metal ions from water and wastewater include technique like decomposition, coagulation, followed by filtration, chemical reduction, precipitation complex, solvent extraction, ion exchange, ion floating, reverse osmosis, precipitation, adsorption and photocatalysis<sup>16</sup>. Most of the processes have disadvantages as continuous input of chemicals, high cost, incomplete removal of metals and these processes needs the high degree of operation skill<sup>17</sup>. Out of the various methods for the removal of metal ions from water and wastewater photocatalysis is very advanced technique and most popular<sup>18-20</sup>. Now days it's widely used process for removal of heavy metals from wastewater effluent<sup>21</sup>. Therefore, in the present investigation, photocatalytic degradation method is used for removal of Lead (II) from liquid industrial effluent. Hence in the present investigation, selections of suitable semiconducting materials like TiO<sub>2</sub>, ZnO and CdS as photocatalyst which can remove Lead (II) from the wastewater<sup>22</sup> was studied. A detailed batch study with the selected photocatalysts has been carried out. The effect of Contact time, pH, concentration of photocatalyst, and kinetic study were also investigated.

## PRINCIPLE

Photocatalysis over a semiconductor oxide such as TiO<sub>2</sub> is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor (ca.3.2 eV for anatase), producing electron-hole (e<sup>-</sup>/h<sup>+</sup>) pairs, as written in the equation 1.



Where cb is conduction band and vb is the valence band.

Consequently, following irradiation, the TiO<sub>2</sub> particle can act as either an electron donor or acceptor for molecules in the surrounding medium. The electron and hole can recombine, releasing the absorbed light energy as heat, with no chemical effect. Otherwise, the charges can move to "trap" sites at slightly lower energies. The charges can still recombine, or they participate in redox reactions with adsorbed species. The valence band hole is strongly oxidizing, and the conduction band electron is strongly reducing. At the excited electron and the hole can take part in redox reactions with adsorbed species such as water, hydroxide ion (OH<sup>-</sup>), 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 OH<sup>-</sup> by the hole produces the hydroxyl radical (·OH), an extremely powerful and indiscriminant oxidant. For a comparison, the oxidation potential of hydroxyl radical (·OH) is 2.8 V relative to the normal hydrogen electrode (NHE); of other substances used for water disinfection: ozone (2.07V), H<sub>2</sub>O<sub>2</sub> (1.78 V), HOCl (1.49 V) and Chlorine (1.36 V). OH radicals rapidly attack pollutants at the surface, and possibly in solution as well, and are usually the most important radicals formed in TiO<sub>2</sub> photocatalysis. An important reaction of the conduction band electron is reduction of adsorbed O<sub>2</sub> to O<sub>2</sub> molecule. This both prevents the electron from recombining with the hole and results in an accumulation of oxygen radical species that can also participate in attacking contaminants<sup>23, 24</sup>.

## MATERIALS AND METHODS

Solution of Pb(II) were prepared Lead nitrate was used as the source of metal ions by using Pb(NO<sub>3</sub>)<sub>2</sub> according to standard method<sup>25</sup>. TiO<sub>2</sub> (anatase), ZnO, CdS were provided by S.D. Fine Chemicals and used as received. Lead (II) was added as Pb(NO<sub>3</sub>)<sub>2</sub> (Merck). Dithizone (Merck), Ethanol (EtOH), NaOH was of A.R. grade (99.9%). HClO<sub>4</sub> was used for pH adjustments. All reagents were A.R. graded and highest purity used without

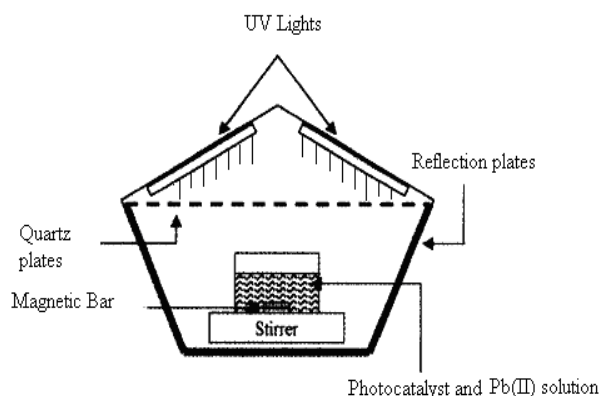
further purification. Deionized water was used throughout the experiment. Lead nitrate reacts with Dithizone produce a greenish colour in slightly acidic solution which is neutralized by addition of NaOH. The absorbance was measured using a UV-Vis spectrophotometer (model Systronic-2203) obtained maximum at  $\lambda_{\text{max}} = 620 \text{ nm}$ . A calibration curve was prepared by measuring the absorbance of known Lead nitrate concentrations in the range of 0.50–100 mg/L. Batch experiments were carried out with different doses (2–6 gm/L) of with  $\text{TiO}_2$ , ZnO and CdS. The Effect of various process parameters on the extent of removal of metals ions was studied. In all photodegradation experiment the values of the percentage removal were calculated.

### **Preparation of Nanosized semiconducting materials:**

Nano sized semiconductors as  $\text{TiO}_2$ , ZnO and CdS are one of the most basic functional materials. For the preparation of anatase  $\text{TiO}_2$  chemicals by using  $\text{TiCl}_3$  (in 20-30% HCl) solution and ammonia were used for the preparation of anatase  $\text{TiO}_2$ . The pH was adjusted by  $\text{NH}_3$  between 10-12. The  $\text{TiO}_2$  particles are formed in the beaker, by the hydrolysis of  $\text{TiCl}_3$ . Surface morphology of  $\text{TiO}_2$  nano particles was analyzed by using XRD. Nano sized ZnO semiconductor was prepared by using Zinc sulphate and sodium hydroxide solution. During the reaction, ZnO is precipitated and it was annealed in the air at  $250^\circ\text{C}$  for half an hour. After annealing ZnO nano sized particles are formed<sup>26, 27</sup>. 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 CdS is formed, the washing of the precipitate to remove soluble cadmium salts followed by calcinations at  $260^\circ\text{C}$  to convert it to the hexagonal form produced a nanosized particles of a CdS. These materials are used for photocatalysis for removal of Cr (VI). After adsorption of Cr (VI) ions the size of the photocatalysts particles are increases.

### **Photoreactor**

The photocatalysis experiments were performed in a 500 ml Pyrex reaction vessel. The intensity of the incident light was measured by the Lux meter (model DT-1301). The reaction vessel was illuminated from the top and continuous stirring of the suspension was provided by mean of magnetic stirrer<sup>28</sup>. The reaction mixture of lead



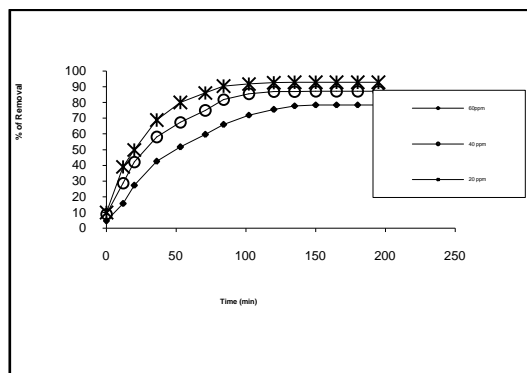
**Fig.1- Schematic diagram of the Photocatalysis experimental device**

nitrate with dithizone extracted mass was irradiated with light source UV lamp (Philips-400Watt) at a distance 30cm from the reaction vessel (fig 1). In each experiment an accurately weighted amount of  $\text{TiO}_2$ , ZnO and CdS was taken in 100 ml lead solution, by adjusting pH of Lead solution with addition of requisite volume of A.R. grade NaOH and  $\text{HClO}_4$  (E. Merck India), in the different flask at pH 2 to 11 the flask were placed under UV lamp the flask with constant shaking by magnetic stirrer, after certain period (15 min. Interval). The semiconducting materials were separated from the solution by centrifugation.

## **RESULTS AND DISCUSSIONS**

In order to interpret the photocatalytic degradation of Pb (II) ions on the surface of semiconductor degrade the metal ions exhibit a strong dependence on the formation of highly soluble metal species.

### Effect of Contact time

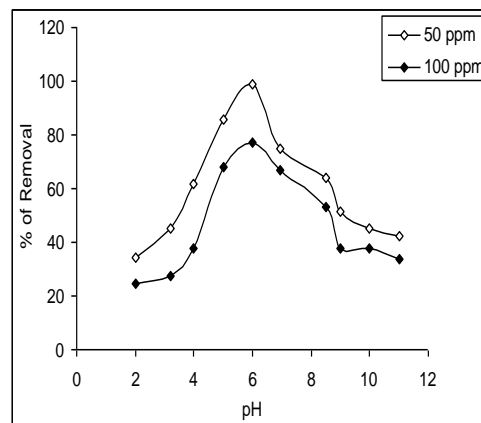


**Fig.2- Effect of contact time of Pb(II) with TiO<sub>2</sub> at pH 6**

with CdS it was 48.2 %, 27.2 % and just 6.3 % of Pb(II) for 60,40 and 20 ppm concentration of Pb(II), respectively . It was observed that the amount of photocatalyst increases from 0.2 g/L to 0.6 g/L, irradiation time for complete degradation of Pb(II) decreases, as the concentration increases of photocatalysts.

### Effect of pH

The removal of Pb(II) from wastewater by semiconducting material is highly dependent on the pH of the solution, which affects the degradation, and the degree of ionization and speculation of adsorbate<sup>29</sup>. Degradation of typical inorganic pollutants from water is increased with decreasing pH. In many cases, this may result from the neutralization of negative charges at the surface of the carbon with increasing hydrogen ion concentration there by reducing hindrance to diffusing and making available more of the active surface of the photocatalysts<sup>30</sup>.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 concentrations is studied The effect of pH shown figure 3. The percentage of removal decreases with the increases in metal ion concentration.

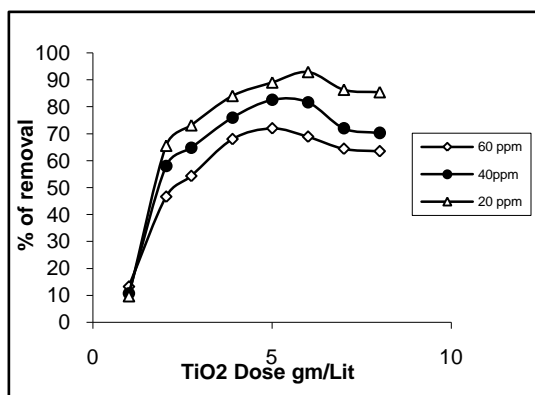


**Fig. 3- pH effect of Pb (II) at different concentrations**

The percentage photodegradation of Pb(II) by the semiconducting materials from the aqueous solution of 50 and 100 mg/L at various pH was examined. The percentage of removal of Pb(II) increased with increased in pH is reached a maximum of 92.7 % and 86.8 % from initial concentration of 50 and 100 mg/L respectively at pH 6. The percentage of removal is decrease beyond pH 6.0 at pH 9.0 it was 61.4 % of removal was observed at initial concentration. pH 6 has highest removal of Pb(II) 96.8 %, pH 6 was choose for the further reaction.

### Effect of photocatalyst dose

The effect of Semiconducting material on removal of Pb(II) form aqueous solution is shows that the percentage removal of Pb(II) increases with increase in semiconductor TiO<sub>2</sub>, ZnO and CdS loading. Further, at lowest quantity loading of the semiconductor removal is more accessible and because of this, the removal per unit weight of Semiconducting material is higher. It was found that the Pb(II) removal rate is increases with increase



in semiconducting material loading (fig 4), that the Pb(II) removal percentage is found to be maximum 84.6 at photocatalyst loading of 6 gm/L of TiO<sub>2</sub>. When the TiO<sub>2</sub>, ZnO and CdS loading is increased from 2 to 6 gm, the Pb(II) removal percentage also increases from 48.7 to 84.6 % with TiO<sub>2</sub>, 40.2 to 66.6 % with ZnO and 32.9 to 52.1% with CdS semiconducting materials.

**Fig.4- Effect of semiconductor dose different concentration of Pb(II) with TiO<sub>2</sub>**

**Kinetic study**

The kinetic study of Pb(II) removal by photocatalytic degradation the pseudo first order and Pseudo second order kinetics models were used to fit in the experimental data, log (qe-qt) Vs t was plotted at different Pb(II) concentrations (fig 5). The pseudo first order model data do not fall on the straight line for the most initial concentration indicating that this model is less appropriate.

The Lagergren first order rate constant (K1) and qe cal determined from the model are presented in table 1 along with the corresponding correlation coefficient. Lagergren first order model express as equation 2.

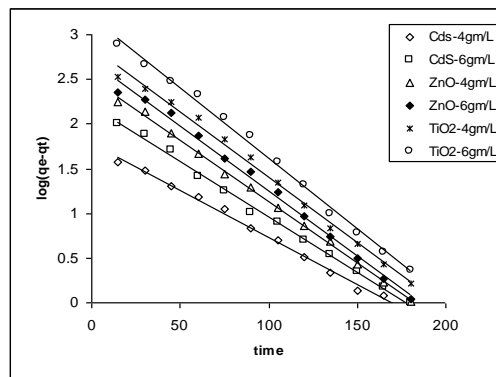
$$\log (q_e - q_t) = \log q_e - (K_1 / 2.303)t \dots \dots \dots (2)$$

Where qe and qt are the adsorption capacity in mg/g at equilibrium at the time t respectively K1 is the rate constant of pseudo first order adsorption (min<sup>-1</sup>). The first order rate constant K1 and qe for first order equation are determined from the slope and intercept. The coefficient of correlation for the first order kinetic model was not high for all adsorbents and concentration. The estimated values (table 1) show that the model is not appropriate to describe the adsorption process. The adsorption kinetics data were explained by the pseudo second order kinetic model.

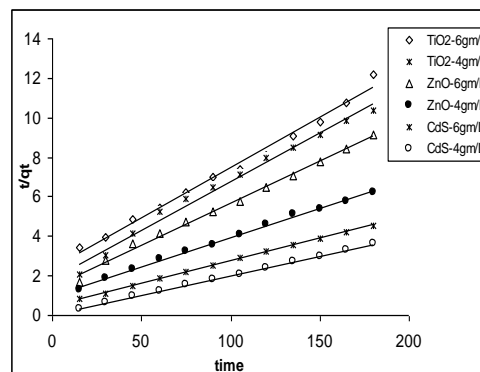
$$t/q_t = 1/K_2 q_e^2 + (1/q_e)t \dots \dots \dots (3)$$

K2 is the second order rate constant (mg<sup>-1</sup>min<sup>-1</sup>), the values of K2 is different initial dye concentration for all adsorbent were calculated from the slope of the representative linear plot of t/qt Vs t, figure 6. The values of correlation coefficient were 0.9967 to 0.9995, suggested a strong relationship between the parameters and also explain that the process follows the pseudo second order kinetics.

**Fig 6. Pseudo Second order of Pb(II) on TiO<sub>2</sub>, ZnO and CdS**



**Fig. 5 Pseudo First order kinetics for removal of Pb(II) with semiconducting nanosized materials 4-6gm/lit**



The experimental kinetics data were further analyzed using the pseudo second order model. By plotting  $t/q_t$  Vs  $t$  at different initial Pb(II) concentration, a straight line was obtained in all cases and using equation 3, the second order rate constant  $K_2$  and  $q_e$  values were determined from the plot. The correlation coefficient obtained were very high of  $\text{TiO}_2$  ( $r^2 > 0.9999$ ) and the theoretical  $q_e$  cal values obtained from this model were closer to the experimental  $q_e$  cal Values obtained from this model were closer to the experimental  $q_e$  values at different initial Pb(II) concentration ( table1). It is important to note that for the first order model the this study,

$R^2 < 0.9778$  at Pb(II) concentration correlation coefficient obtained in this study, ( $R^2 = 0.9999, 0.9995$  and  $0.9986$  for  $\text{TiO}_2$ , ZnO and CdS respectively) at different initial concentration, which is lower as compared to the correlation coefficient obtained from second order model. Moreover from the table 1, it is observed that the experimental values of  $q_e$  exp. are not good in agreement with theoretical values calculated ( $q_e$  cal) from the pseudo first order equation, therefore it can be concluded that the pseudo second order kinetic model provided a better correlation for the adsorption of Pb(II) on  $\text{TiO}_2$ , ZnO and CdS at different initial concentration compared to the pseudo first order model.

**Table: 1 - Initial concentration and dose of semiconducting materials for Lagergrin First Order and Second order reaction of  $\text{TiO}_2$ , ZnO and CdS studied systems**

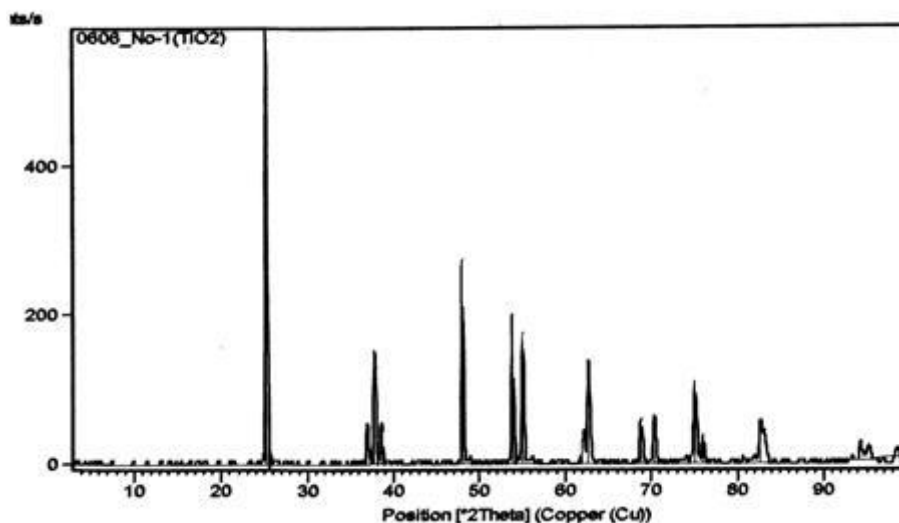
| Adsorbent        | Adsorbent dose g/L | Pb(II) Conc. mg/L | qe expt. mg/g | Pseudo First order |        |        | Pseudo Second order |        |        |        |
|------------------|--------------------|-------------------|---------------|--------------------|--------|--------|---------------------|--------|--------|--------|
|                  |                    |                   |               | qe cal.            | K1     | $r^2$  | qe cal              | K2     | $r^2$  | h      |
| TiO <sub>2</sub> | 6                  | 20                | 18.34         | 9.22               | 0.0184 | 0.9667 | 18.26               | 0.0296 | 0.9981 | 11.792 |
|                  |                    | 40                | 57.11         | 26.77              | 0.0207 | 0.9697 | 56.91               | 0.0014 | 0.9917 | 56.818 |
|                  |                    | 60                | 99.42         | 33.63              | 0.0143 | 0.9999 | 97.68               | 0.0025 | 0.9966 | 24.272 |
| ZnO              | 6                  | 20                | 11.31         | 6.31               | 0.0038 | 0.9922 | 11.72               | 0.0116 | 0.9987 | 01.595 |
|                  |                    | 40                | 58.10         | 17.16              | 0.0187 | 0.9987 | 57.88               | 0.0015 | 0.9939 | 05.347 |
|                  |                    | 60                | 99.06         | 29.62              | 0.0166 | 0.9982 | 98.04               | 0.0033 | 0.9943 | 32.895 |
| CdS              | 6                  | 20                | 08.45         | 2.45               | 0.0156 | 0.9778 | 08.32               | 0.0064 | 0.9957 | 02.458 |
|                  |                    | 40                | 18.56         | 6.78               | 0.0354 | 0.9839 | 18.11               | 0.0038 | 0.9974 | 07.866 |
|                  |                    | 60                | 26.47         | 18.95              | 0.0658 | 0.9989 | 26.85               | 0.0018 | 0.9981 | 13.265 |

#### ***X ray Diffraction:***

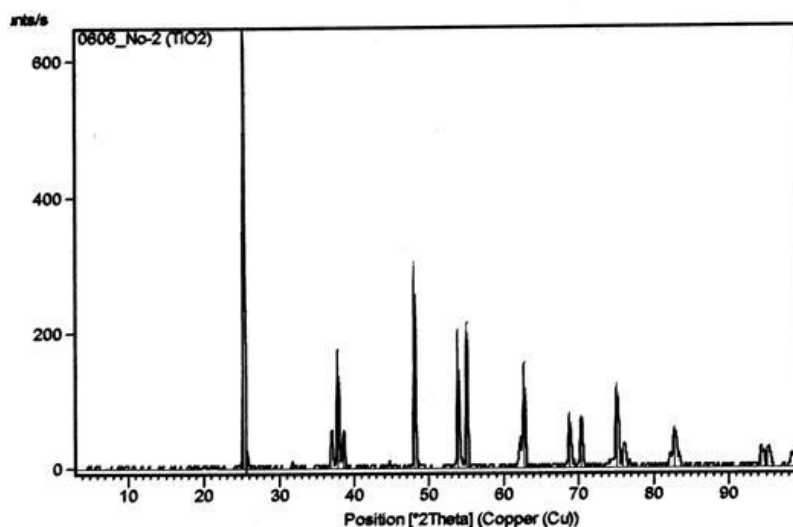
The X ray powder diffraction pattern of  $\text{TiO}_2$  and ZnO shows the peak at 25.25 Å, 31.78 Å the diffraction pattern shows a shift to 25.24 Å and 36.38 Å indicating the interrelation of surfactant ions in the ZnO. X ray diffraction of  $\text{TiO}_2$ , ZnO and CdS were recorded by Philips Holland. Model-Xpert MPD using copper target. The d values obtained for  $\text{TiO}_2$  and ZnO CdS was 0.576, 0.458 and 0.431 correspond to 0.458 0.401 and 0.421 respectively, (Table 2). It indicates that after photocatalytic degradation the size of particles are increases. The diffractogram are shown in figure 7 to 11.

**Table: 2. Nano sized photocatlyst before and after treatment by using XRD**

| TiO <sub>2</sub> |          | ZnO      |          | CdS      |          |
|------------------|----------|----------|----------|----------|----------|
| Before           | After    | Before   | After    | Before   | After    |
| 0.458 nm         | 0.576 nm | 0.401 nm | 0.458 nm | 0.421 nm | 0.432 nm |



**Fig.7 XRD diagram of TiO<sub>2</sub> semiconductor before irradiation with Pb(II)**



**Fig.8 XRD diagram of TiO<sub>2</sub> semiconductor after irradiation with Pb(II)**

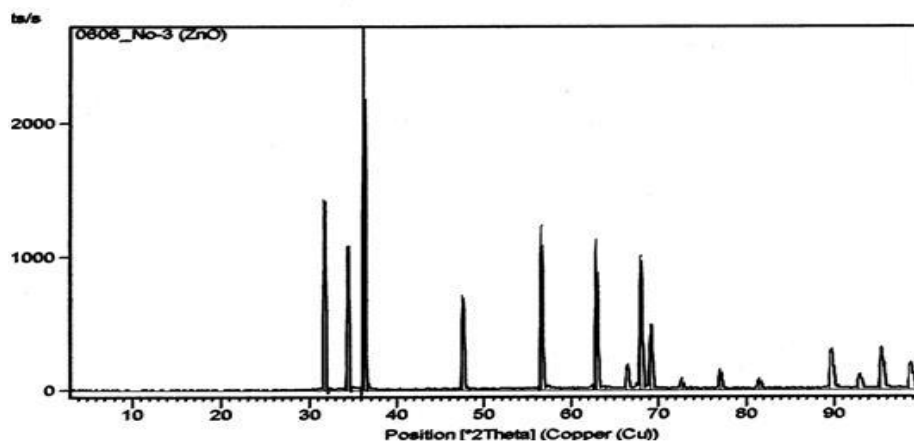


Fig.9 XRD diagram of ZnO semiconductor before irradiation with Pb(II)

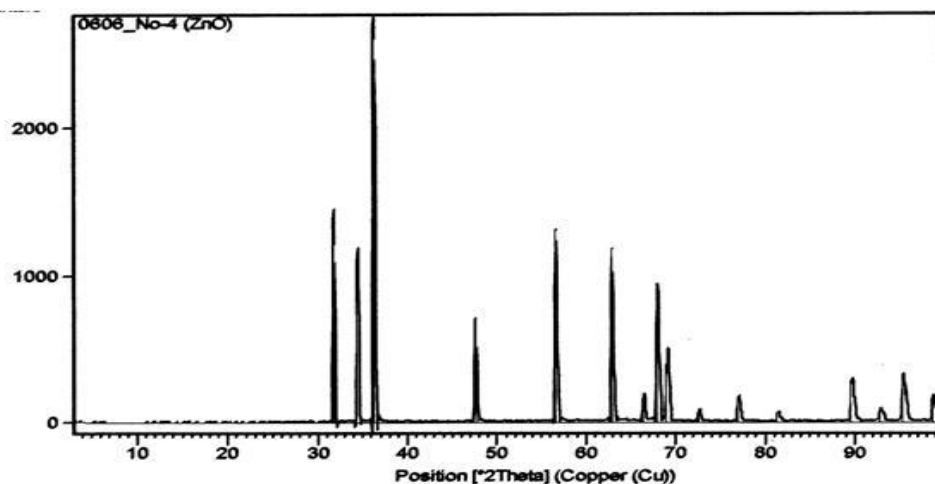


Fig.10. XRD diagram of ZnO semiconductor after irradiation with Pb(II)

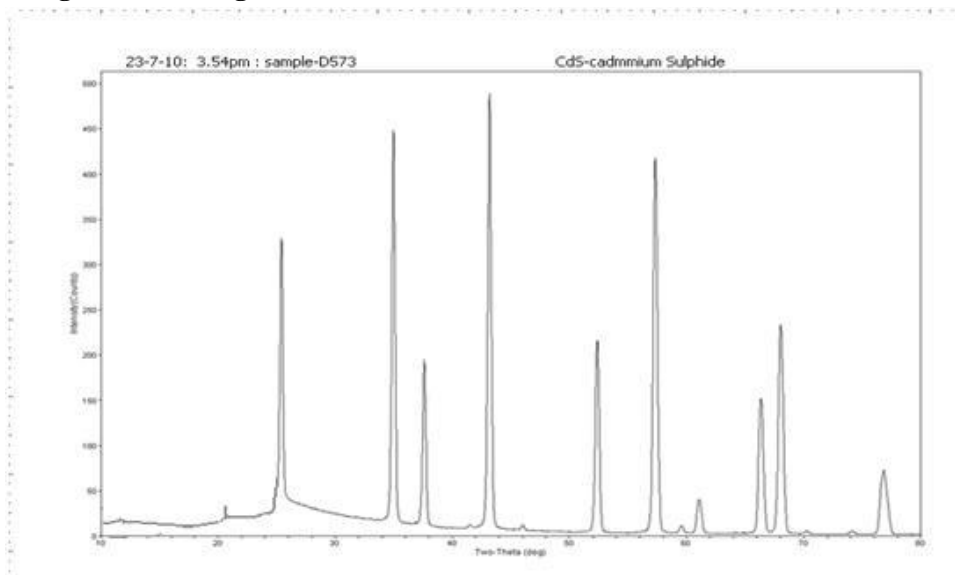
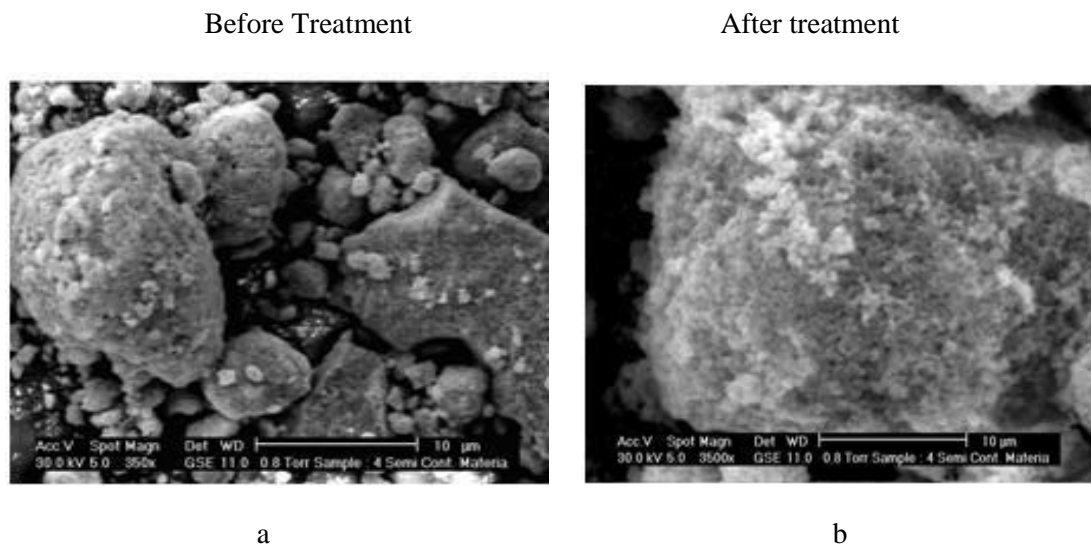


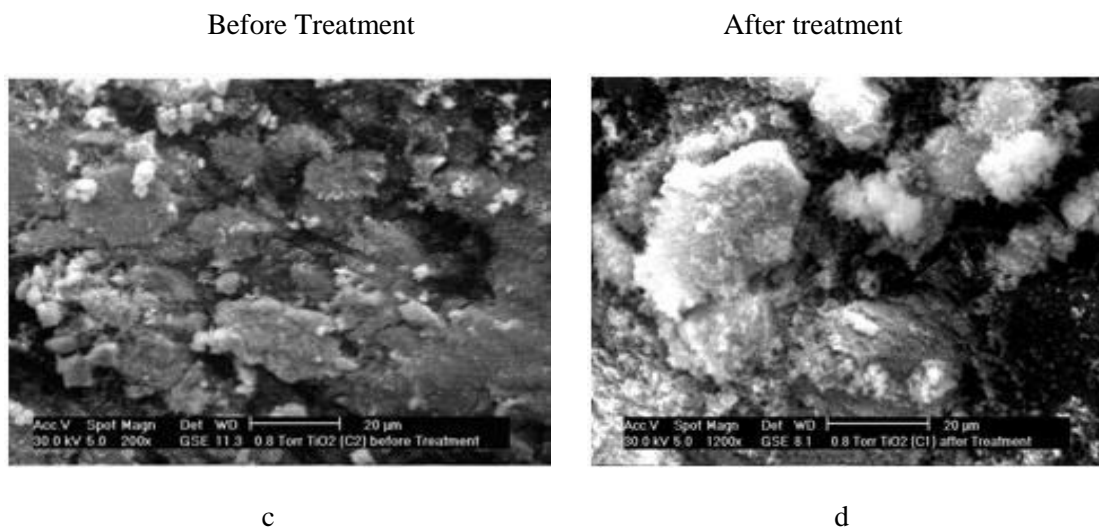
Fig.11 XRD diagram of CdS semiconductor after irradiation

**SEM**

The Scanning electron microscope (SEM) images of the semiconductors before and after photodegradation were recorded. The images of TiO<sub>2</sub>, ZnO and CdS show the presence of micro pores on the surface of semiconducting materials (Figure 12,13). The pores are responsible for the large surface area and having high adsorptive capacity of the heavy metal ions. The images clearly show that the micro pores are more compacted with before image. It indicates that there is good possibility for Pb(II) degradation on TiO<sub>2</sub> as well as ZnO.



**Fig.12 SEM images of ZnO after and before irradiation of Pb(II)**



**Fig.13 SEM images of TiO<sub>2</sub> before and after irradiation of Pb(II)**

**CONCLUSION**

Photocatalysis has been ascertained to be a promising technique for the removal of heavy metals from industrial effluents. In the present investigation, a complete removal of Pb(II) with the help of TiO<sub>2</sub>, ZnO and CdS as semiconducting materials.

Removal of chromium was maximum at pH 6 for different amount of photocatalysts. The removal of Pb(II) at pH 6 values may be attributed to the number of H<sup>+</sup> ions was neutralize the negatively charged group. The Lead (II) removal percentage increases as loading of photocatalysts increases and mass removal rate increases with decrease in adsorbent loading.

Out of these TiO<sub>2</sub> was the most effective for which the removal reached more than 94.5% for Pb(II) at the concentration of 60 ppm. Increase in the dose of photocatalysts, initial concentration of Pb(II) and increase in contact time upto 180 minutes are favorable for all increase the adsorption of Pb(II). The kinetic of the Pb(II) removal with TiO<sub>2</sub>, was found to be best photocatalyst. ZnO was less effective photocatalyst than TiO<sub>2</sub>, and CdS is very poor photocatalyst, remove only 45% Cr(VI). All these three photocatalysts follow first order mechanism.

By using XRD it is found that the size of the photocatalytic particles is 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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