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Photodegradation of Real Pharmaceutical Wastewater with Titanium Dioxide, Zinc Oxide, and Hydrogen Peroxide During UV Treatment

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Abstract:-This paper presents the photocatalytic degradation of real pharmaceutical wastewater from Abbot Laboratories (Private) Limited, Karachi, Pakistan, using TiO_2, ZnO, and H_2O_2. The pretreated sample wastewater was used for degradation experiments and tests were carried out at 38 ^{0}C under pH of 9 and 4 in a stirrer bath reactor equipped with eight ultraviolet tubes. The use of this technique is common in removal of the organic, inorganic pollutants and pathogens. Optimal conditions were selected from reported results of the researchers on advanced oxidation processes (AOPs) for removal of residual pharmaceuticals from real pharmaceutical wastewater. The three catalysts (Titanium dioxide, zinc oxide, and TiO_2/ H_2O_2) used in this study are effective catalysts in photocatalytic degradation of real pharmaceutical wastewater. The maximum degradation achieved was 45.11% by combined use of TiO_2 and H_2O_2 at 38 ^{0}C and pH. The degradation improved at higher pH with Zinc oxide and Titanium oxide. The results indicate that for real pharmaceutical wastewater, combined use of TiO_2/ H_2O_2 is comparatively more effective than ZnO and TiO_2 alone. The degradation of the pharmaceutical wastewater followed pseudo-first-order kinetics. The reaction rate constant was 0.00148/min for TiO_2/ H_2O_2. This study demonstrates that for real pharmaceutical wastewater reacts differently to catalyst than synthetic pharmaceutical wastewater, or formulated wastewater.

Keywords*:-**Hydrogen peroxide, Pharmaceutical wastewater, Photocatalytic degradation, Titanium dioxide, Ultra violet light, Zinc oxide*

I. INTRODUCTION

The pharmaceuticals are found in drug manufacturing wastewater, hospital wastewater, and industrial wastewater of pharmaceutical origin. The pharmaceutical usually consist of biologically active substances designed as lipophilic and are resistant to biodegradation. In aquatic media these substances if discharged to the environment, have potential for accumulation and persistence in the environment. Though they appear at low concentrations, but still may impose serious effects on the environment. During last two decades researchers have focused their attention in searching suitable technologies to destroy the xenobiotic substances and recently been able to report advanced oxidation processes (AOPs) as highly efficient treatment process for pharmaceutical wastewater.

Among many processes the ozone oxidation is adapted as part of the treatment at several water production plants. Treatment of pharmaceutical wastewater by AOPs is expensive, hence photocatalysis is an option considered widely by researchers. In recent years photocatalytic degradation of pharmaceutical wastewater has received attention of the scientific community. The results of past research carried out on real pharmaceutical effluent are comparable to this study; however, the results of studies on aqueous solution, synthetic wastewater, formulation effluent, synthetic wash-water from antibiotics packaging distilled water, industrial wastewater of pharmaceutical origin, hospital wastewater, synthetic wash-water from medium scale drug manufacturing plant, biologically pre-heated pharmaceutical wastewater, actual wash-water from ointment manufacturing plant, effluent from bulk drug manufacturing plant, municipal wastewater, and secondary treated domestic effluent are worth considering. The previous findings on aqueous system indicate degradation of wastewater by TiO_2 and UV alone is negligible [1] and that coupling of TiO_2 with UV greatly enhance degradation rates [2-4]. Only UV processes require long irradiation time [5] and only TiO_2 require high catalyst loading [6]. The variables affecting the degradation rates are catalyst loading, pH and temperature of solution/wastewater, irradiation time and intensity, and use of additional catalyst like H_2O_2 with and without Fe^{2+}. The particle size and surface area/$_{BET}$ of the catalyst (TiO_2) is an important parameter too [3]. The total organic carbon (TOC) removal rate depends on refractory character of the organic-inorganic wastewater content.

Fatemeh reports high degradation of analgesics in water at pH 12 and 50 ^{0}C [7] whereas, Liming found degradation between pH of 3.5 and 9.5 [1]. The synthetic wastewater made from human and veterinary antibiotics show that degradation increases with increasing pH (pH range 7-12), H_2O_2 enhance performance [8,9]. The results of Kaniou et al on Sulfamethzine in distilled water indicate higher removal performance of H_2O_2, and ZnO was more active than TiO_2 [10]. 90% removal of Diclofenac from distilled water is reported by TiO_2 after 60 minutes of irradiation [11]. 55% COD removal from industrial wastewater of pharmaceutical origin is reported by San Sebastian by using H_2O_2 at pH 4 [12]. Xing et al found 94% color and 73% COD removal with Fe^{2+}/ H_2O_2at pH 5 from biologically pre-heated pharmaceutical wastewater [13]. Kulik et al reports 87%-96% COD removal from actual wash water from ointment manufacturing plant with Fe^{2+}/ H_2O_2 [14]. Augmentation of TiO_2 by H_2O_2 is reported by many researchers [15-18] and now it is believed that presence of H_2O_2 enhances degradation performance of the catalyst [9]. The generation of the OH radicals in the UV/ H_2O_2 occurs via reaction (1) [19].

$H_2O_2 + h\upsilon \rightarrow 2\ ^{\cdot}OH$ (1)

The photogenerated electrons can recombine and make their ways to the surface of TiO_2, where they can react with species adsorbed onto the catalyst surface.

$h\upsilon^+ + H_2O \rightarrow {}^{\cdot}OH + H^+$ (2)

$h\upsilon^+ + OH^- \rightarrow {}^{\cdot}OH$ (3)

Organics + $h\upsilon^+ \rightarrow$ products (4)

The photogenerated electrons can also combine with O_2 and organics and produce:

$e^- + O_2 \rightarrow O_2^{-\cdot}$ (5)

Organics + $e^- \rightarrow$ products (6)

The produced hydroxyl radicals ($^{\cdot}OH$) and superoxide radical anion ($O_2^{-\cdot}$) can mineralize organics to water and CO_2 (end products):

Organics + (($^{\cdot}OH$), $O_2^{-\cdot}$, etc.) $\rightarrow$ (7)

Only a few studies have been conducted on industrial wastewater of pharmaceutical origin employingTiO_2andH_2O_2asthecatalystswithvaryingdegradationresults.Itisstillunclearthat how realpharmaceuticalwastewaterwouldrespon to photocatalytic activity of widely used catalysts.ThispaperreportsthefindingsoftheresearchworkemployingTiO_2,ZnO,and $H_2O_2$and the performance of photocatalytic reactor for degradation of a real pharmaceuticalwastewater.Theresultsofthisstudywouldaidtotheapplicationofnanophotocatalyst particles forremovalofcontaminantsfrompharmaceuticalwastewater.

II. EXPERIMENTAL PROCEDURE

2.1 material

Inthisstudy titanium dioxide powder (anatase) formandZincoxide (Dentam) were used as supplied.TheseChemicalsaresuppliedbyBDHwithpurityof99.99%withtheaverageparticle sizeof25± 4nmandspecificsurfaceof55± 8 m^2 g^{-1}.The30%AqueousSolutionofHydrogen peroxidewasalsosuppliedbyBDH.ThepHofthesampleinthereactionvesselwasadjusted withcalculatedvolume/weightof1NHClor1 NNaOH.Thestandardsolutionandreagentswere usedformeasuring theCODinclosed reflux colorimeteraspropose byAPHA [20].These catalystsareknownforoptimalcatalyticefficiencyandgoodinterparticlecontactsinwater[21].

2.2 ultraviolet energy

The selectionofultraviolet(UV)energydependsontheabsorptioncapacityofthemoleculesof thecontaminantin thesamplewater.TheUVenergynotonlyadvancestheoxidationprocessbut sterilizesthewastewaterbydestroyingfivemajorgroupof micro-organism.Thephotodegradation efficiencydependson UVdosage[22].Previousresearch[10,15,23]hasindicatedthat UVlightat wavelength254-579 nm,and 50-150 Wis adequate forsyntheticand realpharmaceutical wastewater withanirradiationtimeof1-4hour.However,occurrence ofmostdegradationis reportedwithinfirsthouroftreatment.Henceisthereasonforselectingoftheparametersforthis study.

2.3 experimental setup

The UV lamp selectedforthisstudywas8.0incheslongwithanUVoutputof11W.Atotal numberofeightUVlamptubes,manufacturedbyJiangsuShenXingPhotoelectricity ApparatusCo., Ltd.China,weresubmersedinthespeciallydesignedreactionvessel(diameter8 inches,volume5 liter)to produce88Wofenergy.Thepretreatedsamplewastewaterwasplacedina 5 literglass cylinderverticalreactoractingasa photoreactioncell.Thecatalystpowderwassuspendedinthe sampleandthesolutionin thecellwaskepthomogenousbyconstantstirringwitha topmounted stirrerandaerationbyusinganairpumpasshowninFig. 1 (actualexperimentalrig).The schematic diagram of the

experimental setupis shown in Fig. 2.The aerial view of the geometricalarrangementoftheUVtubesisshowninFig.3.Thepassingoftheairfacilitated thewastewatercirculationaroundthereactionvesselinordertomaintainthereactiontemperature atthedesired value. Thiscellwasplacedinaconstanttemperaturebath.ThepHmeterandtemperatureprobewasinsertedintothecelltomonitorpHandtemperatureofthewastewater.

Thephotocatalyticdegradationwascarriedoutoversuspensionof TitaniumOxide,ZincOxide and TiO_2/H_2O_2 underultravioletirradiation.

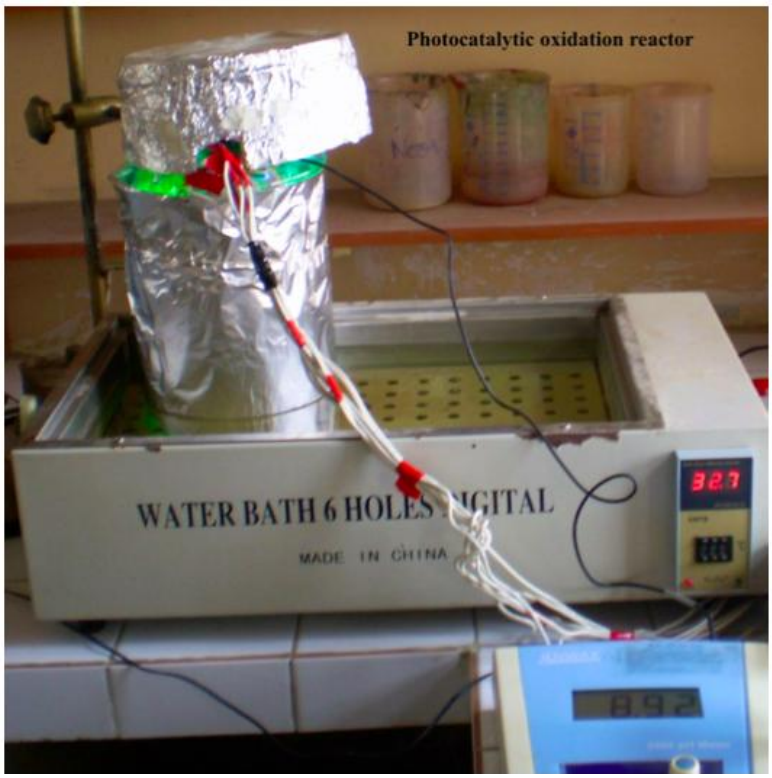

Fig. 1 photocatalytic oxidation reactor

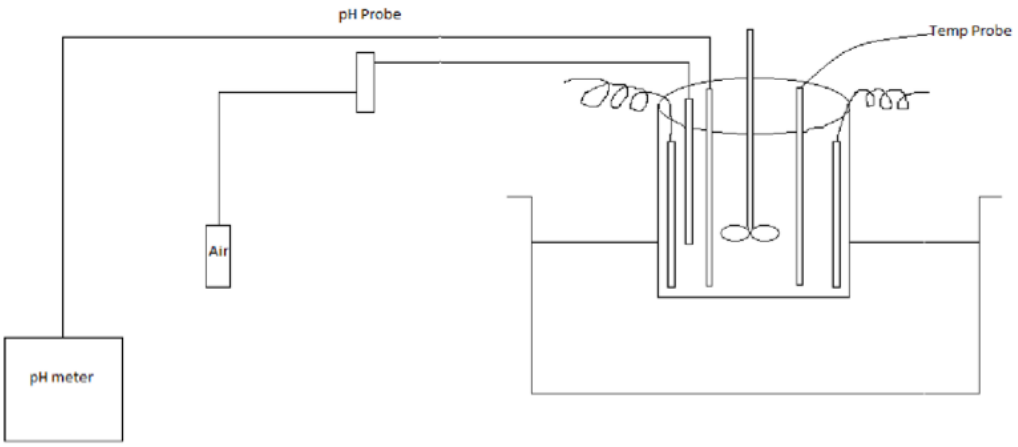

Fig. 2

schematic diagram of the experimental set-up

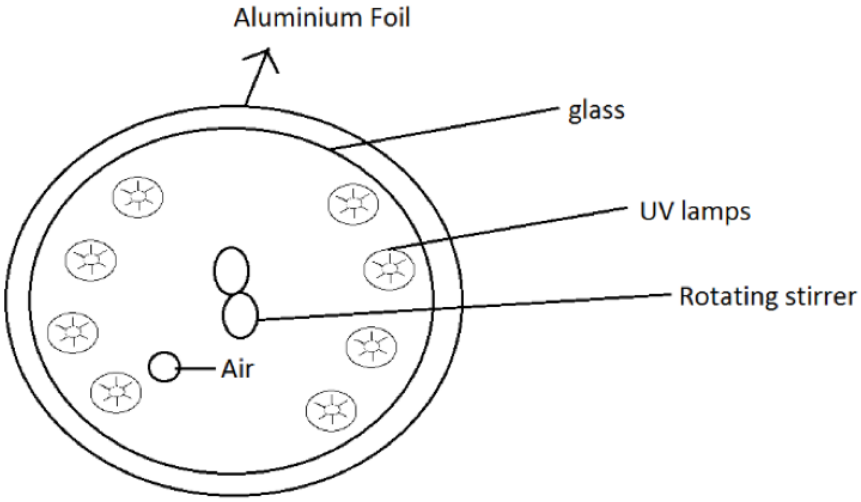

Fig. 3 the aerial view of the geometrical arrangement of the uv tubes in the reactor

TheSpectronic "Genesys 20" Spectrophotometer with wavelength range 325 to 1100 nm, accuracy ± 2.0nm wasused to measure absorbance at λmax of 625 nm. The rate of photodegradation iscalculatedinpercentagewithtimeofirradiation.Testswereconductedfor variablessuchaspHofsamplewastewater,typeofcatalyst,andexposuretimeofUVlight.

2.4 procedure

The optimumconcentrationofTiO_2 reportedbyAlmudena[18,24]wasbetween1.5and2.5g/l, henceinallexperiments6goftitaniumdioxideor4gzincoxidewassuspendedin5literofthe realpharmaceuticalwastewater which isplaced inaphotoreactioncell.Forexperiments with hydrogen peroxide, 2.4 ml $H_2O_2$30% purity wasadded tosample wastewater. The suspensionwassubjectedtoirradiationunderUVlightfor2 hour.Thesuspensionwasstirredand aeratedthroughouttheexperiment.

Atregulartimeintervals,the2cm^3ofirradiatedsamplewastakenoutfromthereactionvessel withthehelpofmicrosyringe,andthenfilteredthroughMilliporefilterof0.45um toseparatethe solidcatalyst.Usingcuvettestheabsorbanceofthesupernatantliquidismeasuredatλmaxof625 nm.

The antibacterial activities of the wastewater before and after the photocatalysis were measured by Abbot Laboratories using HPLC to determine the remaining concentration of the parent antibiotics (Sulfonamide, Fluroquinolones, Bacteriostatics, and Penicillingroup); analgesics (Acetaminophen); parent anti-inflammatory drugs (Diclofenac and Ibuprofen); and CNS stimulant (Caffeine). TABLE 1 lists the characteristics of sampled pharmaceutical wastewater from Abbot Laboratories, and TABLE 2 shows the minimum standard discharge limits for pharmaceutical effluents [25].

Table 1. Characteristics of Sampled Pharmaceutical Wastewater from Abbott Laboratories Limited

Characteristics	Name of Drug	Value
COD ($mgxl^{-1}$)	------	168-240
Antibiotics ($mgxl^{-1}$)	Sulfonamide	0.02-0.52
	Fluoroquinolones	5-43
	Bacteriostatic	0.08-0.33
	Penicillin group	0.002-0.022
Analgesics/Antipyretics	Acetaminophen	10-28.55
Anti-inflammatory drugs	Diclofenac	0.01-480
	Ibuprofen	0.47-885
CNS Stimulant	Caffeine	2.8-10.56
TDS ($mgxl^{-1}$)	-------	980-1240
TSS ($mgxl^{-1}$)	-------	105-200
P^H(dimensionless)	-------	7.4-7.8
Temperature (^OC)	-------	24-30

Table 2. Minimum Standard Discharge Limits for Pharmaceutical Effluents [25]

Parameter	Composition ($mgxl^{-1}$)
COD	250
BOD (3 days, 27 ^{O}C)	10-40
Oil & Grease	10
TSS	100
P^{H} (dimensionless)	6.0-
Mercury	0.01
Arsenic	0.20
Chromium (Cr^{6+})	0.10
Lead	0.10
Cyanide	0.10
Phenolics (C_6H_5OH)	1.00
Chromium (Cr^{6+})	0.10
Sulphides (as S)	2.10
Phosphates (as P)	5.0

Each culture tubes were incubated for 12 hours at 38 ^{0}C. After the incubation, the bacterial growth was measured using the optical density at 625 nm. All bio-assessment tests were repeated for accuracy. The optical density value was converted to growth inhibition, I, and, was calculated in terms of changes in absorption spectra. The degradation efficiency I (%) was calculated as:

$$I = [A]_o - [A]_t/[A]_o \times 100 \quad (8)$$

Where $[A]_o$ is the initial value and $[A]_t$ after any irradiation time. All experiments were carried out at two pH of sample with different photo catalyst. For accuracy of results the absorbance at a given time was compared with a calibration curve. The calibration plot was obtained by using a known percentage of real pharmaceutical wastewater. The calibration of spectrophotometer was done using manual procedure outlined in Spectronic "Genesys 20" and solutions were prepared from BDH products.

III. RESULTS AND DISCUSSIONS

3.1 Effect of Catalyst Type

The results presented in Fig. 4 shows effect of catalyst as an oxidant on degradation ofreal pharmaceuticalwastewaterbyphotoxidationprocessatconstantpH9andFig.5showseffectof pH on degradation ofwastewater withTiO$_2$. The wastewater waseffectively degraded using titaniumdioxideorzincoxideunderpHof9.Themaximumdegradationachievedwithin120 minutesof irradiationtime,wasabout33.23%byusingTiO$_2$and40.23%byusingZnOat 38^{0}C. Therearelimitedresearchfindingsontheuseofcatalystlike ZnO.Mostresearchershavefocused ontheuse of TiO$_2$,H$_2$O$_2$,Fe^{2+}/H$_2$O$_2$,andFe^{2+}/H$_2$O$_2$/UV.Theresultsof thisstudyarenotdirectly comparableto reportedfindingsdueto variationsin theparametersstudied.However,the effectivenessofthecatalyst canbediscussed duetosimilartrendinCODandTOCremoval efficiency. Kaniou reports that ZnO is more active than TiO$_2$[10]. Theyachieved 90% degradationin60minuteswhenTiO$_2$wascombinedwithSiO$_2$.Whereas,Limingfoundmorethan 90%pollutant's(paracetamolinaqueoussolution)degradationin80minutesatpH9.5byTiO$_2$alone[1].Thistrendiscom parable toourfindings.Theeffectiveness ofZnOwashigherthan TiO$_2$atgiven pHandtemp. Reduced effectiveness ofTiO$_2$isduetomediumpHandlower reaction temperature. Fatemeh found higher degradation at 50 ^{0}C. At high pH formation of OH radicals is enhanced [7]. The higher reactivity of ZnO is attributed to the geometry and working conditions of the photo reactor. The saturation level of ZnO under given operating conditions is lower than TiO$_2$.

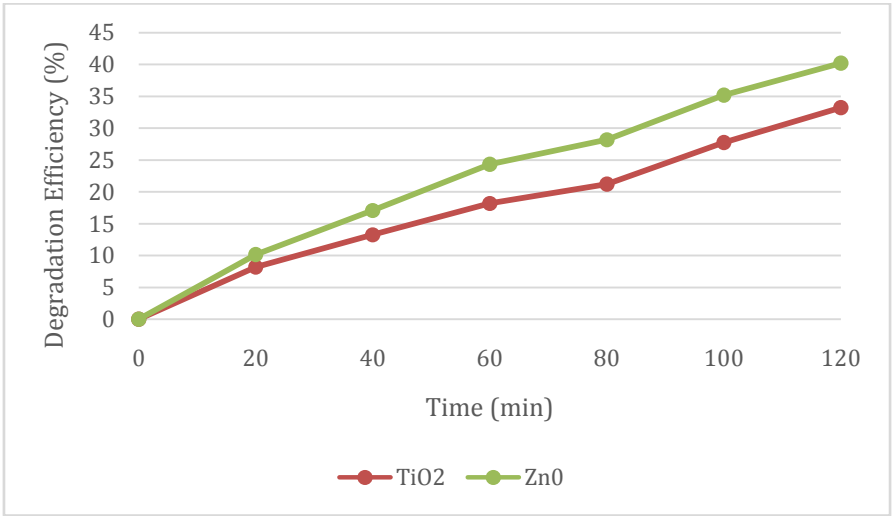

Fig.
4. The effect of catalyst on degradation of pharmaceutical waste water at pH 9.0, T=38°C

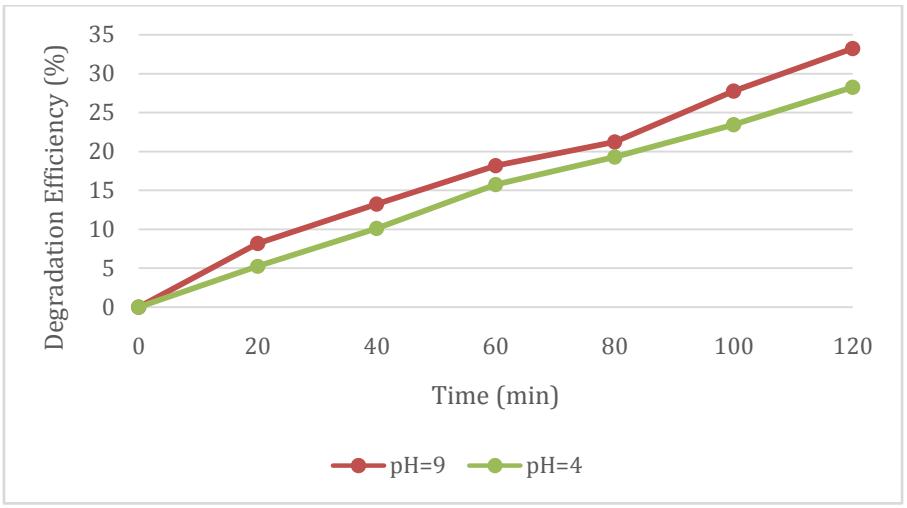

Fig. 5. The effect of pH on degradation of waste water with TiO_2 (Temperature = 37°C)

3.2 Effect of pHwith additional catalyst H_2O_2

TheeffectofpHondegradationofpharmaceuticalwastewaterbyTiO_2/H_2O_2 isshowninFig.6.Themaximumdegradationachievedwithin120minutesofirradiationtime,atpH9wasabout 45.11%.Byaddingthecatalyst$H_2O_2$to TiO_2,thedegradationwasincreasedby12%.Ithasbeen reportedbymanyresearchersthatH_2O_2 additionincreasesdegradationefficiencyofthecatalyst [22,26-30]. Yeon[3 0] foundmorethan99%removalofamoxicillin fromaqueoussolution inthe presenceofH_2O_2.Xiang-RongreportsthatFentonprocessismoreefficientthanUV/H_2O_2inthe absenceofTiO_2[6]asrateofreactionincreaseswithH_2O_2. Itisprovedthatmorethan90% degradationcanbeachievedinaqueoussolutionbutnotinrealpharmaceuticalwastewater.As real wastewater characteristics and chemistry of pollutants are significantly different than syntheticwastewateroraqueoussolution,it is expectedthatdegradationwouldvarywidely.Fig.7 and8 showperformanceofcatalystatconstantpH9 and4respectively.AtpH4 themaximum degradationachievedwithin120minutesofirradiationtime,wasabout40.18%.Itindicatedthat pHplayedanimportantroleandthemoderatephotocatalysisinthepresenceofH_2O_2 isdueto enhancedabsorbanceofUVlightcapacitybythecompound;whichissimilartothefindingsof manyotherresearchers[12,14, 31].EvenwithFentonoxidationprocesswith H_2O_2,the maximum COD removal fromindustrialwastewater ofpharmaceutical origin was 55%. Hence itisnot surprisingtoachieveamaximumdegradationof45%usingrealpharmaceutical wastewater.A possibleexplanationforlowerdegradationcouldbe thatphotocatalyticreactioninrealwastewater

producesseveralintermediateproductsandtheseproductsdonottransformintoCO$_2$to theextent transformedinaqueoussolution.

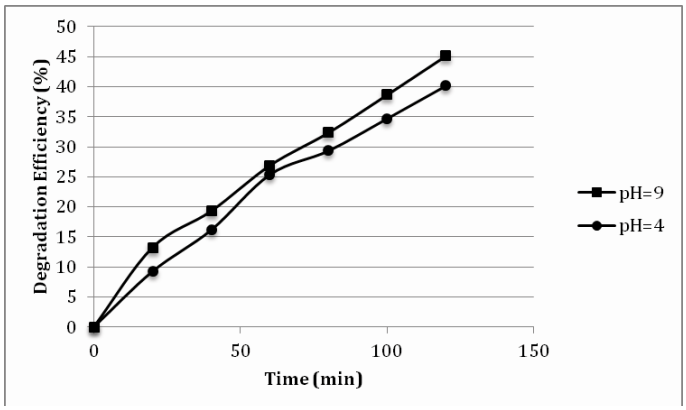

Fig. 6 The effect of pH on degradation of wastewater by TiO_2/H_2O_2

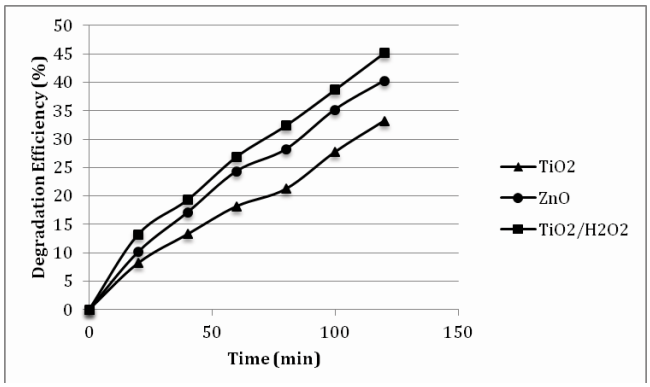

Fig. 7 The performance of catalyst at constant pH of 9

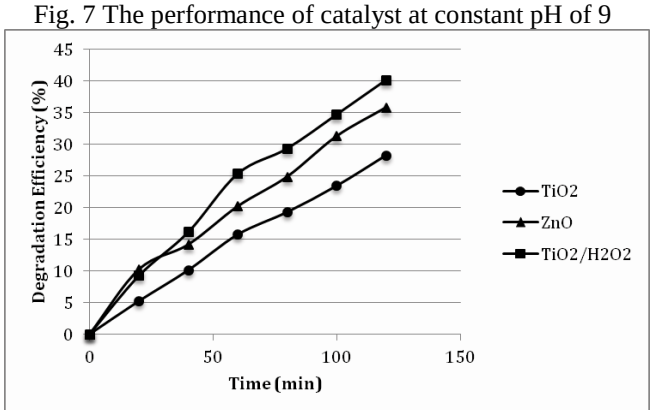

Fig. 8 The performance of catalyst at constant pH of 9

3.3 Effect of reaction time

A linear relationship as shown in Fig. 9 was observed between irradiation time and COD removal. The results show that in oxidation process, the reaction rate plays an important role than adsorption rate. The OH^- radicals can degrade organic pollutants to intermediates and then the intermediates are further degraded to CO_2 and H_2O [7]. The reaction rate attains a maximum value at high pH; and the generation of OH^- radicals by the effect of irradiation on the TiO_2 of the composite may be another factor for increasing reaction rate in basic environment [1]. The maximum COD removal efficiency in 120 min was obtained at pH of 9, which corresponds with the findings of San Sebastian [12,22]. The comparability of reported work on treatment of pharmaceutical in water and wastewater by AOPs with current study is given in TABLE 3.

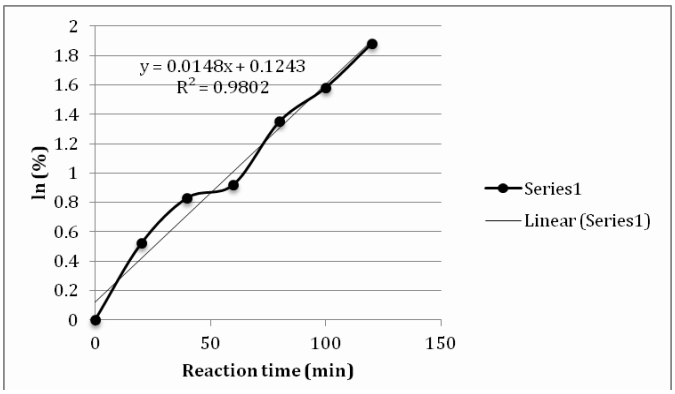

Fig. 9 The linear regression of degradation of pharmaceutical wastewater at pH 9 and temperature 38 ^{O}C

Table 3. Reported Work on Treatment of Pharmaceutical in Water and Wastewater by AOPS

	AOPfeature	Scale	Measureof	Comparability	Reference
Synthetic wastewater	O_3aloneorO_3/H_2O_2;	Bench	COD,TOC,	Yes	[8, 9, 16]
Municipal	O_3alone	Pilot	TOC	No	Notlisted
Formulation Effluent	O_3alone,UValone, orO_3/H_2O_2; Fe^{2+}/H_2O_2	Bench	COD,TOC, BOD_5	Yes	[9, 15, 16]
Syntheticwash-waterfromantibiotic packagingdistilled	O_3alone,O_3/$MnSO_4$	Bench	COD,BOD_5	No	Notlisted
Industrial wastewaterof pharmaceutical origin	UVonly,Fe^{2+}/H_2O_2', UV/H_2O_2	Bench	COD,BOD	Yes	[5, 12]
Hospitalwastewater	Fe^{2+}/H_2O_2	Bench	COD,BOD_5,	Yes	[31]
Syntheticwash-waterfrommedium scaledrug	Fe^{2+}/H_2O_2	Bench and Full	COD,BOD_5	Yes	[17]
Biologicallypre-treated pharmaceutical wastewater	Fe^{2+}/H_2O_2	Bench	COD	Yes	[13]
Actualwash-water fromointment manufacturingplant	Fe^{2+}/H_2O_2	Bench	COD,BOD_7	Yes	[14]
Effluentfrombulk drugmanufacturing plant	TiO_2asanode, Graphiteascathode, Cl^- aselectrolyte	Bench	COD,TOC	No	Notlisted
Distilled water/Deionized Water	O_3alone,UValone, UV/Fe^{2+},UV/Cu^{2+}, TiO_2/UV,	Bench	TOC	No	Notlisted

3.4 Kinetic analysis

The linear regression analysis of degradation of pharmaceutical wastewater with TiO_2/H_2O_2 at pH 9 is shown in figure 9. The plotted data produced a straight line that indicates that the degradation of the pharmaceutical wastewater can be described by the following first-order kinetic model equation.

$$\ln (C_o/C_t) = k_1 t \quad (9)$$

Where C_o is the initial concentration value, k is the reaction rate, and t is the time. The equation (9) presents kinetic expression and the correlation between $\ln(C_o/C_t)$ and reaction time t was linear with R^2=0.9802 for TiO_2/H_2O_2. The value of determination coefficient R^2 clearly indicates that this degradation process follows pseudo-first-order kinetics. The figure 9 also shows the rate constant (0.0148/min). These results are very close to the findings of SunJianHui[28]. Similar to previous studies[13,21,32]. More precise rate of reaction can be calculated if effects of photon absorption are included to the kinetic model equation.

3.5 Pharmaceutical Wastewater and Mineralization Study

The composition of pharmaceutical wastewater iscomplex andmaycontaindifferent typesof organicpollutants. Atthetimeofstudy,AbbotLaboratories wereprocessing formulations for antibiotics,analgesics,anti-inflammatorydrugsandCNSstimulantaslistedinTABLE1. Henceitis assumedthatthesamegroupofcompoundswouldbe presentin wastewater.TheHPLCresults confirmedtheconcentrationofthesecompoundslistedinTABLE 1.

During the degradation process, some intermediate products are formed which may be more difficult to degrade. The measurement of COD is related to total concentration of organic compounds in the waste and treated water. Hence the change in COD before and after treatment reflects degree of mineralization. The COD of sampled wastewater was in the range of 168 to 240 mgl/l, which is within the standard discharge limits. However, the composition of the treated water suggests that nearly all of the intermediates were mineralized by photocatalysis under given conditions. It is most likely that the treated water is free from toxic compounds. This study confirms that photocatalytic degradation can completely mineralize pharmaceutical wastewater but still lacks in comprehensive study that encircles the comparison of the effect of TiO_2, ZnO, and other catalysts under different operating parameters. Therefore, in order to commercialize the photocatalytic wastewater technology, several key parameters like catalyst development, reactor design and process optimization need to be further investigated.

IV. CONCLUSIONS

All three catalystsnamelyTitaniumdioxide,zincoxide,andTiO_2/H_2O_2usedinthisstudyare effectivecatalystsinphotocatalyticdegradationof realpharmaceuticalwastewater. However,the maximumdegradationachievedwas45.11%bycombineduseofTiO_2andH_2O_2at38^{O}CandpH of9, within 120 minutes of irradiations. Withthesamecatalyst atpH of 4 thedegradation decreasedto35.82%.Thedegradationat higherpHsupportsthenotionthatpHisoneofthemost importantoperatingparameterthataffectthephotcatalyticreactivityof thecatalyst.Themaximum degradationwithZnOwas40.23%andwithTiO_2was33.23%atpH9.Thedegradationofthe pharmaceutical wastewater followedpseudo-first-orderkinetics.Thereactionrateconstantwas0.0148/minfor TiO_2/H_2O_2.Theresultsindicatethatforrealpharmaceuticalwastewater,combined useof $TiO_2/H_2O_2$is comparatively moreeffectivethan ZnO andTiO_2alone.This study demonstrates thatrealpharmaceuticalwastewater reacts differently tocatalysts than synthetic pharmaceuticalwastewater,orformulatedwastewater.

Theresultsofthisstudyindicatedthatphotocatalyticdegradationcanbe usedforthereal pharmaceutical wastewater contaminated bydifferent inorganic-organic pollutants. Inorder to achievemorethan90%degradation,pretreatedeffluentismoresuitableforAOPtreatment.Due to low consumptionofchemicalsand energy, heterogeneous photocatalysis seems to be a promisingmethodundermoderntechnologywithbroadapplicationin treatingwastewaterform pharmaceuticalindustry,hospitalsandmunicipalities.However,furtherstudiesare requiredfor i) identifying thebioactivity ofunknown intermediate products andby-products, ii)inhibition of photocatalyticactivitybynaturalorganicmatterpresentinthewastewater,andiii)comparisonof theeffectofTiO_2,ZnO,andothercatalystsunderdifferentoperatingparameters.

V. ACKNOWLEDGEMENT

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