Nanotechnology Perceptions
ISSN 1660-6795
www.nano-ntp.com

Photocatalytic Degradation Studies of Actual Wastewater With and Without Dilution by ZnO, TiO_2 and MgO Nanoparticles

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The present research was selected to evaluate the feasibility of treating pharmaceutical wastewater by photocatalytic degradation and using nanoparticles. The trends of degradation were found to be same as that of Photocatalytic degradation of wastewater without dilution. However, higher removal efficiencies were observed with diluted wastewater compared to wastewater without dilution. Even these higher removal efficiencies were recorded at much lower catalyst dosage and irradiation time as compared to removal efficiencies achieved in case of wastewater without dilution. Same trends were observed for other constituents of wastewater studied. Maximum colour removal of 99.2%, 95.8% and 92.0% by ZnO, TiO_2 and MgO respectively were recorded at catalyst dosage of 0.6 g/l and irradiation time of 90 min. These values at catalyst dosage of 1.6 g/l and 150 min were found to be 78.0, 72.5 and 66.7% respectively by ZnO, TiO_2 and MgO nanoparticles. Potential of ZnO was found to be higher followed by TiO2 and MgO. The COD removal was maximum at catalyst dosage of 1.6 g/l and irradiation time of 150 min, values being 88.5% (ZnO), 81.01% (TiO_2) and 71.6% (MgO). Accordingly, the minimum removal values recorded at catalyst dosage of 0.6 g/l and irradiation time of 90 min were 45.8%, 42.7% and 29%. Again, higher removal efficiencies of other constituents of wastewater were recorded at catalytic dosage of 1.6 g/l and irradiation time of 150 min. In nut shell it can be said that the removal all constituents of wastewater tried by ZnO is higher compared to TiO2 and MgO. Finally, to treat the actual wastewater with dilution of 1:3 by Photocatalytic degradation adopting catalyst dosage of 0.6 g/l and irradiation time of 90 min employing ZnO preferably. Further, treatment of wastewater to

achieve disposal standards specified for constituents of wastewater, as found feasible could be considered. However, author also opine to work out the techno economic feasibility of dilution of wastewater, selection of particular nanoparticles etc, before recommending to treat the wastewater.

Keywords: Photocatalytic, ZnO, Adsorbent, TiO_2, Methylene Blue, MgO, Methyl Orange, Photocatalytic Degradation.

1. Introduction

With the development in science, nanotechnology as found to have wider range of application in each and every aspects of life science. This majorly includes pharmaceuticals, health-care, construction, energy, environment, electronics, agriculture, food processing, information technology etc. In particular treating industrial wastewaters with nanomaterials is important and wide spread. Nanotechnologies have advantages in treating wastewaters, since they eliminate contaminants and help in the recycling process. Such a processes leads to reduction in labour, time, and expenditure to industry solving various environmental issues. Opportunities and challenges of using nanomaterials in the purification of surface water, groundwater and industrial wastewater stream is a matter of continuing concern. The development of different nanomaterials like Nano adsorbents, Nano catalyst, zeolites, and non-structured catalytic membranes have made it possible to disinfect disease causing microbes, removing toxic metals and organic and inorganic solutes from water/ wastewater. To meet the one of the objectives of present research work, Photocatalytic degradation studies were carried out to assess the degradation potential of nanoparticles in degrading actual wastewater. Combinations of experimental investigations carried out are listed below. The pH, Chemical Oxygen Demand and Colour removal efficiencies were estimated by varying catalyst dosage and irradiation time. Further, employing optimum catalyst dosage and irradiation time arrived from above findings, investigations were carried out to assess the treatment potential of actual wastewater for its various contents viz pH, Colour, Chemical Oxygen Demand, Total Solids, Total Dissolved Solids, Nitrate, Sulphate and Chlorides. Also, the experimentations were carried out on the same lines mentioned above with actual wastewater but with 1:3 (Actual wastewater: Distilled water) dilution.

2. Literature Review

2.1 Photocatalytic Treatment of Actual Wastewater

Zhao and Zhang et al., (2008) [13] have discussed the treatment of different wastewaters by photocatalytic oxidation and the influence of variables on the process.

- They reported the increase in COD removal with increase in ZnO quantity upto 3g/l and beyond this they observed the decrease in COD removal. They attributed that such behaviour is due to less hole numbers at lesser dosage and at higher dosage of ZnO, the grains will produce dispersion of light leading to decline in reaction rate. Further they have reported the highest COD removal at pH-10 and stated that the wastewater pH will influence the stability of the catalyst as the ZnO is an amphoteric oxide. They have also observed the increase in COD removal rate with increase in light intensity.
- Increase in COD removal rate with increase in irradiation time in treating printing and dyeing wastewater by photocatalytic degradation has been reported by the authors. Same

effect has been reported by [14] stated that, regardless of using ZnO or TiO2 as photocatalyst, the treatment efficiency of semi synthesis wastewater of Cephalosporin remained same.

[1] Increase in COD removal with increase in irradiation time has been reported by Abdulraheem et al., (2012) [2]. They observed the small decrease in COD during the first step of oxidation process, at which time the sample will be still coloured. They writes that the dye molecules are decomposed to lower molecular weight compounds resulting in intermediates which might have contributed to the COD of wastewater. Further, sharp decrease in COD after the decolourisation has been observed. This indicates the complete oxidation of stable compounds and almost complete mineralisation of intermediates.

[2] Studies to evaluate the Photocatalytic degradation of (Sunlight, ZnO) textile wastewater with diverse composition have been carried out by Byrappa et al., (2006) [21]. The wastewater was diluted to get COD of 1278 mg/l and used for experimentation. They have reported increase in COD reduction from 20% to 86% with increase in exposure time from 1 hour to 10 hour. The confirmed the destruction of organic molecules in the effluent, along with colour removal due to photocatalytic treatment. They concluded that the photocatalytic treatment is versatile, economic and efficient method of treatment.

[3] Based on the studies carried out on UV based photocatalytic degradation (assisted by ZnO) of effluent from an industry manufacturing intermediates for dyes, [15] reported the linear relationship between COD and BOD reduction and irradiation time. Reduction in COD from 3885 mg/l to 90 mg/l in 20 hour of exposure time has recorded by them. Also they have noticed the BOD reduction from 851 to 19 mg/l in irradiation time of 20 hour.

[4] Studies to evaluate the treatment of highly polluted paper mill wastewater by solar and UV based photocatalytic degradation (in conjunction) using synthesised nano TiO_2 as a catalyst has been carried out by Montaser et al., (2011) [16].70.5% COD removal by solar photocatalytic oxidation in conjuction with TiO_2 (0.75g/l) at pH-6.5, the irradiation time being 180 minutes has been reported by them. However they have recorded very low COD removal with TiO2 alone. This is attributed to the photocatalytic reaction of the semiconductor particles. They reported the increase in COD removal from 43.2% to 72.1% with increase in pH from 3 to 10, under specified experimental conditions. They inferred that the COD removal will be faster in alkaline solution. Chang et al., (2004) [20] stated that the low pH value, the agglomeration of TiO2 results in reduction of adsorption as well as photon absorption. Further the excess concentration of H+ ions in the acidic range interact with aromatic linkage of the organic pollutants present in the paper mill wastewater and thus decreases the electron densities at the polycyclic groups. Consequently, the reactivity of hydroxyl radical by electrophilic mechanism decreases. The authors have also reported the 80.4% of the TSS from the wastewater at optimum TiO2 loading of 0.75g/l at pH of 6.5.

[5] Batch experiments (Nanoparticles not Photocatalytic degradation) performance of nano ZVI in the removal of colour and COD of textile mill wastewater revealed the increase in COD removal with decrease in pH Hegde and Tuppad et al., (2016) [19], 80, 81, 87v of COD reduction at pH 6, 5 and 3 was observed.

[6] Marcela et al., (2009) [17] carried out studies to treat pharmaceutical and cosmetic factory employing combined electrocoagulation and TiO2 photo assisted treatment and for

convenient and efficient to treat these wastewaters by photo catalysation if the COD is less that 800 mg/l. Therefore, Marcela et al., (2009) [17] Preferred to treat the said wastes by photodegradation after pre-treating this waste by electrocoagulation, so that the COD can be reduced from 1753 mg/l to lower value. The COD of electro coagulated sample was 160 mg/l. They inferred that the better removal can be achieved at acidic and neutral pH. They recorded the COD removal of 75% and 63% at pH 3 and 7 respectively (TiO_2 dosage - 0.25g/l, irradiation time-4 hour). The studies also revealed that a pH-3.0, the strong photo-oxidative environments causes nitrite oxidation to nitrate ions. Further the authors opined that, the treatment of these wastewaters at lower pH was favoured, because these wastewaters at lower pH was favoured, because these wastewaters present particles with negative charge density due to the anions adsorption in the suspended materials and the presence of oxygen, carboxylate and other negatively charged groups in these organic molecules. Further near pH-6.5 the point zero charge of the TiO_2 occurs. In nutshell the authors concluded that, to treat effectively and efficiently the wastewaters considered for study in industrial scale, the electrocoagulation and photocatalysis can be employed.

[7] In the review paper on photocatalytic degradation for environmental applications, Dhananjay et al., (2004) [18], made an attempt to take stock of role of constituents of wastewater and effect of various variables and the rate of degradation of pollutants. Based on the review of papers, they inferred that, all types of organic and inorganic substances can be degraded using photocatalysis. They opined that, streams containing inorganic pollutants such as heavy metals can also be treated using photocatalysis.

Further the reviews revealed that, photocatalytic degradation rate will be less affected by presence of sulphate, phosphate and nitrate in wastewater. They will decrease the photocatalytic degradation rate as they decrease the adsorption of the substrate. However, the presence of chlorides in wastewater considerably decrease the photocatalytic degradation rate, as chloride ions absorb UV light. Further the author writes that carbonates and bicarbonates have the largest effect on the photocatalytic degradation rates. This may be due to decrease in the adsorption their reaction with HO radical. It is also documented that; the knowledge of dissolved salts is essential in view of their inhibiting effects on photocatalytic degradation.

3. Materials and Methodology

The area of present research work is to evaluate the adsorption potential of nanoparticles in adsorbing methylene blue and methyl orange from aqueous solutions under varied experimental conditions. In depth discussions on materials and methodology adopted for the present study are documented in sections and subsections as below. The conceptual framework formulated to carry out the proposed research work is shown in Figure 3.1

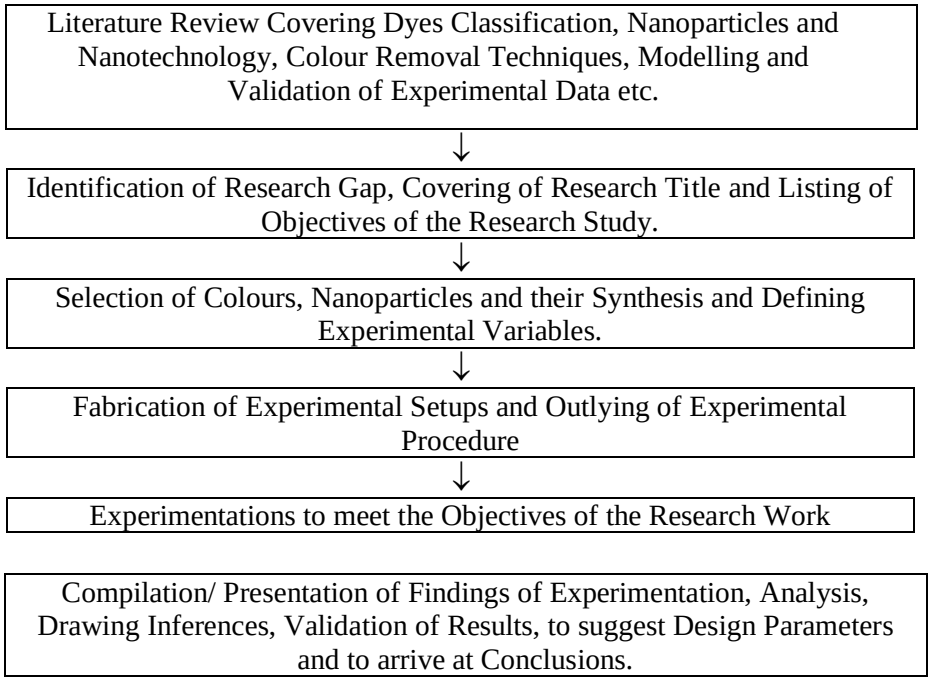

Figure 3.1: Conceptual Framework

3.1 Saturation Studies

Saturation studies were carried out for set of optimized conditions derived from the studies. Sample was passed through the column and effluent was analysed for its characteristics by collecting the sample once in five hours. Adsorbent system is considered saturated corresponding to treatment efficiency of around 5% less than optimized removal efficiency of pollutant/parameters studied. Corresponding to the saturation attainment the quantity of sample passed and thereby the pollutants passed are determined. Such a value are linked with quantity/weight of the adsorbent used for experimentation and thereby saturation adsorption capacity of adsorbent for different parameters are arrived.

3.2 Preparation of Aqueous Coloured Samples

Commercially available Analytical Grade Methyl Orange and Methylene Blue dyes were procured from colour tex. By dissolving 1g of dye in 1litre of double distilled water the stock solution of concentration 1000 mg/l is prepared. Further by diluting calculate the quantity of stock solution using double distilled water colour concentration of samples adopted for present work were prepared.

3.3 Adsorption Isotherms

Colours to assess the behavior of nanoparticles as an adsorbent in adsorbing an attempt has been made to fit the equilibrium data into Langmuir and Freundlich isotherm models. It is very

well established that adsorption isotherm describe how solutes interacts with adsorbent and such a data is critical in optimizing the use of adsorbent. Experimentations were carried out by varying the metal concentrations and keeping the agitation time constant equal to as obtained in kinetic studies. Further adsorbent dosage was kept constant for all concentrations tried by using the formulae and the concept for Langmuir and Freundlich isotherms as discussed in the section of this present research report, graphs were drawn and calculations were made.

3.4 Effect of pH

pH is one of the most important operating parameter which affects the adsorption of pollutants by the photo catalysts on their surfaces. pH affect the charge on the catalyst particles, size of the catalyst aggregates and the position of conductance and valence bands [3]. Therefore, for the photocatalytic degradation of wastewaters, the pH value of the aqueous solution plays an important role. Wastewaters from industries viz dairy, pharmaceutical, textile etc were generally found to have wide range of pH values. Further for the photocatalytic degradation, generation of Hydroxyl radicals is necessary which depends largely on pH of the solution. Thus researchers across the globe have made attempts to investigate the effect of pH in treating wastewater employing solar and ultraviolet irradiations. Further the studies have been carried out to evaluate the influence of pH (acidic and alkaline range) photocatalytic degradation of anionic, cationic and neutral dyes in wastewater, as the wastewaters produced from industries have wide range of pH values.

4. Results and Discussions

Effect of Variables on Photocatalytic Degradation of Actual Wastewater (Without dilution)

The depicts the findings of experimentations carried out to evaluate the influence of Irradiation time and catalyst dosage on Photocatalytic degradation of actual wastewater (without dilution) with respect to constituents viz pH, Chemical Oxygen Demand and Colour. The results are also presented graphically.

In this combination also, the trends of degradation was found to be same as that of Photocatalytic degradation of wastewater without dilution. However, higher removal efficiencies were observed with diluted wastewater compared to wastewater without dilution. Even these higher removal efficiencies were recorded at much lower catalyst dosage and irradiation time as compared to removal efficiencies achieved in case of wastewater without dilution. Same trends were observed for other constituents of wastewater studied.

Maximum colour removal of 99.2%, 95.8% and 92.0% by ZnO, TiO2 and MgO respectively were recorded at catalyst dosage of 0.6 g/l and irradiation time of 90 min. These values at catalyst dosage of 1.6 g/l and 150 min were found to be 78.0, 72.5 and 66.7% respectively by ZnO, TiO2 and MgO nanoparticles. Potential of ZnO was found to be higher followed by TiO2 and MgO. The COD removal was maximum at catalyst dosage of 1.6 g/l and irradiation time of 150 min, values being 88.5% (ZnO), 81.01% (TiO2) and 71.6% (MgO).

- The removal of colour from actual wastewater increased with increase in catalyst dosage from 0.5 to 1.2 g/l and then decreased with increase in dosage beyond 1.2 g/l (upto 3.0 g/l tried).
- Similarly, same trend has been observed with irradiation time. With increase in irradiation time from 50 min to 150 min, increase in removal efficiency has been observed. Colour removal efficiency further reduced with increase in irradiation time beyond 150 min (upto 300 min).
- Maximum colour removals were 95.3, 91.7 and 88.5% by ZnO, TiO_2 and MgO respectively at 150 min and catalyst dosage of 1.2 g/l. Again, degradation potential was found to follow the sequence of ZnO>TiO2>MgO.

Accordingly, the minimum removal values recorded at catalyst dosage of 0.6 g/l and irradiation time of 90 min were 45.8%, 42.7% and 29%. Again, higher removal efficiencies of other constituents of wastewater were recorded at catalytic dosage of 1.6 g/l and irradiation time of 150 min. In nut shell it can be said that the removal all constituents of wastewater tried by ZnO is higher compared to TiO2 and MgO.

Comparison of Photocatalytic degradation of actual wastewater with and without dilution revealed that, the better removal at lower values of catalyst dosage and irradiation time can be achieved with dilution which could be techno economically feasible.
Further, it is suggested to treat wastewater employing catalyst dosage and irradiation time at which maximum colour removal was observed. So that after achieving the highest colour removal by Photocatalytic degradation, the wastewater can be treated for its other constituents by employing any other physico-chemical treatment technologies suggested elsewhere in literature by other researchers. It is opined so because the colour removal by Photocatalytic degradation is more feasible technology followed by treatment of wastewater for its remaining constituents employing other feasible treatment options.

Finally, it is suggested to treat the actual wastewater with dilution of 1:3 by Photocatalytic degradation adopting catalyst dosage of 0.6 g/l and irradiation time of 90 min employing ZnO preferably. Further, treatment of wastewater to achieve disposal standards specified for constituents of wastewater, as found feasible could be considered. However, author also opine to work out the techno economical feasibility of dilution of wastewater, selection of particular nanoparticles etc, before recommending to treat the wastewater.
Experiments were terminated after 300 min of irradiation time, as the removal of COD at 200 and 300 min were not significantly varying within statistical limitations. Further, the removal efficiency was found to decrease with increase in catalyst dosage from 2.5 to 3.0 g/l. Thus, it is inferred that the maximum removal of COD could be achieved with catalyst dosage of 2.5 g/l and irradiation time of 300 min. Maximum removal of COD recorded at these optimum operating parameters were found to be 75.6%, 70.1% and 67.3% by ZnO, TiO2 and MgO nanoparticles respectively.

Further the reviews revealed that, photocatalytic degradation rate will be less affected by presence of sulphate, phosphate and nitrate in wastewater. They will decrease the photocatalytic degradation rate as they decrease the adsorption of the substrate. However, the presence of chlorides in wastewater considerably decrease the photocatalytic degradation rate, as chloride ions absorb UV light. Further the author writes that carbonates and bicarbonates have the largest effect on the photocatalytic degradation rates. This may be due to decrease in the adsorption their reaction with HO radical. It is also documented that; the knowledge of dissolved salts is essential in view of their inhibiting effects on photocatalytic degradation.

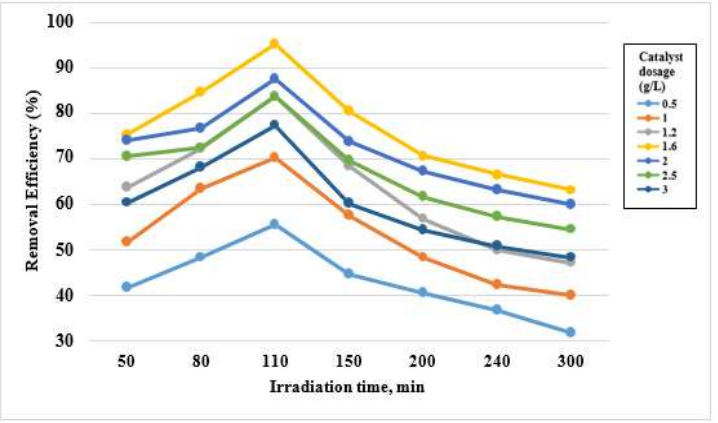

Figure 1: Effect of Irradiation Time on Colour Removal from Actual Wastewater by ZnO (Without dilution)

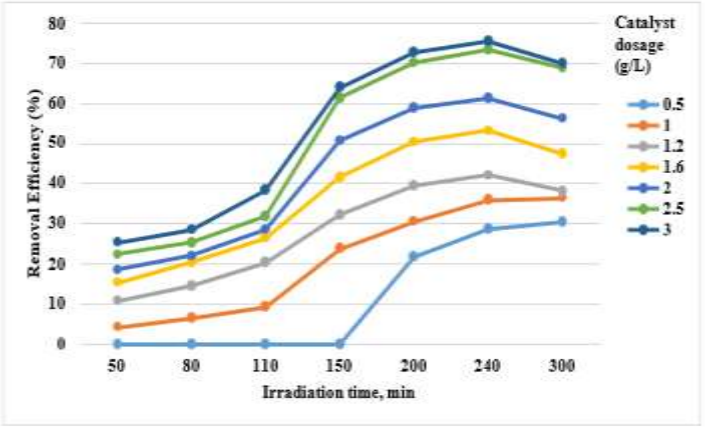

Figure 2: Effect of Irradiation Time on COD Removal from Actual Wastewater by ZnO (Without dilution)

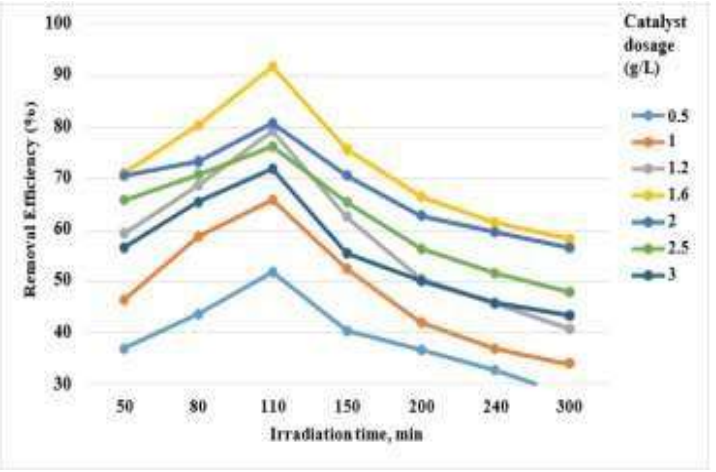

Figure 3: Effect of Irradiation Time on Colour Removal from Actual Wastewater by TiO_2 (Without dilution)

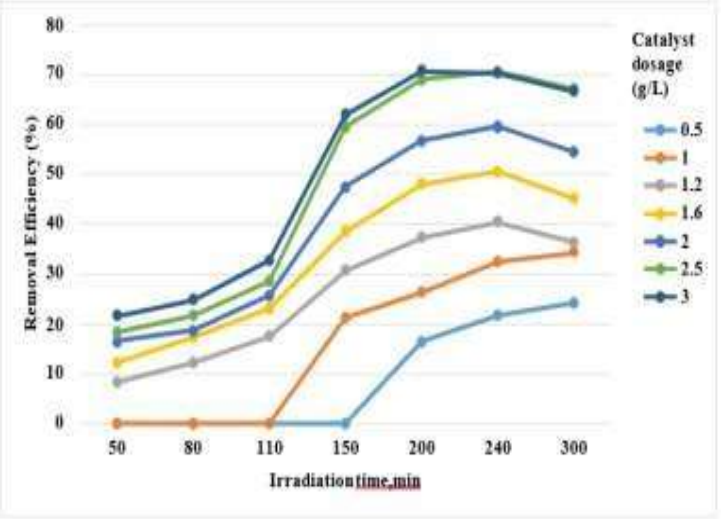

Figure 4: Effect of Irradiation Time on COD Removal from Actual Wastewater by TiO_2 (Without dilution)

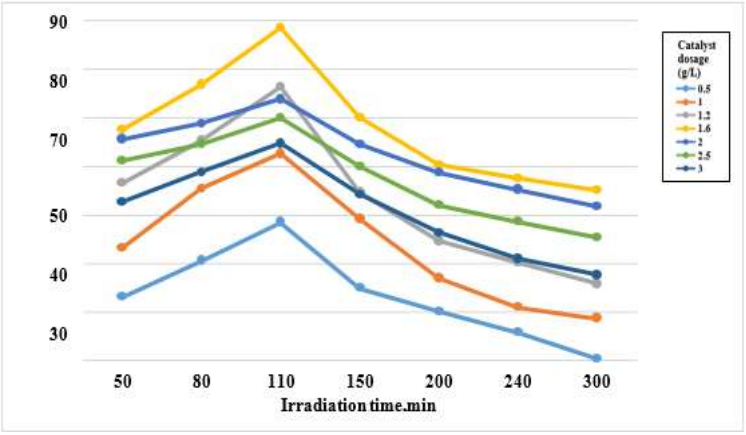

Figure 5: Effect of Irradiation Time on Colour Removal from Actual Wastewater by MgO (Without dilution)

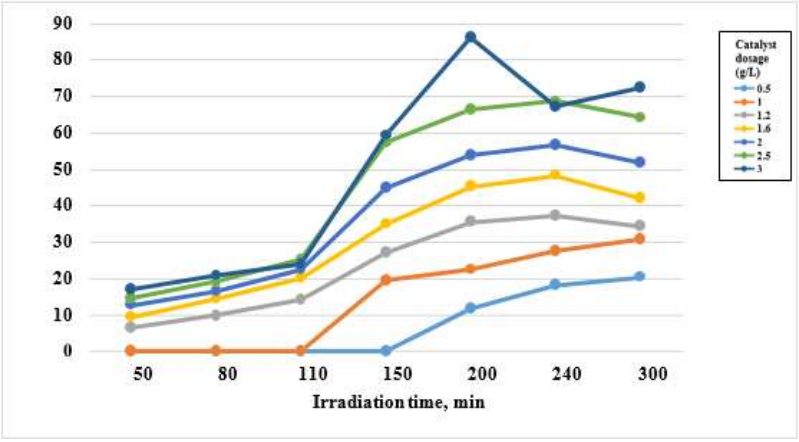

Figure 6: Effect of Irradiation Time on COD Removal from Actual Wastewater by MgO (Without dilution)

Table 1: Studies on Treatment of Actual Wastewater COD, Colour Intensity (Co) (Lower dosage and Irradiation time, pH

Catalyst dosage g/l	Parameters	Removal Efficiency (%) at Stated Irradiation time (min) by Stated Catalyst																			
		50			80			110			150			200			240			300		
		ZnO	TiO_2	MgO	ZnO	TiO_2	MgO	ZnO	TiO_2	MgO	ZnO	TiO_2	MgO	ZnO	TiO_2	MgO	ZnO	TiO_2	MgO	ZnO	TiO_2	MgO
0.5	pH	7.3	7.2	7.2	7.1	7.0	7.1	7.0	7.0	7.0	7.0	7.1	7.2	7.0	7.1	7.2	7.3	7.0	7.1	7.2	7.0	7.0
	Colour	41.6	36.8	33.1	51.6	46.3	43.2	63.7	59.2	56.5	75.3	71.0	67.5	74.0	70.4	65.5	70.5	65.7	61.2	60.4	56.5	52.6
	COD	NM	NM	NM	4.2	NM	NM	10.8	8.3	6.5	15.3	12.2	9.6	18.5	16.4	12.8	22.3	18.2	14.6	25.4	21.5	17.2
1.0	pH	7.3	7.1	7.2	7.2	7.1	7.2	7.2	7.0	7.0	7.1	7.0	7.1	7.2	7.0	7.1	7.1	7.1	7.0	7.2	7.1	7.0
	Colour	48.3	43.5	40.6	63.4	58.6	55.4	72.3	68.6	65.3	84.6	80.3	76.8	76.7	73.2	68.8	72.4	70.7	64.6	68.2	65.4	58.8
	COD	NM	NM	NM	6.5	NM	NM	14.6	12.2	10.0	20.5	17.3	14.7	22.0	18.5	16.7	25.2	21.5	19.2	28.6	24.7	21.0
1.2	pH	7.2	7.0	7.1	7.4	7.2	7.3	7.2	7.1	7.0	7.2	7.2	7.2	7.1	7.0	7.1	7.2	7.2	7.0	7.1	7.0	7.1
	Colour	55.5	51.6	48.5	70.2	65.7	62.5	83.81	79.2	76.4	95.3	91.7	88.5	87.5	80.6	73.8	83.6	76.2	70.0	77.4	71.8	64.7
	COD	NM	NM	NM	9.3	NM	NM	20.3	17.4	14.3	26.4	23.0	20.3	28.5	25.5	22.6	31.8	28.4	25.2	38.5	32.7	24.1
1.6	pH	7.1	7.2	7.1	7.1	7.3	7.3	7.1	7.1	7.1	7.2	7.3	7.1	7.3	7.3	7.1	7.1	7.1	7.1	7.1	7.0	7.0
	Colour	44.6	40.2	34.9	57.5	52.3	49.1	68.5	62.4	54.6	80.4	75.6	70.0	73.8	70.4	64.5	69.6	65.3	60.0	60.2	55.3	54.2
	COD	NM	NM	NM	23.8	21.2	19.5	32.2	30.6	27.3	41.6	38.4	35.1	50.8	47.3	45.0	61.4	59.3	57.3	64.0	61.8	59.4
2.0	pH	7.1	7.3	7.2	7.1	7.1	7.1	7.3	7.2	7.1	7.2	7.1	7.3	7.1	7.2	7.3	7.2	7.1	7.1	7.2	7.1	7.1
	Colour	40.5	36.5	30.2	48.3	41.9	37.0	56.8	50.3	44.6	70.6	66.4	60.3	67.2	62.6	58.7	61.6	56.3	52.0	54.4	50.0	46.3
	COD	21.8	16.3	11.8	30.6	26.2	22.5	39.4	37.2	35.6	50.4	47.9	45.3	59.0	56.5	54.0	70.2	68.8	66.3	72.8	70.5	86.2
2.5	pH	7.3	7.1	7.0	7.1	7.2	7.2	7.2	7.2	7.1	7.2	7.1	7.3	7.1	7.2	7.2	7.1	7.1	7.1	7.2	7.1	7.1
	Colour	36.7	32.5	25.8	42.3	36.8	31.0	50.0	45.5	40.1	66.5	61.3	57.5	63.2	59.5	55.2	57.3	51.5	48.6	50.8	45.7	40.9
	COD	28.7	21.5	18.3	36.0	32.4	27.6	42.1	40.3	37.5	53.2	50.5	48.4	61.4	59.3	56.8	73.5	70.4	68.7	75.6	70.1	67.3
3.0	pH	7.1	7.0	7.0	7.2	7.2	7.2	7.1	7.2	7.2	7.0	7.1	7.1	7.1	7.0	7.0	7.0	7.2	7.0	7.0	7.1	7.2
	Colour	31.8	27.6	20.4	40.0	33.8	28.7	47.1	40.6	35.8	63.0	58.2	55.0	60.0	56.5	51.8	54.5	47.8	45.4	48.3	43.2	37.6
	COD	30.5	24.0	20.5	36.5	34.2	30.8	38.2	36.3	34.5	47.4	45.1	42.3	56.3	54.2	51.9	68.9	66.9	64.2	70.1	66.5	72.4

Table 2: Studies on Treatment of Actual Wastewater COD- 8100 mg/l pH- 7.4

Catalyst dosage g/l	Parameters	Removal Efficiency (%) at Stated Irradiation time (min) by Stated Catalyst						
		50	80	110	150	200	240	300
		ZnO	ZnO	ZnO	ZnO	ZnO	ZnO	ZnO
0.5	pH	7.3	7.1	7.0	7.0	7.0	7.3	7.2
	Colour	41.6	51.6	63.7	75.3	74.0	70.5	60.4
	COD	NM	4.2	10.8	15.3	18.5	22.3	25.4
1.0	pH	7.3	7.2	7.2	7.1	7.2	7.1	7.2
	Colour	48.3	63.4	72.3	84.6	76.7	72.4	68.2
	COD	NM	6.5	14.6	20.5	22.0	25.2	28.6
1.2	pH	7.2	7.4	7.2	7.2	7.1	7.2	7.1
	Colour	55.5	70.2	83.81	95.3	87.5	83.6	77.4
	COD	NM	9.3	20.3	26.4	28.5	31.8	38.5
1.6	pH	7.1	7.1	7.1	7.2	7.3	7.1	7.1
	Colour	44.6	57.5	68.5	80.4	73.8	69.6	60.2
	COD	NM	23.8	32.2	41.6	50.8	61.4	64.0
2.0	pH	7.1	7.1	7.3	7.2	7.1	7.2	7.2
	Colour	40.5	48.3	56.8	70.6	67.2	61.6	54.4
	COD	21.8	30.6	39.4	50.4	59.0	70.2	72.8
2.5	pH	7.3	7.1	7.2	7.2	7.1	7.1	7.2
	Colour	36.7	42.3	50.0	66.5	63.2	57.3	50.8
	COD	28.7	36.0	42.1	53.2	61.4	73.5	75.6
3.0	pH	7.1	7.2	7.1	7.0	7.1	7.0	7.0
	Colour	31.8	40.0	47.1	63.0	60.0	54.5	48.3
	COD	30.5	36.5	38.2	47.4	56.3	68.9	70.1

Table 3: Studies on Treatment of Actual Wastewater Cd-1.2 g/l, t-150 min (Colour Optimised values) (for allparameters)

Wastewater Constituent	**Actual Value**	**Removal Efficiency (%) by Stated Catalyst**		
		ZnO	**TiO_2**	**MgO**
pH	7.4	7.1	7.1	7.1
Colour	-	96.3	93.6	90.2
COD, mg/l	8100	27.0	24.4	20.2
TS, mg/l	3783	31.6	30.5	29.5
TDS, mg/l	740	18.3	24.8	30.6
NH_3-N, mg/l	210	36.8	32.5	28.9
SO_4, mg/l	94.3	47.9	46.4	41.5
Cl, mg/l	2632	28.4	26.3	24.2

Table 4: Studies on Treatment of Actual Wastewater Cd-2.5 g/l, t-300 min (COD Optimised values) (for allparameters)

Wastewater Constituent	**Actual Value**	**Removal Efficiency (%) by Stated Catalyst**		
		ZnO	**TiO_2**	**MgO**
pH	7.4	7.2	7.0	7.1
Colour	-	51.6	45.2	44.5
COD, mg/l	8100	76.5	72.4	68.0
TS, mg/l	3783	52.8	51.0	48.0
TDS, mg/l	740	39.4	35.7	32.3
NH_3-N, mg/l	210	58.3	54.6	50.2
SO_4, mg/l	94.3	69.5	67.5	62.8
Cl, mg/l	2632	50.0	47.0	45.5

Table 5: Studies on Treatment of Actual Wastewater Cd-2.5 g/l, t-240 m (for all parameters)

Wastewater Constituent	**Value**	**Removal Efficiency (%) by Stated Catalyst**		
		ZnO	**TiO_2**	**MgO**
pH	7.4	7.1	7.1	7.1
Colour	-	98.8	93.6	90.2
COD, mg/l	8100	73.5	70.4	68.7
TS, mg/l	3783	31.6	30.5	29.5
TDS, mg/l	740	18.3	24.8	30.6
NH_3-N, mg/l	210	36.8	32.5	28.9
SO_4, mg/l	94.3	47.9	46.4	41.5
Cl, mg/l	2632	28.4	26.3	24.2

Table 6: Studies on Treatment of Actual Wastewater but Diluted (1:3) Wastewater (Lower dosage and Irradiation time)

Catalyst dosage g/l	**Parameters**	**Removal Efficiency (%) at Stated Irradiation time (min) by Stated Catalyst**											
		20			**40**			**60**			**90**		
		ZnO	**TiO_2**	**MgO**	**ZnO**	**TiO_2**	**MgO**	**ZnO**	**TiO_2**	**MgO**	**ZnO**	**TiO_2**	**MgO**
0.2	pH	7.2	7.1	7.1	7.2	7.1	7.1	7.2	7.2	7.1	7.1	7.1	7.1
	Colour	61.3	55.8	52.4	68.5	62.6	59.4	75.7	70.2	67.5	82.6	76.7	73.2
	COD	9.5	NM	NM	16.3	12.2	NM	24.6	20.3	17.2	32.5	27.4	24.5
0.4	pH	7.0	7.1	7.1	7.1	7.0	7.0	7.2	7.1	7.0	7.1	7.2	7.2
	Colour	70.3	65.8	62.4	77.2	71.6	68.5	82.6	76.4	73.0	90.3	85.8	83.4
	COD	17.8	12.5	9.8	23.6	19.2	16.4	31.3	26.8	23.5	39.8	36.2	33.0
0.6	pH	7.0	7.2	7.1	7.1	7.0	7.1	7.1	7.0	7.1	7.0	7.1	7.1
	Colour	78.6	74.5	71.8	84.5	80.5	76.5	91.6	86.0	82.7	98.9	94.2	91.8
	COD	23.5	19.2	16.4	30.8	26.5	22.8	39.0	35.2	32.2	46.5	41.2	37.5
0.9	pH	7.1	7.1	7.0	7.0	7.2	7.1	7.0	7.1	7.1	7.2	7.0	7.1
	Colour	76.5	71.8	67.4	82.7	77.4	73.5	89.2	83.1	79.5	96.3	91.6	88.4
	COD	29.2	26.4	23.0	37.4	33.0	31.1	46.5	42.2	39.3	57.3	53.5	50.2

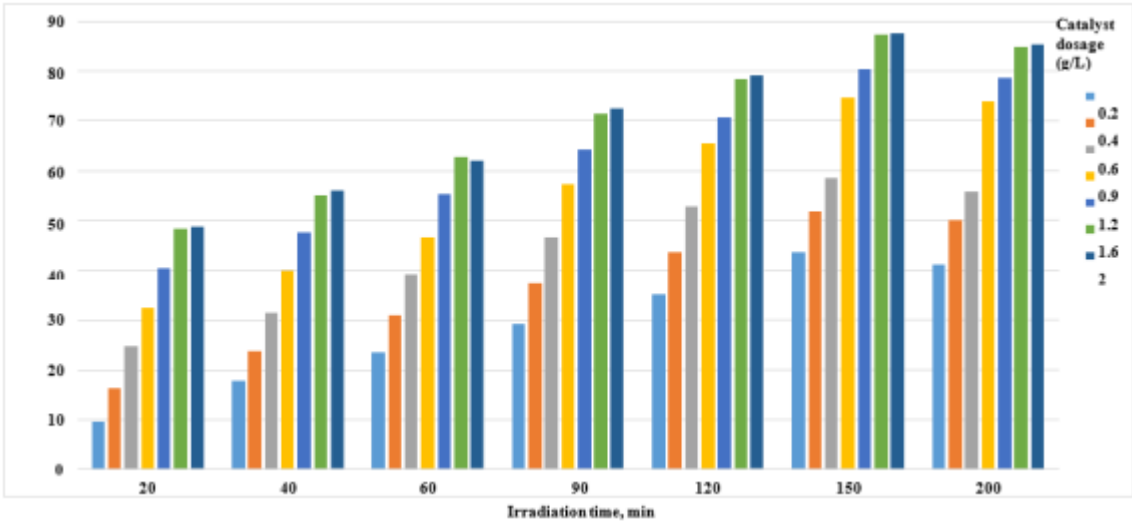

Figure 7: Effect of Irradiation Time on COD Removal from Actual Wastewater by ZnO (With dilution)

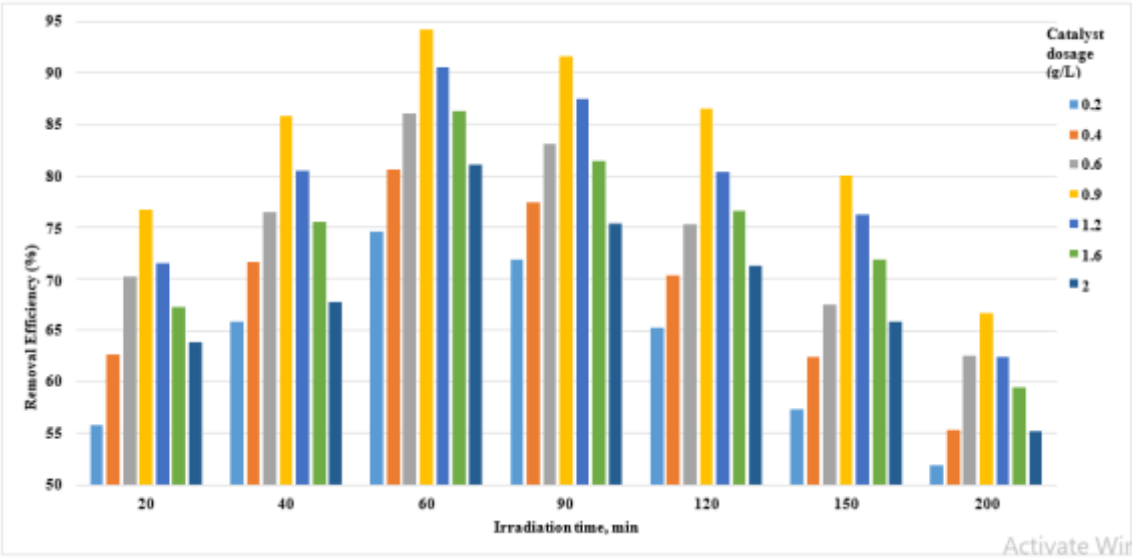

Figure 8: Effect of Irradiation Time on Colour Removal from Actual Wastewater by TiO_2 with dilution

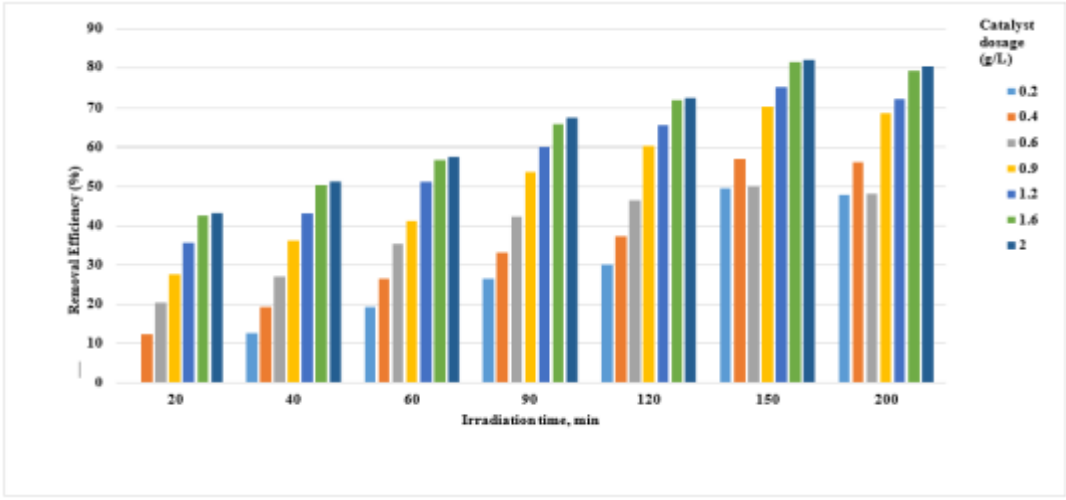

Figure 9: Effect of Irradiation Time on COD Removal from Actual Wastewater by TiO_2 (With dilution)

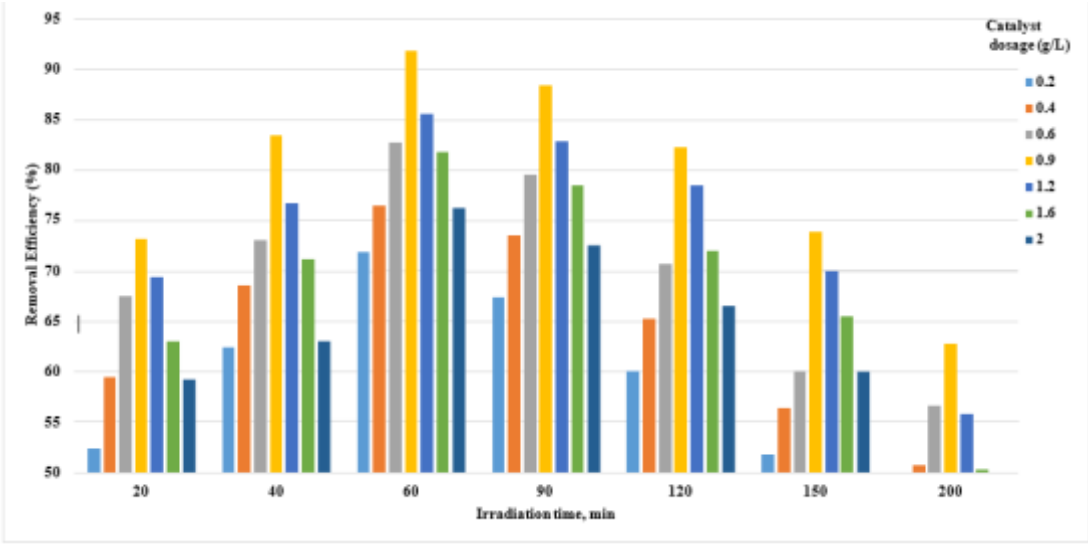

Figure 10: Effect of Irradiation Time on Colour Removal from Actual Wastewater by MgO (With dilution)

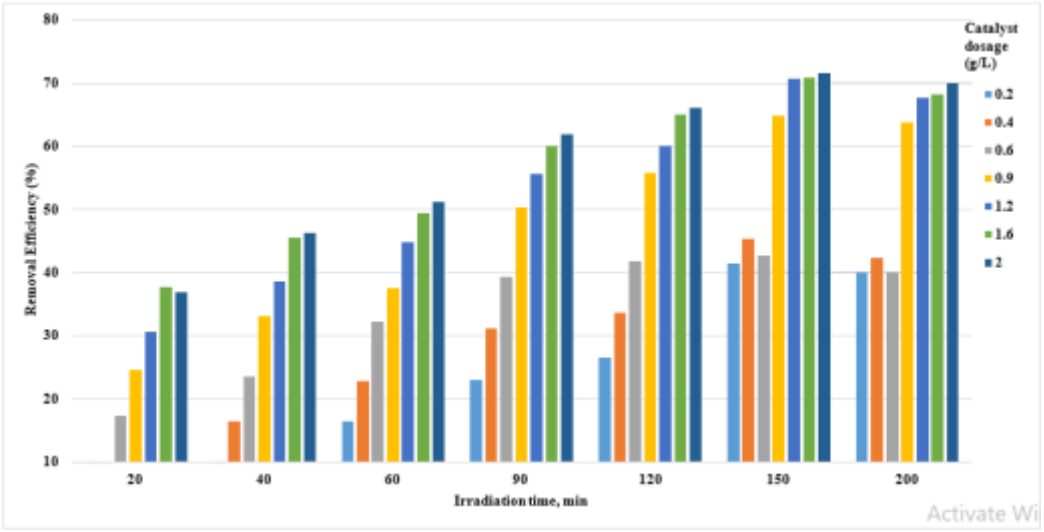

Figure 10: Effect of Irradiation Time on COD Removal from Actual Wastewater by MgO (With dilution)

5. Conclusion

The experimentations on photocatalytic studies with combination of nanoparticles, lead to a conclusion that, to achieved higher Photocatalytic degradation of colours, it is better to use nanoparticles separately instead of in conjunction. The studies on actual wastewater with (1:3) and without dilution, lead to an conclusion that, with dilution the actual pharmaceutical wastewater can be more efficiently photocatalytically treated for its constituents viz, Colour, COD, pH, TS, TDS, NH3-N, SO4 and Cl using nanoparticles. The sequence of preference would be ZnO>TiO2>MgO. Cost economics analysis of various treatment techniques studied in the present research work could not be carried out, as such a exercise demands huge data to be established from indepth laboratory and field investigations, wherein the present research work reveals the data pertaining only to optimized operating conditions.

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