A Bench-Scale Photoreactor For Performing Photocatalytic Degradation Studies

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Abstract: - Several investigations have been published across the globe and also discussing more on the applicability of photocatalytic activity for the treatment of industrial dye effluents. Photocatalytic process involves the removal of contaminants and organic waste from effluent streams that are chemically stable and resistent to biodegradation. This process has shown a great potential being cost effective, ecofriendly and complete mineralisation, use of low cost catalyst system and in the field of sustainable treatment with zero waste discharge. The principle of photocatalysis relies on in-situ generation of hydroxyl radicals under ambient conditions which are capable of generating a wide spectrum of toxic organic compounds including non-biodegrdables into relatively less toxic end products. Photocatalytic process of removal of colour from aqueous solutions also indicated the better removal of methylene blue compared to methyl orange. It was interestingly to note that, photocatalytic degradation of both the colours by all nanoparticles studies is more effective than the removal by batch studies. Further the adsorbent dosage required for photocatalysis was found to be very less compared to batch studies. The removal percentage of methylene blue by using ZnO was
99.6%, TiO2 was 96.3% and MgO was 93.4% respectively under optimum experimental conditions. Accordingly, these values for methyl orange were found to be 96.2% for ZnO, 91.1% for TiO2 and 85.8% for MgO respectively. In the present research work, the combination of different nanoparticles are used to remove the colour from aqueous solutions of industrial dye effluents by using photocatalytic process are also presented.

Keywords: Photocatalytic, ZnO, Adsorbent, TiO_2, Methylene blue, MgO,Methyle orange

1. Introduction:

The researchers across the globe have been published papers and discussing more on the applicability of photocatalytic process for treating industrial wastewaters. Photocatalytic process involves the removal of contaminants from waste streams that are chemically stable and resistant to biodegradation. This process has shown a great potential being cost effective environment friendly complete mineralization, use of low-cost catalyst system and in the field of sustainable treatment with zero waste discharge. The principle of photocatalysis relies on in-situ generation of hydroxyl radicals under ambient conditions which are capable of generating a wide spectrum of toxic organic compounds including non-biodegrdables into relatively less toxic end products. The rapid industrialization in developing countries has began to introduce harmful organic pollutants into receiving bodies. In particular, textile industries that consume a large quantity of water in the process of dying and washing of fabrics and thus release huge quantities of coloured effluents. In this regard the development of inexpensive and green methods to treat and purify pollutant streams has been focal subject in technological developments. Amongst many strategies photocatalysis is regarded as most viable one. It is attributed to its usage of sunlight to decompose organic pollutants.

2. Literature Review:

Specific Reviews

Colour removal from actual textile mill wastewater using Nano CaO has been investigated by Anitha et al., (2005) [1]. They have recorded 62% and 55% of colour removal at pH 6.0 and 5.2 (actual pH of wastewater).

Hegde and Tuppad (2016) [2] carried out batch experiments to evaluate performance of ZVI in the colour and COD from textile mill wastewater. They reported the increase in colour removal with decrease in pH. At optimum conditions of

experimentation, viz: contact time of 150 minutes, adsorbent dosage of 1.5 gm, pH of 2.48, the authors recorded 85% and 55% of COD and colour removal respectively.

Removal of textile dyes from its aqueous solutions using biosynthesized silver nano particles have been explored by Khatoon and Sardar M (2017) [3]. The study revealed the effective dye removal at alkaline pH 9. The study suggested that the silver nano particles are eco-friendly and highly efficient adsorbents in removal of dyes from textile industry.

Abiyu Kerebo et al., (2016) [4] carried out batch experiments to investigate the effect of contact time, pH, initial dye concentration on removal of methyl violet from synthetic wastewater using nano aluminum oxy hydroxides. The optimum removal of dye was achieved at pH of 10, contact time of 85 minutes and adsorbent dosage of 9 mg/l. The authors interfere that Langmuir model is the best model fitted to equilibrium data.

Over 96% removal of chromium and lead from diluted electroplating wastewater using titanium oxide nanoparticles has been reported by Sudarshan et al., (2015) [5]. Arafat et al., (2015) [6] carried out batch adsorption studies to evaluate the colour removal from textile dying industry effluents using chitosan-ZnO nano composite.

The author recorded, 99% of original colour of the effluent at adsorbent dosage of 2 g/L and at contact time of 60 minutes. Use of ZnO nanoparticles has low cost, efficient adsorbents for the removal of methylene blue colour from synthetic wastewater has been reported by Kulkarni (1998) [7]. The author's observed 98% colour removal at pH 6.5 and at stated optimum conditions of experimentation. The uptake capacity was found to be about 200 mg/g. Langmuir isotherm model fitted well to the data obtained.

Capacity of decolorizing various types of dyes such as disperse, reactive, Sulphur and vat dyes (which are used in textile processing) by using zero valent iron nanoparticles has been reported. The effective decolorization of dye solutions in the pH range of 3-10 has been reported. But the better decolorization was recorded at acidic pH of 3 to 6. The nanoparticles showed maximum adsorption of 5.3 mg/g of reactive red dye. The attempt has been made to validate the applicability of MgO nano particles for the removal of Rhodamine-B (cationic dye) from the effluent wastewaters [8]. At the optimum experimental conditions, 100% color removal is recorded. The authors tried Langmuir, Freundlich and Temkin models to evaluate the adsorption behavior and found that data fitted well to Langmuir and Temkin adsorption isotherms.

Merve et al., (2018) [9] successfully investigated the removal of 100% methyl violet, methylene blue, brilliant green and brilliant cresol blue colours from wastewaters using resins coated with nickel/nickel boride nanoparticles. Adsorption of these dyes was found to obey the Langmuir isotherm model and was endothermic. The isotherms revealed the adsorption capacities of these colors varying from 66.7 mg/g (methylene blue) to 44.9 mg/g (methyl violet). Further the authors investigated the three kinetic models and concluded that the pseudo second order kinetic model fit the cationic dyes best.

H.N. Jayasimha et al., (2024) [10] the green synthetic method employed for the synthesis of CuO materials has proven to be effective for the degradation of AR88 dye and the sensing of ciprofloxacin. The synthesized CuO catalyst exhibited high dye degradation efficiency, with a degradation percentage of 97.35 % achieved after 80 min of UV light exposure. This indicates that the synthesized CuO material is a promising candidate for the degradation of AR88 dye, highlighting its potential for industrial pollutant treatment. Furthermore, the CuO material demonstrated excellent sensing capabilities for ciprofloxacin.

Batch studies to investigate the adsorption of methyl orange dye on multiwalled carbon nanotubes from aqueous solutions have been carried out by Donglin et al., (2013) [11]. Linear relationship between adsorption and variables like concentration of colour, dosage of adsorbent has been observed. The kinetic study demonstrated that, the adsorption was in a good accordance with the pseudo second order kinetic model. Behanjady et al., (2006) [12] stated that, the photocatalyst concentration beyond certain limit results in increase in the turbidity of the suspension which leads to decrease in UV light penetration and is the reason for decrease in degradation rate. Saktivel et al., (2003) [13] based on the degradation experiments they carried out (degradation of azodyes by TiO2 and ZnO) reported the increase in degradation rate with increase in the light intensity. Kormann et al., (1991) [14] and Neppolian et al., (2002) [15] when they examined the influence of the light intensity on photocatalytic degradation of phenol and chloroform, reported square root dependence. Further they noticed a linear relationship of the rate of degradation at lower light intensities. Sampa and Binay et al., (2004) [16] reported about 45 and 70% of decolorization of Eosin Y by ZnO photocatalyst within first 30 min or irradiation time, initial concentration of dye being 50 and 25 mg/l. Konstantinou and Albanis (2004) [17] carried out the studies to evaluate the TiO2 assisted photocatalytic degradation of azo dyes in aqueous solution. They reported the increase in degradation rate of azo dyes with decrease in pH. Further they reported that, the electrostatic attraction of the positively charged TiO2 with the dye at pH less than 6 resulted in the strong adsorption of the dye on the TiO2 particle. Falah and Thekraw et al., (2010) [18] have carried out studies to investigate the photocatalytic degradation of actual and prepared (simulated) textile dyeing wastewaters by ZnO. For both the wastewaters they noticed the increase in decolorization efficiency with increase in catalyst mass up to 250 mg/l under stated experimental conditions. Beyond 250 mg/l of dosage, they reported the decrease in degradation efficiency.

K. G. Chandrappa. et al, (2019) [19] the successful synthesis of ZTO nanoparticles offers an opportunity to examine their photocatalytic activity. The as-prepared and calcined ZTO nanoparticles were selected for the evaluation of photocatalytic activity with MB dye under the illumination of UV light. In order to study the effect of UV light on degradation of MB dye, a blank experiment was performed under UV light without the addition of photocatalysts (ZTO). The results indicated that MB dye of 10 mg/L was photolyzed up to 5% in 2 hr. This degradation efficiency was negligible when the different sized (24, 35 and 53 nm) nanoparticles were added to the solution under illumination. When there was no UV light, the concentration of MB dye with the addition of ZTO photocatalysts remains unchanged for 2 hr. From these blank experiments, it can be concluded that UV light and photocatalysts are the necessary factors in the photocatalytic process.

MB dye absorbs light in the visible region (550-700 nm) with the absorption maxima at 664 nm. A series of experiments were carried out with different sizes (24, 35 and 53 nm) ZTO nanoparticles in MB dye solution.
In a review paper on "Removal of dyes from wastewater by nanomaterials" Wenqian et al., (2019) [20] presented extensive literature information with regard to removal of dyes by nanomaterials. The table given by the authors based on the review of papers of the other researchers is presented below.

Table 1: Removal of Industrial Dye Effluents by Different Nanomaterials

Adsorbents	**Preparation /modification**	**Adsorbate**	**Efficiency**
Fe3O4 Nanomaterials	NPs were Synthesized by Chemical Precipitation Method Using CTAB	Acridine Orange Coomassive Brilliant Blue R-250 Congo Red	0.056 (mol/g) 0.082 0.078
HA- Fe3O4	Fe3O4 NPs were modified by humic acid	Rhodamine B	Adsorption qmax-161.8 mg/g (98.5%)
Fe3O4 Nanomaterials	Ionic Liquid were used to modify Fe3O4 Nanoparticles.	Reactive Red 120	166.67 mg/g
Fe3O4 Nanomaterials	Silica Based Cyclodextrin Immobilized on Magnetic Nanoparticles	Direct Blue 15	98%
MgO Nanoparticles	Coprecipitation Method	Reactive Black 5	500mg/g
MgO Nanoparticles	-	Reactive Orange	333.34 mg/g
MgO Nanorods	Artinite and MgO Nanorods Prepared by Precipitation Method	Malachite Green and Congo Red	95.1% 86.28%
MgO Nanostructures	Hierarchical Hydromagnasite and MgO Nanostructures Prepared by Reflux Method	Malachite Green and Congo Red	99.98% 99.94%
MgO Nanoflakes	Hydromagnasite and MgO Nanoflakes Prepared by Hydrothermal Method	Malachite Green and Congo Red	97.42% 92.68%
MgO Nanoparticles	Activated Carbon Immobilised on MgO Nanoparticles	Rhodamine B	16.2mg/g
Rice Straw Charcoal/ MgO Nano Composite	Rice Straw Charcoal Immobilized on MgO	Reactive Blue 221	27.78mg/g
GO	-	Methylene Blue	714 mg/g
Magnetite/Reduced Graphene Oxide	-	Rhodamine B	91%
nZVI/rGO	-	Malachite Green and Rhodamine B	94% 87.22%

The photocatalytic properties of semiconductors depend generally on several factors namely:
- The mobility and mean lifetime of photo generated electrons and holes.
- The position of energetic level.
- The nature of the interface.
- The light adsorption coefficient.

The basic mechanism of photocatalytic reaction is governed by the generation of electron-hole pair into the semiconductor material and its transportation to reaction with organic pollutants. These types of reaction are activated by absorption of photon with sufficient energy (equal to or higher than the band gap energy; Eg of the Catalyst. The absorption leads to a charge separation due to promotion of electron(e-) from the valence band (vb) of semiconductor catalyst to the conduction band (cb) thus generating a hole (h+) the valence band [21]. For photo catalyzed reaction to occur as for as possible the recombination of the electrons and the hole should be prevented. The ultimate goal of the process is to have a reaction

between the activated electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reactant to produce an oxidizer product. The process is schematically presented in the Figure 1.

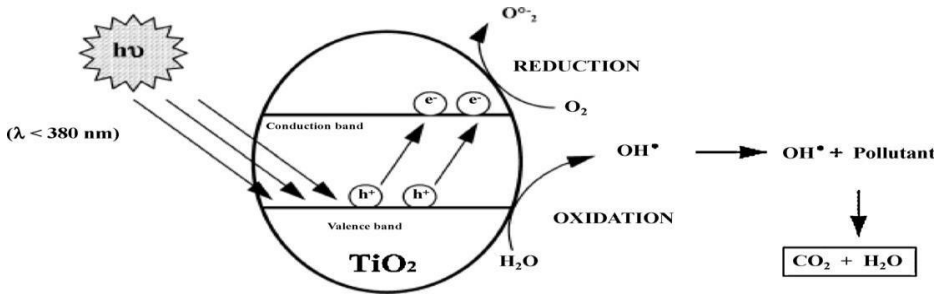

Figure 1: General Mechanism of the Photocatalysis

The mechanism is also shown in equations below

Photocatalysts (TiO_2/ZnO) +hv $\xrightarrow{UV}$ e-+h+vb → (1)

h+vb+H_2O→H++OH– → (2)

h+vb+ OH–→OH+ → (3)

2e-+O_2→O_2- → (4)

e-+H_2O_2→OH++OH- → (5)

ecb-+O_2→O_2- → (6)

Organic pollutants O2-or OH- CO_2+H_2O + other degradation products

Where hυ is photon energy required to excite the semiconductor electron from the valence band region to conduction band region.

Thus, basic process of photocatalysis consists of ejecting an electron from the valence band region to the conduction band of the semiconductor catalyst creating an h+ hole in the valence band.

This is due to ultraviolet radiation of the catalyst with and energy equal or superior to the band gap (ZnO>3.30ev, TiO2>3.30ev) (equation 1). This is followed by formation of extremely reactive radicals (like OH-) semiconductor surface and or a direct oxidation of polluting species (equation 2-5). The ejected electron reacts with electron acceptors such as oxygen adsorbed or dissolved in water (equation 6).

The oxidation of pollutants and the reduction process of oxygen in the photocatalysis of organic pollutants do not occurs concurrently. Here there is an accumulation of electrons in the conduction band of the photo catalyst, thus helping a recombination of negatively charged electron and positive hole.

Therefore, to encourage photocatalytic oxidation process, efficient utilization of electrons is necessary. In case if semiconductors are used as photocatalyst for environmental remediation, Photon induced electron hole pairs help in redox reactions and produces hydroxyl free radicals (OH+) and superoxide ions (O2-). Further harmful organic pollutants in the wastewater are disintegrated by the generated species (powerful oxidizers) and converted into carbon dioxide and water.

Interplay between surface and electronic characteristics determine the photo activity. This parameter is defined as the ratio between the rate of photo induced events and the flux of the absorbed photon.

But due to extensive light scattering, it is often impossible to accurately estimate the absorbed photons in the real system. Consequently, for practical reasons, many studies assume that all the radiation is absorbed. Thus, the photonic efficiency an alternative photo performance index can be adopted. This index is defined as the quotient between the rate of the photocatalytic events and the photon flux.

Table 2.: Energy Band Gap for Some Common Semiconductor Materials

Semiconductors	Bandgap energy (ev)
Diamond	5.4
ZnO	3.36
TiO_2	3.03
Cu_2O	2.172
CdS	2.42
ZnS	3.6
WO_3	2.76
Fe_2O_3	2.3
PbS	0.286
SnO_2	3.54
CdSe	1.7
ZrO_2	3.87

3. Methods and Materials:

Description of photocatalytic reactor with UV light to be used for experimentation is outlined below. About 1-liter cylindrical reactor/vessel with a quartz tube at the centre of the reactor to house medium presence of mercury lamp (Source of UV Irradiation 120 Watt/m^2) is selected. To adjust the temperature, the reactor is placed in water bath. For mixing of suspension the cylindrical reactor is placed on magnetic stirrer. The line diagram of photocatalytic reactor is shown in Figure 2.

A set of photocatalytic experiments are conducted in borosil silicate glass cylinder (Photoreactor) under UV light irradiation. The light source was mercury lamp of 125 watts. The experiments are performed at ambient temperature and are conducted to evaluate optimum photocatalytic condition such as pH, irradiation time, initial concentration of time but keeping constant photo catalyst dosage of 0.3 g/L. The reactor is placed on a magnetic stirrer and contents are stirred during irradiation to keep the suspension homogenous. After specific pre-decided times of irradiation, a suitable aliquot of samples is withdrawn and analyzed after centrifugation using Ultra Violet (UV) spectrophotometer.

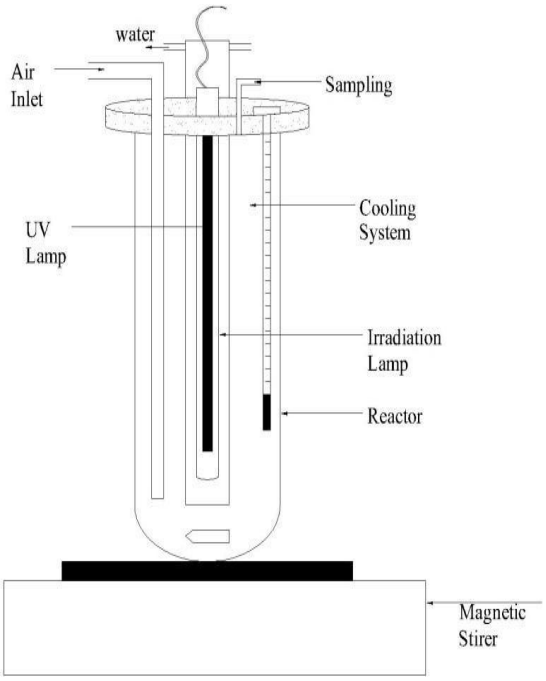

Figure 2: Photocatalytic Reactor with UV Lamp

The outcome of Nano photocatalytic studies carried out to access the nano photocatalytic degradation of methyl orange using MgO nanoparticle under varied experimental conditions. An attempt has been made to analyze the effect of irradiation time, pH and initial dye concentration on the removal efficiency of dye from aqueous suspensions.

3. Results and Discussion:

Initially, the experiments were conducted to investigate the influence of irradiation time, initial concentration of colour, pH and at constant catalyst (Nanometal oxide) dosage of 0.3 g/L. Further, the corresponding parameters at which the maximum removal efficiency was recorded in the first step, an attempt has been made to optimize the catalyst dosage. In the first step of experimentation, the photocatalytic degradation studies on methyl orange using different nano catalyst are presented and the respective findings are listed as below.

- Increase in the removal efficiency with increase in irradiation time from 10 to 40 min for ZnO and 10 to 50 min for TiO_2 and MgO has been recorded. Whereas beyond 40 min (50 min and upto 60 min) for all the nano catalyst were studied, the inverse relationship between removal efficiency and irradiation time was observed.
- Again, maximum removal efficiency was recorded with pH=7 of the aqueous sample.
- Also, inverse relationship between removal efficiency and initial concentration has been recorded. With initial colour concentrations of 10 mg/L and 90 mg/L the removal efficiency was found to be maximum and minimum respectively.
- Further the removal potential of three catalysts found to follow the sequence: ZnO>TiO_2>MgO. In the present research work, the maximum adsorption percentages of methyl orange from aqueous solutions and at optimum operating conditions tried by catalysts ZnO is 94.1%, TiO_2 is 86.8% and MgO 72.3% respectively. Optimum conditions are being used, the irradiation time was 40 min for ZnO and 50 min for both TiO_2 and MgO, pH=5, Co=10 mg/L.
- Minimum removal efficiencies corresponding to operating conditions of Co=90 mg/L, Irradiation time was 10 min, pH=3 were found to be 43.5% for ZnO, 42.9% for TiO_2 and 27.2% for MgO.

In the second step, adopting the optimum operating conditions evaluated in the first step, viz, Co=10 mg/L, Irradiation time of 50 min, pH=5, experimentations were conducted to optimize the catalyst dosage varying 0.05 to 1.2 g/L. The maximum removal efficiencies were found to depend on the catalyst.

Accordingly, maximum colour removal of 96.2% by ZnO was recorded with catalyst dosage of 0.25 g/L. Similarly, the removal efficiencies by TiO_2 and MgO were 91.6% (Co=0.5 g/L) and 85.8% (Co=0.7 g/L).

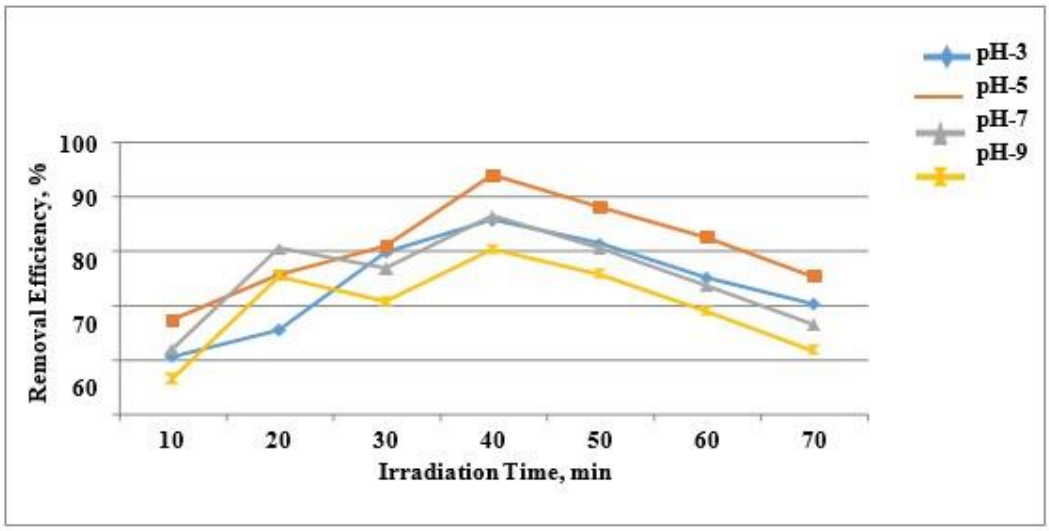

Figure 3: Effect of irradiation time on removal efficiency of Methyl orange by ZnO (Co=10 mg/l)

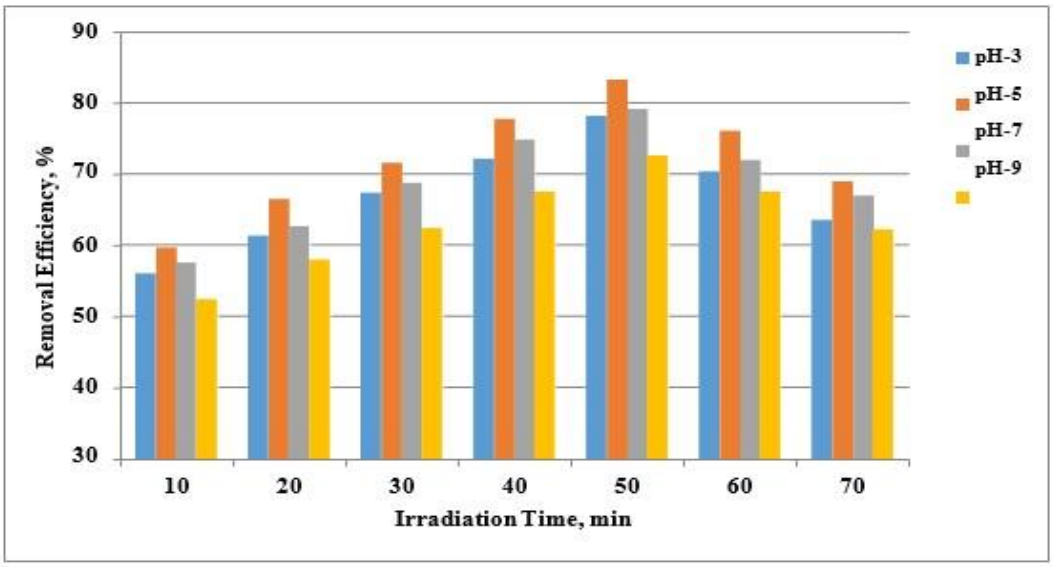

Figure 4: **Effect of irradiation time on removal efficiency of Methyl orange by TiO_2 (Co=70 mg/l)**

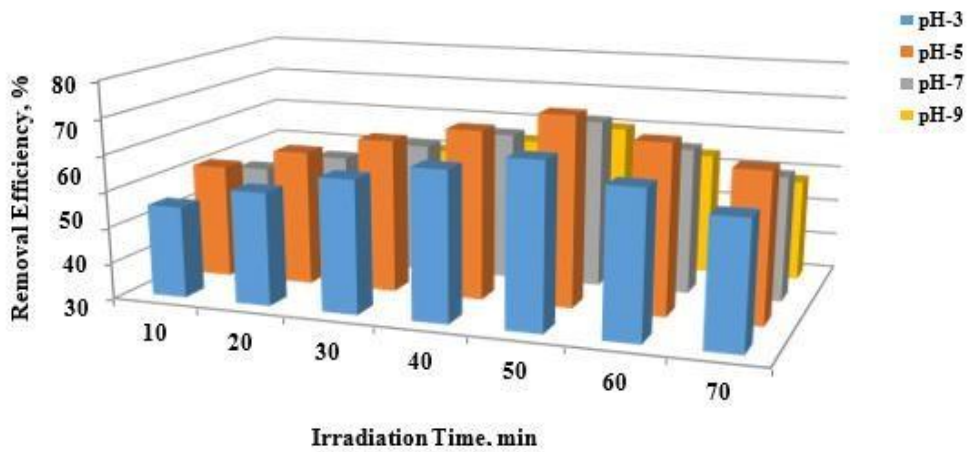

Figure 5: Effect of irradiation time on removal efficiency of Methyl orange by MgO (Co=10 mg/l)

Potential of ZnO in photo catalytically degrading Methylene Blue (99.6%) is higher than Methyl Orange (96.2%). Also, the optimum catalytic dosage corresponding to these removal efficiencies were 0.15 g/L (Methylene Blue) and 0.25 g/L (Methyl Orange). However, pH was found to be colour dependent and thus optimum pH s were 5 and 9 for Methyl Orange and Methylene Blue respectively. Similarly, the higher removal of Methylene Blue by TiO_2 compared to Methyl Orange were observed and values were respectively 96.3% and 91.1%, optimum catalytic dosages being respectively 0.3 g/L and 0.5 g/L. On the other hand, maximum removal of 93.4% (Methylene Blue) and 85.8% (Methyl Orange) by MgO were recorded at catalytic dosages of 0.7 g/L for both the colours.

4. Conclusion

- Based on photocatalytic studies, it is concluded that, photocatalytic degradation of colours by nanoparticles with higher efficiencies compared to Batch degradation can be achieved.
- It is concluded that, photocatalytic degradation is also more effective in degrading Methylene Blue colour compared to Methyl Orange by nanoparticles employed for degradation studies.
- It is concluded that, the dosage of nanoparticles required for photocatalysis is very much less than required by Batch removal. Corresponding to maximum removal 0.9g/L of optimum dosage for all colours removal by all nanoparticles by Batch studies were recorded. While optimum catalytic dosages of 0.25g/L (ZnO), 0.5g/L (TiO_2) and 0.7g/L (MgO) for maximum removal of Methyl Orange by photocatalysis were observed.
- On the other hand, these values for Methylene Blue were found to be 0.15g/L (ZnO), 0.3g/L (TiO_2) and 0.7g/L (MgO).
- It is concluded that the maximum removals of Methylene Blue, in the order of 99.6% (by ZnO), 96.3% (by TiO_2) and 91.1% (by MgO) can be achieved by photocatalytic degradation. While these values for Methyl Orange were found to be 96.2%(by ZnO), 91.6% (by TiO_2) and 85.8% (by MgO) respectively.
- Thus, it is inferred that for better degradation of both the colours namely Methylene Blue and Methyl Orange from aqueous solutions, ZnO catalyst can be successfully used. And with respect to dosages also ZnO being found to be economical.

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