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UV-TiO_2 process for Landfill Leachate Treatment: Optimization by Response Surface Methodology

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Abstract - Landfill leachate contains variety of organic compounds, some are recalcitrant in nature. Those compounds are difficult to convert into inorganic compounds by conventional biological methods. For which, advanced oxidation processes (AOPs) plays very crucial role for their treatment. Among AOPs, photocatalytic degradation process was employed in the present study. In this method, ultraviolet (UV) irradiation with photocatalyst titanium dioxide (TiO_2) is producing highly reactive hydroxyl radicals (HO°). The generated (HO°) are highly reactive and non-selective in nature, which converts complex organic compounds into simple harmless inorganic compounds. In the present study, experiments were designed by Central Composite Design (CCD) method in Response Surface Methodology (RSM) approach by using Design Expert-10 software and performed the experiments accordingly. In the (CCD) method, three factors were adopted, i.e. reaction time, TiO_2 dosage and dilution factor (D.F) with one response, percentage chemical oxygen demand (COD) removal. Using the multivariate effect of the factors, the optimization conditions were achieved for UV-TiO_2 process for landfill leachate treatment. At optimized conditions more than 60% COD removal were achieved and the experimental results were in agreement with the predicted value with R^2 = 0.91. It is noticeable from the results, UV assisted TiO_2 photo catalysis could be useful for high strength wastewater treatment. From the results, it is analyzed that beyond a certain limit of the parameters, the organic contaminants removal decreased. The UV-TiO_2 photo catalysis system suggested may be an economical method for landfill leachate treatment. This process also helps in enhancing the biodegradability of landfill leachate.

Keywords* — *Central Composite Design, Chemical oxygen demand, Landfill leachate, Photocatalytic degradation, Response surface methodology, Titanium dioxide

I. INTRODUCTION

In India the generation of municipal solid waste is about 62 million tons per year, having an annual average growth rate of 4% [1].The rapid urbanization and population explosion are the main culprits behind the severity of Municipal solid waste (MSW) problem. The anticipated population of India in 2051 would be 1823 million having a MSW generation of about 300 million tons per annum [2].Hence, proper disposal of the MSW is the need of hour. The different disposal methods that are primarily adopted for MSW involve, composting, incineration, recycling and landfilling.

Landfilling is one of the most widely applied methods of municipal solid waste disposal all over the world. However, the generation of highly contaminated leachate is an unavoidable and undesirable effect of the existing practice of waste management [3]. This highly toxic leachate is formed when the rain falls over the landfill and percolates down, combining with the decomposed waste under different biological, physical and chemical conditions [4]. The refractory nature of the contaminants, high COD, presence of various recalcitrant compounds, heavy metals and other toxicants make its remediation a difficult task [5]. Due to the diverse nature of the leachate the conventional biological treatments face various drawbacks. Hence, a generalized treatment does not exist. However numerous kinds of physical and chemical treatment processes have been developed in the last decades such as Chemical Oxidation, Coagulation–Flocculation, Electrochemical treatment etc. which are adopted in combination with the biological treatments in order to optimize the total treatment efficiency.

Despite its drawbacks, biological treatment is still the best treatment method for young and intermediate leachates because of their high biodegradability (BOD_5/COD >0.4) and lower molecular weight fraction. They show good elimination efficiency, are relatively cost effective and uncomplicated in nature. However, these treatments prove to be ineffective when it comes to mature leachate because of their refractory nature i.e. (BOD_5/COD<0.2), greater

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molecular weight fraction, high ammonia, humic substances and increased levels of heavy metals concentration [6]. Keeping these demerits in mind, researchers came up with processes that are especially designed for removal of recalcitrant organic pollutants present in the mature leachate i.e. Advanced oxidation processes(AOPs).They consists of a number of chemical treatment procedures that use oxidation through reactions with highly reactive radicals (mainly hydroxyl) for the removal of vast range of organic contaminants. These are used as a pre and post treatment method for the leachates. These hydroxyl radicals having high oxidation potential are generated by oxidants like (O_3 and H_2O_2) in the presence of catalysts (like Fe^{2+}, ZnO, CuO_2, and TiO_2) under radiations like (UV light)[7].

As per past literature [8] [9], AOPs are mainly oxidizing organic compounds by generated in situ strong oxidants. There are various advanced treatment technologies, particularly UV based treatment are well recognized and applied to the field as well [10].The use of catalysts in photocatalytic degradation process for oxidation has been considered over the last decades [11]. The application of TiO_2 with their photocatalytic properties utilized well, having certain reaction based on the solubility of the catalyst: [12]:

$$TiO_2 + h\nu \rightarrow (e^- + h^+)$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH$$

For photocatalysis there are various process are utilized in reaction mechnisms, but other AOPs are based only on ●OH reactions [10].The limitation of this process for application at full-scale is mainly by separation of colloidal catalyst from effluent [13].

Heterogeneous photocatalytic oxidation is one of the most widely researched and talked about technique under AOPs due to its relatively high efficiency and eco-friendly approach towards solving environmental issues. It deals with using a solid metal oxide semiconductor catalyst (generally TiO_2), in the presence of light (solar or UV) of an appropriate wavelength for the oxidation of organic contaminants into CO_2 and water (also called, mineralization of pollutants). The reason why TiO_2 has been so extensively used as a photo catalyst is all thanks to its stable nature, cost effectiveness and distinctively high photocatalytic efficiency [14].

Organic compounds are oxidized by the positive holes while the electrons reduces the molecular oxygen into highly reactive radicals like (•OH) which further convert organic contaminants into harmless inorganic ions [15]. Among AOPs, heterogeneous photocatalysis seems as a most effective and suitable option, which allows for mineralization of most organic molecules under UV radiation with the catalyst (e.g., titanium dioxide) and air.

$$R + HO^\circ \rightarrow R\,(HO^\circ) \rightarrow R_1 + R_2 \rightarrow \text{Inorganic substances (i.e. } CO_2 + H_2O) \quad (1)$$

The objective of the present study is to evaluate the effectiveness of UV–TiO_2 based advanced oxidation processes for the treatment of landfill leachate. A statistical approach is applied in the present study for designing the experiments and for analyzing the multivariate effect of the adopted factors (such as TiO_2 dosage, reaction time and dilution factor) for the response, COD removal efficiency. Optimization of the factors adopted were carried out, and the results obtained were in agreement with the experimental values.

II. MATERIALS AND METHODS

Landfill leachate was collected from Ghazipur landfill site located in the capital city of India, Delhi. The samples were directly sent to the lab, categorized and cooled in refrigerator to stop any biological activity. Three samples of leachate were taken and the characteristics like pH, total nitrogen (TN), COD, TDS, and BOD_5 were measured. Table 1 shows the initial characteristics of the leachate. The suitable probes (HACH) were used for pH and total dissolved solids (TDS) measurement. The measurements of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were done as per the Standard Method. DR5000 (HACH, USA) UV/V spectrophotometer was used for measurements of total nitrogen (TN). The experiments were performed at ambient temperature and pressure. The percentage removal of COD was calculated as follows:

$$\textbf{\% COD removal} = (C0 - C/C0) \times 100$$

Table: 1. Initial characteristics of raw leachate

S.No.	Parameters	Values in (mg/L) except pH
1.	pH	8.30
2.	TN	1050
3.	COD	8900
4.	TDS	18320
5.	BOD_5	2200

The apparatus used to carry out the experimental work namely UV photo reactor. All the analysis were done as per standard methods. Experimental chart was prepared for 20 runs of experiments by the software used (Design Expert-10), the central composite design (CCD) methodology were used in response surface methodology (RSM) approach as per the adopted factors with their suitable range shown in table 2.

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Table: 2. Range of the adopted factors

Name	Unit	- alpha	+ alpha
R. Time [A]	minutes (min.)	5	60
TiO_2 dose [B]	(gm/L)	0	5
D.F [C]		1	10

From the adopted factors experimental runs were obtained and performed accordingly. For each run of experiment diluted sample were collected in the tube, obtained from UV photo reactor and the required dosage of

catalyst (TiO_2) added and placed in the reactor for assigned UV exposure time. After completion of the reaction, sample were taken out from the photo reactor and COD of each were checked. Similarly, for each run of the experiment COD removal were checked as our target response.

After performing all the experiments, the obtained response data were filled in the software tool for further analysis of the process and suggested model with significant value were obtained. The process further modified for best outcome and optimization conditions were achieved by targeting maximum COD removal. The obtained process variables with their predicted values were cross checked by performing experiments and suitable agreement were achieved.

III. RESULTS AND DISCUSSION

When a catalyst is exposed to UV radiation, after several reactions in the solution hydroxyl radicals (*OH) generated and attack the organic compound to form other intermediate species and finally mineralize end product. The rate of oxidation process and treatment efficiency depend on various operational parameters such as TiO_2 concentration and irradiation time. In the present study, the effect of operational parameters on leachate treatment was observed. After required reaction time COD removal of the sample were analyzed. As shown in Fig 1, the COD removal efficiency increases with concentration of photocatalyst and exposure time up to certain level. The dissimilarities in reported exposure time are mainly due to the wide variation of the characteristics of the leachate. The variety of the refractory compounds could be degraded into simpler compounds by UV/TiO_2 photocatalytic process. Thus, UV-TiO_2 process not only removes a major part of COD of the leachate, but also increases the biodegradability of the solution [16]. The ANOVA results obtained from the software presented in the table 3.

Table: 3. Analysis of variance (ANOVA)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	970.43	6	161.74	22.16	< 0.0001	Signifi-cant
A-R.Time	*3.00*	*1*	*3.00*	*0.41*	*0.5326*	
B-TiO_2 dose	*54.10*	*1*	*54.10*	*7.41*	*0.0174*	
C-D.F	*597.42*	*1*	*597.42*	*81.86*	*< 0.0001*	
AB	*160.56*	*1*	*160.56*	*22.00*	*0.0004*	
BC	*132.52*	*1*	*132.52*	*18.16*	*0.0009*	
B^2	*22.84*	*1*	*22.84*	*3.13*	*0.1004*	
Residual	94.87	13	7.30			
Lack of Fit	*82.32*	*8*	*10.29*	*4.10*	*0.0685*	***not signifi-cant***
Pure Error	*12.56*	*5*	*2.51*			
Std. Dev.	2.70	**R-Squared**	**0.9109**			
Mean	52.52	Adj R-Squared	0.8698			
C.V. %	5.14	Pred R-Squared	0.7241			
		Adeq Precision	19.563			

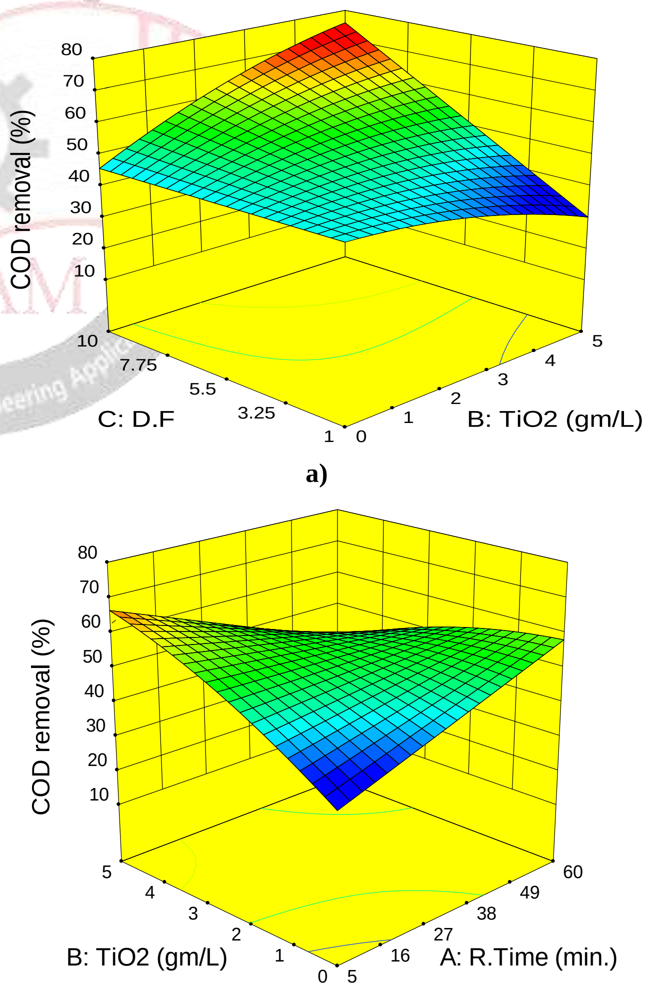

Fig.1: 3D surface plots of process variables with response COD removal.

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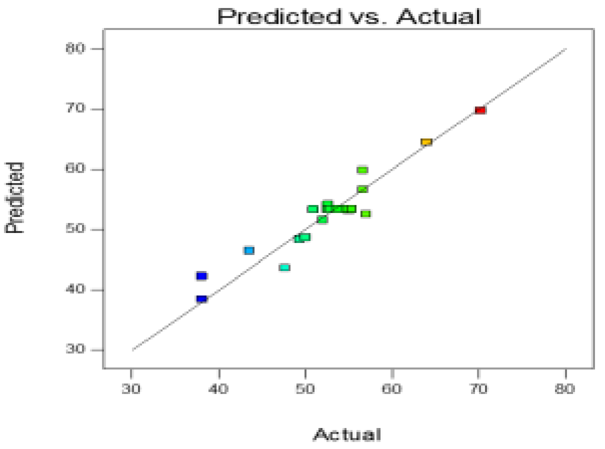

Fig.2: Predicted vs actual plot.

The relation between the process variables and the response was obtained by graphical analysis wherein the analysis of variance (ANOVA) was used. The coefficient of determination (R^2) expressed the quality of the fit polynomial model.

The coefficient of determination (R^2) evaluated using p-values (probability) with confidence level of 95% were 0.91 (greater than the cut off value 0.8).Hence a perfect adjustment of the quadratic model to the experimental data is ensured and satisfactory agreement between the observed and calculated results is illustrated. The adequate precision value in our study was 19.56 (higher than 4) hence desirable and therefore the predicted models can be to navigate the space defined by the CCD. [17]

Empirical relationships among the variables and COD removal were presented by equation shown below:

Final Equation in Terms of Coded Factors:

COD removal= +53.38 -0.47*A+1.99*B +6.61*C-4.48* AB +4.07 * BC -1.25* B^2.

The initial characteristics of leachate and amount of photo-catalyst are the factors that affect the efficiency of photo degradation [18]. In figure 2 the predicted versus actual data very near to straight line clears that model is significant the model equation is obtained one can use it for more details to know about the process. From the fig 1 it is

clear that as reaction time increases COD removal efficiency increases but after certain value again efficiency decreases similarly for TiO_2 there is some mixed relationship occurs for best COD removal here [17].

It was found that excess of the catalyst has opposite effect as it increase the turbidity in the wastewater and hinders the absorption of the sunlight thereby reducing the active site on the surface of the photo catalyst [19].

IV. CONCLUSIONS

In the present study, the removal of pollutants from landfill leachate was obtained. At the optimized condition, more than 60% chemical oxygen demand (COD) removal efficiency was achieved. From the results, it was noticeable that UV based AOPs are the good option for enhanced COD removal. From the adopted factors it was clear that high dosages of chemicals were not always favorable. The multivariate analysis is proved to be better than single variate analysis. The suggested model by RSM were in agreement with the experimental values. The adopted factors such as reaction time and catalyst dosage are major influencing parameters in photocatalytic degradation process. The process variables should be maintained properly, otherwise, COD removal will decrease. It can be concluded that UV-TiO_2 based AOPs are suitable option for landfill leachate treatment and if its characteristics are complex then integrated processes would be more suitable for effective treatment.

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