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Photocatalytic degradation of 2, 2, 4 trimethyl pentane (isooctane) in aqueous solution

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ABSTRACT

This work deals with photocatalytic degradation of 2, 2, 4 – trimethyl pentane (isooctane) in batch slurry photo-reactor using solar radiation. The effect of various parameters such as pH, initial concentration of pollutant, catalyst dose, oxidant, and time variation were studied. The determination of the best catalyst was studied amongst the four catalysts (TiO_2, ZnO, PSA and SSA) used. The kinetics of degradation of isooctane was also studied. The results show that TiO_2 was the best catalyst with a degradation rate of 57%. Also, the optimum conditions for the degradation of the isooctane were; 50mg/L of initial concentration, pH 8 and catalyst dose of 4.0g/l. The kinetics analysis for the degradation of isooctane reveals that it follows pseudo – first- order reaction kinetics. The Langmuir – Hinshelwood model shows a better fitting with reaction rate and adsorption equilibrium constants of 3.0 mg/L.h and 1.53 $\times 10^{-3}$ L/mg respectively and the regression was 0.979.Finally adsorption equilibrium isotherms study shows that degradation of isooctane pentane fits both Langmuir isotherm and Freundlich isotherm with maximum adsorption capacity of 18.12 mg/g and n = 2.26 respectively.

Keywords: Photocatalysis;2, 2, 4 Trimethyl Pentane(Isooctane);TiO_2catalyst; Adsorption

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1. INTRODUCTION

Photocatalysis has been proposedas an alternative for the treatment of organic pollutants in recent years as it is an attractive technique for the complete destruction of undesirable contaminants (pollutants) in liquid phase by using artificial light or solar illumination (Zhao et al., 1998). It is a natural phenomenon in which a substance, termed the photo catalyzer, alters the speed of a chemical reaction through the action of light. By exploiting the energy of light, photo catalyzers induce the formation of strongly oxidizing reagents which can cause the decomposition of some organic and inorganic substances present in the water (Blanco et al., 2003). The advantages of photocatalysis include low operation temperature, low cost and significantly low energy consumption. These factors have led to the relevant application of photocatalysis to the stage of commercialization (Chao et al., 2002). Photocatalytic processes are based on the generation of hydroxyl radicals HO• (Okamoto et al., 1985; Serpone, 1996). The pollutant, isooctane is a colourless liquid with the odour of gasoline; it is also one of two chemicals used in establishing the octane rating for gasoline. The octane value is a number that reflects the resistance of a gasoline mixture to knocking when used as fuel in an internal combustion engine. The source of isooctane is mainly from the production of petroleum products, it is also an organic pollutant that is very toxic and is easily found in the environment. Therefore, the photo degradation of 2, 2, 4 trimethyl pentane (isooctane) as the target compound in this study can not only provide useful information for the treatment of isooctane but also be viewed as the primary method of inquiry for dealing with complicated organic pollutants. Many examples of complete photo-oxidation of organic compounds have been reported. The photocatalytic degradation of some organics both in TiO_2 aqueous suspensions and over immobilized TiO_2 thin films has been studied (Matthews et al., 1990). In most of the above studies, Langmuir–Hinshelwood model was used to describethe degradation rate expressions in terms of the disappearance of compounds or the formation of CO_2 (Pelizzetti et al., 1987). It has been demonstrated that catalyst dosage, initial concentration of pollutants, effect of hydrogen peroxide, and pH of the solution are the main parameters affecting the degradation rate. It is well known that kinetic modelling of the photocatalytic process is essential to any practical applications (Prudenet al., 1983). The objective of this study is to degrade isooctaneusing solar radiation and different catalyst such as TiO_2, ZnO, Periwinkle shell and Snail shell ashes, to know the best catalyst for this study. In this study, analysis was conducted to know the effects of operational parameters such as pH, initial concentration, oxidant, catalyst dose, on the degradation rate. The adsorption of isooctane is further evaluated by the common isotherms (e.g., Langmuir, Freundlich isotherms) and kinetic models (e.g., Langmuir – Hinshelwood, pseudo – first – order, pseudo – second – order).

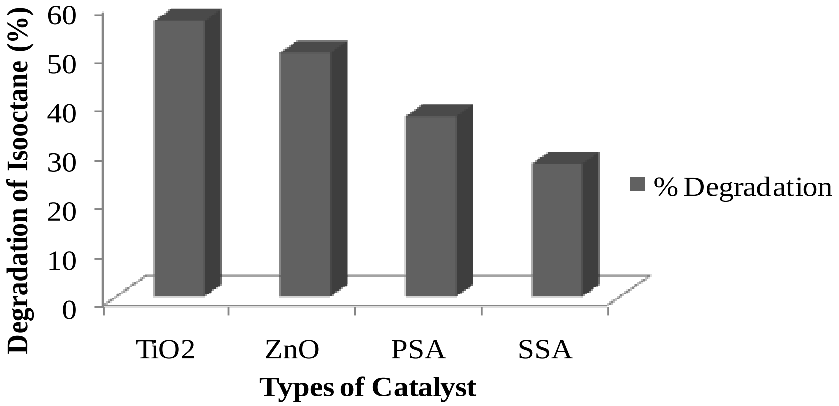

Figure 1

Percentage degradation of isooctane using different catalysts

2. MATERIALS AND METHODS

2.1. Materials

The photocatalyst TiO_2 P-25 (mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30, ZnO grade material 99% purity (Emory), was procured from Whosco Ventures Nigeria Limited. Periwinkle shell and snail shell ashes were prepared in the laboratory. Isooctane compound was purchased from Stanvac, hydrogen peroxide, (0.1, 1M) HCl and NaOH were obtained from Stanvac, and distilled water was also used.

2.2. Methods

The photocatalytic tests were conducted using the batch slurry system under light condition, it was carried out in order to evaluate the adsorption of isooctane on the surface of the four catalysts (TiO_2, ZnO, periwinkle shell and snail shell ashes),and so as to obtain the most efficient catalyst needed for the study. Analysis involving fundamental parameters such as catalyst dosage, oxidant, pH, time variation and different initial concentrations of isooctane were also studied.

2.2.1. Determination of the best catalyst

100ml of the 200mg/L solution was taken and put into four conical flasks of 250ml, was added 5g the optimum amount of different catalysts (TiO_2, ZnO, periwinkle shell and snail shell ashes) into each of the conical flasks and shaken for 2hrs in the sun with an orbital shaker. The catalysts were filtered from the sample by Whattman filter paper (0.7µm) was then analyzed using UV – Vis spectrophotometer.

2.2.2. Effect of Catalyst dose

250ml of 200mg/L isooctane solutions was placed in six conical flasks with various catalyst doses of 2.0 – 12.0g/L of TiO_2 and shaken under the sun for 1h. The samples arefiltered and analyzed with UV spectrophotometer to obtain optimum catalyst dose.

2.2.3. Effect of initial concentration of Isooctane

200ml of 50 – 300mg/L of isooctane concentration were placed in six conical flasks and 4.0g/L titanium dioxide (TiO_2) was added to each solution and exposed to the sun for a period of 1hr and analyzed to obtain optimum concentration.

2.2.4. Effect of pH

100ml of 50mg/L (best concentration) was placed in six conical flasks whose pH was adjusted using 0.5M HCL and 0.1M NaOH solution and then measured with pH meter. The pH values were varied from 2.0 – 12.0 and the samples were shaken under the sun for 2hrs filtered and analyzed to obtain optimum pH for best degradation rate.

2.2.5. Effect of oxidant (H_2O_2)

100ml of 50mg/L (best concentration) was placed in six conical flasks with catalyst dose of 4.0g/l TiO_2, at a pH of 8.0 and different volumes of hydrogen peroxide(2 – 12ml). Samples were analyzed to evaluate the effect of oxidant on photo degradation. Each of these samples was also placed on an orbital shaker, shaken for a period of 2 hrs. to allow equilibrium to be reached, then filtered and analyzed with UV spectrophotometer.

2.2.6. Effect of Exposure time

200ml of 50mg/L (best concentration) was placed in one conical flask adjusted to a pH of 8.0 (optimum pH) and fixed catalyst dose of 4.0g/L and placed on an orbital shaker. The sample was shaken under the sun for 2 hrs. with an interval of 20mins for 10ml of sample to be withdrawn with a syringe, filtered and analyzed using UV spectrophotometer.

2.2.7. Photocatalytic Degradation using solar radiation

In the analysis investigating photocatalytic degradation, TiO_2 was used as photocatalyst because it was found to be the best among the other catalysts with a percentage degradation of 57%.In the analysis using solar radiation,200ml of varying concentration (50 - 300 mg/L) of isooctane adjusted to a pH of 8.0 were placed in six conical flasks and 4.0g/l titanium dioxide (TiO_2) was added to each solution and place on an orbital shaker. All samples were shaken with a regulated speed of175 rev/min under the sun to allow the penetration of light for a period of 2hrs.with an interval of 20 min for 10ml of the sample to be taken with syringe, filtered with Whattman filter paper (0.7µm)and analyzed with UV spectrophotometer with a wavelength of 246nm.

2.3. Analysis

In using the UV spectrophotometer, it was switch on for at least 20mins to enable it warm up properly. After then, it was turn to the UV mode and the wavelength was adjusted to 246nm. A blank solution of 50% ethanol was prepared for zero checking the reading of the UV spectrophotometer. Then the filtered isooctane solution was poured into thoroughly washed glass Cuvette to at least 2/3 of its total height. One Cuvette is filled with the reference compound and the other one with the compound (ethanol) whose absorbance has to be measured at λ max. The Cuvette was placed in the Cuvette chamber inside the UV machine and was closed. Then, the absorbance reading was displayed on the screen and it was recorded. To get the relationship between concentration and absorbance of the compound, a calibration curve is made. Calibration solutions are

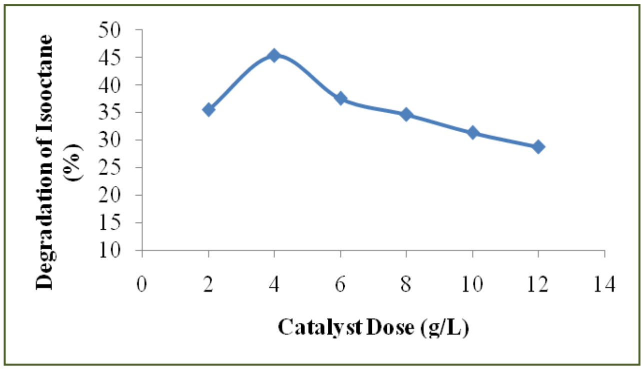

Figure 2

Percentage degradation of isooctane for varied catalyst dose (TiO_2)

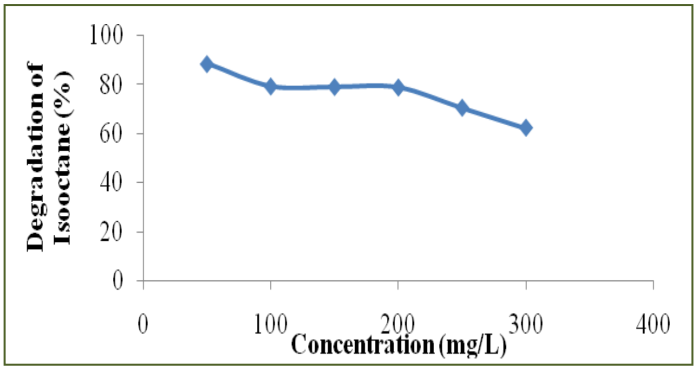

Figure 3

Percentage degradation of isooctane for varied initial concentration using TiO_2 catalyst dose of 4.0g/L

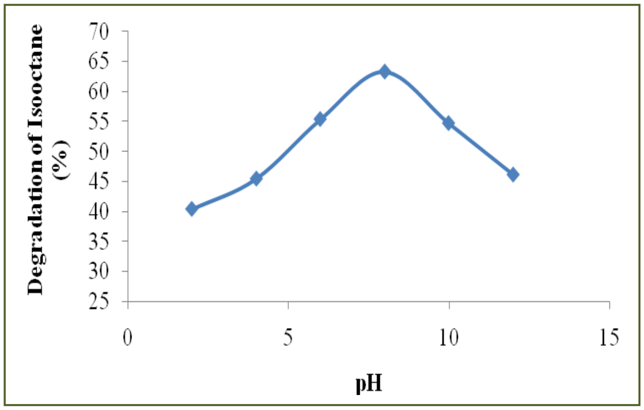

Figure 4

Effect of initial pH on photocatalytic degradation of isooctane for the Conc. = 50mg/L TiO_2 = 4.0g/L

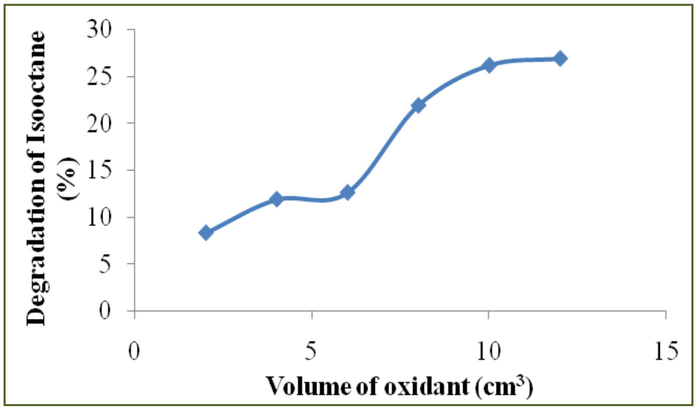

Figure 5

Percentage degradation for varing volume of oxidant (H_2O_2) using TiO_2 Catalyst

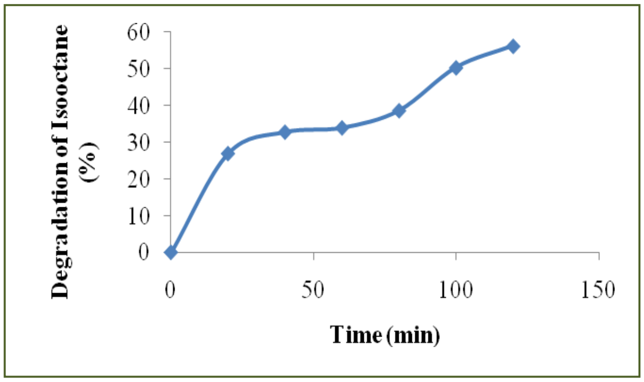

Figure 6

Percentage degradation of isooctane at pH 8.0 for varied time using TiO_2 catalyst dose of 4.0g/L

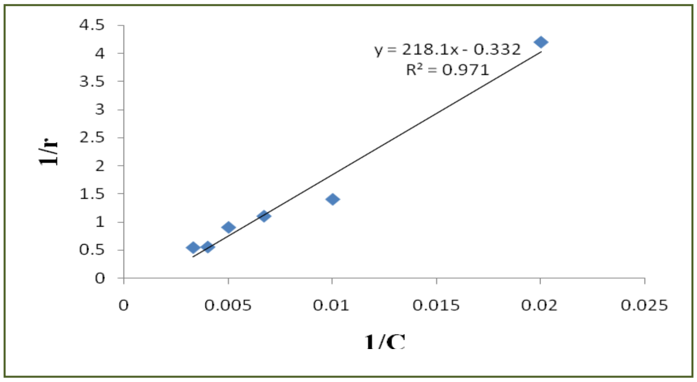

Figure 7

Langmuir – Hinshelwood model for the photodegradationofisooctane using TiO_2 catalyst

made from standard solutions of known concentration. The absorbance is plotted against known concentration of the samples. This standard curve is used to calculate the value of concentration of unknown sample from the absorbance reading. This was repeated for each of the filtered sample taken after time t and the results recorded.

3. RESULTS AND DISCUSSION

3.1. Effect of Catalyst Type

The catalyst efficiency of TiO_2, ZnO, PSA and SSA was 57%, 50%, 37% and 27.3% respectively. As a result the rate of degradation of isooctane was observed to be decreasing; this tells that UV from the sun increased the rate of degradation of isooctane. TiO_2 was the best catalyst compare to the other catalysts. In the case of the commercial and the local catalysts, the commercial catalysts (TiO_2, ZnO), the rate of degradation using TiO_2 was higher than ZnO and for the local catalyst (PSA, SSA), PSA was more effective than SSA (Figure 1).

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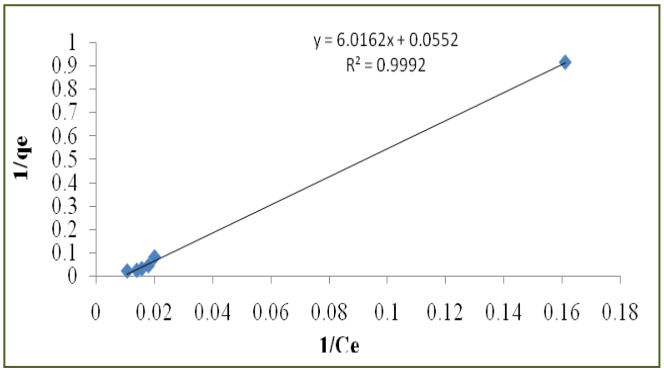

Figure 8

Langmuir Isotherm

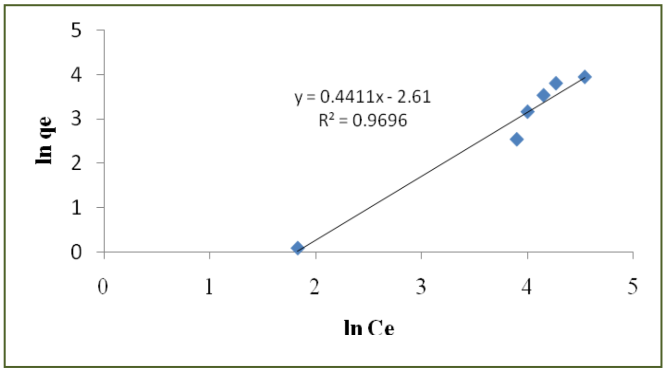

Figure 9

Freundlich Isotherm

3.2. Effect of Catalyst dosage

Photocatalyst (TiO_2) dosage was varied from 2.0g/l to 12g/l during reactions for studying the isooctane degradation rate at different concentrations. It was observed that degradation rate of isooctane increases with increased catalyst dose and becomes constant above a certain level as shown in (Figure 2) and after one particular optimize dose the degradation rate of the isooctane starts to decrease. The reasons for this decrease in degradation rate are:

(i) Aggregation of TiO_2 particles at high concentrations causing a decrease in the number of surface active sites and

(ii) Decrease in opacity and light scattering of TiO_2 particles at high concentration. Therefore the optimum dose at which the highest degradation was observed was 4g/l

3.3. Effect of Initial Concentration

Initial concentration was varied from 50 – 300mg/L, at constant catalyst dose of 4g/L. It was observed from the graph (Figure 3) that increasing concentration of compound solution from 50 – 300mg/L decreases the percentage degradation rate and it was found that at 50mg/L concentration, degradation was 88.3% at 246nm and for 300mg/L compound concentration, percentage degradation was reduced to 62.2% at 246nm. The reason behind this behaviour may be due to the increase in the extent of adsorption on the catalytic surface at reference compound concentration which reduces the catalytic activity of TiO_2. The increases in the isooctane solution concentration also decrease the path length of photon entering into the solution. Therefore 50mg/L was the optimal concentration with a percentage degradation of 88.3%.

3.4. Effect of pH

The pH was varied from 2–12.The result shown in Figure 4 indicates that degradation of the increases with an increase in solution pH from 2 to a range of 8, and then led to a drastic decrease which result implies that the degradation of isooctane was favorable at alkaline conditions, and the optimum initial solution pH is 8(63.03%). This may be due to the fact that pH affects the state of reaction in solution and catalyst surface.

3.5. Effect of Oxidant (H_2O_2)

Another important data from these experiments is the effect of the addition of hydrogen peroxide. As can be seen in Figure 5, the addition of hydrogen peroxide has a positive effect on the degradation. The experiment was conducted by varying the hydrogen peroxide volume from 2.0 to 12 ml per 200ml of the isooctane sample. It was observed that the degradation of isooctane sample increased with increase oxidant, showing that the use of TiO_2 by added hydrogen peroxide molecules to generate hydroxylradicals is more effective for this photocatalyst.

3.6. Effect of Time Variation

Figure 6 shows the percentage degradation of isooctane at pH 8.0, and at 50mg/L concentration for varying time using TiO_2 catalyst dose of 4.0g/L. It can be clearly seen that under light radiation with increasing the time of irradiation up to 2h, the amount of isooctane evolved increased from 0 - 56.3% almost proportionally to the irradiation time in the investigated period. This is because with an increase in irradiation time the photons absorbed on the surface of the photocatalyst become greater which in turn helps in the photocatalytic process.

4. KINETICS AND MODELING OF PHOTOCATALYTIC PROCESS

The destruction rates of organics in photocatalytic oxidation have been modeled by different kinetic models. Langmuir-Hinshelwood (L-H) kinetics seems to describe many of the reactions fairly well. The rate of destruction is given by Eq.1:

$$\frac{-dC}{dt} = \frac{k1\ k2\ C}{(1+k2C)} \qquad 1$$

In the ideal case, for which the L-H model is derived, C is the bulk solute concentration, k1 the reaction rate constant, k_2 the equilibrium adsorption constant and t represents time. The L-H reaction rate constants are useful for comparing the reaction rate under different experimental conditions. Adsorption of organic substrate onto the catalyst can be modeled by mathematical models such as Langmuir and Freundlich model. The mathematical formulae of Langmuir and Freundlich models are shown in Eqn. (2) and (3) respectively; both equations can be rewritten into linear form as shown in Eqn. 4 and Eqn. 5 respectively.

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad 2$$

$$q_e = K_F C_e^{1/n} \qquad 3$$

Table 1
Linear regression analysis of kinetics of isooctane degradation

Conc. (mg/L)	Pseudo-first order		Pseudo - second order	
	-r= KC		-r = KC²	
	$\ln\frac{C_o}{C} = K_1 t$		$\frac{1}{C} - \frac{1}{C_0} = K_2 t$	
	$K_1 \times 10^{-3}$	r^2	$K_2 \times 10^{-5}$	r^2
50	142	0.766	1.0	0.694
100	48	0.991	70	0.926
150	59	0.869	70	0.809
200	54	0.927	60	0.904
250	73	0.986	70	0.974
300	61	0.989	50	0.973

Table 2
Reaction rate, Equilibrium constants and regression for isooctane using Titanium dioxide (TiO_2)

Equations	Reaction rate and adsorption equilibrium constants		Regression
$r = \frac{kK_{LH}}{1 + kK_{LH}}$	K_{LH} (mg/L.h)	k (L/mg)	r^2
$\frac{1}{r} = \frac{1}{kK_{LH}}\frac{1}{C} + \frac{1}{K_{LH}}$	3.00	1.53×10^{-3}	0.9715

Table 3
Equilibrium constants for the Pseudo first and second order model

Adsorption model	Pseudo-first-order		Pseudo-second-order	
Equation	$\frac{dq_t}{dt} = k_{e1}(q_e - q_t)$		$\frac{dq_t}{dt} = k_{e2}(q_e - q_t)^2$	
Linear form	$Ln\,(q_e - q_t) = Ln\,(q_e) - k_{e1}t$		$\frac{t}{q_t} = \frac{1}{k_{e2}q_e^2} + \frac{t}{q_e}$	
Plot	$Ln\,(q_e - q_t)$ against t		$\frac{t}{q_t}$ against t	
Conc. (mg/L)	k_{e1}	r^2	k_{e2}	r^2
50	0.0242	0.971	1.142	0.726
100	0.0071	0.814	0.255	0.013
150	0.01	0.921	0.536	0.777
200	0.014	0.900	0.547	0.815
SS250	0.0214	0.931	0.332	0.807
300	0.0194	0.943	0.289	0.558

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_L q_m} \quad 4$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad 5$$

Where
K_F = Freundlich constant for adsorption capacities (L/mg)
K_L = Langmuir constant (L/mg)
1/n = Freundlich exponent (surface heterogeneity)

4.1. Kinetics and Modeling

Table 2 shows the linear regression analysis of the kinetics of isooctanedegradation using photocatalysis. These results were used to analyze the rate of adsorption and possible adsorption mechanism of isooctane into TiO_2 catalyst using pseudo-first-order and pseudo-second-order models. From the Table 1, the first order regression range from 0.766 - 0.991 while that of second order from 0.694 – 0.974. Hence, pseudo first order gave a better regression. As a result, the photodegradation of isooctanefollows the Pseudo – first order.

4.2. Langmuir – Hinshelwood Model

The results confirm the Langmuir-Hinshelwood relationship and indicate that adsorption represents the initial step in the photocatalytic process. The k and K_{LH} values calculated from the slope of the straight line ($r^2 = 0.9715$) and from the ordinate were 1.53×10^{-3} L/mg and 3.00 mg/L.h respectively. Hence the value for adsorption is lesser than K_{LH} for reaction. This implies that degradation was basically as a result of reaction and the photocatalytic degradation of isooctane under optimized working conditions follows satisfactorily the Langmuir – Hinshelwood model. This explanation is similar to that reported by Guettaai et al. (2005).

4.3. Adsorption Isotherms

In order to evaluate the efficacy of the photodegradation procedure, the equilibrium adsorption of isooctanewas studied as a function of equilibrium concentration. Adsorption isotherms were studied to estimate the adsorption capacity (Figure 7). The adsorption process of isooctanewas tested with Langmuir and Freundlich isotherm models. Figure 8 shows the Langmuir Isotherm. From the plot, the maximal adsorption quantity (q_m) and the Langmuir adsorption constant (K_L) were found to be 18.12 mg/m² and 9.175× 10^{-3}L/mg respectively. Also, Figure 9 shows the Freundlich Isotherm. From the plot, the Freundlich adsorption constant (K_F) was found to be 0.07353 L/mg and n to be 2.26.This explanation is similar to that reported by Alina et al, (2011). The isotherm models gave good correlation coefficients with $r^2 \geq 0.999$. The applicability of the two isotherm models implies that both monolayer adsorption (that is only a limited number of surface sites are adsorbing sites for the isooctane molecules) and heterogeneous surface conditions exist under experimental conditions studied (Figure 10).

4.4. Adsorption Kinetic Modeling

Several Kinetic models are used to explain the adsorption mechanism. Pseudo – first order and Pseudo – second – order kinetics allow the computation of the first and second order constant, k_1 and k_2 and of linear regression correlation coefficient, r^2. From the table 3, it can be deduced that pseudo – first- order model fits the photodegradation of isooctane on TiO_2 catalyst withr^2range of 0.814 – 0.971 which is far better than the pseudo – second – order model with r^2range of 0.013 – 0.815 (Figure 11).

5. CONCLUSIONS

Photocatalytic process can efficiently degrade isooctane using sunlight radiation sources. The observations, clearly demonstrates the importance of choosing optimum degradation parameters to obtain high degradation rates which is most essential for any practical applications of photocatalytic oxidation processes. The optimum conditions for photo degradation of isooctane are 4g/L catalyst dose, 50mg/L concentration, and 8.0 pH. The photocatalytic degradation of isooctaneusing TiO_2 catalyst under solar radiation followed Langmuir-Hinshelwood kinetics with reaction rate and adsorption equilibrium constants of 3.00mg/L.min and 1.52 x 10^{-3}L/mg respectively. Also the Adsorption isotherm study shows that degradation of isooctane fit both Langmuir isotherm and Freundlich isotherm with maximum adsorption capacity of 18.12mg/g and n = 2.26 respectively. It also show that pseudo – first- order model fits the photodegradation of isooctane on TiO_2 catalyst withr^2range of 0.814 – 0.971 which is far better than the pseudo – second – order model with r^2range of 0.013 – 0.815.From the results so far, isooctane was seen to be a rapidly degrading organic compound.

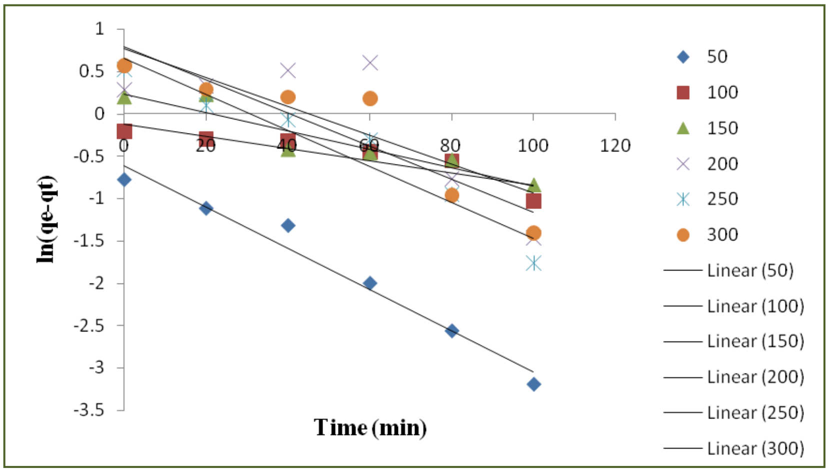

Figure 10

Pseudo – first – order reaction kinetics for isooctane adsorption on TiO_2 catalyst. Condition: pH 8.0, catalyst dosage 4g/L

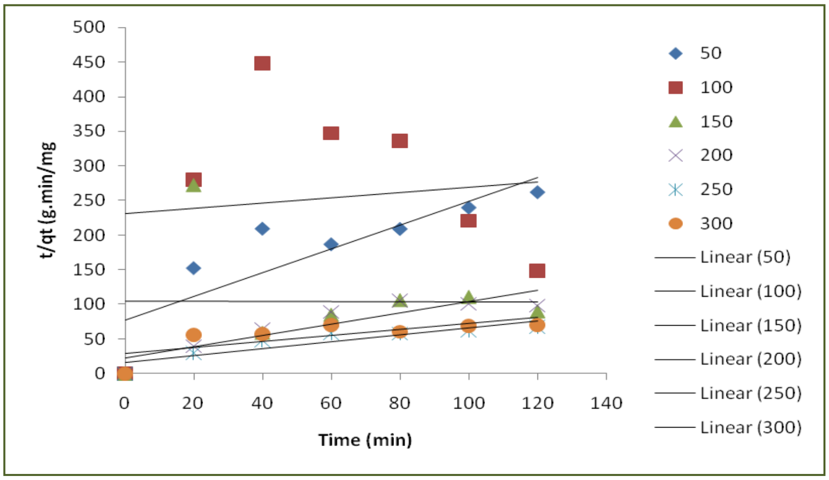

Figure 11

Pseudo – second – order reaction kinetics for isooctane adsorption on TiO_2 catalyst. Condition: pH 8.0, catalyst dosage 4g/L

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