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Photocatalytic degradation of Methylene blue dye and Chromium metal from wastewater using nanocrystalline TiO₂ Semiconductor

V. S. Shrivastava

Nano Chemistry Research Laboratory, G. T. P. College, Nandurbar, (M.S.) India

ABSTRACT

This paper describes the basics of photocatalysis on semiconductors, mainly on TiO₂ and the application of photocatalytic processes for water purification from organic and inorganic matter as well as metal removal introduced in order to improve the photocatalytic action of titanium dioxide. The photocatalytic activity of anatase phases of nanocrystalline TiO₂ for the degradation of different substances under UV light irradiation. The higher photocatalytic activity was obtained in anatase phase of TiO₂. In the present investigation, result indicates that removal of dye methylene blue (MB) and metal chromium Cr (VI) has been studied by considering influent concentration, loading of photocatalyst, pH and contact time as operating variables. The percentage removal of dye MB and Cr(VI) increase with increase in contact time. The optimum contact time was fixed at 180 minutes for TiO₂. The results of this study reveal that the dyes could be removed by semiconducting nanomaterials assisted photocatalytic degradation. The kinetics study of experimental data were analyzed using the pseudo first order kinetics of Lagergren and Pseudo second order model to determine adsorption rate constant. The semiconducting nano materials was characterized by EDX, XRD and SEM for determining the contents and the size of particles.

INTRODUCTION

Contaminants from industrial effluents often pose a major environmental problem. Semiconductor photocatalysis is one technique that has great potential to control aqueous organic as well as inorganic contaminants or air pollutants [1].

It holds several advantages over conventional oxidation processes, such as complete mineralization of the pollutants [2], use of near-UV or solar light, [3] no addition of other chemicals, and operation at near room temperature [4]. Although photocatalytic degradations of trace toxic organic compounds in water or air have been investigated intensively in the past decade. Advanced Oxidation Processes (AOP) is very fresh chemical techniques used for water purification now days [5,6]. Among the various oxide semiconductor photocatalysts, TiO₂ is an important photocatalyst due to its strong oxidizing power [7]. In this article the mechanism of the heterogeneous photocatalysis on semiconductors, mainly on TiO₂, and applications of the methods to water purification are described. Textile dye produces huge amount of polluted effluents that are normally discharged to surface water bodies and ground water aquifers [8]. These wastewater causes damages to the ecological system of the receiving surface water capacity and certain lot of disturbance to the ground water resources [9]. Most of the dyes and poisonous metals are used in the textiles industries are stable to light and are non biodegradable [10]. In order to reduce the risk of environmental pollution from such waste, it is necessary to treat them before discharging it receiving in the

environment [11]. Today more than 10,000 dyes have been incorporated in colour index [12]. In order to remove hazardous materials like dyes, poisonous metals, and toxic organic and inorganic substances from wastewater is very difficult [13,14]. There are various methods for removal of organic and inorganic compounds from the wastewater as filtration, electrolysis, precipitation, ion exchange and adsorption process [15]. Most of these methods require high capital and recurring expenditure and consequently they are not suitable for small scale industries [16]. Among all the above-mentioned methods, photocatalysis is highly effective and cheap process than the other methods. TiO₂ is an important photocatalyst, because they are most efficient and shows the highest quantum yield. It is safe and inexpensive material, stable to photocorrosion and insoluble in water [17,18]. In the present investigation, TiO₂ is used as photocatalyst which can remove dyes as well as metals like chromium from the wastewater [19]. Large amounts of chromium are introduced into the environment through dyeing and printing in textile industries, chemical manufacture, leather tanning metal plating and a many other industrial effluents thus making them available to plants, animals and human [20]. Chromium exists in two oxidation state Cr(III) and Cr(VI). The hexavalent form is 500 times more toxic than the trivalent [21]. It is toxic to the micro organism, plants, animals and humans [22]. Several studies have shown that the trace amount of chromium (VI) is considered to be essential for normal metabolic processes [23]. However, intakes at higher levels have been found to be toxic mainly to the kidney and liver [24,25]. The human toxicity includes lung cancer as well as liver and gastric damage [26,27]. Chromium discharged in to the sewage system causing serious environmental impact.

Chromium ions in liquid state wastes occur mainly in trivalent form which gets further oxidized in chromium (VI) due to the presence of organics [28]. The maximum level permitted in wastewater are 0.05mg/l for chromium (VI), with this limit it is essential for industries to treat their effluent to reduce the Cr to acceptable level [29]. A detailed batch study with the TiO₂ has been carried out in the present investigation. The effect of pH, contact time, concentration of photocatalyst, and first order study were also investigated.

MATERIALS AND METHODS

3.1 Methylene Blue: The basic dye used in this study is Methylene blue, it is a heterocyclic aromatic compound. A.R. grade supplied by S.D. Fine Chemicals Mumbai. MB in commercial purity was used without further purification. The accurate weighted quantity of the dye was dissolved in double distilled water to prepare the stock solution (0.5g/L) experimentally dilution [33]. Dye concentration was determined by using absorbance value measured before and after the treatment with UV-Visible Spectrophotometer.

3.2 Chromium:

Hexavalent chromium was prepared by dissolving K₂Cr₂O₇ (A.R. Grade) and reacted with diphenyl carbazide (DPC) to produce a reddish purple colour in slightly acid solution which neutralized by addition of NaOH. The absorbance was measured using a UV-VIS spectrophotometer (model: systronic-2203) obtained maximum at λ_{max} = 540 nm. A calibration curve was prepared by measuring the absorbance of known chromium concentrations in the range of 0 – 0.5 mg/L. Batch experiments were carried out with different doses (1– 5gm/L) of with semiconductor [34].

3.3 Preparation of nanosize TiO₂ :

A nano crystalline TiO₂ of anatase phase was synthesized by hydrolysis of titanium tetra isopropoxide. The mixture of dry ethanol (100 ml) and titanium tetraisopropoxide (30 ml) was taken in a 250 ml round bottom flask. It is very soluble in water and continuously stirred for 30 min, followed by Absorption 628 nm ultrasonication for 30 min. Hydrolysis of titanium tetra isopropoxide solution was carried out by adding distilled Tri aryl methane water (25 ml) slowly at the rate of 0.5 ml/min with continuous stirring. The solvent from the obtained mixture was removed using roto vapour at 343 K under reduced pressure [35]. The powder was then kept in oven at 393 K over night. The dried sample was calcined at different temperatures of 753 under air for 12 hr, and the calcined samples are termed as AT (anatase TiO₂). from the solution by centrifugation. The absorbance of the supernatant solution was estimated to determine the dye concentration and values of the percentage of dye removal was found to be maximum at pH 3 therefore pH was finalized at pH-3.

3.4. photocatalysts:

Many studies have confirmed that the anatase TiO₂ is superior photocatalytic material. The bleaching of Methylene blue was carried out in presence of semiconductor TiO₂ [36, 37]. The photocatalytic degradation of MB for both initial concentration and irradiation sample was determined by mean of UV-Visible Spectrophotometer (Systronic-

2203). The dye solution was separated from the dye solution by centrifuging. All the kinetic experiment were carried out at pH 7 [38].

3.5. Photocatalytic Study:

The removal of the dye was observed by spectrophotometer (Systronic Model 2203). The calibration curve of Methylene blue dye was obtained at 665nm. The dye solution was exposed to UV light (PHILIPS-400Watt) by addition of TiO₂ and ZnO at a distance 30 cm from the reaction vessel (fig.2). Double distilled water was used through out the experiment. UV-spectrophotometer in glass cuvette with path length 1.00 cm and the progress of photocatalytic reaction can be observed .the sample separated from the photocatalysts by centrifuging. Samples were withdrawn at different time interval (15min.). To study the effect of important parameters like pH, contact time, initial concentration and photocatalyst dose on the MB dye, A batch experiment were conducted for each experiment. The kinetics were determine by analyzing decolourization of dye from aqueous solution at different time intervals [39]. A batch experiment were conducted for each experiment. The kinetics study was determine by analyzing decolourization of dye from aqueous solution at different time intervals. In the photocatalysis the nano sized photocatalytic materials can degrade the metals as well as organic dyes and the nanoparticle can be reused.

3.6. Effect of pH :

In the study of effect of variation of pH, It was found that as pH of the reaction mixture was raised, the rate of Photocatalytic degradation also increases. About 0.2 gm of photocatalyst were added in the solution in different concentration from 10 mg/L to 50 mg/L . Solutions were irradiation by UV light for given time interval and the percentage of removal was determined [40]. Initial pH was adjusted by adding HCl and NaOH (0.05M). pH where the highest percentage was chosen for the study of photocatalysis. The rate of photocatalytic bleaching of Methylene blue was found increase with increase in pH [41].

3.7. Effect of concentration :

The concentration of the MB and Cr(VI) dependent and the as the percentage of removal is increased with decreasing the initial concentration of Methylene blue [42]. The equilibrium time is taken for the maximum removal of MB and Cr(VI) by increasing in photocatalyst. The equilibrium time was found to be 180 min for 10 mg/L to 50 mg/L of the MB dye concentration and 20 mg/L to 50 mg/L. The removal of the dye is rapid in the initial stage of contact time and gradually decreases with the increasing the time [43].

RESULTS AND DISCUSSION

Batch experiments were carried out by shaking different dosages of (1-5 gm) with TiO₂ 100 ml aqueous solution of chromium in the flask with a constant speed of 200 rpm. With stirring. During this investigation, the influent chromium concentration is varied from 10 to 50 mg/L and the pH is varied form 3 to 11.0. The results obtained during the present investigation are discussed as follows.

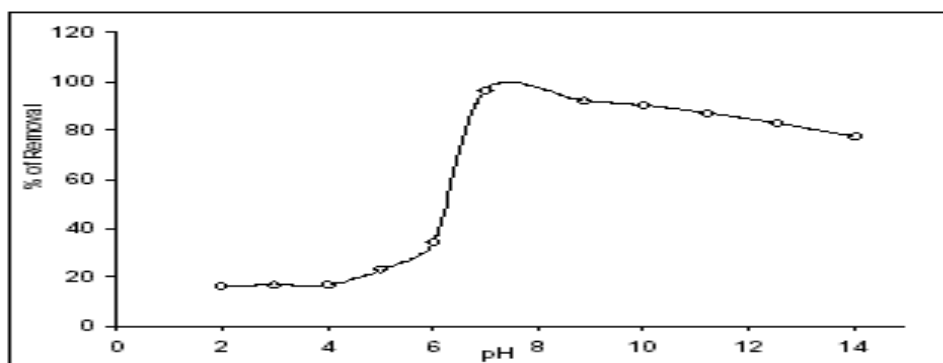


Fig.3. Effect of pH on adsorption of Methylene blue on TiO₂

5.1 Effect of pH on Methylene blue removal

The pH of the dye solution on the percentage of removal of MB was studied by varying the pH. It is one of the most important factor controlling the removal of dye on photocatalysis. The pH increases 4 to 7 the percentage of removal

increases from 34.2 to 91.4 % and from 7 to 14 the removal decreases from 91.4 to 77 % fig.3 show the effect of pH (2-14) on the percentage removal of M.B. The higher percentage removal was obtained at pH 7.0 is 91.4 %, pH 7 was suitable for further study.

5.2 Effect of pH on chromium removal

The removal of chromium from wastewater by adsorption is highly dependent on the pH of the solution, which affects the surface change of the adsorbent, and the degree of ionization. Adsorption of typical inorganic pollutants from water is increased with decreasing pH. The degradation of Cr (VI) is maximum at the pH range of 1–3, Fig.4. This is probably due to the neutralization of the anionic sites and negative potential of the surface of the adsorbent at lower pH. The reduced adsorption at higher pH may be attributed to the abundance of hydroxyl ion and consequent ionic repulsion between surface potential negative charge and chromate ions.

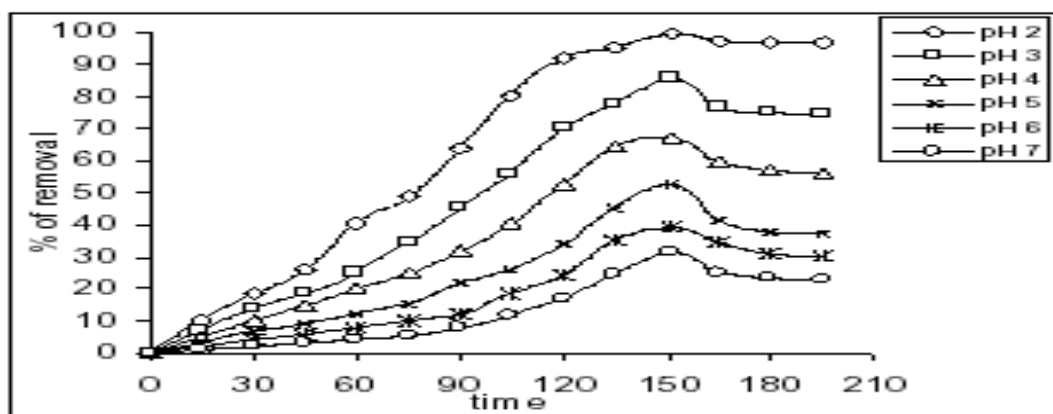


Fig.4 Effect of pH on removal of Cr(VI) ion 5gm/l at pH 7 in the absence of photocatalyst

5.3 Effect of Contact Time:

Effect of contact time and dye concentration on the removal of Methylene Blue from aqueous solution is presented in fig. 5 and 6 by TiO₂. The experiments were carried out at 200 rpm 5.0 g/L mass adsorbent at room temperature, pH 7.0 and the dye concentrations of Methylene Blue (10 to 50 mg /L) for different time intervals up to 180 min. The percentage dye removal decreases with increasing the dye concentration. Though the percentage removal decreases with increase in dye concentration and remained nearly constant after equilibrium time [44]. Photocatalytic degradation capacity at equilibrium for MB increased from 15.5 to 85 mg/g for 50 ppm, 20.7 to 95.4 mg/g for 30 ppm, and for 10 ppm it is very high 21.4 to 99.8 mg/g respectively for TiO₂. The equilibrium established within 180 min for both photocatalyst for all the concentration studies. It is established that removal of dye depends upon the concentration of dye. It is observed that the amount of photocatalyst increases from 0.2 g/L to 1.0 g/L. Irradiation time for complete degradation of MB decreases, as the concentration increases, because when all dye molecule are degrade on TiO₂ surface, any further addition of TiO₂ could have no effect on the degradation efficiency [45].

5.4 Effect of Photocatalyst loading

5.4.1 Methylene Blue

In order to examine the effect of Photocatalyst dose on the removal efficiency of MB degradation experiments were set up with varying the dose (1.0 mg/L, to 5.0 mg/L) for TiO₂ while keeping initial dye conc. of 40 g/L and temp was 30 ± 0.1 °C and pH 7.0. The percentage removal was increased and equilibrium time and was decreases with adsorbent dose Fig.7. The percentage removal increases from 61 to 92 % as the TiO₂ dose was increased from 2.0 to 5.0 g/L at the equilibrium time. Maximum dye was sequestered from the solution within 180 min. after the start of experiment. The rate of reaction increases with increase in amount of TiO₂. As the amount of semiconductor increases the exposed surface area of the semiconductor also increases

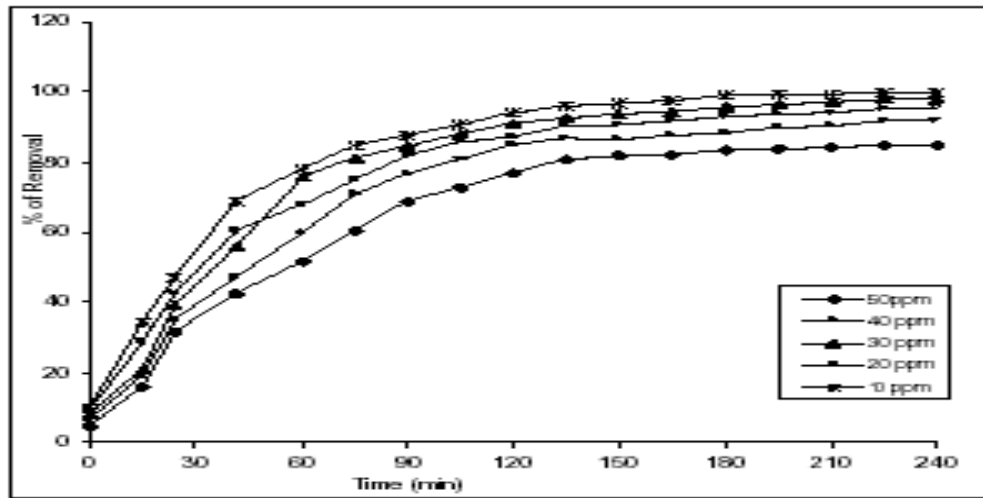


Fig.5. Effect of Contact time with % of removal of different initial concentration of Methylene blue on TiO₂ (dose .5gm/100ml at pH 7)

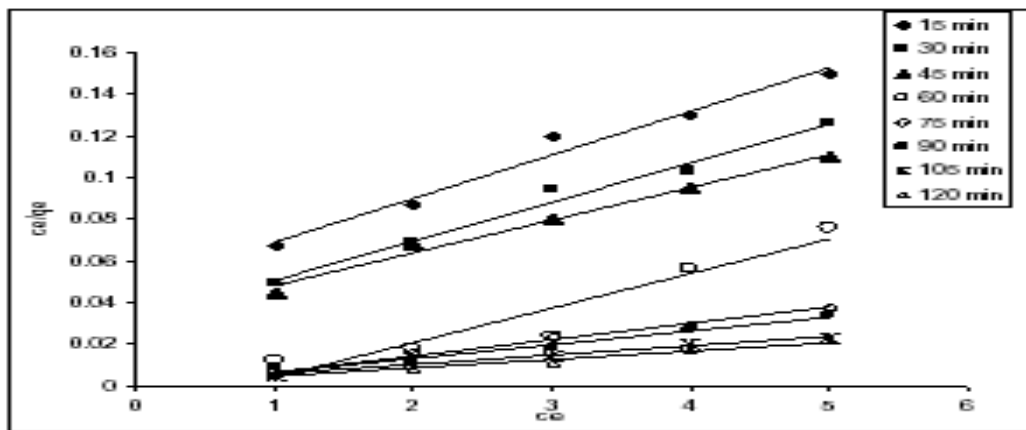


Fig.6. Effect of Contact time with % of removal of different initial concentration of Cr(VI) on TiO₂

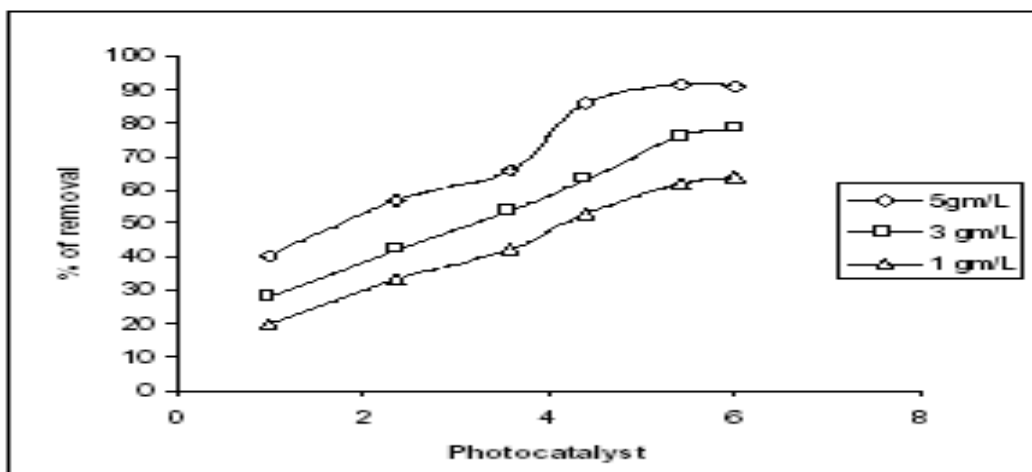


Fig. 7 Effect of Photocatalysts loading for removal of MB removal

5.4.2 Chromium (VI)

The effect of adsorbent loading on removal of chromium from aqueous solution is shown in figure 8. From the figure it can be observed that, the percentage removal of chromium increases with increase in adsorbent loading. Further, at lowest adsorbent loading the adsorbate is more accessible and because of this, the removal per unit weight of adsorbent is higher. It can be inferred that the chromium removal rate (that is removal per unit mass of adsorbent) increases with decrease in adsorbent loading. It can be observed from the figure 6 that the chromium removal percentage is found to be 86.2 at loading of 1 gm TiO₂. As the loading is increased from 1 to 5 gm, the chromium removal percentage also increases from 87.5 to 95%. Similarly the mass removal rate is found to be 0.815 gm/gm m³ at an adsorbent loading of 1 gm. When the adsorbent loading is increased from 1 to 5 gm, the mass removal rate also increases from 0.815 to 0.217 gm/gm m³

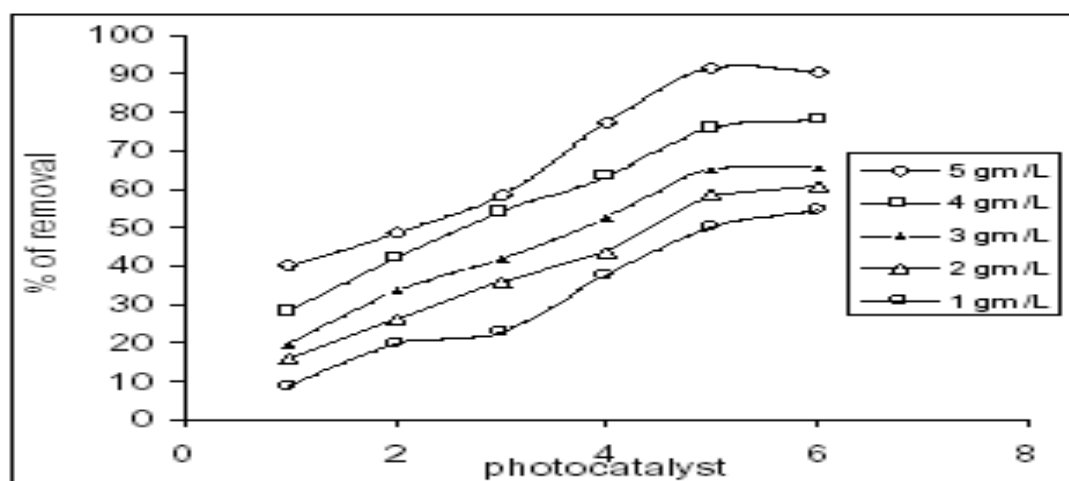


Fig. 8 Effect of Photocatalysts loading for removal of Cr (VI)

5.6 Kinetic Study :

The kinetic study of MB and Cr (VI) removal by photocatalytic degradation the pseudo first order and Pseudo second order kinetics models were used to fit in the experimental data, $\log (q_e - q_t)$ Vs t was plotted at different concentrations figure 9. In Chromium (VI) the pseudo first order model data do not fall on the straight line. The photocatalytic degradation of MB with TiO₂ obeys pseudosecond order kinetics at different concentration. for the most initial concentration indicating that this model is less appropriate. The Lagergren first order rate constant (K_1) and q_e cal determined from the model are presented in table 2 along with the corresponding correlation coefficient .Lagergren first order model express as eqn 1.

$$\log (q_e - q_t) = \log q_e - (K_1/2.303)t \dots \dots \dots (1)$$

Where q_e and q_t are the adsorption capacity in mg/g at equilibrium at the time t respectively K_1 is the rate constant of pseudo first order adsorption (min^{-1}). The first order rate constant K_1 and q_e 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.

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

K_2 is the second order rate constant ($\text{mg}^{-1}\text{min}^{-1}$), the values of K_2 is different initial dye concentration for all adsorbent were calculated from the slope of the representative linear plot of t/q_t 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.

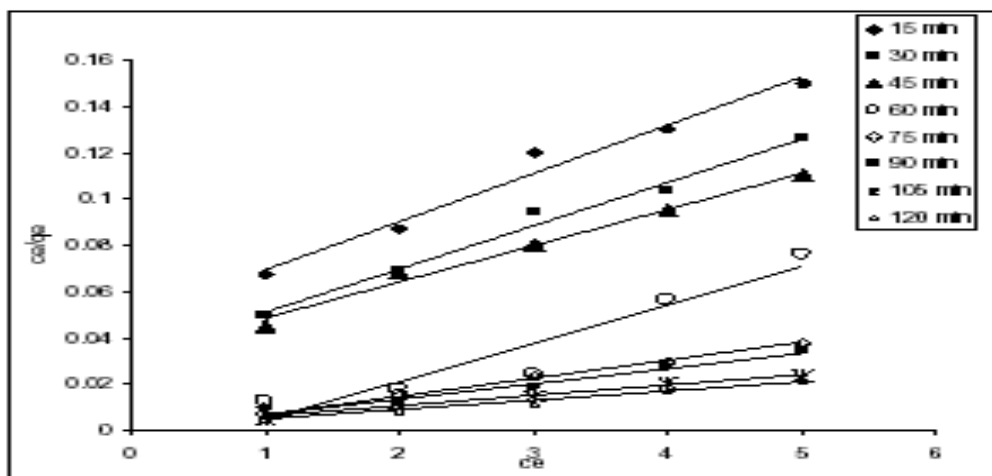


Fig.9. Pseudo First order kinetics for MB with TiO_2 - 5gm/lit

The experimental kinetics data were further analyzed using the pseudo second order model. By plotting t/q_t Vs t at different initial concentration, a straight line was obtained in all cases and using equation 1, the second order rate constant K_2 and q_e values were determined from the plot. The correlation coefficient obtained were very high of TiO_2 ($r^2 > 0.9999$) and the theoretical $q_{e\text{ cal}}$ values obtained from this model were closer to the experimental $q_{e\text{ exp}}$ values. Values obtained from this model were closer to the experimental q_e values at different initial concentration (table 1). It is important to note that for the first order model the this study. The concentration correlation coefficient obtained in this study, ($R^2 = 0.9999$ for TiO_2) 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 $q_{e\text{ exp}}$ are not good in agreement with theoretical values calculated ($q_{e\text{ cal}}$) 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 on TiO_2 at different initial concentration compared to the pseudo first order model.

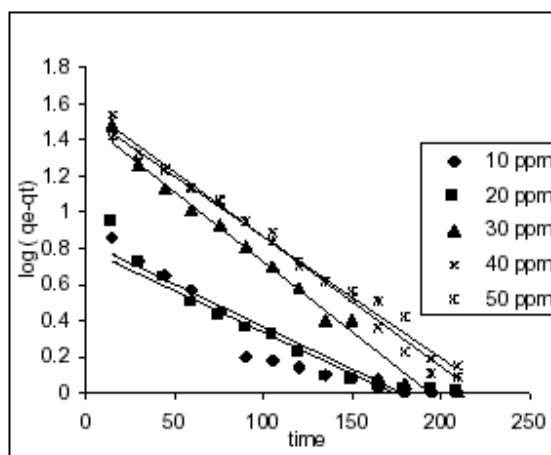


Fig.10. Pseudo Second order kinetic for adsorption of Cr (VI) with TiO_2

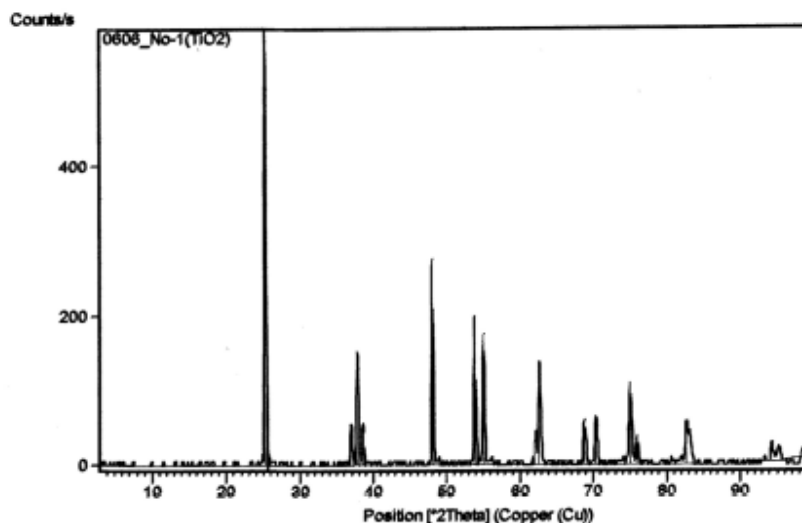


Fig.12 XRD diagram of TiO₂ semiconductor before irradiation

5.7 Catalyst characterization:

5.7.1 X ray Diffraction :

The X ray powder diffraction pattern of TiO₂ and ZnO shows the peak at 25.25 A° and 31.78.A° the diffraction pattern shows a shift to 25.24 A° and 36.38 A° indicating the interrelation of surfactant ions in the ZnO. X ray diffraction of TiO₂ and ZnO was recorded by Philips Holland. Xpert MPD model using copper target. The d values obtained for TiO₂ and ZnO was 0.5764, 0.4706 correspond to 0.4583 and 0.4012 respectively, Table 3 indicates that after photocatalytic degradation the size of particles are increases fig.12,13. X ray diffraction (XRD) pattern obtained on a Philips Holland. Xpert MPD model using Cu K α radiation at a scanning rate [46]. Equation for determining the size of particle is

$$D = k\lambda/\beta\cos\theta$$

Where D is grain size,k is constant taken to be 0.94,B is full width at half maximum(FWHM) and λ is wavelength of X-ray.

5.7.3. SEM:

Scanning electron microscope (SEM) Phillips XL-30 has been a primary tool for characterizing the surface morphology of the adsorbent. SEM is widely used to study the morphological features and surface characteristics, as well as its useful to determine particle shape, size porosity and appropriate size distribution of the adsorbent materials. The electromagnetic lenses which focus the beam towards the sample. When the beam hits the sample, other electrons are dispersed or ejected from the sample. All non-metals need to be made conductive by covering the sample with a thin layer of conductive material. This s done by using a device called a "sputter coater"[47]. he sputter coater uses an electric field and argon gas. The sample is laced in a small chamber that is at a vacuum. Argon gas and an electric field ause an electron to be removed from the argon, making the atoms positively.charged. The argon ions then become attracted to a negatively charged gold foil. he highest SEM resolution at high beam energies (0.4 nm at 30 kV) is obtained with the Phillips XL-30 At low beam energies with the best resolution is achieved by the SEM.The scanning electron micrographs are recorded with Phillips XL-30 SEM analyzer are used for characterization the surface morphology of TiO₂ photocatalyst, given figure 13 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 TiO₂ has rough surface with heterogeneous porous nature . It indicates that there is good possibility for adsorption Cr(VI)on TiO₂ fig.14,15.

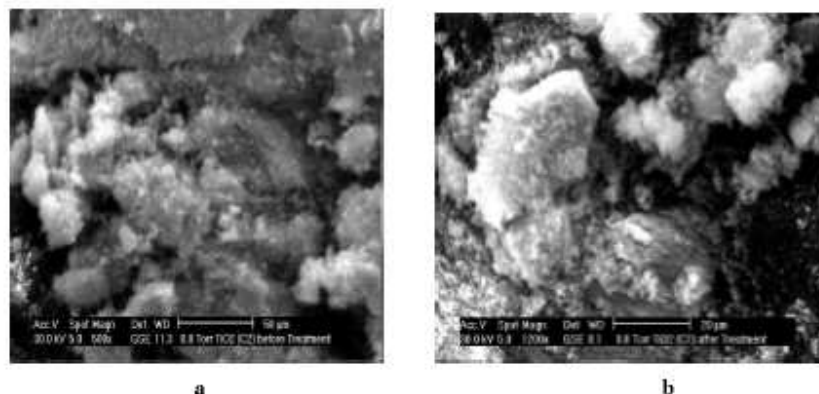


Fig.14. SEM images of TiO₂ a) before treatment b) after treatment

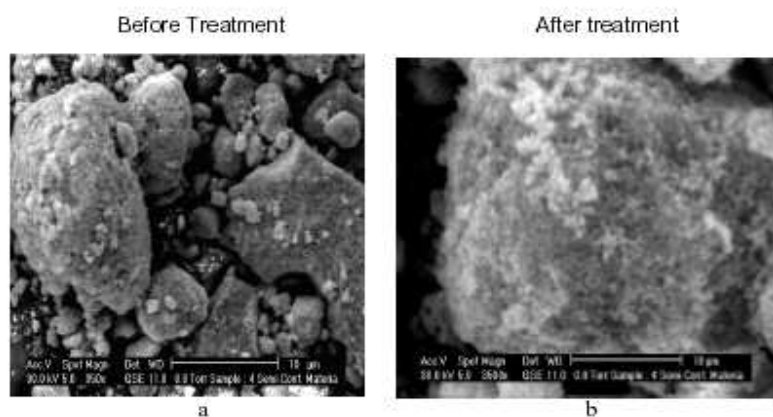


Fig.15 SEM images of TiO₂ after and before irradiation with Cr(VI)

CONCLUSION

A wide variety of semiconductors have been examined for their photocatalytic capacity and thus for TiO₂ have been shown to be the most active among the others. TiO₂ was selected as the photocatalyst for this project because it is insoluble under most conditions, photo stable, nontoxic and has higher photocatalytic efficiency and relatively inexpensive. The photocatalytic oxidation using a semiconducting material TiO₂ with UV light was successfully applied for the degradation of dye and metal species. TiO₂ can remove the dye and metal from aqueous solution. The degradation rate was increased significantly by increasing the amount of semiconductor, while on increasing substrate concentration decolorisation decreases. pH condition were found to be affected the degradation of metal as well as dye.

6.1. Methylene Blue:

Photocatalytic degradation of Methylene Blue can be achieved by using nanomaterials as TiO₂, (semiconductor). The experimental results indicate that the kinetics of degradation process TiO₂/UV, fit well with pseudo second order reaction. From this experiment it is possible to obtain decolorized water in a convenient time scale. The rate of degradation of dye is found to be more at 0.5 g/L than the in 1.0 g/L. TiO₂ is more efficient photocatalyst in the removal of Methylene Blue. The experimental results indicate that the degradation process,

TiO₂ /UV, system is very effective compared with different natural and artificial adsorbent available. In this system there is hundred percent of removal of dye is possible in a practical time scale. By using XRD it is found that the size of the photocatalytic particles size increases after the dye reacted with these particles. SEM photographs show that the TiO₂ has heterogeneous pores in nature as well as the surface is rough in nature.

6.2 Chromium (VI)

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 chromium on TiO₂, has been processed with the help of Langmuir and Freundlich isotherms. Removal of toxic hexavalent form of Cr(VI) from solutions was possible using photocatalysts like TiO₂. The removal is maximum at lower pH (that is less than 3) for different amount of photocatalysts. The removal of Cr(VI) at lower pH values may be attributed to the large number of H⁺ ions was neutralize the negatively charged or convert a neutral group. The chromium removal percentage increases as loading of photocatalysts increases and mass removal rate increases with decrease in adsorbent loading. TiO₂ was the most effective for which the removal reached more than 98% for Cr(VI) at the concentration of 100ppm. Increase in the dose of photocatalysts, initial concentration of Cr(VI) and increase in contact time upto 180 minutes are favorable for all increase the adsorption of Cr(VI). This photocatalysts follow first order mechanism. By using XRD it is found that the size of the photocatalytic particles are increases after the dye reacted with these particles. SEM photographs shows that the TiO₂ and ZnO has heterogeneous pores in nature as well as the surface is rough in nature.

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