Photocatalytic Treatment of Landfill Leachate Using Pure Tio_2 Nanoparticles

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Abstract: Sanitary landfilling is one the most common and oldest method for disposal of the solid waste worldwide. Landfill site has many advantages. In spite of the major disadvantage is production of the by-products like bio-gas and leachate. Leachate is main and major polluted which have heavy metal, chemical composition. It is creating adverted impact on the environment. Many distinctive methods are used to treat the landfill leachate. Major treatment processing has divided into two categories like biological and physical/ chemical treatments. But all these strategies are less compelling for treated the leachate. Advanced Oxidation process is new way to treated landfill leachate. In this process, photocatalyst is mainly used with TiO_2 nanoparticle as catalyst and UV light source as irradiation source. These nanoparticles are synthesis by sol-gel method. These nanoparticles are Characterization by XRD and DLS method. Finally, study and get resulted of photocatalyst degradation of leachate by synthesis TiO_2 nanoparticle. Which give best results at acidic media at 6 pH with maximum 3 hours contacted time.

key words – Landfill leachate, Photocatalysis Process, synthesis, TiO_2 nanoparticles, XRD, COD

I. INTRODUCTION

In all over the world, solid waste is one of the critical to manage. Solid waste is the unwanted and used materials generated from many ways like industrial, residential and commercial activities. Solid waste management is reduced negative impact on environment and human health and supports economic development. Investigate appears that burying of waste within the ground harmed the groundwater. Solid waste required proper management otherwise it can cause air, land, and water pollution, spread of different types of vector-borne diseases, and aesthetic deterioration of the environment. It shows that municipal solid waste management (MSWM) is most imported of any government in the all over the world. In MSWM most imported part is the last phase which is the disposal of waste. Disposal of solid waste is a most differed phase in base on economically and technology. So, 90% of solid waste in the open dump. Just 8-9% of solid waste is dumped in a proper way of disposal in Indian (R. Joshi,2016).

The sanitary landfill is best, effective and economical method of disposing of the solid waste material. It is widely accepted and used all over the world. The concept of the sanitary landfill was introduced by the United Kingdom in 1912. Most of the developed and developing countries nowadays use design criteria that take into account topography, site geology, and hydrogeology, along with engineering, economic, and legal requirements for the construction and operation of landfills. Sanitary landfills have primary By-products are landfill gases and leachate. Leachate is a contaminated liquid emanating from bottom of the landfill site. Leachate contains organic and inorganic compounds with suspended particles. Amount of leachate and contaminations of polluted depended on weather and type of waste disposed at landfill site. Measuring of leachate contamination, their parameters are chemical oxygen demand (COD), Biological oxygen demand (BOD) and ammonium for discharging the leachates into natural waters. But, the main parameter is biodegradability (BOD_5/COD) of leachate, which varies with age of landfill site. This ratio indicates biodegradable materials in leachate (C. Bernard.1997). Environmentally, leachate generation is a major concern for the society. Treatment of landfill leachate is most difficulted, it is a main environmental concern. Many biological and physio-chemical processes have been designed for landfill leachate treatment for the last couple of decades. Conventional biological treatment is hindered by the presence of certain bio-recalcitrant compounds, especially in the case of mature leachate.

Advanced oxidation processes (AOPs) (processes in which oxidation of organic contaminants occur primarily through reactions with hydroxyl radicals, using the combination of strong oxidants (e.g. O_3, H_2O_2), irradiation, e.g. ultraviolet (UV) light and ultrasound catalysts, e.g. Fe^{2+} and photocatalyst, e.g. titanium dioxide (TiO_2) and produce hydroxyl radicals. TiO_2 shows relatively chemical and reactivity stability under UV light, sunlight and visible light. The main effecting factors of this process are light source and type of photocatalyst. Many different types of semiconductors like ZnO, In_2O_3, CuO_2 and TiO_2 are used as photocatalyst (H.X. Zhu,2016). All of these semiconductors are nontoxic, Inexpressive, stable and available. But, Titanium dioxide (TiO_2) is strong oxidation and reduction power of photoexcited it discovery by Honda-Fujishima (Honda-Fujishima, 1972). TiO_2 can be synthesized in a nanocrystalline or crystalline phase of rutile, anatase and brookite (M. Hassan,2016).

Chemlal (R. Chemla,2012) investigated that photocatalytic process with TiO_2 and UV light source on leachate. landfill leachate has COD range 26,000 to 30,000 mg/L and it can change with pH. At optima condition where pH is 5. This system gives COD removal efficiency around 92% with treatment time of 30 hrs. This result show that TiO_2 nanoparticle can be used for any type of pollutant. Various parameters such as pH, dose of TiO_2 nano-particle, phase of TiO_2 nano-particle, temperature (which affects on phase of nanoparticles), intensity UV light, an initial concentration of pollutants affect photocatalysis process (M. Hassan,2016).

In this study, TiO_2 nanoparticles are used for leachate treatment under UV light irradiation. Some parameters like pH, calcination temperature of particles, dose of TiO_2 nanoparticles, treatment time with the leachate as independent variables and leachate COD concentration are considered for photocatalyst digression process.

II. Materials and methods

2.1 Photocatalysis and its basic principle

Photocatalysis is most advanced oxidation process (AOP), which generated a higher reactive radical species, mainly those are hydroxyl radicals ($HO^{\bullet}$) and superoxides ($O_2^{\cdot -}$) ions, using energy source as solar, UV or any other light source (U.I. Gaya,2008). This process has a capacity to degraded complex organic and inorganic compound, change into non-hazardous from or simple from like carbon dioxide, water, ammonia. These methods have many advantages like good efficiency, less energy demand (solar source), process can work under many phases like gaseous phase, aqueous solutions etc., process can detoxify waste.

Photocatalytic reactions are stated when semiconductor catalyst is illuminated under light source (UV light) with required energy which equals or more then band gap energy of semiconductor ($h\nu \geq \Delta Eg$). The commonly postulated chain reactions in photocatalytic process are as follows:

Photocatalyst illumination (electron-hole pair generation)

$$Hv + \text{photocatalyst} \rightarrow e^{-} + h^{+} \quad \text{...... (1)}$$

Mineralization of pollutant

$$h^{+} + \text{Organics} \rightarrow CO_2 + H_2O \quad \text{..... (2)}$$

The electron and hole pairs were generated by the light illumination with heat. This system photogenerated electrons and irons are oxidized organic pollutant compounds.

2.2 Titanium Dioxide (TiO_2)

Titania is second name of titanium dioxide. It is a white inorganic solid substance which stable, insoluble in water, non-hazardous according to the United Nations (UN) globally harmonized system. Titanium dioxide is widely used in an industrial level like dye-sensitized, catalyst support. In addition, TiO_2 used as semiconductor in photocatalysts process in research scale projects.

TiO_2 is one of the widely used semiconductor photocatalysts, but it is often not considered a viable alternative alone. In TiO_2 catalysis, two types of reactions occur, i.e. adsorption-desorption equilibrium in dark reaction and photocatalysis under irradiation. It has been considered as promising techniques for landfill leachate treatment. The demand for photocatalysis in wastewater remediation is increasing, but the practical application of TiO_2 as a photocatalyst for large-scale operations is limited by one major drawback. The wide band gap of anatase TiO_2 (3.2eV). So, Pure TiO_2 is only active in the ultraviolet (UV) range.

Table 1 Physical and structural properties of Titanium dioxide (X. Chen,2007)

Property	Unit for measurement	Value
Phase	-	Anatase
Molecular weight	g/mol	79.9
Crystal structure	-	Tetragonal`
Lattice Constant	A°	a=b= 3.784, c= 9.515
Density	g/cm^3	3.894
Melting point	°C	1825
Bandgap	eV	3.12
Light adsorption	nm	<390

2.3 TiO_2 nanoparticles synthesis

In this study, TiO_2 nanoparticle is synthesized by the sol-gel method (R. Akbarzadeh,2010). There is step by step process conducted for synthesized TiO_2 nanoparticles. First add 4ml of TTIP (Titanium isopropoxide) to 18.9 ml of IPA (Isopropyl alcohol) solution (20% wt. of solution) preparade by adding appropriate amount of each. In this continued process add ammonia drop by drop in this IPA and TTIP solution under continuous stirring process for achieved pH of 9-10. After some time, solution makes dented solution as semi-gel form. This gel solution washed with IPA and filtered. Second step is put this solution on dry place at room temperature for 2 Hrs and then put in hot air oven at 80°C for 12 Hrs. third step is dried gel solution required calcination for 4 Hrs at 400°C. After 4 Hrs, obtained white powder for TiO_2 nano-particle.

2.4 Characterization of TiO_2 Nanoparticles

In this study, two methods are used for characterized of synthesis TiO_2 nanoparticles. To determine the structural characteristics and crystalline phases of nanoparticles, X-ray diffraction (XRD) method is used. For determination of size distribution profile of nano-particles which in suspension or polymers in solution, Dynamic light scattering (DLS) is used.

X-ray diffraction (XRD)

XRD is used of analysis for crystalline compounds with Qualitative and Quantitative parameter. This method gives an information about phase identification, unit cell dimensions, structure type, size of unit structure and composition of particles etc.

XRD patterns were recorded by Phillips PW 1710 diffractometer using monochromatic higher intensity Cu Kα radiations (λ = 0.15418 nm) with angle range of 2θ =20-100°. The crystallite size is calculated by peaks of anatase (101), brookite (121) and rutile (110) reflections, by using this Debye- Scherrer equation

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \text{...... (3)}$$

Where D is the crystallite size, k is a constant 0.9, λ is an X-ray wavelength of Cu, β is full width at half maximum (FWHM) of the peak and θ is the Bragg's angle in radians.(H. Zhang,2000)

2.5 DLS (Dynamic Light Scattering)

Dynamic light scattering (DLS) is a technique in physics that can be used to determine the size distribution profile of small particles in suspension or polymers in solution. DLS software of commercial instruments typically displays the particle population at different diameters. If the system is monodispersed, there should only be one population, whereas a polydisperse system would show multiple particle populations. Poly Dispersity Index is preferred to be less than 0.5.

III. Standard photocatalysis Degradation of landfill leachate under UV light

The photocatalysis degradation of landfill leachate is carried out in a sample method which show in the picture. In this method first step is to add 2mg of Titania as photocatalyst into the 200 ml of landfill leachate with any suspend contaminated. Put this solution into the sonicator for sonication process in which titania mixed with leachate for 10 min. After 10 min, keep the solution and put in the UV reaction chamber. First 30 min, UV lamp is off. At this time initial adsorption on nanoparticles is done and after it photocatalysis reactions is started. Sampling for leachate is taken regular interval of 1 hours till next 3 hours and also, take the initial sample of adsorption of nanoparticles after 30 min. for calculation. Then samples are tested under standard method of COD (chemical oxygen demand) (standard method committee,1997 (5220)) for finding a percentage reduction of organic and inorganic compounds of landfill leachate.

Understand degradation process of leachate requited fixed some parameter which directly affected degradation process of leachate like pH of the leachate, contacted time and catalyst does. So, pH is bound round 7. pH can vary only 6, 7, 8. Contacted time is limited up to 3 hrs and catalyst dose fixed 1 g/L.

Figure 1 sonicator for proper mixed of nanoparticles

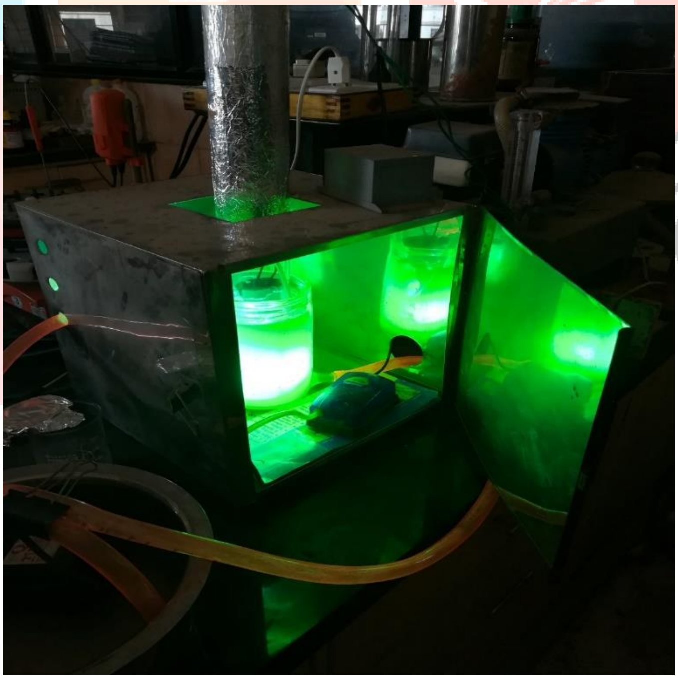

Figure 2 Photocatalysis process under UV-light

IV. RESULTS AND DISCUSSION

4.1 **XRD Analysis**

The XRD analysis performed on the pure TiO_2 nanoparticles. XRD pattern of the sample shows the two phases. Both phases are anatase and rutile phase. The diffraction peaks at a 2θ show in the figure. Peaks are showing both phases of the nanoparticle. The XRD peaks at a $2\theta = 25.36^{\circ}$ (101) and $2\theta = 27.4^{\circ}$ (110) are peaks of anatase and rutile phases of nanoparticles, respectively. Pure TiO_2 crystallite size is 28 nm and volume percentage of the Anatase and rutile phase are 67.2, 32.8 respectively. Cell volume of particle is 132.59 $(A^{\circ})^3$.

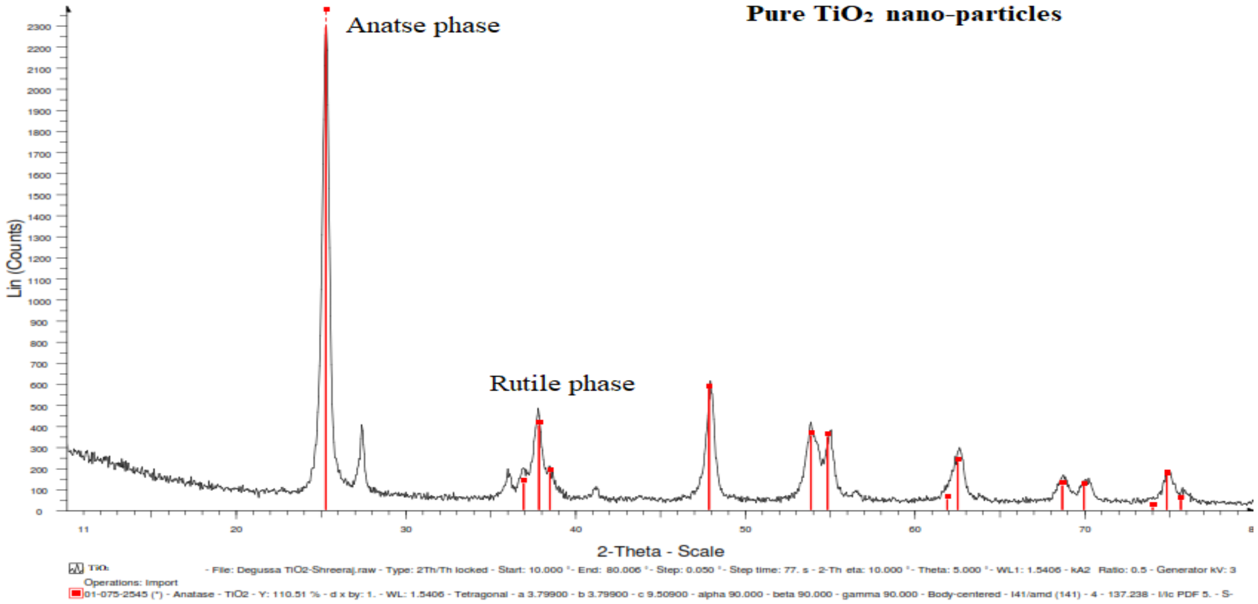

Figure 3 XRD patterns of TiO_2 nanoparticles, calcined at 300°C

4.2 DLS Analysis

The DLS analysis gives a size distribution report by number. This analysis was done at room temperature (25°C) at duration of 5 min with measurement position of 4.65 mm. The results show that Z-average diameter of nano-particle is 435.7 nm with width of 90.17 and PDI (polydispersity index) ratio 0.510. This ratio is more than 0.5 but it acceptable.

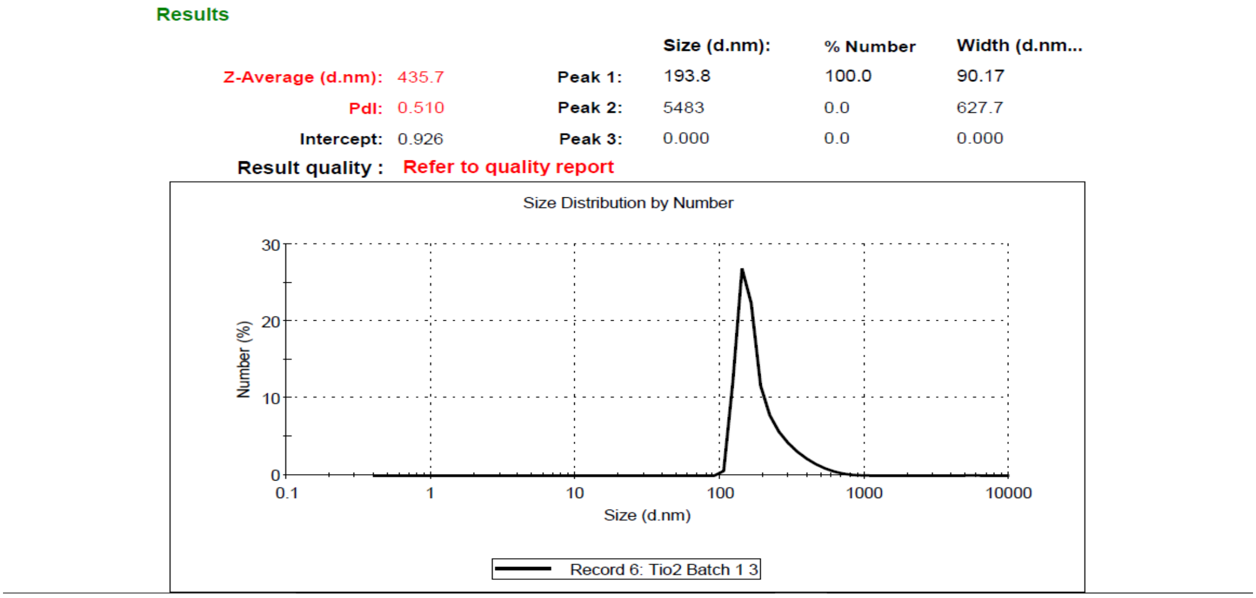

Figure 4 DLS Analysis results of the pure TiO_2 nanoparticles

4.3 COD results

Initial COD of landfill leachate is calculated by the standard method (5220). Resulted show that initial COD is 2560 mg/l. after the photocatalyst degradation of leachate, percentage of COD reduction under different condition. value is shown in below into the table:

Table 2 only UV light as irradiation, without TiO_2 catalyst

pH	-	6	7	8
Contact Time (Hrs)	0.5	1.04	1.45	1.12
	1	4.19	4.26	4.2
	2	6.12	6.04	6.00
	3	7.65	7.45	7.05

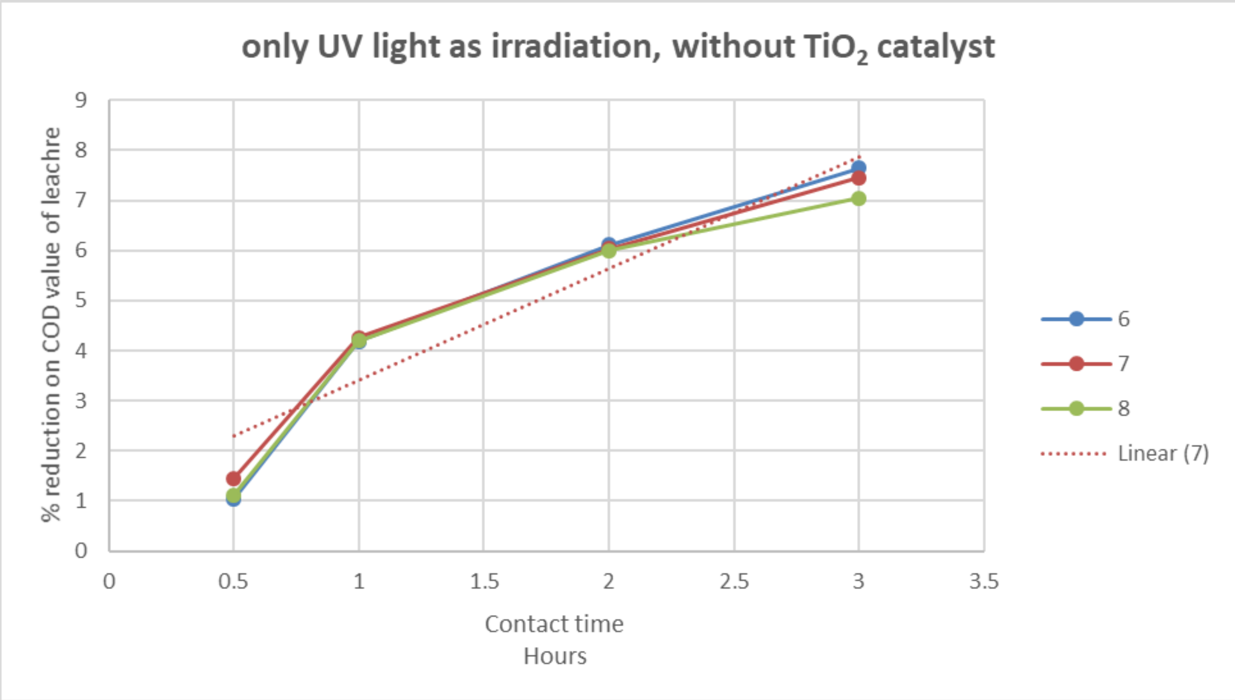

Figure 5 only UV light as irradiation, without TiO_2 catalyst

Table 3 (1 g/L dose) TiO_2 catalyst with UV light source as irradiation

pH	-	6	7	8
Contact Time (Hrs)	0.5	3.24	4.25	4.55
	1	10.45	13.5	13.86
	2	28.5	27.45	26.23
	3	60.14	57.64	56.83

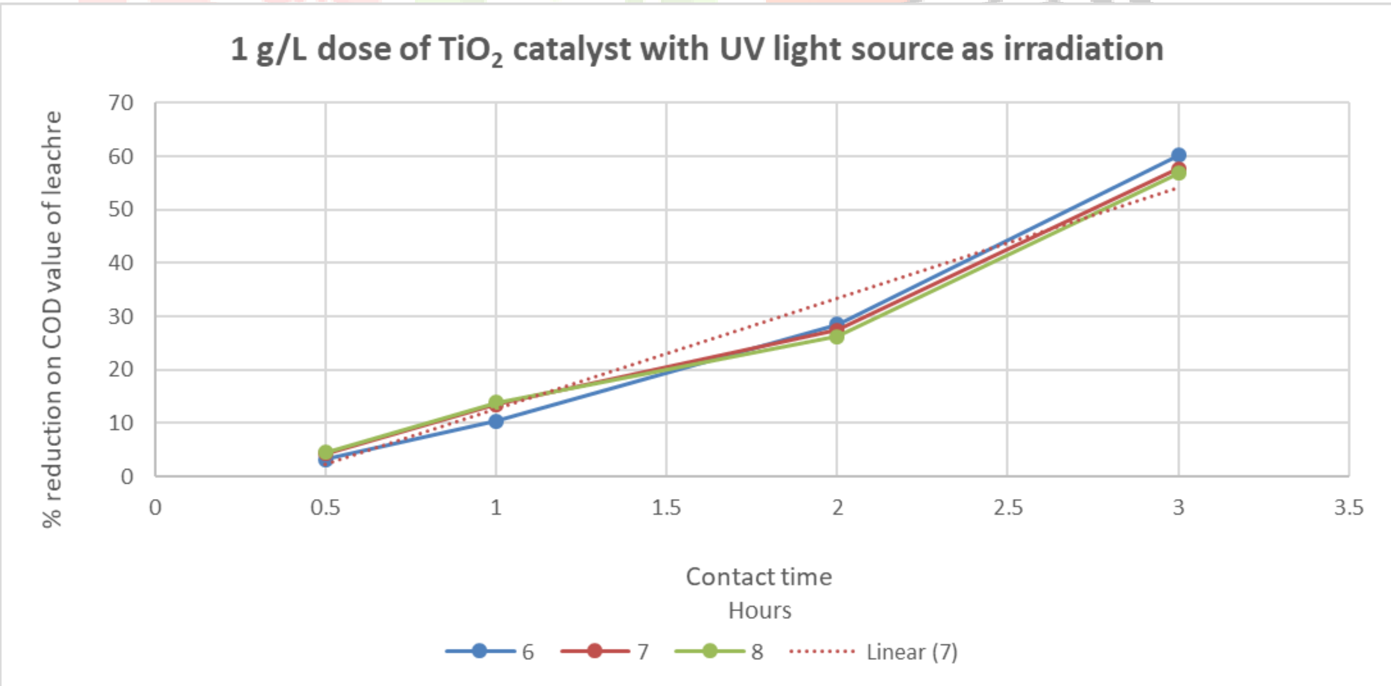

Figure 6 (1 g/L dose) TiO_2 catalyst with UV light source as irradiation

Table 4 Competition of Performance to removal efficiency of TiO_2 catalyst and UV light source

pH	-	only UV light and without TiO_2 catalyst	UV light and With **TiO_2 catalyst**
Contact Time (Hrs)	0.5	1.45	4.25
	1	4.26	13.5
	2	6.04	27.45
	3	7.45	57.64

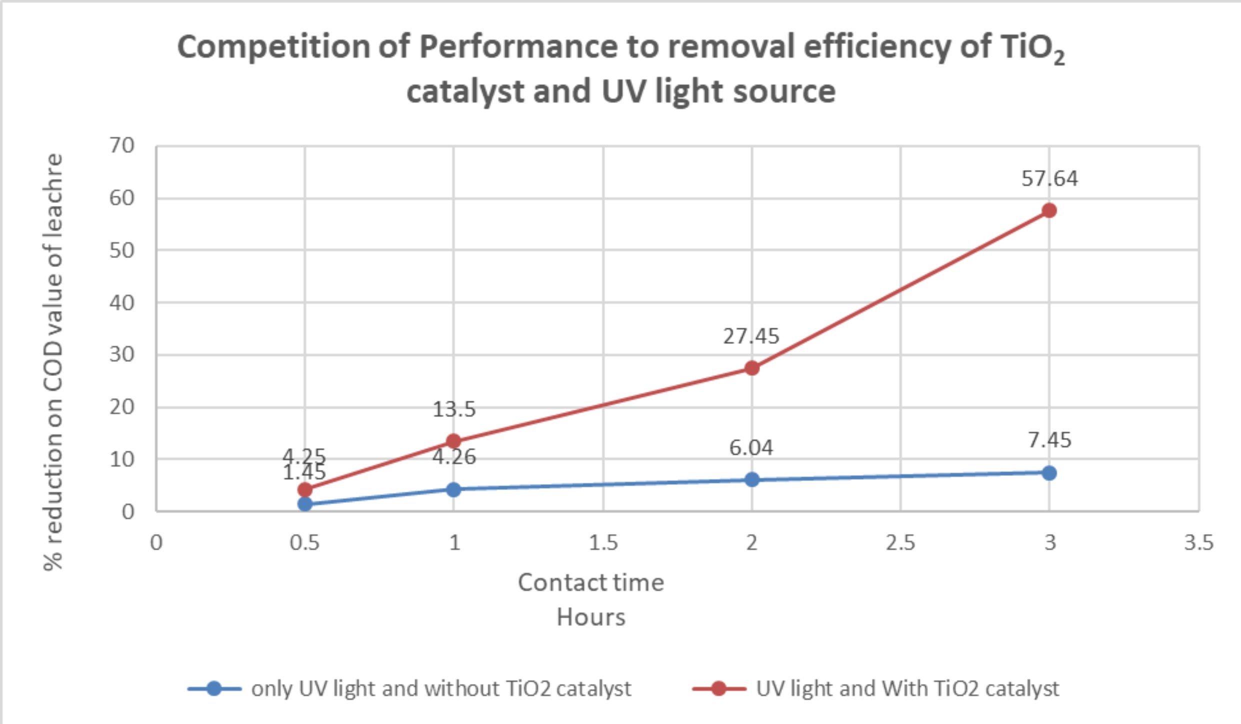

Figure 7 Competition of Performance to removal efficiency of TiO_2 catalyst and UV light source

V. Conclusion

This graph (figure-7) shows that UV light is not directed affected to the degradation of organic and inorganic compound. But its effective irradiation light source. Some percentage of degradation by UV is only by temperature variation. UV light intensity can increase degradation process.

This is study, investigate the perforce of Pure TiO_2 nanoparticle in a photocatalytic treatment of landfill leachate under UV light irradiation. Main influential parameters are contact time, catalyst doses and pH of leachate considered on the photocatalytic treatment process as indented variable. All that parament is directly affected to COD removal of leachate in photocatalyst process. So, COD is depended variable. The condition to get best result is at pH 6 with maximum contact time. This result shows that photocatalyst process can efficiently work below 7 pH.

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