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Refinery wastewater degradation with titanium dioxide, zinc oxide, and hydrogen peroxide in a photocatalytic reactor

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ABSTRACT

This paper presents the photo-catalytic degradation of real refinery wastewater from National Refinery Limited (NRL) in Karachi, Pakistan, using TiO_2, ZnO, and H_2O_2. The pretreatment of the refinery effluent was carried out on site and pretreated samples were tested at 32–37 °C in a stirrer bath reactor by using ultra-violet photo oxidation process. The degradation of wastewater was measured as a change in initial chemical oxygen demand (COD) and with time. Optimal conditions were obtained for catalyst type, and pH. The titanium dioxide proved to be very effective catalysts in photo-catalytic degradation of real refinery wastewater. The maximum degradation achieved was 40.68% by using TiO_2 at 37 °C and pH of 4, within 120 min of irradiations. When TiO_2 was combined with H_2O_2 the degradation decreased to 25.35%. A higher reaction rate was found for titanium dioxide. The results indicate that for real refinery wastewater, TiO_2 is comparatively more effective than ZnO and H_2O_2. The experiments indicated that first-order kinetics can successfully describe the photo-catalytic reaction. The ANOVA results for the model showed satisfactory and reasonable adjustment of the second-order regression model with the experimental data. The ANOVA results also showed that pH is significant than reaction time and catalyst dosage of TiO_2; and in case of ZnO, reaction time is significant than pH and catalyst dosage. This study proves that real refinery wastewater reacts differently than synthetic refinery wastewater, oil field produced water or oil water industrial effluent.

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Keywords: Photo-catalytic degradation; Refinery wastewater; Ultra-violet light; Titanium dioxide; Zinc oxide; Hydrogen peroxide

1. Introduction

The aliphatic and aromatic organic compounds present in refinery wastewater are a major source of aquatic environmental pollution (Wake, 2005). The petroleum refineries use huge amount of water in refining crude oil and subsequently generate high volume of wastewater. Due to rapid increase in demand for oil worldwide, the wastewater effluent will continue to rise and ultimately be discharged to main water sewer in the vicinity (Doggett and Rascoe, 2009; Marcilly, 2003). The refinery wastewaters vary in composition depending on type of crude oil, refining processes configuration, and procedures.

The COD levels of refinery wastewater are generally between 100 and 600 mg l^{-1} (WBG, 1999). Due to extreme toxicity of contaminants in refinery wastewater, there is a need to develop an economical technique to remove the pollutants from the effluent. The refinery wastewater is not suitable for photo-degradation unless passed through pretreatment.

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Through pretreatment organic contaminant are transferred to another medium. An attractive technique of chemical oxidation is proposed by Huang and Shu (1995) but limited in application due to huge volume of wastewater (Guo and Al-Dahham, 2005). Through photo-catalysis, the toxic organic pollutants present in the refinery wastewater can be completely degraded into harmless inorganic compounds like CO_2 and H_2O.

During last decade a lot of work is done in advancing the oxidation processes. Most of the oxidation processes use TiO_2, ZnO, H_2O_2, and Fe^{2+} alone or in combination employing ultraviolet (UV) light (Chong et al., 2010; Fox and Dulay, 1993; Jiang et al., 2009). Titania loaded nano-composite has proved to increase photo-catalytic degradation (Daraei and Ghasemi, 2012). The phenol removal by the use of TiO_2/UV and H_2O_2 is also obtained (Soltanian and Behbahani, 2011; Luenloi et al., 2011). The benzene–toluene–xylene in refinery wastewater was successfully degraded to 73% by ZnO and TiO_2 combined with SnO_2 and WO_3 (Mohd Hir et al., 2011; Saien and Nejati, 2007). The photo-catalysis was used as a tertiary treatment for petroleum refinery wastewater and removal of 93% of phenols was achieved (Santos et al., 2006; Liwsirisaeng et al., 2012). The enhancement of degradation is achieved by the use of H_2O_2 with UV light (Stepnowski et al., 2002).

This paper reports the findings of the research work employing TiO_2, ZnO, and H_2O_2 and the performance of photo-catalytic reactor for degradation of a real refinery wastewater. The results of this study would aid to the application of nano-photocatalyst particles for removal of contaminants from refinery wastewater.

2. Experimental procedures

2.1. Pretreatment

The refinery wastewater was pretreated in two steps. The suspended solids, immiscible liquids, solid particles, and suspended substances were reduced significantly by gravity in separation tanks at National Refinery Limited (NRL) site, Karachi, Pakistan. Then concentration of heavy metal and small sized suspended solids were reduced in second step in Chemical Engineering Labs at Karachi University (KU), Karachi, Pakistan. The pretreated refinery wastewater samples were tested for measurement of parameters. After upgrading and expansion completed recently, the NRL is designed to process 53,000 bpsd crude oil of local and Arabian Gulf origin; 6600 bpsd of lube fraction; and producing premium products by deeper conversion of the low value high sulfur fuel oil and asphalt. Table 1 shows the characteristics of the pretreated refinery wastewater; and Table 2 shows the minimum standard discharge limits from refinery effluents (Ma et al., 2009; Hami et al., 2007; Santos et al., 2006; Environmental Health Safety Guidelines, 2009).

Table 1 – Characteristics of sampled refinery wastewater from NRL.

Characteristics	Value
COD ($mg\,l^{-1}$)	200–240
BOD ($mg\,l^{-1}$)	110–230
TDS ($mg\,l^{-1}$)	510–620
TSS ($mg\,l^{-1}$)	15–27
pH (dimensionless)	6.5–7.5
Turbidity (NTU)	70–100
TKN ($mg\,l^{-1}$)	3.7
Ammonia-N ($mg\,l^{-1}$)	1.4
Phenols ($mg\,l^{-1}$)	9
Sulphides ($mg\,l^{-1}$)	13–17

Table 2 – Minimum standard discharge limits for refinery effluents.

Parameters	Composition ($mg\,l^{-1}$)
COD	100–200
BOD	10–40
DOC	20
TSS	30–70
pH (dimensionless)	6.0–9.0
Ammonia	15–70
Phenols	3.7
Sulphides	1

2.2. Materials

In this study titanium dioxide powder (anatase) form and zinc oxide (Dentam) were used as supplied. These chemicals are supplied by BDH with purity of 99.99% with the average particle size of 25 ± 4 nm and specific surface of $55 \pm 8\,m^2\,g^{-1}$. The 30% aqueous solution of hydrogen peroxide was also supplied by BDH. The pH of the sample in the reaction vessel was adjusted with calculated volume/weight of 1 N HCl or 1 N NaOH. The standard solution and reagents were used for measuring the COD is closed reflux colorimeter as proposed by APHA (1989). These catalysts are known for optimal catalytic efficiency and good interparticle contacts in water (Ohno et al., 2011).

2.3. Ultraviolet energy

The selection of ultraviolet energy depends on the absorption capacity of the molecules of the contaminant in the sample water. The ultraviolet (UV) energy not only advances the oxidation process but sterilizes the wastewater by destroying five major group of micro-organism. Previous research (Alkdasi et al., 2004) has indicated that UV light at wavelength 200–678 nm, and 50–150 W is adequate for pretreated composite water with an irradiation time of 1–4 h. Hence is the reason for selecting of the parameters for this study.

2.4. Experimental setup

The UV lamp selected for this study was 8.0 in. long with an UV output of 11 W. A total number of eight UV lamp tubes, manufactured by Jiangsu Shen Xing Photo-electricity Apparatus Co. Ltd. China, were submersed in the specially designed reaction vessel (diameter 8 in., volume 5 l) to produce 88 W of energy. The preheated sample wastewater was placed in a 5 l glass cylinder vertical reactor acting as a photoreaction cell. The catalyst powder was suspended in the sample and the solution in the cell was kept homogenous by constant stirring with a top mounted stirrer and aeration by using an air pump as shown in Fig. 1. The aerial view of the geometrical arrangement of the UV tubes is shown in Fig. 2. The passing of the air facilitated the wastewater circulation around the reaction vessel in order to maintain the reaction temperature at the desired value. This cell was placed in a constant temperature bath. The pH meter and temperature probe was inserted in to the cell to monitor pH and temperature of the wastewater. The photo-catalytic

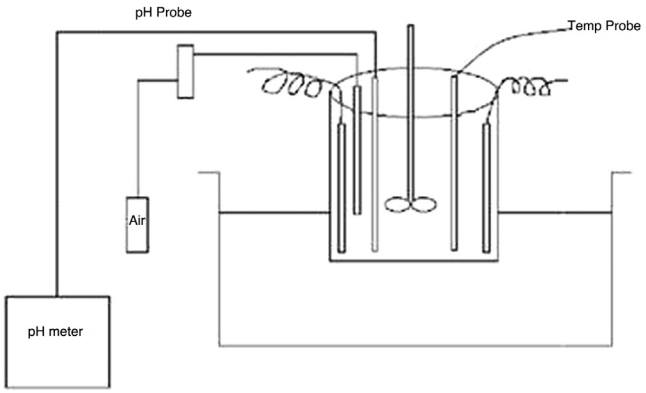

Fig. 1 – Schematic diagram of the experimental set-up.

degradation was carried out over suspension of Titanium Oxide, Zinc Oxide and TiO_2/H_2O_2 under ultraviolet irradiation.

The Spectronic "Genesys 20" Spectrophotometer with wavelength range 325–1100 nm, accuracy ±2.0 nm was used to measure absorbance at λ_{max} of 625 nm. The rate of photo-degradation is calculated in percentage with time of irradiation. Tests were conducted for variables such as pH of sample wastewater, type of catalyst, catalyst dosage and exposure time of UV light.

Many researchers have reported that the effect of temperature is insignificant (Basheer et al., 2011) because the process' true activation energy is zero, which clearly indicate the functionality of the process at ambient temperature. Regarding catalyst concentration a linear relationship is reported between the mass of the catalyst and the initial rates of reaction (Hermann, 1999). Higher catalyst concentration beyond a certain limit does not result in any significant change in the efficiency of photo-catalytic degradation (Al-Sayyed et al., 1991; Alhakimi et al., 2003a,b). Therefore, in this study, effect of temperature was not investigated. All the tests were performed in the range of 32–37 °C and with varying concentration of the catalysts. A reduction of only 5% in COD was reported by Javad and Fatemeh (2012), after 150 min of irradiation with 100 mg l^{-1} of TiO_2. This low reduction is attributed to very low absorption of organic compounds by nano-titania particles. Based on the published results of researchers who used the similar setup, the operating parameters like temperature, pH, irradiation time, catalyst dosage and type were selected. The effects of three different types (titanium dioxide, zinc oxide and hydrogen peroxide) were investigated.

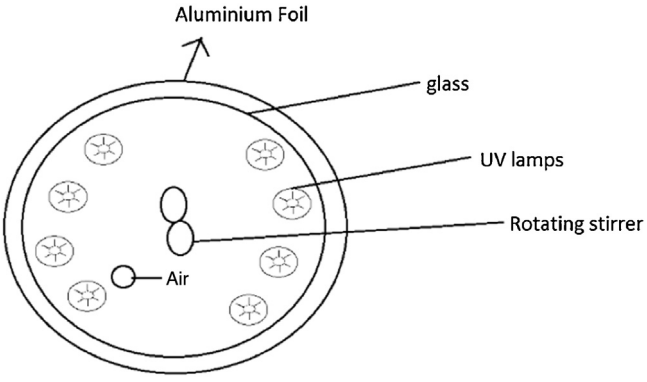

Fig. 2 – The aerial view of the geometrical arrangement of the UV tubes in the reactor.

2.5. Procedure

In all experiments 1–10 g of titanium dioxide or 1–6 g zinc oxide is suspended in 5 l of the real refinery wastewater which is placed in photoreaction cell. For experiments with hydrogen peroxide, 2.4 ml H_2O_2 with 30% purity was added to sample wastewater. The suspension was stirred and aerated throughout the experiment.

At regular time intervals, the 2 cm^3 of irradiated sample was taken out from the reaction vessel with the help of micro syringe, and then filtered through Millipore filter of 0.45 μm to separate the solid catalyst. Using cuvettes the absorbance of the supernatant liquid is measured at λ_{max} of 625 nm. The rate of degradation was calculated in terms of changes in absorption spectra. The degradation efficiency (X%) was calculated as:

$$X = \frac{[COD]_0 - [COD]_t}{[COD]_0} \times 100 \quad (1)$$

where $[COD]_0$ is the initial value $[COD]_t$ after any irradiation time. All experiments were carried out with samples of pH in the range of 2–9 with different photo catalyst. The COD analysis was done using the standard reagents and solutions, digested for 2 h and measured by Thermo Orion aqua fast II AQ 2040 COD meter. 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 refinery wastewater. The calibration of spectrophotometer was done using manual procedure outlined in Spectronic "Genesys 20" and solutions were prepared from BDH products.

3. Results and discussions

3.1. Effect of catalyst type

The effect of catalyst as an oxidant on degradation of real refinery wastewater by photoxidation process at constant pH is shown in Fig. 3. It should be noted that Figs. 3–12 are drawn with standard error bars. The wastewater was effectively degraded using titanium dioxide or zinc oxide at pH of 9. The maximum degradation achieved within 120 min of irradiation time, was about 32.25% by using TiO_2 and 30.18% by using ZnO at 34 °C. There are limited research findings on the use of catalyst like ZnO. Most researchers have focused on the use of TiO_2, H_2O_2, Fe^{2+}/H_2O_2/UV. The results of this study are not directly comparable to reported findings due to variations in the parameters studied. However, the effectiveness of the

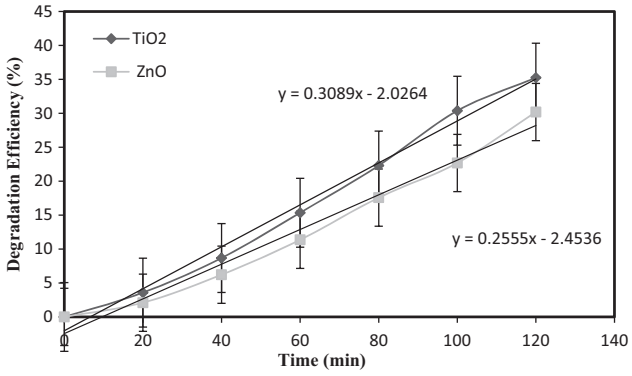

Fig. 3 – Effect of catalyst on degradation of wastewater at constant pH.

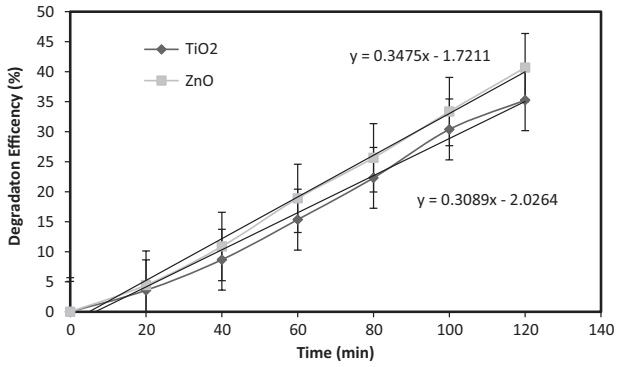

Fig. 4 – Effect of pH on degradation of wastewater with TiO_2.

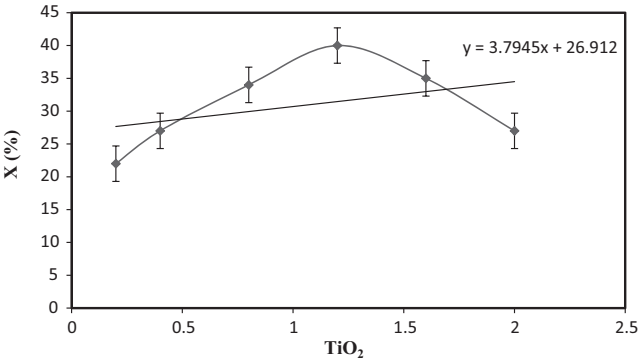

Fig. 5 – Saturation effect of titanium dioxide on degradation of wastewater; pH 4.0, $T = 35\,°C$ and reaction time 120 min.

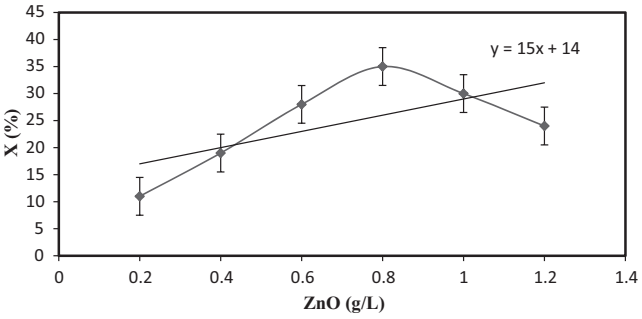

Fig. 6 – Saturation effect of zinc oxide on degradation of wastewater; pH 4.0, $T = 35\,°C$ and reaction time 120 min.

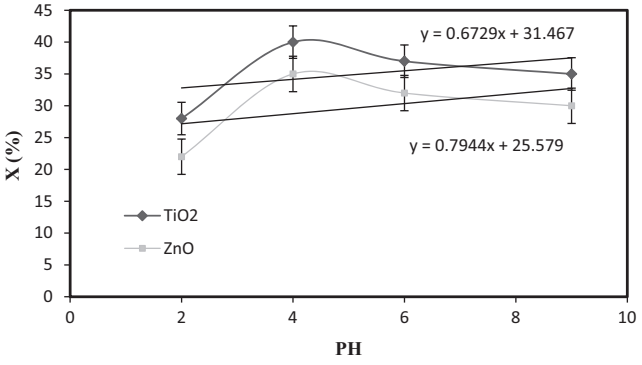

Fig. 7 – Effect of pH on degradation of wastewater at $[TiO_2] = 1.2$ g/l, $[ZnO] = 0.8$ g/l, $T = 35\,°C$ and reaction time 120 min.

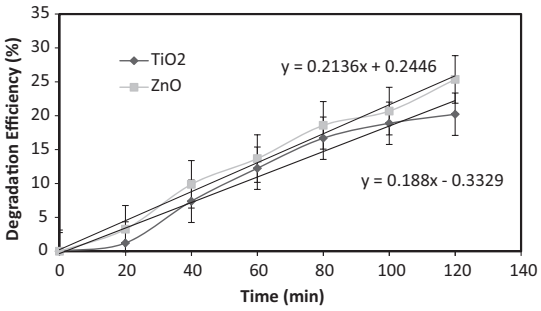

Fig. 8 – Effect of pH on degradation of wastewater by TiO_2/H_2O_2.

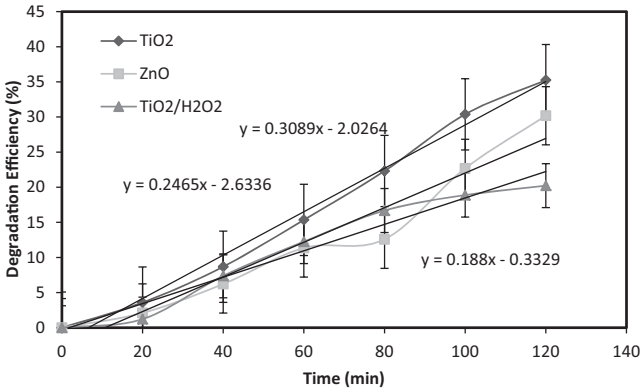

Fig. 9 – Performance of catalyst at constant pH of 9.0.

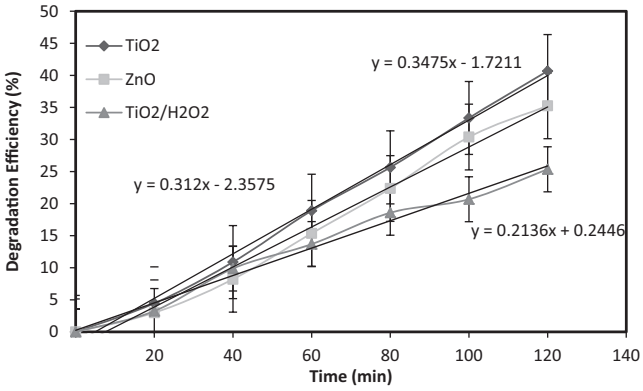

Fig. 10 – Performance of catalyst at constant pH of 4.0.

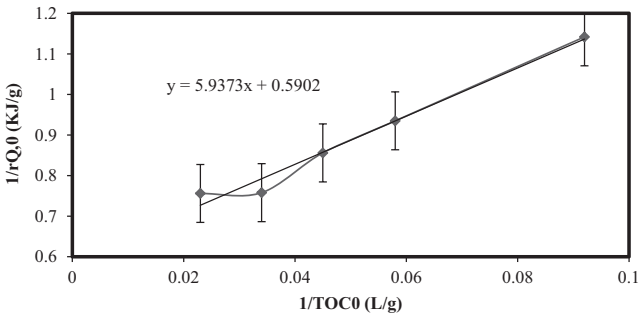

Fig. 11 – A plot of $1/r_{Q,0}$ vs. $1/TOC_0$.

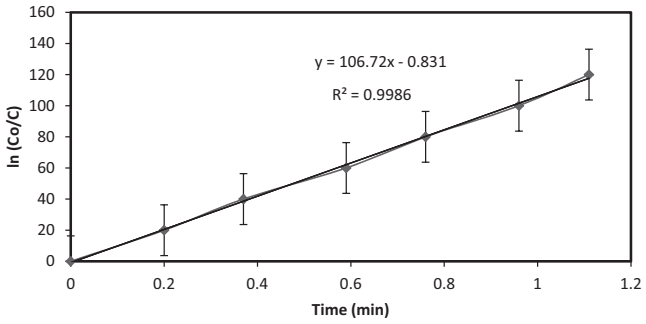

Fig. 12 – The linear regression analysis of degradation of refinery wastewater at pH 4.0 and temp. 37 °C.

catalyst can be discussed due to similar trend in COD removal efficiency. A 76% reduction in COD by TiO_2 at pH 6.5, and temperature 20 °C under 120 min of reaction time is reported by Javad and Fatemeh (2012). Another study of Fatemeh reports a maximum COD reduction of 83% by TiO_2 at pH 4 and temperature 45 °C under 120 min (Fatemeh et al., 2012). Saien and Nejati (2007) have founded 61% COD reduction at pH 7 and within 120 min reaction time. This trend is comparable to our findings. The effectiveness of TiO_2 was higher than ZnO at given pH and temperature. Reduced effectiveness of TiO_2 is due to high pH and lower reaction temperature. As shown in Fig. 4, a 5% increase in COD removal was obtained when pH was reduced to 4. The higher reactivity of TiO_2 is attributed to the geometry and working conditions of the photo reactor.

3.2. *Saturation effects of the catalyst*

Fig. 5 shows that with TiO_2 dosage up to 1.2 g/l, the degradation increases and then decreases gradually with increasing dosage. The similar effect is observed for ZnO. Fig. 6 shows that with ZnO dosage up to 0.8 g/l the degradation increases and then decreases gradually at 35 °C temperature and 120 min of reaction time. The linear regression shown in both Figs. 5 and 6 shows a gradual increase of degradation with an increase in catalyst dosage. This behavior (saturation effect) of the catalyst is not surprising and is in agreement with the findings of Saien et al. (2003) and Saien and Soleymani (2007). The similar results are reported by other researchers (Bickley et al., 2005; Mengyne et al., 1995; Rideh et al., 1997). Among various reasons for deviation from linearity at high dosage, the more convincing reason is the level of turbidity of the waste water due to aggregation of free catalyst particles causing excessive opacity of the wastewater (Mehrotra et al., 2003; Heredia et al., 2001). It can be assumed that the absorption of UV light by catalyst particles and catalyst surface are limiting the photons absorption within the reactor. The optimum concentration of TiO_2 and ZnO in this study was 1.2 and 0.8 g/l respectively, which is far less than the range reported by Alhakimi et al. (2003a,b). The saturation level of TiO_2 under given operating conditions is lower than ZnO.

3.3. *Effect of pH*

It is known that the surface of the catalyst can assume different ionization states and affect the extent of adsorption. The pH of waste water affects the surface of catalyst by protonation or deprotonation. The effects of varying pH from 2 to 9 are presented in Fig. 7 at 35 °C and 120 min reaction time. The maximum degradation of waste water by both catalysts (TiO_2 and ZnO) was obtained at pH of 4. The point zero charge (PZC) for TiO_2 is determined by Pelizzetti et al. (1993) and Hoffman et al. (1995) as 6.25 and 6.28 (Alaton et al., 2002). The adsorption of anions is favored when $pH < pH_{(zpc)}$. The effects of pH on degradation efficiency in this study are in agreement with findings of other researchers. The point zero charge of ZnO is reported as 8 (Selvam et al., 2007). The maximum adsorption was observed at pH of 4 for ZnO too; the surface of ZnO catalyst is also positively charged, hence, the maximum degradation occurs, which is in agreement of reported values in literature (Selvam et al., 2005). It is clear from this study that an acidic medium can also favor degradation. The higher efficiency in degradation is due to strong adsorption from electrostatic attraction between the cationic catalysts and dianionic pollutants in wastewater.

The effect of pH on degradation of refinery wastewater by TiO_2/H_2O_2 is shown in Fig. 8. The maximum COD reduction achieved within 120 min of irradiation time, at pH 4.2 was about 23.35%. Adeyinka used alum with 30% solution of H_2O_2 and found 45.83% reduction in COD at pH 8 (Adeyinka and Rim-Rukeh, 1999). More than 70% COD removal rate was found by Fenton's reagent ($Fe^{2+}/H_2O_2/UV$) coupled with UV source at more or less similar conditions but using real wastewater from a car-wash facility (Maha et al., 2009). A 21% COD reduction is reported by Coelho with advance oxidation process under 60 min of reaction time (Coelho et al., 2006). Santos found the use of H_2O_2 ineffective and degradation decreases as pH value tends to neutrality due to consumption of generated OH radical H_2O_2 (Santos et al., 2006) via Eqs. (2) and (3).

$$H_2O_2 + {}^{-}OH \rightarrow H_2O + HO_2 \quad (2)$$

$$HO_2 + {}^{-}OH \rightarrow H_2O + O_2 \quad (3)$$

The current study suggests that the use of TiO_2/H_2O_2 is more effective in COD removal under acidic environment if coupled with optimized dosage of the catalyst.

The performance of catalyst at constant pH of 9 and 4 is shown in Figs. 9 and 10, respectively. At both pH and COD reduction was higher by TiO_2 alone. However, the highest reduction of 40.68% by TiO_2 was achieved at low pH of 4. The maximum COD removal achieved at pH around 3 is also reported by Javad and Fatemeh (2012). The findings of this study support the argument that TiO_2 has an amphoteric character and adsorption of the anions is favored under conditions when pH is less than pH of zero point of charge. Hence, under low pH the adsorption of anions, reduces the chance of adsorption of organic material into catalyst surface and the rate of oxidation is reduced. Moreover, the generation of OH radical via Eqs. (2) and (3) by UV-light on the catalyst is another factor in increasing the reaction rate at low pH.

3.4. *Effect of reaction time*

A linear relationship 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 the intermediates are further degraded to CO_2 and H_2O (Fatemeh et al., 2012). The reaction rate attains a maximum value at a very low 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 acidic environment (Chen et al., 2001). The maximum COD

Table 3 – Multiple linear regression analysis and ANOVA results from the data of zinc oxide.

	Coefficient estimate	Standard error	Sum of square (SS)	Mean square (MS)	*p* value
X (%)	0.133	0.055	0.031	0.006	0.135
A	−0.041	0.044	34.833	6.967	0.457
B	−0.222	0.250	1.073	0.215	0.467
C	0.004	0.001	15,533.333	3106.667	0.062

removal efficiency in 120 min was obtained at pH of 4, which corresponds with the findings of Saien and Nejati (2007).

3.5. *Kinetic analysis*

3.5.1. *Mathematical empirical model*

The Design Expert Software, Version 6.0.6, was used for data analysis. As all the experiments were performed at constant temperature, the three most important system variables were pH (A), catalyst dosage (B) and reaction time (C) for optimum removal of TCOD using response surface methodology (discoloration of waste water) with TiO_2 and ZnO catalyst particles. The same approach in modeling is used by Fatemeh et al. (2012) and others (Sun et al., 2008; Tanaka et al., 2000; Luenloi et al., 2010). The coefficients of the polynomial model were calculated using the following equation (Fatemeh et al., 2012; Khuri and Cornell, 1996).

$$Y = \beta_0 + \beta_i X_i + \beta_j X_j + \beta_{ii} X_i^2 + \beta_{jj} X_j^2 + \beta_{ij} X_i X_j + \cdots \quad (4)$$

where *i* and *j* are the linear, and quadratic coefficients, respectively, β is the regression coefficient and the goodness of the fit was expressed by the coefficient of determination R^2 (0.9986), and its statistical significance by probability value. The *p*-values for *A*, *B* and *C*, shown in Table 3 (for ZnO) and Table 4 (for TiO_2) range from 0.107 to 0.720 for titanium dioxide and 0.062–0.467 for zinc oxide. The *p*-values for ZnO indicate that reaction time is a significant variable and pH and catalyst dosage are not significant. In the case of TiO_2, pH is significant and catalyst dosage and reaction time are not significant. The Design Expert Software was found capable of predicting the values of three design variables. There was deviation (6–10%) in predicted values from experimental values. The fitting of the data to linear and quadratic model and their analysis of variance (ANOVA) was adequate and indicated that photo-catalytic degradation of waste water can be described with quadratic polynomial model. The goodness of the fit of the model (R^2) for the given range of the variables was adequate to high (91–99%). The fitting of the variables with an acceptable variance range implies that the empirical model proposed and the constant variance assumptions are confirmed.

3.6. *Langmuir–Hinshelwood (L–H) kinetic model*

The discoloration of wastewater can also be described by discoloration kinetics UV–vis analysis and TOC degradation. The process can be described by the following equation.

$$r = -\frac{dC}{dt} = K_{disp.} C \quad (5)$$

where $K_{disp.}$ is reaction rate constant, and *C*, the concentration of pollutants in the sampled waste water, when $t > 0$. Integration of Eq. (5) leads to a linear plot of $\ln(C_0/C)$ versus *t* with a slope of $K_{disp.}$, the rate constant (Eq. (6)).

$$\ln\left(\frac{C_0}{C}\right) = K_{disp.} t \quad (6)$$

where C_0, initial concentration of waste water and *t*, is irradiation time. The disappearance of the color in waste water can be linked to the disappearance of the organic compounds (pollutants) in the waste water during photo-catalytic treatment. Many researchers (Ghanem et al., 2006; Tanaka et al., 2000; Saquib and Muneer, 2003) have reported for textile waste water that disappearance of organic compounds have higher rate than degradation of total organic carbon (TOC). The experimental data of this study were fitted to L–H kinetic model (Eq. (7)) that is widely used for solid-liquid reactions (Tang and An, 1995). The main assumption in this model is the rapid adsorption of the pollutants on the surface prior to photo-catalytic reaction.

$$r = -\frac{dTOC}{dQ_{uv}} = \frac{(kK \times TOC)}{(1 + K \times TOC)} \quad (7)$$

where *r* degradation rate of the waste water (mg k/J); Q_{uv}, total UV energy (kJ/l); TOC, total organic carbon ($mg\,l^{-1}$); *k* reaction rate constant (mg k/J); and *K*, adsorption coefficient (l/mg).

Fig. 11 shows the curve for inverse of the initial rate of reaction ($r_{Q,0}$) as a function of $1/TOC_0$. Where, TOC_0, is initial total organic carbon ($mg\,l^{-1}$). Since reaction rate constant is a zero-order constant thus Eq. (8) can be derived from Eq. (7).

$$\frac{1}{r_{Q.0}} = \left(\frac{1}{k}\right) + \left(\frac{1}{k \times K \times TOC_0}\right) \quad (8)$$

The plot of Fig. 11 enables us to determine the relationship between adsorption constant and degradation rate. This figure suggests that the initial rate increases with increasing initial TOC until TOC_0 is 1.2 g/l and reaction rate becomes constant. This finding implies that high adsorption capacity is associated with the occurrence of photo-catalytic degradation process on the interface of the solid photo-catalyst and waste water. The model further suggests that at high

Table 4 – Multiple linear regression analysis and ANOVA results from the data of titanium dioxide.

	Coefficient estimate	Standard error	Sum of square (SS)	Mean square (MS)	*p* value
X (%)	0.139	0.129	0.036	0.007	0.393
A	−0.071	0.025	34.833	6.967	0.107
B	−0.153	0.371	2.453	0.491	0.720
C	0.006	0.005	15,533.333	3106.667	0.305

TOC_0, all catalytic sites are occupied, and 1.2 g/l TiO_2 is the optimum amount for maximum degradation. The same approach is used by Ghanem et al. (2009) in optimizing the flow rate of waste water for degradation of commercial textile azo dyes.

The kinetics of degradation of refinery wastewater with TiO_2 at pH 4 is shown in Fig. 12. The plotted data produced a straight line that indicates that the degradation of the refinery wastewater can be described by the following first-order kinetic model equation.

$$\ln\left(\frac{TCOD_0}{TCOD}\right) = kt \quad (9)$$

where $TCOD_0$ is the initial TCOD value. The linear regression analysis for correlation constants for $R^2 = 0.9986$ for TiO_2. The value of determination coefficient R^2 clearly indicates that first-order kinetics with reasonable precision exists. These results are very close to the findings of Fatemeh et al. (2012). More precise rate of reaction can be calculated if effects of photon absorption are included to the kinetic model equation.

4. Refinery wastewater

The composition of refinery wastewater is complex and may contain different types of organic pollutants. The refinery wastewater for investigation by researchers during last two decades varied in composition. However, oil and grease, ammonia, phenols, sulphides, trichloroethylene, toluene, furfural, dodecane, oxalic acid, and benzoic acid were among the common pollutants. A number of researchers used synthesized wastewater including effluent from a car-wash facility near a refinery. Most of the effluents were not analyzed for identification of organic pollutants using GC/MS except Javad and Fatemeh (2012) who report that their pretreated wastewater consisted of methyl-tetrabutyl ether, phenol, 2,3,5,6-tetramethylphenol, naphthalene, xylene, tetradecane, 4-chloro-3-methylphenol, and 3-tert-butylphenol. For this type of wastewater, a maximum degradation of 78% was achieved (Javad and Fatemeh, 2012). All above mentioned pollutants were degraded with high efficiency. It is well known that photo-catalytic degradation can completely mineralize refinery 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 photo-catalytic wastewater technology, several key parameters like catalyst development, reactor design and process optimization need to be further investigated.

5. Conclusions

Titanium dioxide, zinc oxide, and TiO_2/H_2O_2 are effective catalysts in photo-catalytic degradation of real refinery wastewater. The maximum degradation achieved was 40.68% by using TiO_2 at 35 °C and pH of 4, within 120 min of irradiations. At pH of 9.13 the degradation decreased to 32.25%. The degradation at lower pH supports the notion that pH is one of the most important operating parameter that affect the photo-catalytic reactivity of the catalyst. When TiO_2 was combined with H_2O_2 the maximum degradation was about 25.35% at pH 4.2. A higher reaction rate was found for titanium dioxide. The results indicate that for real refinery wastewater, TiO_2 is comparatively more effective than ZnO and H_2O_2. The experiments indicated that first-order kinetics can successfully describe the photo-catalytic reaction. The ANOVA results for the model showed satisfactory and reasonable adjustment of the second-order regression model with the experimental data. The ANOVA results also showed that pH is significant than reaction time and catalyst dosage of TiO_2; and in case of ZnO, reaction time is significant than pH and catalyst dosage. This study demonstrates that real refinery wastewater reacts differently to catalysts that synthetic refinery wastewater, oil field produces water or oil water industrial effluent.

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