

Use of semiconductor Nano-photo catalysts composite for removing moieties from waste water

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ABSTRACT-The photo catalytic removal by using semiconductors especially TiO₂ and SiO₂ composite (TSC) were used out in presence of light to observe good semiconducting property. Preparation, characterization and applications of semiconducting materials were studied. The purification of the Wastewater in presence of photo catalysts were carried out. The fate of degradation by-products were also investigated in this study. The photo catalytic removal of dyes, heavy metals and hardazous organic compound. The time required for photo catalytic 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. Results of the study showed that dyes removal in the dark was very low for the three types of Nano materials under the study conditions used. However, appreciable removal of dyes and metals was observed when using TSC for UV lights, the degradation of the dye by using semiconducting materials were characterized by XRD, and SEM analysis before and after application of photo catalysts.

KEYWORDS: Photo catalysis, TiO₂, SiO₂ semiconductors, XRD, SEM.

I. INTRODUCTION

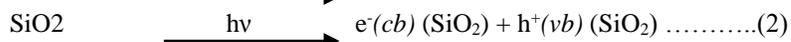
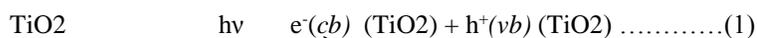
Increasing demand for clean water due to rising population and pollution from industrial, Agricultural and domestic activities are among the factors affecting the quality of available water resources [1]. Chemical pollutants in the form of organics, inorganics and heavy metals are usually present in water bodies at generally low levels; however it is their high toxicity and potential to cause harm to humans that is of greater concern [2]. Nanotechnology holds great potential in advancing water and wastewater treatment to improve treatment efficiency as well as to augment water supply through safe use of unconventional water sources. Last few decades numerous research effect in the field of Photocatalysis by using semiconductor materials through particular system has been studied [3,4]. Dyes, heavy metals and hardagious organic compound produces huge amount of polluted effluents that are normally discharged on the surface water bodies and ground water aquifers [5]. 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 [6]. In order to reduce the risk of environmental pollution from such as wastewater, it is necessary to treat before discharging it into the environment [7]. Study shows that toxic effects of these synthetic dyes as well as metals are observed in the presence of the ultraviolet component of sunlight (285-400 nm) [8].

Photocatalysis has large capability for the water treatment. It can be utilized for the decomposition of organic and inorganic compounds and removal of dyes [9]. A wide variety of semiconductors have been examined for their

photocatalytic capacity shown to the most active amongst the other [10]. TiO₂ and SiO₂ composite (TSC) were selected as the photocatalyst for this project because it is insoluble in water, photos table, nontoxic, less expensive and It has higher photocatalytic efficiency[11]. Water treatment by using nanoparticles has high technology demand; its usage cost should be managed according to existing competition in market [12]. There are various recent advances on different nanomaterials (Nano structured catalytic membranes, Nano sorbents, Nano catalysts, bioactive nanoparticles, biomimetic membrane and Carbon Nanotubes for removing toxic metals, disease causing microbes, organic and inorganic solutes from water[13].The difficulty with the traditional waste water treatment techniques as adsorption, coagulation, chlorination, ionization, 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: mechanism

Photocatalysis over a semiconductor oxide such as TiO₂ 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 1 and 2.



(Where *cb* is conduction band and *vb* is the valence band.)

The TiO₂ and SiO₂ composite 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.

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 semiconducting forms a pair of valence band (Vb) hole and conduction band (Cb) electron as in case of zinc oxide and titanium dioxide. Titanium dioxide having band gap (3.23eV) semiconductor, is transparent to visible light. The usual excited semiconductor has separated the hole and electron pairs that induced the photocatalytic reaction and hence the band gap energy has important role to play. The band gaps of different photocatalysts are summarized in Table 1.

Table 1. Band gap of different photocatalysts

Sr.No.	Semiconductor	Band Gap
1	PbS	0.30
2	CdS	2.50
3	ZnO	3.20
4	ZnS	3.80
5	TiO ₂	3.80
6	SiO ₂	3.62

II. MATERIALS AND METHODS

2.1 Preparation of Nano sized photocatalysts:

Nano sized semiconductors as TiO_2 , as well as SiO_2 are one of the most basic functional materials for photocatalytic 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 mixture 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 known as anatase TiO_2 [17].

2.2 Preparation of SiO_2 Nanoparticles:

The materials required for the synthesis of SiO_2 nanoparticles prepared by using trimethoxyvinylsilane (TMVS 98% pure), Butanol (99% pure), and ammonium hydroxide solution 5 M (31.5% NH_3 pure).. All these chemicals were of analytical graded, 5.5 mL TMVS was dissolved in 200 mL of de-ionized water. The mixture was stirred for 15 minutes before 200 μL of prepared NH_3 (1 mL NH_3 solution was dissolved in 1 mL de-ionized water) was added to ensure the pH is maintain in the range 9 - 11. Then, butanol was added into the mixture and continuously stirred for five minutes. The mixture was then transferred into a preheated reactor at the set temperature and continuously stirred at 320 rpm for one hour. After an hour, trimethoxyvinylsilane (TMVS) as SiO_2 precursor was added. The mixture was left overnight with continuously stirred at const. temperature, filter the precipitated clean SiO_2 several times and calcination for 3hrs at 400°C [18].

2.3 Spectrophotometric Study:

The photo degradation of waste water was followed by measuring absorbance periodically, by using Systronics-2203 spectrophotometer. The study of the absorbance characteristics of the effluents. The corresponding absorbance values for the wastewater 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.

In the experiment an accurately weighted amount of TiO_2 and SiO_2 composit (TSC) 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 (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].

2.4 Source:

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electroless depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals wastes result from printed circuit board (PCB) manufacturing. Tin, lead, and nickel solder plates are the most widely used resistant over plates, inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium. Nanotechnology-enabled water and wastewater treatment promises to not only overcome major

challenges faced by existing treatment technologies, but also to provide new treatment capabilities that could allow economic utilization of unconventional water sources to expand the water supply[20].

III. RESULT AND DISCUSSION

3.1 X ray Analysis:

The XRD pattern of TiO₂ and SiO₂ particles and TiO₂-SiO₂ composite(TSC) shows that TiO₂ shows broad peak, It indicates that the size of the particles is very small. The average crystalline size and morphology of the prepared and commercial TiO₂ and SiO₂ powder were determined separately from XRD pattern. The X ray diffraction pattern of TiO₂, SiO₂ and TiO₂-SiO₂ composite (TSC) shows the peak at 25.25° for TiO₂ & SiO₂ at 21.68° the diffraction pattern shows a shift to 25.24 and 23.38 indicating the interrelation of surfactant ions in the SiO₂. X ray diffraction of TiO₂ SiO₂ and TiO₂-SiO₂ composite (TSC) were recorded by Philips Holland. Xpert MPD model using Cu-Kα target.

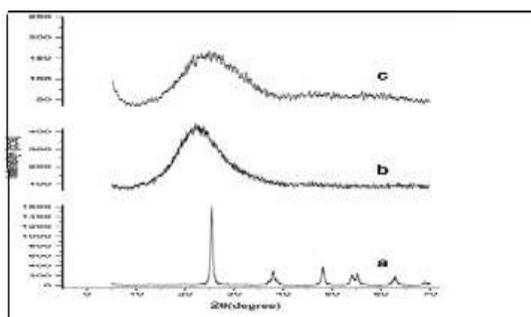


Fig. 1. XRD pattern of the TiO₂ a-nanoparticles, b-SiO₂ nanoparticles and c- TiO₂/SiO₂ nanocomposite

3.2 Effect of pH:

The pH of is one of the most important factor controlling the photocatalysis process of dye on to the the photocatalyst. The removal of Acid blue was maximum at pH 8.0 was reported 76.4 % removal, Maximum removal of Congo red dye was 89.4% at pH 8.0. it was increases from 3 to 6 and decreases from pH 8 to 11. Fig. 2

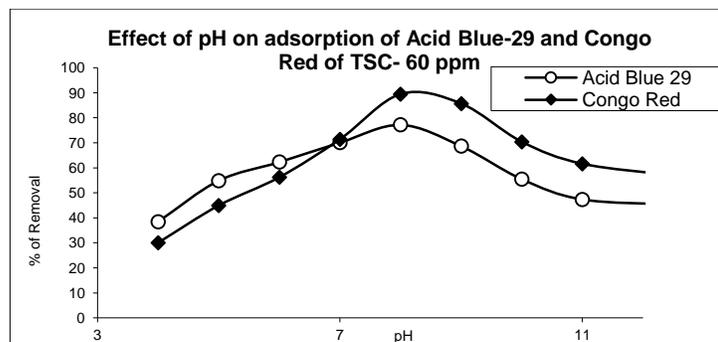


Fig 3. Effect of pH for removal of the dye

3.3 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 TiO₂ and ZnO dose with 0.2 g/l to 0.6 g/l at pH 8 (figure 3). 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. 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 TiO₂ –SiO₂ Composite for the dye 5 gm/Lit, It was 84.2 % and decreases up to 86.4 % at 6 gm / (Fig.3).

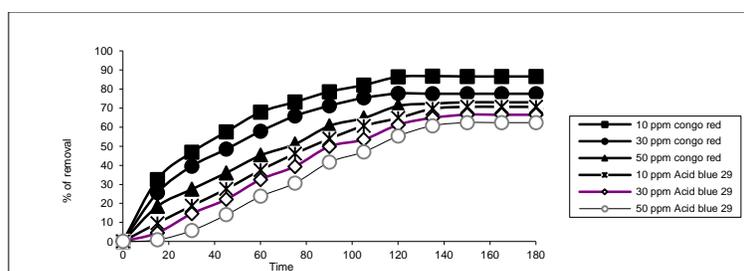


Fig.4 . Effect of photocatalyst dose on Dyes

3.4 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 TiO₂ 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. 4.

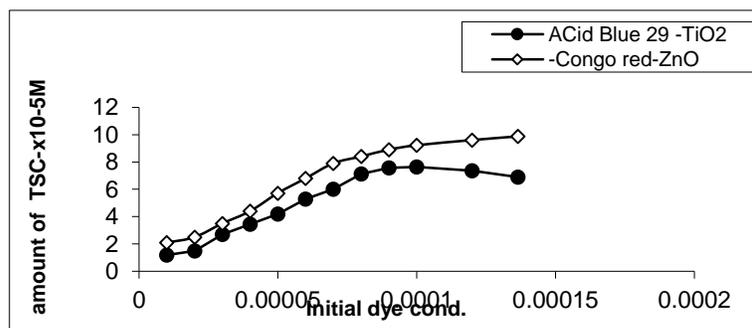


Fig.5. Effect of contact time with TiO₂ at pH 6

3.5 SEM :

The scanning electron micrographs are recorded with Philips XL-30 SEM analyzer for characterization the surface morphology of TiO₂ and SiO₂ photocatalyst (fig.5 before and after degradation. The SEM Photographs depict the surface texture and porosity, before and after treatment of photo catalysts, it is clear that TiO₂ has rough surface with heterogeneous porous nature. It indicates that there is good possibility for degradation on TiO₂ (Fig. 5)

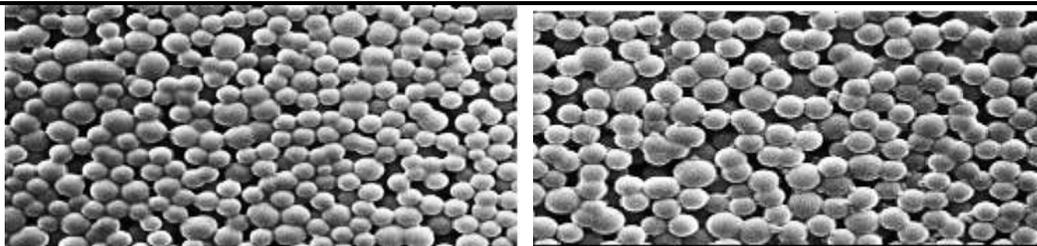


Fig. 6. SEM images before & after Treatment

IV. CONCLUSION

Nanotechnologies have made great improvements for handling water contamination problems and will clearly make further advancements in future. Nanotechnology based treatment has offered very effective, efficient, durable and eco friendly approaches. These methods are more cost-effective, less time and energy consuming with very less waste generations than conventional bulk materials based methods. However certain precautions are to be taken to avoid any threat to human health or environment due to the nanoparticles. The technology should be cost effective and friendly with ease in establishment and use. The results of this study clearly establish that TiO₂ 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 (TiO₂) = 5 gm/L. Initially the decrease in concentration the degradation of dyes were fast. Photocatalytic oxidation using TiO₂ 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 photocatalyst. pH condition were found to be significantly affected the degradation of dye. TiO₂ as a photocatalyst was an effectively for the remove the dyes. Nano sized anatase TiO₂ can remove the dye from aqueous solution. Its possible to obtained a wastewater free from dye as well as trace metal by using TiO₂ as well as SiO₂.

REFERENCES:

- [1] V. Likodimos, D. D. Dionysiou, and P. Falaras CLEAN WATER: water detoxification using innovative photocatalysts, *Reviews in Environmental Science and Biotechnology*, vol. 9, pp. 87–94,(2010).
- [2] B. S. Tawabini, M. Atieh, Effect of UV light on the Efficiency of NanoPhoto-Catalyst (UV/ CNTs/TiO₂) Composite in Removing MTBE from Contaminated Water, *International Journal of Envir.l Science and Development*, Vol. 4, 2,148-151 (2013.)
- [3] A.L.Castro, M.R. Nunes, Synthesis of anatase TiO₂ nanoparticle with high temperature stability and photoconductivity activity. *Solid State Sci* 10:602–606 (2008).
- [4] Karishma K. Chorawala, Mehali J. Mehta, Applications of Nanotechnology in Wastewater Treatment, *International Journal of Innovative and Emerging Research in Engineering* Vol. 2, No. 1, 21-26 (2015).
- [5] N. Kuburovic, M. Todorovic, V. Raicevic, A. Orlovic, L.,Removal of methyl tertiary butyl ether from wastewaters using photolytic, photocatalytic and microbiological degradation processes, *Desalination*, vol. 213, pp. 123–28, (2007).
- [6] NEERI. Manual on water and wastewater analysis. National Environmental Engineering Research Institute, Nagpur.(1988).
- [7] J. Pandey, R. Khare, M. Kamboj, S. Khare and R. Singh, Potential of Nanotechnology For The Treatment of Waste Water, *Asian Journal of Biochemical and Pharmaceutical Research*, Issue 2 (Vol. 1),272-277(2011).
- [8] Muhammad Kaved Iqbal, Muhammad Naeem Ashiq, *Jour. of Research Science*, Pakistan,,18(2),91-99(2007)

Volume 1, Issue 7, December 2015

- [9] R.S. Dave and A.R.Patel ,photochemical and photocatalytic of cypermethrin under UV radiation, *Der pharma chemica*, 2(1), 152-158 (2010).
- [10] M.J.Iqbal and S.Zahoor, Synthesis and characterization of nanosized lithium manganate and its derivative, *J. Power Sources*, 165, 393-397 (2007).
- [11] Mills, A. and J. S. Wang., Photobleaching of Methylene blue sensitized by TiO₂, *Jour. Photochem. Photobiol A.*, 127-123(2009).
- [12] R. A. Crane, Scott T. B., Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. *J Hazard Mater*, Vol-4 pp 211-212(2012).
- [13] Prachi, Pranjali Gautam, Deepa Madathil, A. N. Brijesh Nair, Nanotechnology in Waste Water Treatment: A Review, *International Journal of ChemTech Research*, Vol.5, No.5, pp 2303-2308, (2013).
- [14] W.Y.Lin, C.Weil, and K.Rajeshwar, Photocatalytic reduction and immobilization of hexavalent chromium at titanium dioxide in aqueous basic media, *Journal of Electrochemical society*, 140(9), 2477-2482 (2003).
- [15] J.Aguado , Grieken R.V. Comprehensive study of the synthesis Characterization and activity of TiO₂ and mixed TiO₂/SiO₂ photo catalyst. *Applied Catalysis A: General* 312:202–212,(2006)
- [16] S.Senthilkumar, P.Kalaamani, K.Porkodi, P.R.Varadarajan and C.V. Subburaam , Adsorption of dissolved Reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste., *Biosour.Technology*, 97, 1618-1625(2006).
- [17] K. Lee, N.H. Lee, S.H. Shin, H.G. Lee, S.J. Kima, Hydrothermal synthesis and photocatalytic characterizations of transition metals doped nano TiO₂ sols *Mater. Sci. Engg. B*, 129, 109–115(2006).
- [18] D. Arun Kumar, J merline Shyla, Synthesis and Charectrization of TiO₂ and SiO₂ nano composites for solar cell application, *Appl. Nano Science* , Vol.2 429-436(2012).
- [19] Nilchi A, Janitabar-Darzi S, Rasouli-Garmarodi S Sol-gel preparation of nanoscale TiO₂/SiO₂ composite for eliminating of congo red azo dye. *Mater Sci Appl* 2:476–480,(2011).
- [20] Thomas Hanemann and Dorothee Vinga Szabo, Polymer-Nanoparticle Composites: From Synthesis to Modern Applications, *Materials*, VOL.3, 3468-3517,(2010)