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Preparation, Characterization and Applications of Nanostructure Photocatalysts

K. M. Joshi, B. N. Patil and V. S. Shrivastava

Nanochemistry Research Laboratory, G.T.P. College, Nandurbar(India)

ABSTRACT

The photocatalytic degradation on semiconductors especially on TiO_2 and ZnO were carried out in presence of light to observe good semiconducting property. In this paper the preparation, charectrization and applications of semiconducting materials were studied. The purification of wastewater in the presence of photocatalysts were carried out. The photocatalytic degradation of dyes Methylene blue, Acid blue-29, and Alizarin red-S were used in this experiment. A Total time required for photocatalytic degradation is different for different effluent samples, varied from 60 to 180 min. Parameters like band gap; Dose of Catalysts concentrations of effluent, pH, etc were studied. Studies The TiO_2 shows more photocatalytic efficiency than ZnO. The degradation of the dye by using semiconducting materials were characterized by XRD, SEM and EDX analysis before and after application of photocatalysts.

Keywords: Photocatalysis, semiconductors, XRD, SEM, EDX.

INTODUCTION

Photcatalysis has large capability for the waterwater treatment. It can be utilized for the decomposition of organic and inorganic compounds and removal of dyes [1]. A wide variety of semiconductors have been examined for their photocatalytic capacity and thus for TiO_2 have been shown to the most active amongst the other [2]. TiO_2 and ZnO were selected as the photocatalyst for this project because it is insoluble in water, photostable, non toxic, less expensive and It has higher photocatlayitic efficiency [3]. Titanium dioxide (TiO_2) shows its unique photocatalytic activity at an excellent choice of photo catalysis application [4, 5].

Last few decades numerous research effect in the field of photocatalysis by semiconducting materials through particular system has been studied [6,7]. Textile dye produces huge amount of polluted effluents that are normally discharged on the surface water bodies and ground water aquifers [8]. This wastewater causes damages to the ecological system of the receiving surface

water capacity and certain a lot of disturbance to the ground water resources. Most of the dyes used in the textiles industries are stable to light and non biodegradable [9]. In order to reduce the risk of environmental pollution from such as wastewater, it is necessary to treat them before discharging it into the environment [10]. Study shows that toxic effects of these synthetic dyes are observed in the presence of the ultraviolet component of sunlight (285-400 nm) [11]. However, the aqueous phase photochemical degradation of dyes like Methylene blue, Acid blue-29 and Alizarin red-S etc. has been studied in the presence of semiconducting oxide like TiO_2 and ZnO [12]. Characterization and application of TiO_2 ZnO as photocatalyst is also studied [13].

The difficulty with the traditional waste water treatment techniques as adsorption, coagulation, chlorination, ozonisation, precipitation, ion exchange and reverse osmosis [14]. Most of these methods require high capital and recurring expenditure and consequently they are not suitable for small scale industries [15-16]. In the present investigation, photocatalytic degradation method is used for removal of dye from liquid industrial wastewater. Beside the above a study of the effect of pH, contact time, dosage of photocatalyst, and characterization of semiconductors were studied.

1.1 Mechanism of Photocatalysis:

Photocatalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor (.3.2 eV for anatase), producing electron-hole (e^-/h^+) pairs, as written in the equation 1and 2.

$$TiO_2 \xrightarrow{h\nu} e^-_{cb}\,(TiO_2) + h^+_{vb}\,(TiO_2) \quad \text{……(1)}$$

$$ZnO \xrightarrow{h\nu} e^-_{(cb)} + h^+_{(vb)}\,(\,ZnO) \quad \text{……..(2)}$$

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

The TiO_2 particle can act as either an electron donor or acceptor for molecules in the surrounding medium. 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 (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 OH^- by the hole produces the hydroxyl radical (OH^*), an extremely powerful and indiscriminant oxidant fig.1.

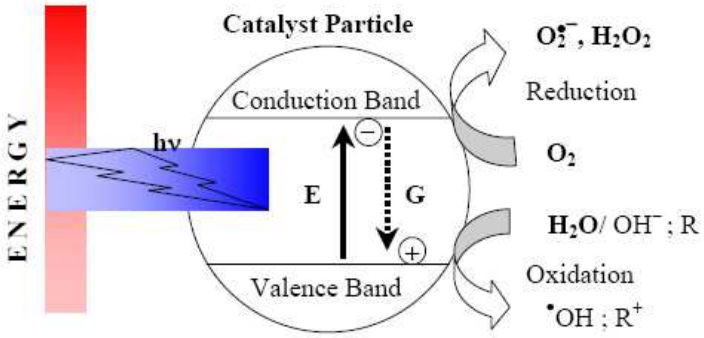


Fig.1. Simplified mechanism for the Photo-activation of a semiconductor catalyst

1.2 Effect of band gap of semiconductor

As a semiconductor is irradiated with light having energy (E= hγ) equal to or more than band gap energy, a heterogeneous photocatalyst reaction occurs on surface of semiconducting materials. The semi conducting forms a pair of valence band (V_b) hole and conduction band (C_b) electron as in case of zinc oxide and titanium dioxide. Titanium dioxide having band gap (3.23eV) semiconductor, is transport to visible light. The usual exited semiconductor has separated the hole and electron pairs that induced the photo catalytic reaction and hence the band gap energy has important role to play. The band gaps of different photo catalysts are summarized in Table 1.

Table 1.Band gap of different photo catalysts

Sr.No.	Semiconductor	Band Gap
1	PbS	0.30
2	CdS	2.50
3	ZnO	3.20
4	ZnS	3.80
5	TiO2	3.80

MATERIALS AND METHODS

2.1 Materials and Methods:

The Dyes Methylene blue, Acid blue-29, and Alizarin red-S were used in this experiment procured from BDH India Ltd. was used. The stock solution was prepared by dissolving 0.1g L^{-1} of dye in water and made up a stock solution in volumetric flask. By making 20, 40, 60 ppm solution. The concentration of the dye solution was determined spectrophotometerically.

2.2 Preapration of Nanosized photocatalysts:

Nano sized semiconductors as TiO_2, and ZnO are one of the most basic functional materials for photcatalytic degradation. For the preparation of anatase TiO_2 by using Titanium isopropoxide and ethanol stirred continuously for 30 min. Hydrolysis of titanium isopropoxide by adding distilled water slowly with continuous stirring. Solvent from the mixiture was removed. The compound was heated at 393 K overnight. The dried sample was calcined at 753 K under air for 8 hrs. and the calcined samples are termed as AT (anatase TiO_2) [17]. Nanocrustalline ZnO was preapered by using the precipitation method $ZnSO_4$ $7H_2O$ and NaOH form a slurry. It is

contieously stirred for 12 hrs and washed with deionized water . The weight powder was dried to form ZnO . Finally the Powder was calcined in air at 482 K to produced nanosized ZnO photocastalysts[18]. The average crystalline size and morphology of the prepared and commercial TiO_2 and ZnO powder were determined from XRD pattern. These materials are used for photocatalysis for removal of dyes. After degradation of dyes the size of the photocatalysts particles are increases.

2.3 Spectrophotometric Study:

The photodegradation of dyes was followed by measuring absorbance periodically, using Systronics-2203 spectrophotometer. The study of the absorbance characteristics of the effluents. The corresponding absorbance values for the dyes were different as Methylene blue was 665nm, Acid blue-29 was 620nm and Alizarine red-S was 430 nm. The reaction mixture was irradiated with light source UV lamp (PHILIPS-400Watt) at a distance 30cm from the reaction vessel fig.2. Double distilled water was used through out the experiment. After each 15 minutes intervals sample was determined from aqueous solution and by centrifugation photocatalyst is separated.

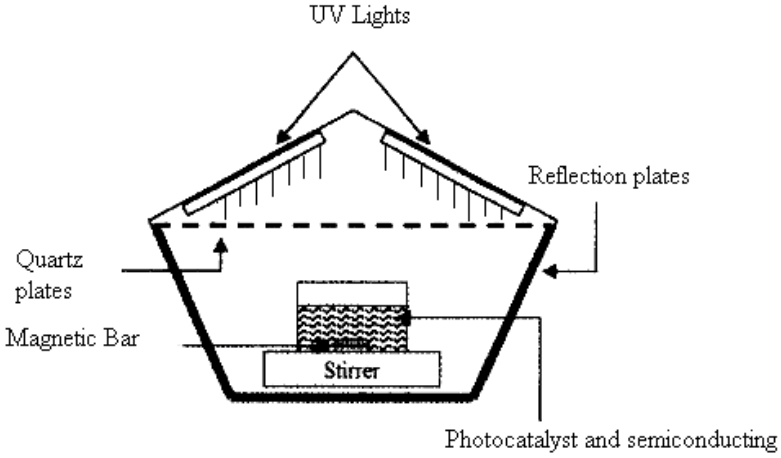


Fig.1. Schematic diagram of the Photocatlaysis experimental device

In the experiment an accurately weighted amount of TiO_2 and ZnO was added in flask in 100 ml dye solution. The pH of the dye solution was adjusted in between 3 to10 with addition of requisite volume of NaOH and HCl (E.Merck India). The absorbance of the supernatant solution was estimated to determine the dye concentration, and values of the % of dye removal were found to be maximum at different pH for different Dyes [19].

RESULT AND DISCUSSION

3.1 Effect of pH:

The pH of is one of the most important factor controlling the photocatalysis process of dye on to the photocatalyst. The removal of Methylene blue was maximum at pH 7.0 was reported 92 % removal, Acid blue was maximum at pH 6.0 was reported 88.5% removal, and the maximum removal of Alizarin red-S dye was 84.4% at pH 8.0. it was increases from 3 to 6 and decreases from pH 8 to 10. Fig. 3

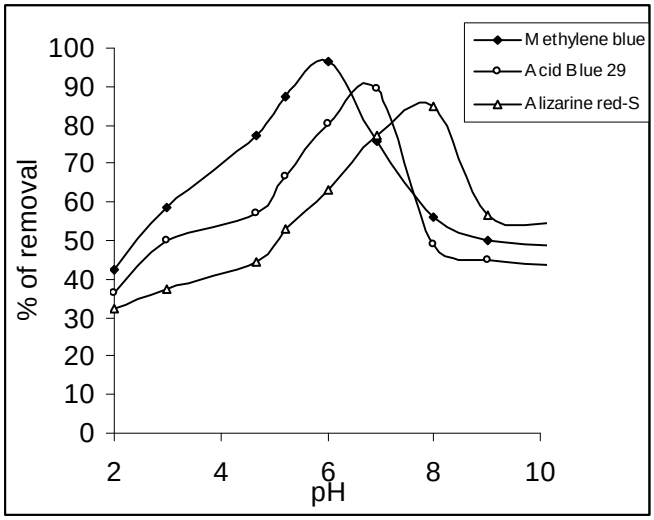


Figure 3. Effect of pH for removal of the dye

3.2 Effect of photocatalyst dose:

The photocatalyst dose was studied with 100 ml solution of different dyes with the concentration 20, 40 and 60 ppm with varying photocatalysis as TiO_2 and ZnO dose with 0.2 g/l to 0.6 g/l at pH 8 (figure 4). The percentage removal of the dyes increase with increase in dosage of the photocatalyst. The amount of the photocatalyst increased with an increasing the dye concentration However, the % removal rate decreases with an increase in the dye concentration. It is also noted that the rate of the removal of the dye is as faster at the lower concentration and decreases with an increase in the concentration of photocatalyst.

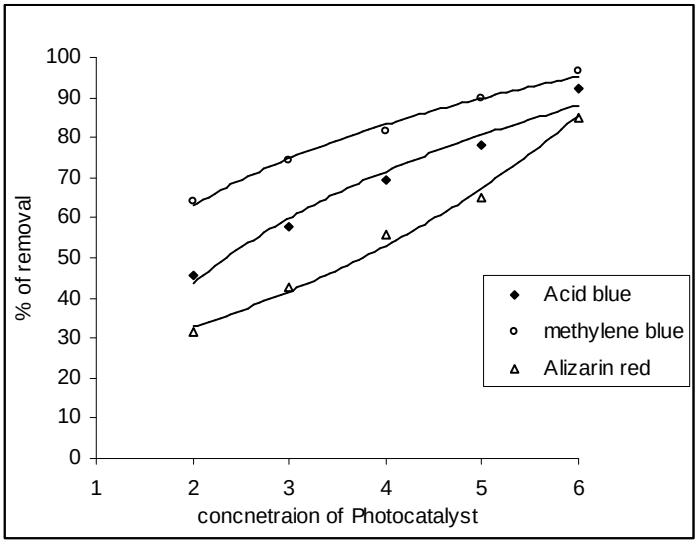


Fig.4 . Effect of photocatalyst dose on Dyes

It is found that with decreasing concentration of the dye from 1 g/Lit to 6 gm/Lit .The percentage removal of Acid blue-29 increases from 32.5 to 84.6%. The removal of the dye was

found to increases constantly with increasing the concentration of TiO_2 for the dye Methylene blue at 5 gm/Lit, It was 94.2 % and decreases up to 86.4 % at 6 gm / (Fig.5).

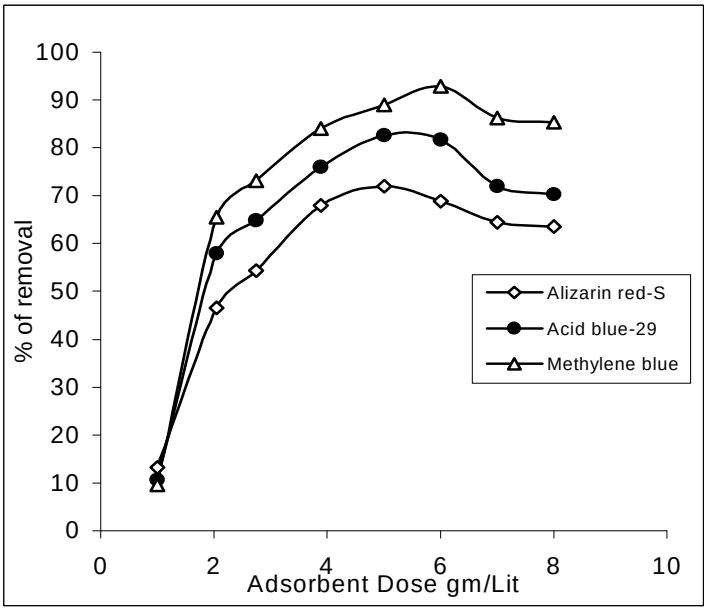


Fig.5 Effect of contact time of Alizarin red-S red with TiO_2

3.3 Effect of contact time:

The effect of contact time on the amount of Alizarin red S adsorbed was investigated using 20, 40, 60 ppm initial concentration with 0.5g/l of TiO_2 and ZnO, respectively. It was observed that the photocatalysis percentage was found to be maximum at 120 minutes increases. As concentration of the dye is increases the percentage of photocatalysts should increases for complete removal of the dye from 92.9 to 78.5% Fig. 6.

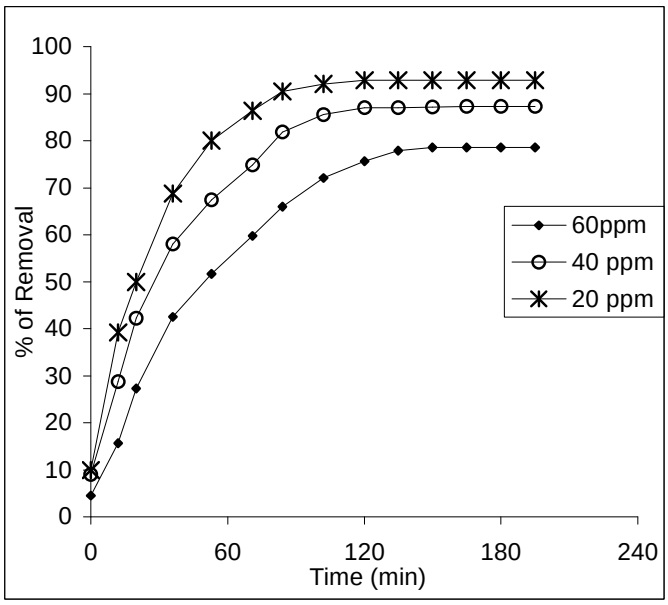


Fig.6. Effect of contact time of Methylene blue with TiO2 at pH 6

Charectrization :

3.4.1 XRD Analysis :

The X ray diffraction pattern of TiO_2 and ZnO shows the peak at 25.25°, 31.78° the diffraction pattern shows a shift to 25.24° and 36.38° indicating the interrelation of surfactant ions in the ZnO. X ray diffraction of TiO_2 and ZnO was recorded by Philips Holland. Xpert MPD model using Cu-Kα target. The d values obtained for TiO_2 and ZnO was 0.5764, 0.4706 correspond to 0.4583 and 0.4012 respectively, Table 3. It indicates that after photcatlalytic degradation the size of particles are increases. The diffractogram are shown figure 7 and 8.

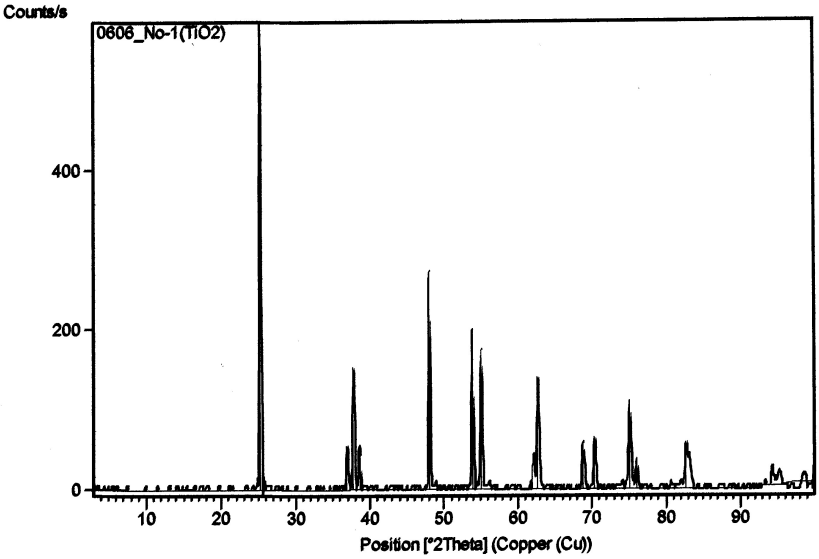


Fig.7. XRD diagram of TiO_2 semiconductor before irradiation

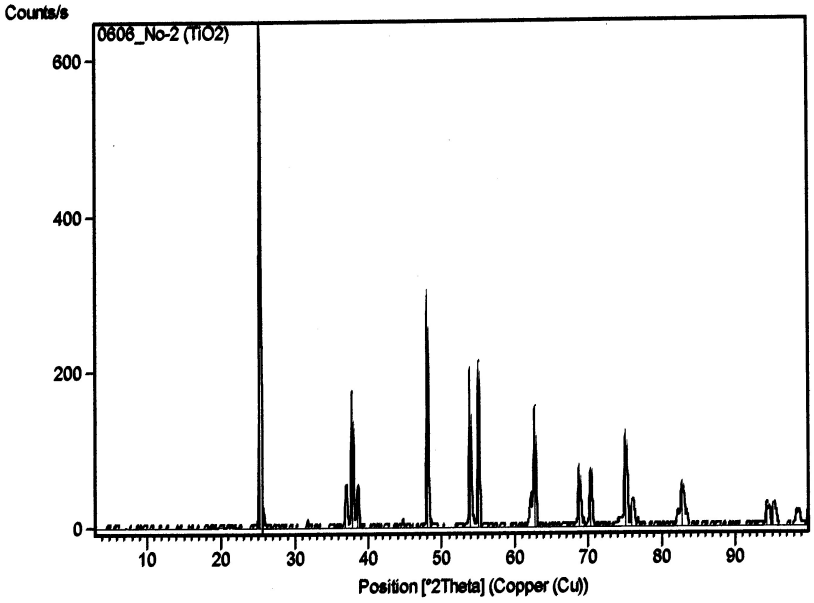
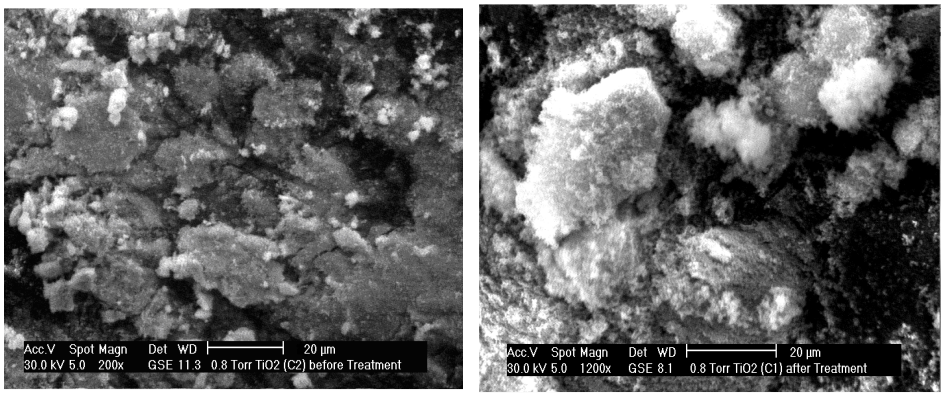


Fig.8 XRD diagram of TiO_2 semiconductor after irradiation

3.4.2 SEM :

The scanning electron micrographs are recorded with Philips XL-30 SEM analyzer for characterization the surface morphology of TiO_2 and ZnO photocatalyst(fig.9, 10) 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_2 has rough surface with heterogeneous porous nature. It indicates that there is good possibility for adsorption Cr(VI) on TiO_2.

Before Treatment **After treatment**



c d

Fig.9 SEM images of ZnO after and after irradiation with Acid blue-29

3.4.3 EDX :

Energy dispensive X ray spectroscopy (EDX) is chemical microanalysis technique used co-junction with SEM , EDX analysis was used by characterized the element composition of the typical EDX pattern of TiO_2 is shown in the figure 11. The Chemical composition of TiO_2 was found to be Ti= 68%, Si = 21%, O = 8% and carbon =3.12%was confirm that presence of TiO_2

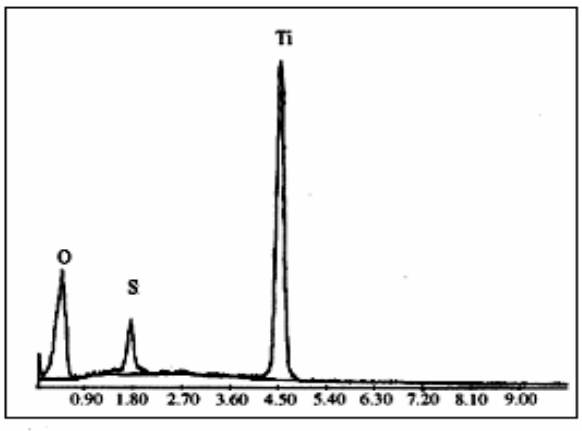


Fig.7 EDX Spectrum of TiO2 powder

4. Applciations of phtocatlaysts;

In recent years applications have been directed towards environmental clean-up. Later, other applications of photocatalysis have been implemented in many fields such as, drinking water

treatment, industrial, and health applications. Many other uses are known; example is found in catalysis as TiO_2 are also using full self cleaning [20], self sterilizing [21].Titanium dioxide work effectively under low UV light intensities and also applicable to indoor and outdoor environments. Photocatalysis has large capability for the water treatment. It can be utilized for the decomposition of organic and inorganic compounds, and removal of trace metals as well as destruction of viruses and bacteria.

4.1 Removing trace metals

A water free from hazardous metal are essentially and important for human health and water quality. [22]. Trace metal such as mercury (Hg), chromium (Cr), lead (Pb) Cadmium (Cd), lead (Pb), Arsenic (As), nickel (Ni) Copper (Cu) and others metals are highly health hazardous. Photocatalysts can remove these toxic metals by using TiO_2 and ZnO .

4.2 Destruction of organics

Photocatalysis has been used for the destruction of organic compounds such as alcohols, carboxylic acids, phenolic derivatives, or chlorinated aromatics, into harmless products as carbon dioxide, water, and simple mineral acids [23, 24].

4.3 Removing inorganic compounds

In addition to organic compounds, wide ranges of inorganic compounds are sensitive to photochemical transformation on the catalyst surfaces. Inorganic species such as bromate, or chlorate azide, halide ions, nitric oxide, palladium and rhodium species, and sulfur species can be decomposed by photocatalysis [25].

4.4 Water disinfections

Photocatalysis can also be used to destroy bacteria and viruses. Streptococcus mutans, Streptococcus natuss, Escherichia coli, scaccharomyces cerevisisas, were destructed effectively using heterogeneous photocatalysis [26].

CONCLUSION

The results of this study clearly establish that TiO_2 semiconductor photocatalysis can be efficiently used for the degradation of the dyes and other organic compounds in dyeing and printing effluents. In order to determine the rate of photochemical degradation of dyes in different effluent samples, the absorbance values at different irradiation times were measured periodically at fixed (TiO_2) = 5 gm/L. Initially the decrease in concentration the degradation of dyes were fast. Photocatalytic oxidation using TiO_2 and UV light was successfully applied for the degradation of dye. The degradation rate was increased significantly by increasing the amount of catalyst, while on increasing concentration of photoctalyst. pH condition were found to be significantly affected the degradation of dye. TiO_2 as a photocatalyst was an effectively for the remove the dyes. Nano sized anatase TiO_2 can remove the dye from aqueous solution. its possible to obtained a wastewater free from dye as well as trace metal by using TiO_2 as well as ZnO.

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