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A COMPARATIVE STUDY ON PHOTO DEGRADATION OF METHYLENE BLUE DYE EFFLUENT BY ADVANCED OXIDATION PROCESS BY USING TiO_2/ZnO PHOTO CATALYST.

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ABSTRACT

The effluent from the textile, paper, and food industries containing dye is strongly colored & reveals very harmful effects on living things. In order to reduce water pollution, the degradation of dye into non-toxic form is desirable. The photo catalytic degradation of methylene blue is reported in the present paper. The irradiation of aqueous solution of methylene blue (MB) dye in presence of photo catalyst & UV light were carried out in the batch photo reactor. Titanium dioxide (TiO_2) & zinc oxide (ZnO) were used as photo catalyst for the study. The rate decolorisation was estimated from residual concentration spectrophotometrically. Effects of some operating parameters such as the initial P^H, H_2O_2/COD ratio, & the amounts of catalyst on the degradation of the dyes were investigated. Results show that ZnO is a better alternative photo catalyst compared to TiO_2 in terms of percentage degradation of MB. The maximum decolorizing efficiency was occurred in less than 90min with 50mg/750ml of ZnO catalyst dose.

Kyewords: methylene blue**,** Photo –catalyst, decolorisation, spectophotometrically

INTRODUCTION

Dyes and pigments are widely used, mostly in the textiles, paper, plastics, leather, food and cosmetic industry to color products. Textile industries generate 100-170 lit dye effluent per kg of cloth processed which could be characterized by strong odour, high COD & wide range of P^H [1]. The treatment of waste-water from textile dyeing is an *environmental* problem that has received considerable attention. The effluent from textile processing is often discharged to municipal sewage treatment plants or directly to waterways [2-4] .The conventional technologies currently used to degrade the color of the dye contaminated water include primary (adsorption, flocculation), secondary (biological methods) and chemical processes (chlorination, ozonization).

However these techniques are non-destructive since they only transfer the non biodegradable matter into sludge, giving rise to a new type of pollution which needs further treatment[5-7].Use of conventional dye wastewater treatment methods are becoming increasingly challenging for existing plants due to recent guides lines adopted by water authorities. The US department of commerce has projected a 3.5 fold increase in textile production between 1975 and 2020 [8]. As a result of these problems, advanced oxidation processes (AOPs) have been considered as an effective technology in treating organic chemical dyes in wastewater. AOPS are a group of processes that are based on the generation of hydroxyl radicals, which are highly reactive oxidants. AOP are able to oxidize a wide range of compounds that are otherwise difficult to degrade. Heterogeneous catalysis, employed by advanced oxidation processes (AOP's), have emerged as a potential destructive technology leading to the total mineralization of most of organic pollutants [9-11]. Photo catalytic systems are the combination of a semiconductor (like TiO_2, ZnO, Al_2O_3, RuO_2, SiO_2, WO_3, SnO_2, ZrO_2, CdS etc.) and UV light.

Titanium dioxide (TiO_2) is found to be more efficient catalyst for photo catalytic degradation of pollutants due to faster electron transfer to molecular oxygen[12], due to its non selectivity for environmental engineering application; it is nontoxic, insoluble, reusable, photo stable[13]. TiO_2 is most widely used catalyst in photo catalytic degradation of pollutants due to its suitable band gap energy of P^H [14]. However widespread use of TiO_2 for large scale water treatment is uneconomical. Thereby interest has been drawn towards the search for suitable alternatives to TiO_2. ZnO appears to be a suitable alternative to TiO_2 since its photo degradation mechanism has been proven to be similar to TiO_2 [15]. ZnO is an n-type semiconductor with many attractive features. Zinc oxide has a wide band gap of 3.17 eV as compared to TiO_2 (E_{bg} anatase = 3.2 eV). It is capable to generate hydroxyl radicals in sufficient quantity. It is transparent to most of the solar spectrum. Efficiency of ZnO has been reported to be particularly noticeable in the photo oxidation of pulp mill bleaching effluent[16] and textile mill wastewater [17].

Methylene blue is a cationic dye. It is most commonly used for coloring paper, temporary hair colorant, dyeing cotton wools and so on. MB, although not considered to be a very toxic dye it can reveal very harmful effects on the living things. After inhale symptoms such as difficulties in breathing, vomiting, diarrhea and nausea can occur in humans[18].

The molecular formula of MB is $C_{16}H_{18}N_3SCl$.Its IUPAC name is 3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride. The structural formula is as shown below in Fig1.

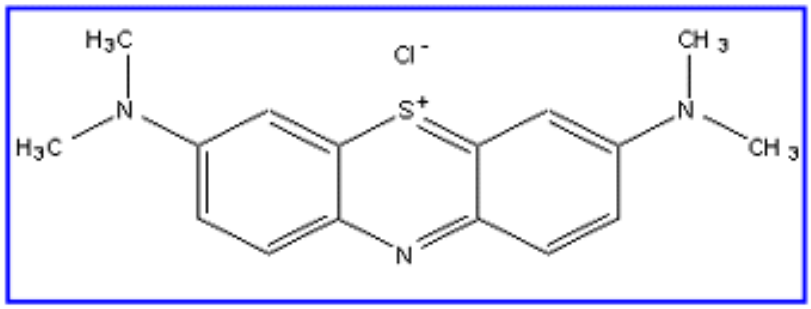

Fig.-1:Structure of methylene blue

The present study investigates the degradation of methylene blue using H_2O_2, ZnO & TiO_2 in presence of UV light. Subsequent experiments were conducted to investigate the effects of various amounts of catalyst dosing on the process performance.

EXPERIMENTAL

Materials

Methylene blue is a dye that was purchased from Merck and used without further purification. Zinc oxide & TiO_2 (AR) (surface area 50m^2/g) were obtained from s-d fine chemical India & were used as received. Double distilled water was used for preparation of various solutions. pH of the solution was adjusted with 1M HCl or 1M NaOH. HCl & NaOH were obtained from Merck, India. Hydrogen peroxide (30% w/v, density 1.11 g/ml) was obtained from Qualigen.

Experimental setup

Studies were conducted using a laboratory photo reactor system made up of borosilicate glass, as shown in Fig.2. A double walled immersion well, made up of quartz was placed inside the glass reactor which was fitted with a standard joint. The capacity of photo reactor was 850 ml. But the total volume of the solution taken was 750ml. The 8W pressure mercury vapors lamp was placed inside the immersion well. This entire setup was placed on a magnetic stirrer for uniform dissipation of heat produced during the reaction. Also TiO_2 & ZnO can be uniformly dispreads in the solution when the sample was degraded by UV light. The spectra were taken with double beam UV-VIS spectrophotometer spectra scan UV 2600 (Chemito). P^H meter Equiptronics -model EQ -621 was used to adjust the P^H of the solution.

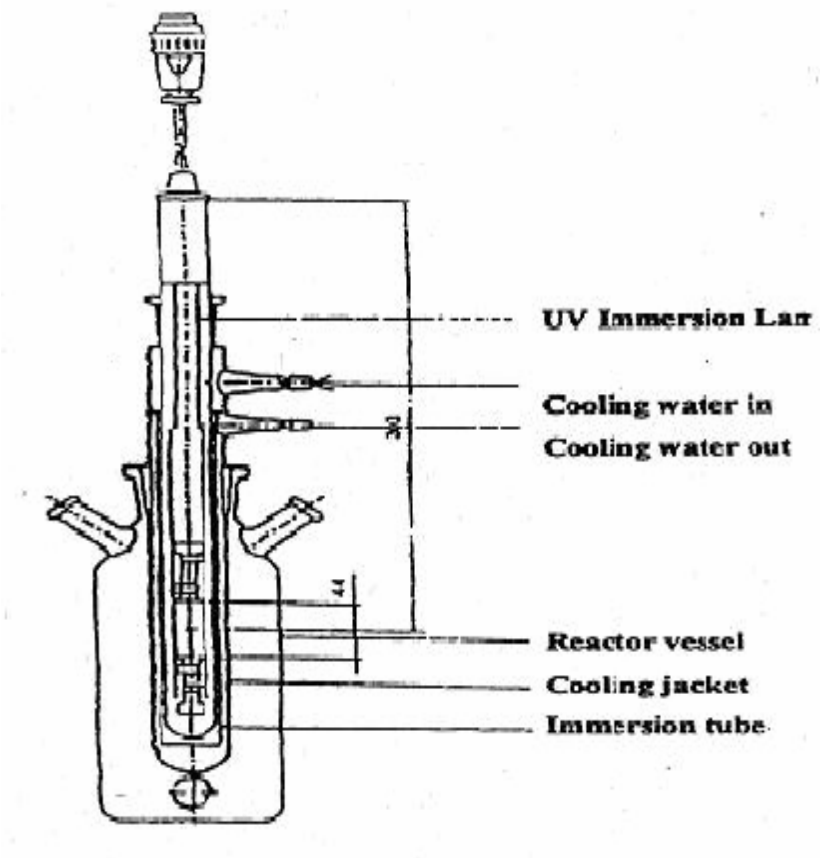

Fig.- 2: Photoreactor

Procedure and analysis

In order to determine the concentration of methylene blue dye using the colorimetric techniques, a calibration curve was generated from the standard solution of methylene blue. A blank sample using distilled deionized water was used to zero the spectrometer. The calibration curve between absorbance and concentration of MB dye gave a high linear regression coefficient of 0.99 at 663 nm. For the degradation experiments, $1.5x10^{-5}$ M dye solution was prepared. 750 ml of this dye solution was taken in the photo reactor and 10mg of photo catalyst TiO_2 /ZnO was added to the dye solution and the suspension was subjected to irradiation under UV lamp of 8W. The aq. solution was magnetically stirred throughout the experiment. Aliquot was taken out at different time intervals with the help of glass syringe. Then a centrifugation process was applied to separate TiO_2 /ZnO catalyst particles after photo catalysis. This degraded solution was taken for spectra measurement .The absorption spectra were recorded & the rate of decolorisation was observed in terms of change in intensity at Λ_{max}=663nm. The % of degradation was calculated from the following eq.-

$$\% \text{ Degradation} = (1 - A_t/A_o) \times 100$$

A_t = the absorbance after time t min

A_o = the absorbance at time t =0 min

RESULTS AND DISCUSSION

The results of the various studies in the present investigation are presented subsequently.

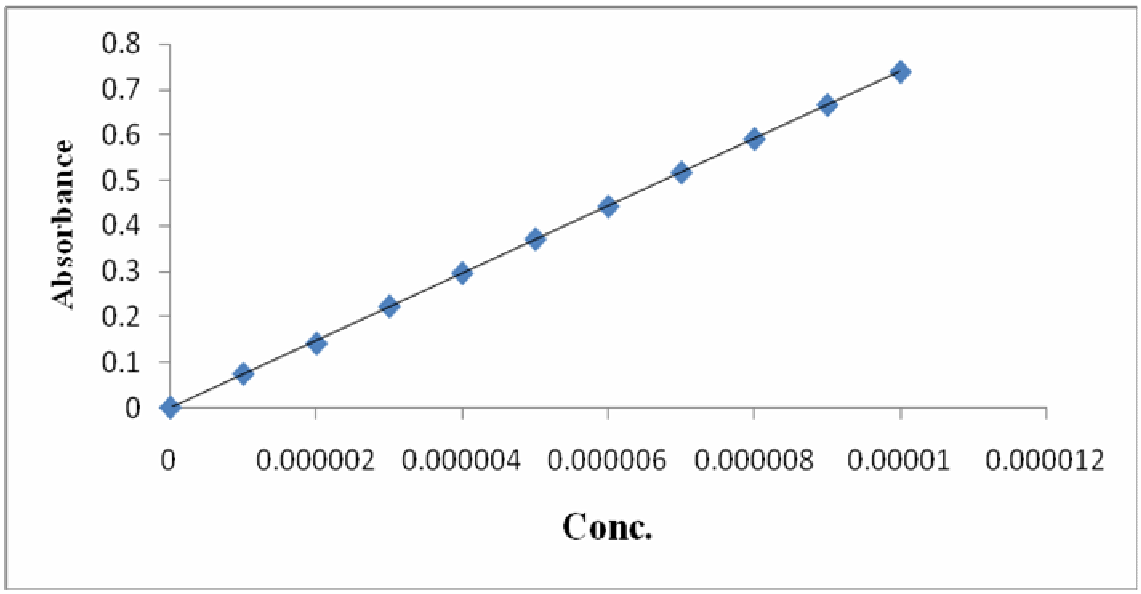

Fig.- 3: Calibration plot of methylene blue at 663 nm.

Effect of pH

pH is most important parameter to study because wastewater containing dyes is discharged at different P^H. Therefore the role of pH on the decolorisation was examined at different pH conditions namely 2, 3, 4, 5, plane water & 8. Fig.4 shows the color removal efficiency of MB as a function of P^H .It has been observed that the decolorisation efficiency increases with the increase in P^H exhibiting maximum rate of degradation at pH 2. This can be explained on the basis that the pH influences at the same time both (i) surface state of catalyst & (ii) ionization state of ionisable organic molecules .The net effect is direct influence of pH of the solution on the heterogeneous photo catalytic process.

Role of hydroxyl radicals

The decolorisation efficiencies increased significantly when H_2O_2 was used in the presence of UV radiation as shown in Fig4. This is because free hydroxyl radicals which the second most powerful oxidizing agent after fluorine are generated by the dissociation of H_2O_2 in the presence of UV radiations[19]. Moreover, high concentration of hydroxyl peroxides act as scavenger itself, thereby decreasing the conc. of hydroxyl radicals & reducing compound elimination efficiency[20]. Therefore, H_2O_2 should be added at an optimum concentration to achieve the best degradation. The hydroxyl radicals generated attack the MB framework at different sites like, unsaturation points etc. In several such attacks the MB gets converted into CO_2 & hetero-atoms which are further mineralized.

Effect of catalyst concentration

The experiments were conducted by varying catalyst doses from 10mg/750ml to 90mg/750ml for the dye solution at maximized pH=2. Maximum degradation is observed with 50mg/750mlof catalyst ZnO & thereafter the rate of degradation decreases. Addition of excess of TiO_2 & ZnO above this dosage did not significantly enhance the degradation as shown in Fig.6. This is due to aggregation of catalyst particles, which reduced the interfacial area between the reaction solution & the photo catalyst. The increases in opacity & light scattering by the particles may be other reasons for the degradation rate[21-22].

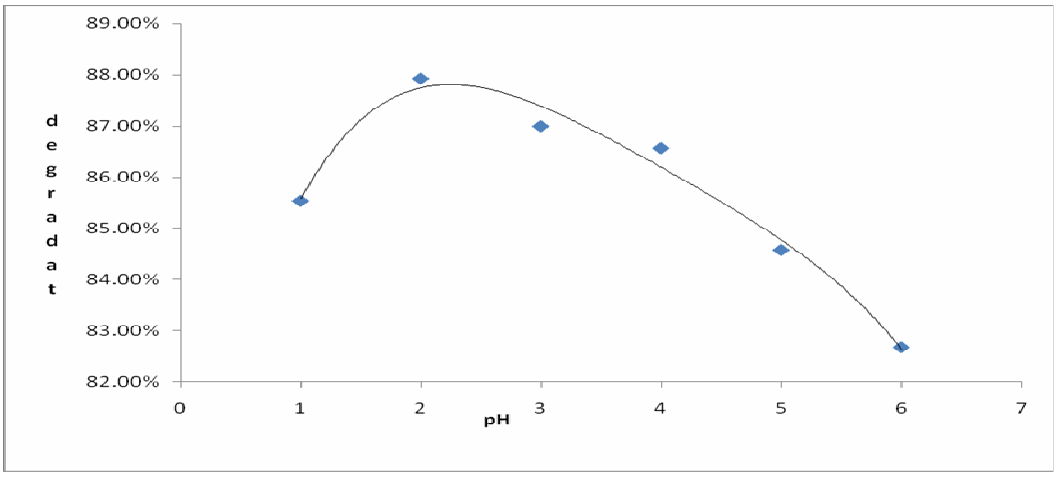

Fig.-4: %degradation of MB with pH

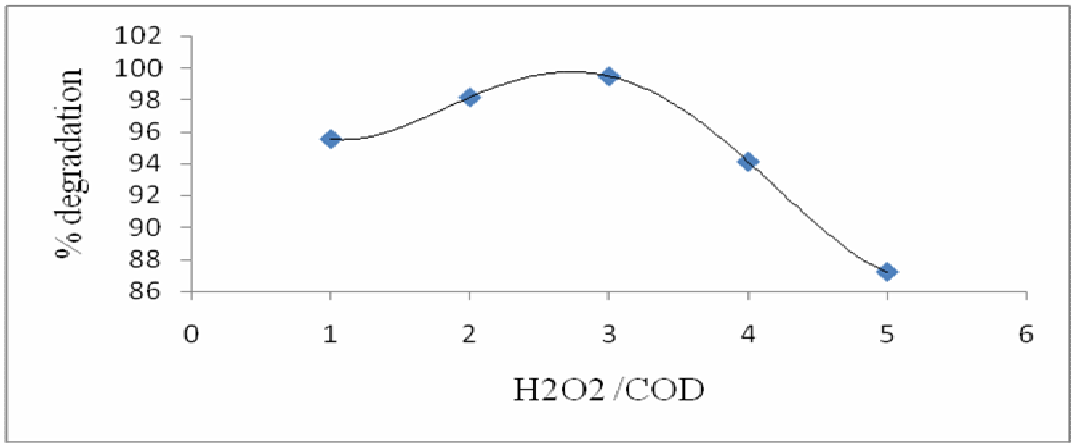

Fig.-5: %degradation of MB with H_2O_2/COD ratio

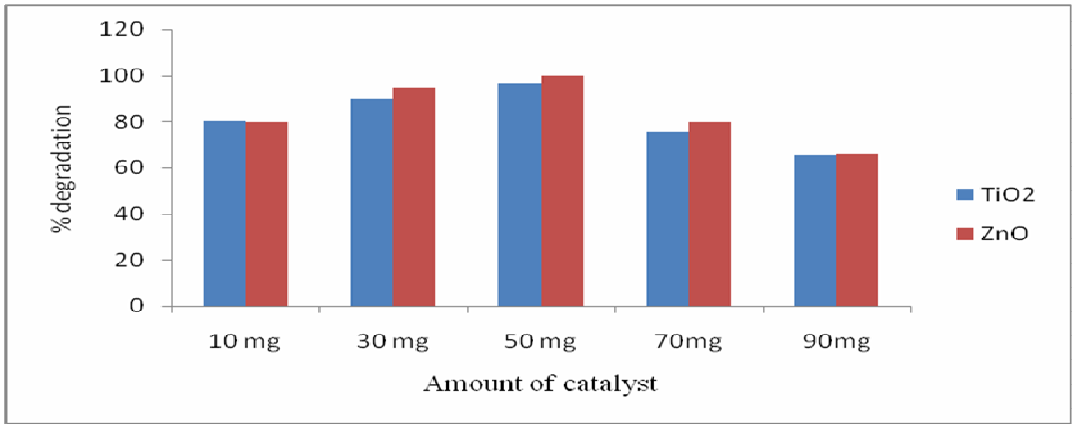

Fig.-6: Bar diagram showing rate of degradation of TiO_2&ZnO

CONCLUSION

The results obtained in the present study show the efficiency of AOP's in removing dyes, which resists other conventional treatment processes. Photo oxidative degradation appears to be a promising technology that has many applications in environmental cleanup systems.

A detailed feasibility study has been carried out on photo catalytic degradation of MB using TiO_2 & ZnO powder as a photo catalyst under UV radiation. It was observed that pH; catalyst dosages and H_2O_2/COD ratio all significantly affect the photo catalytic degradation of MB. The Results of the study indicate that ZnO is very effective & suitable alternative to TiO_2. The best reaction dosage of ZnO catalyst is about 50 mg/750ml.The maximum degradation efficiency of dye was achieved with the combination of UV+ H_2O_2+ZnO.The maximum decolorisation occurred in ≤ 90 min. The photo degradation of MB is 99.99%. It follows the first order kinetics.

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