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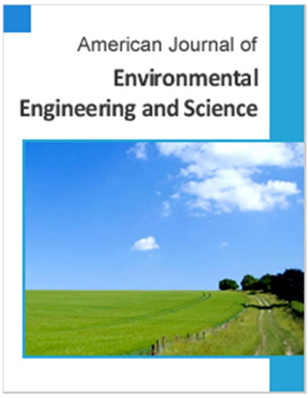

Photocatalytic Degradation of Ethylbenzene on Aqueous Solutions Using Titanium Dioxide as Catalyst

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Abstract

Photocatalysis is an effective treatment method for the removal of toxic pollutants from industrial wastewater. In this research work, the photocatalytic degradation of ethylbenzene was studied in a batch slurry system using solar radiation. Four catalysts; Titanium oxide and Zinc oxide (commercial catalysts), Periwinkle Shell Ash and Snail Shell Ash (local catalysts), were used for the study. The catalysts were used to determine the most efficient catalyst needed for the degradation of ethylbenzene from aqueous solutions using UV from sunlight. The effect of various parameters such as catalyst loading, initial substrate concentration, pH, Oxidants and time variation were studied. The results of the study showed that the difference in percentage degradation between the four catalysts was statistically significant (ANOVA, $p < 0.05$). Titanium oxide was the best catalyst having the highest percentage degradation of 50%. Langmuir–Adsorption Isotherm was used to test the experimental data. The optimum conditions for the degradation of ethylbenzene initial concentration was found to be 100mg/l, pH 6.0 and titanium oxide catalyst dose of 2.0g/l. According to experimental data, the photocatalytic degradation of etylbenzene follows Pseudo–first order kinetics with a regression range of 0.979-0.983.

1. Introduction

Water is one of the most important natural resources essential for sustaining of life on the planet. In the process of rapid industrialization and increase in human population, the demand for portable water is increasing. Huge amount of fresh water is used in different chemical process industries such as petroleum and petrochemical, organic and inorganic, pharmaceutical, dyes and pigments, fertilizer, chlor-alkali, paints, textile, pulp and paper industries (Vimal *et al.,* 2012). These chemical process industries generate a large amount of waste water containing toxic and complex pollutants. Water pollution is a major cause of concern in most of the countries such as Nigeria and other developing nations. Several methods of industrial wastewater degradation have been practiced across the globe (Abdullah *et al.,* 1990; Caliman *et al.,* 2002; Attaia *et al.,* 2008);

approximately 23% of the world's population live in developed countries, consume 78% of the resources and produce 82% of the waste products (Blanco *et al.,* 2003).

Photocatalysis is a promising technique, for photodegradation of various hazardous chemicals that are encountered in waste waters (Mills *et al.*, 1993). The great significance of this technique is that, it can detoxify various complex organic chemicals, which has not been addressed by several other methods of purification. The object of destructive oxidation process is to mineralize organic contaminants, i.e., convert them to carbon dioxide, water and to oxidize inorganic anions of any heteroatoms present. These processes frequently include the addition of oxidizing agent, such as hydrogen pereoxide and ozone in the presence of a catalyst or UV light. Hydroxyl radicals are known to be involved in most of these processes. Examples include UV/H_2O_2, Fenton's Reagent, UV/O_3, H_2O_2/O_3, O_3/pH, high energy radiation and photocatalytic oxidation.

In recent years, the TiO_2 catalyzed photocatalytic degradation in the presence of UV and oxygen has attracted attention of researchers for remediation of hazardous pollutants in water. The advantages of photocatalytic degradation over conventional treatment techniques are degradation of a broad range of organic pollutants, lower cost, and mild operating conditions (Mills *et al.,* 1993). The aims of this study is to investigate the photocatalytic degradation of model organic compound; ethylbenzene which is a persistent non-biodegradable pollutant in the presence of UV light, determine the best catalyst to use for the degradation process and investigate the effect of catalyst dose (TiO_2), initial substrate concentration, oxidant (H_2O_2), pH variation, time variation, and identify the kinetics of the photocatalytic reaction.

2. Materials and Methods

2.1. Preparation and Characterisation of Catalysts

The photocatalysts employed in this study were titanium dioxide (TiO_2), Zinc oxide (ZnO), Periwinkle shell ash, and Snail shell ash. Titanium dioxide and zinc oxide were obtained from Bamidele Ibeh (Nig) Enterprises, shop 3 Uniben shopping centre, University of Benin, Nigeria. Ethylbenzene was obtained from STANVAC laboratory, 78 New Lagos Road, Benin City, Edo State, Nigeria. TiO2 and ZnO were without further purification. Other chemicals used were of analytical grade and used as such without further purification. The water used in all the experiments was distilled water. Periwinkle shells and Snail shells were obtained from the department of Chemical Engineering, University of Benin, Nigeria. The shells were washed and dried in an oven at a temperature of 110°C to a constant mass. The shells were calcined at 600°C in a muffle furnace, and were crushed, sieved to obtain fine particle size (L350mm). The Periwinkle shell ash was tagged (PSA), while the Snail shell ash was tagged (SSA).

2.2. Determination of the Best Catalyst

To determine the best catalyst, 50ml of 200mg/l of ethylbenzene was measured in a measuring cylinder and put into four conical flask of 250ml. 5g of the four catalysts (TiO_2, ZnO, PSA, and SSA) was measured using the analytical weighing balance into each of the conical flask, and shake for 2 hours in the sun on an Orbital shaker. About 10ml of the samples were withdrawn in an interval of 20mins. The samples were filtered, and analyze for their concentrations using the UV/Vis spectrophotometer and calculated for:

The quantity of catalyst $({}^{x}/_{m}) = (\frac{Co-Ci}{M})$v

Or

$$\% \text{ degradation for catalyst} = (\frac{Co-Ci}{Co}) \text{ x } 100 \tag{1}$$

Where;

x/m (mg/g) is the amount of ethylbenzene absorbed onto the photocatalyst at equilibrium.

Co (mg/l) is the initial concentration before irradiation by sunlight.

Ci (mg/l) is the final concentration.

M (g) is the mass of catalyst.

V (l) is the volume of standard solution.

2.3. Photocatalytic Degradation Using TiO_2

Heterogeneous photocatalysis is a technology based on the irradiation of a catalyst, usually a semiconductor, which may be photoecited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidizing sites), providing great scope as redox reagents. Heterogeneous photocatalysis can be carried out in aqueous solutions, gas phase or pure organic liquid phases. The overall process of heterogeneous photocatalysis can be explained by five basic steps;

(i) Transfer of the reactants in the fluid phase to the surface of photocatalyst.

(ii) Adsorption of at least one or more reactants on the surface.

(iii) Reaction in the adsorbed phase.

(iv) Desorption of the product/products.

(v) Removal of the products from the interphase.

The photocatalytic reaction occurs in the adsorbed phase. The only difference between the conventional catalysis and photocatalysis is the mode of activation energy. In the photocatalysis, thermal activation energy is replaced by the photonic activation.

2.4. Mechanism of Photocatalytic Oxidation

Fig. 1 presents the schematic of photocatalytic oxidation using TiO_2 as the photocatalyst. During the photocatalytic oxidation, the most important step of photoreaction is the formation of hole-electron pairs which need energy to overcome the band gap between the valence band (VB) and conduction band (CB) (Hufschmidt *et al.,* 2004). When the photon energy is equal to or greater than the band gap energy

(Eg) of the semiconductor (3.2 eV for anatase phase titanium dioxide) which are incidents upon its surface semiconductor, the electron-hole pairs are created in the semiconductor, dissociating into free photoelectrons in the conduction band and photoholes in the valence band, respectively. Simultaneously, the photo-oxidation and reduction reactions occur in the presence of air, oxygen and pollutant molecules. During the reactions, the hydroxyl radical (OH), coming from the oxidation of adsorbed water or OH−, is highly reactive. In addition, the reducing power of the electrons can induce the reduction of molecular oxygen (O_2) to superoxide O^-_2. The highly reactive species OH and O^-_2 show strong ability to degrade microorganisms (Kikuch *et al.*, 1997; Agrios *et al.*, 2005) as well as organic (Agrios *et al.*, 2005; Demeestere *et al.*, 2007) and inorganic pollutants (Demeestere *et al.*, 2007; Toma *et al.*, 2004). TiO_2 photocatalysis is capable of destroying many organic contaminants completely (Cao *et al.*, 1999; Gaya *et. al.*, 2008; Hoffmann *et al.,* 1995). A photo-excited TiO_2 generates an electron (e^-) and hole (h^+) when photon energy equal to or greater than the band gap of the semiconductor (3.2 eV for anatase phase titanium dioxide) are incidents upon its surface as shown in Fig. 1.

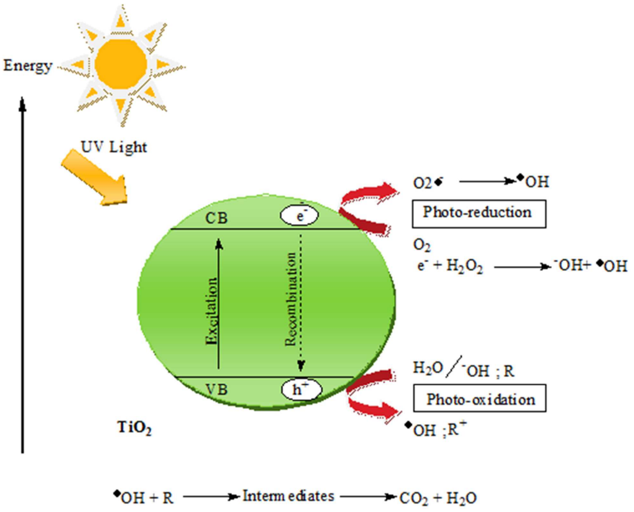

Fig. 1. *Irradiated TiO_2 Semi-Conductor Particle.*

$$TiO_{2\,+}\,hv \rightarrow e^- + h^+ \qquad (2)$$

Electron transfer from the adsorbed substrate (RX_{ad}), adsorbed water or the OH_{ad} ion, to the electron-hole.

$$h^+ + RX_{ad} \rightarrow RX^+_{ad} \qquad (3)$$

$$h^+ + H_2O_{ad} \rightarrow {}^\bullet OH_{ad} + H^+ \qquad (4)$$

$$h^+ + OH^-_{ad} \rightarrow {}^\bullet OH_{ad} \qquad (5)$$

The third step is due to high concentration of OH $^-$, water dissociates into ions.

$$H_2O \rightarrow OH^-_{ad} + H^+ \qquad (6)$$

Molecular oxygen (O_2) acts as an acceptor species in the electron-transfer reaction.

$$e^- + O_2 \rightarrow O_2^- \qquad (7)$$

Super – oxide anions (O_2^-) can be involved in the following reactions.

$$O_2^- + H^+ \rightarrow HO_2^\bullet \qquad (8)$$

$$H^+ + O_2^- + HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad (9)$$

Photoconversion of hydrogen peroxide gives more $^\bullet$OH free radical groups.

$$H_2O_2 + hv \rightarrow 2^\bullet OH \qquad (10)$$

Finally, $^\bullet$OH radicals oxidize organic adsorbed molecules (RX_{ad}) onto the surface of the titanium dioxide particles.

$$^\bullet OH_{ad} + RX_{ad} \rightarrow \text{Intermediates} \rightarrow CO_2{+}H_2O \qquad (11)$$

The $^\bullet$OH radicals are very active oxidizing agent and attack the pollutant molecule to degrade it into mineral acids including carbon dioxide and water.

2.5. Photocatalytic Degradation Studies

All the photocatalytic degradation experiments were carried out under atmospheric conditions. The experimental set-up was a batch system. It consists of six beakers (25ml each) containing 5g of TiO_2 catalyst, and ethylbenzene solutions of various initial concentrations ranging from 50-300mg/l. These were firmly placed on an Orbital shaker with the help of a masking tape. The set-up was left in the sun to shake for 2hours at a regulated speed of 175 rev/min for degradation to occur. About 10ml of the sample were withdrawn in an interval of 20mins. The samples were filtered with 110mm x 100 circles, Whatman filter paper to separate suspensions of TiO2 catalyst. The filtered samples were analyzed using a T 70 UV-Vis spectrophotometer at wavelength of 275.5nm. The experiments were conducted on an open space outside the Chemical Engineering Departmental Laboratory, University of Benin, Benin City, Nigeria.

3. Results and Discussion

3.1. Percentage Degradation of Different Catalysts

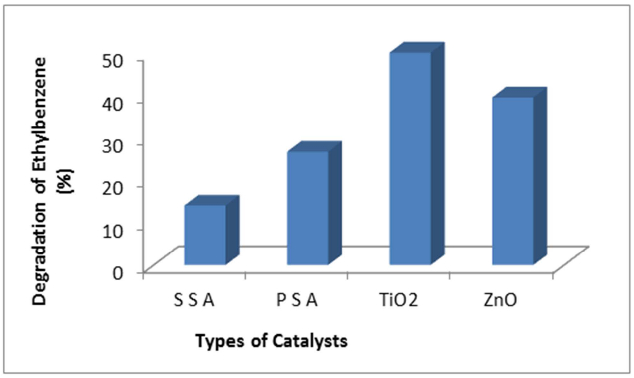

Fig. 2. *Percentage Degradation of Ethylbenzene using Different Catalysts.*

Fig. 2 shows the percentage degradation of ethylbenzene using different catalysts. The highest percentage degradation of ethylbenzene was achieved using TiO_2 photocatalyst, and the percentage obtained was 50%. However, the lowest degradation rate was SSA (14.75%). The difference in percentage degradation between the four catalysts was statistically significant (ANOVA, $p < 0.05$). The percentage degradation by TiO_2 was significantly higher than ZnO, PSA, and SSA. The percentage degradation by ZnO was significantly higher than PSA and SSA. The percentage degradation by PSA was also found to be significantly higher than SSA. The results indicated that higher photocatalytic activity exhibited by TiO_2 photocatalyst might be due to the increasing of charge separation by extending energy range of photoexitation. Subsequently, their characteristic or physical properties significantly modified. Therefore, such factor might contribute to increasing of percentage degradation.

3.2. Effect of Catalyst Dose (TiO_2)

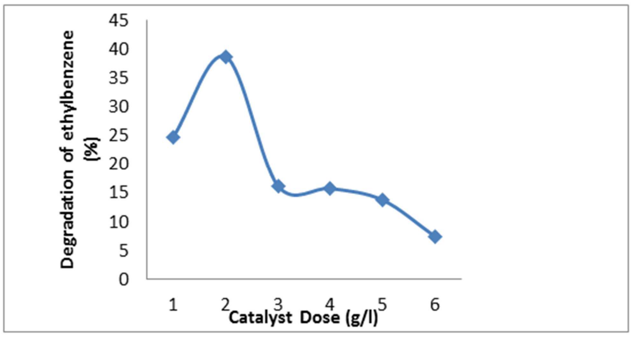

Fig. 3. Percentage Degradation of Ethylbenzene with Catalyst Dose.

The rate of photodegradation and ethylbenzene concentration exhibits a quadratic behavior which has an optimum value at 2.0g/l and a percentage degradation of 38.64%. It is a non-linear function of ethylbenzene concentration. The difference in percentage degradation between the catalysts doses considered was statistically significant (ANOVA, $p < 0.05$). The percentage degradation at the optimum value 2.0g/l was significantly higher than 1.00g/l, 4.00g/l, 6.00g/l, 8.00g/l and 10.00g/l. The reason for this behavior may be related to the probability interaction between ethylbenzene and TiO_2 surface. At very low ethylbenzene concentration, the probability of interaction between ethylbenzene molecules and surface of TiO_2 decrease. Hence, photodegradation rate decreases. The probability of interaction between substrates molecules and oxidizing species is increased by increasing ethylbenzene concentration, leading to an enhancement in the degradation rate (Al-Ekabi *et al.,* 1986; Konstantinou *et al.,* 2004).

3.3. Effect of Initial Substrate Concentration

The effect of initial concentration of ethylbenzene on the photocatalytic degradation rate was investigated over the concentration range of 50 - 300mg/l. The data in Figure 4 shows that degradation rate depend on the initial ethylbenzene concentration. The result shows that for catalyst dose ranging from 50 - 350mg/l and a fixed irradiation period, percentage degradation of ethylbenzene increased from 35.6% to 37.0%, and gradually decreases to 27.8, then decreases sharply down to 15.0%. This may be due to the fact that more ethylbenzene molecules were absorbed onto the surface of TiO_2 from 100mg/l – 300mg/l, which resulted in gradual decrease in degradation rate followed by sharp decreased. However, for a constant light intensity, TiO_2 loading and dissolved oxygen concentration, concentration of $OH^\bullet$ remains practically the same. Also it is likely that competitive adsorption of ethylbenzene, photoproducts and $OH^\bullet$ is responsible for the observed decrease in degradation rate. At higher concentration, the concentration of photoproducts formed during photocatalytic degradation is high thereby reducing the number of available active sites on TiO_2 for adsorption of H_2O/OH^- (required for $OH^\bullet$ formulation) and ethylbenzene, causing a decrease in the degradation rate. Therefore, 100mg/l was the optimum concentration with a percentage degradation of 37.0%. The difference in percentage degradation between the initial concentrations considered was statistically significant (ANOVA, $p < 0.05$). The percentage degradation at the concentration 100mg/l was significantly higher than 50mg/l, 150mg/l, 200mg/l, 250mg/l and 300mg/l.

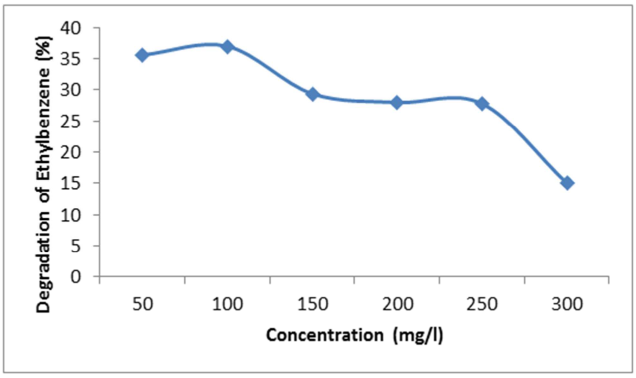

Fig. 4. Percentage Degradation of Ethylbenzene of Initial Concentration.

3.4. Effect of Oxidant (H_2O_2)

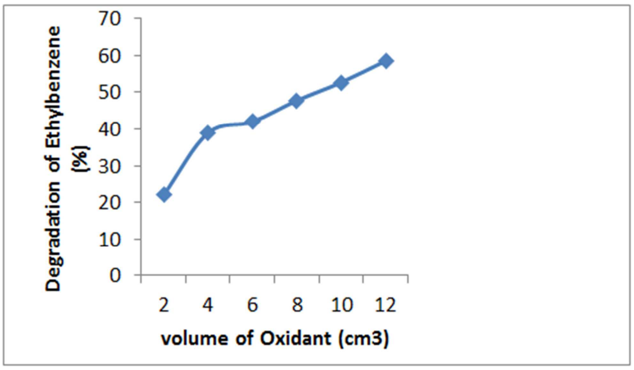

Fig. 5. Percentage Degradation of Varying Volume of Oxidant (H_2O_2) using TiO_2 Catalyst.

A set of photodegradation analysis were carried out to investigate the degradation of ethylbenzene affected by hydrogen peroxide, the experimental results are illustrated in

Fig. 5. These result shows that the percentage degradation of ethylbenzene increased from 22.02% to 58.54% when H_2O_2 increased from 2 to $12cm^3$. The difference in percentage degradation between the oxidants considered was statistically significant (ANOVA, $p < 0.05$). The percentage degradation at the oxidant $12.00cm^3$ was significantly higher than $2cm^3$, $4cm^3$, $6cm^3$, $8cm^3$, and $10cm^3$. The degradation of ethylbenzene by H_2O_2 may be due to the formation of hydroxyl free radicals in photocatalytic processes supplied by the reaction of positive hole with water and OH^- on the surface of TiO_2. This is because H_2O_2 becomes water (H_2O) and oxygen (O_2) by their resolution, and O_2 reacts with H_2O. The excited electrons are to generate hydroxyl and peroxide radicals necessary for the degradation of ethylbenzene. This explanation is supported by Dong *et al.,* 2010, where he stated that the peroxide radical ($O_2^{\bullet-}$) and hole (h^+) can react with water (H_2O) to produce hydroxyl radicals ($OH^\bullet$) which can enhance the degradation of ethylbenzene in solution. The primary oxidizing species in the photocatalytic oxidation processes is the hydroxyl radical ($OH^\bullet$). It produces carbon dioxide (CO_2) and water (H_2O) when it reacts in the oxidation reaction.

$$OH^\bullet + C_8H_{10} \rightarrow 8CO_2 + H_2O$$

3.5. Effect of pH Variation

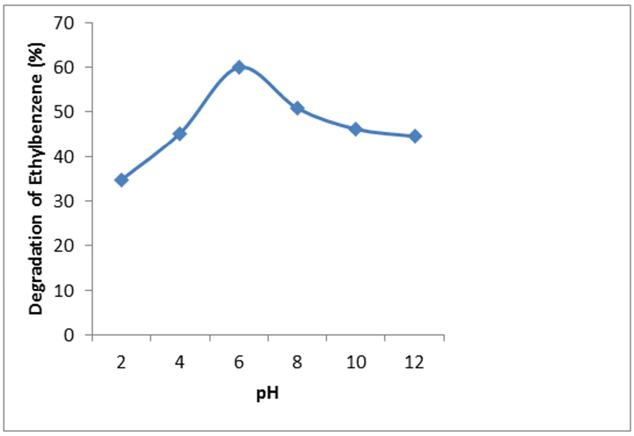

Fig. 6. *Percentage Degradation of Ethylbenzene for Varied pH.*

The pH solution influences adsorption, catalyst surface change, oxidation potential of valance band, and other physicochemical properties. The effect of pH on photocatalytic degradation of ethylbenzene were studied at pH range of 2 to 12, using initial optimum concentration of 100mg/l and optimum value of catalyst loading of 2.0g/l. The pH value was adjusted using PHS-25 model, pH meter by adding dilute NaOH or HCl solution. The effect of pH on the reaction rate of ethylbenzene is shown in Fig.6. As can be seen from this figure, the maximum degradation of ethylbenzene occurs at pH 6 in the acidic range, and the degradation rate is 60.0% respectively. The difference in percentage degradation between the pH considered was statistically significant (ANOVA, $p < 0.05$). The percentage degradation at the pH 6.00 was significantly higher than 2.00, 4.00, 8.00, 10.00, and 12.00. This may be due to the fact that increased in pH which affects the surface charge of catalyst increased the availability of OH ions (Konstantinous *et al.,* 2004). Further increased in pH from 6.0 to 12.0 decreased the degradation rate from 60.0% to 44.59%. This indicated that for pH value above 6.0, more OH^- will compete with the electron rich ethylbenzene for adsorption and catalyst surface. Some results were reported by Sharad *et al.,* 2007 in the photocatalytic bleaching of Evans Blue. Kahan *et al.,* 2007 presented a contradictory result for photolysis of Polyycyclic Aromatic Hydrocarbons (PAHs) on water and ice surfaces, stating that the photolysis rate of PAHs generally increased with decreasing pH, but agreed that few PAHs react more quickly at a higher pH in water.

3.6. Effect of Time Variation

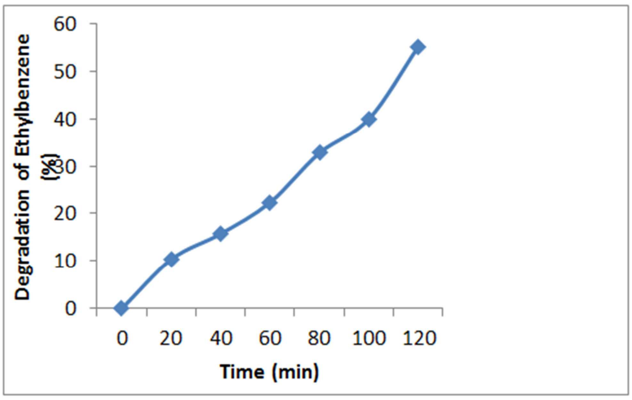

Fig. 7. *Percentage Degradation of Ethylbenzene for Time Variation.*

Fig.7 shows the percentage degradation of ethylbenzene at pH 6.0 for varying time using Tio_2 catalyst dose of 2.0g/l. These results show that as time progresses from 0 to 2hrs, the percentage of degradation increased from 0% to 55.90%. The difference in percentage degradation between the times considered was statistically significant (ANOVA, $p < 0.05$). The percentage degradation at the time 120 was significantly higher than 0.00, 20.00, 40.00, 60.00, 80.00, and 100.00. This may be due to the fact that as time progresses, ethylbenzene molecules are being adsorbed on the surface of TiO_2 and degraded, which means that the concentration of ethylbenzene in the aqueous solution reduces with time.

3.7. Kinetics and Modeling

The Langmuir-Hinshelwood kinetic model has been used to describe many mineralization process kinetics that reactions take place at the surface of the catalyst particle (Ajmera *et al.*, 2002; Turchi and Ollis, 1990; Hussein and Serpone, 1988, and Al-Ekabi and Serpone, 1989). The rate of reaction can be written as:

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \qquad (12)$$

Where; r is rate of the reaction (mg/L min), dC/dt is the rate of degradation, k is the apparent reaction rate constant, K is the adsorption coefficient of the substance to degraded, and C is the concentration of ethylbenzene. If the concentration of the substances to be degraded exceeds the saturated coverage of the TiO_2 surface, i.e. KC >> 1, equation (12) simplifies to a zero-order rate equation.

$$(dC/dt) = k \tag{13}$$

For very low concentration (i.e., KC <<), Langmuir-Hinshelwood equation (12) simplifies to a Pseudo-first order kinetic equation.

$$\mathrm{In}\frac{C_o}{C_t} = kt \tag{14}$$

Where C_o is the initial concentration of ethylbenzene at time t = 0, and C_t is the concentration of ethylbenzene at reaction timt t.

The apparent Pseudo-first order reaction rate constant, k is given as:

$$k = \frac{\mathrm{In}\, C_o/C_t}{t} \tag{15}$$

A plot of In C_o/C_t versus time gives a straight line, and the slop of the straight line gives the value of reaction rate constant, k.

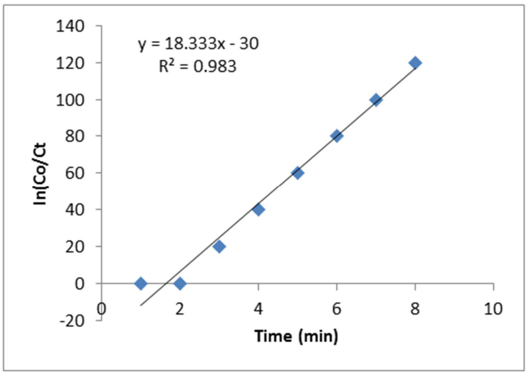

Fig. 8. *Pseudo-first order kinetics for photocatalytic degradation.*

Table 1. *Linear Regression Analysis of Kinetics of Ethylbenzene Degradation.*

	Pseudo first order $-r = KC \,\mathrm{In}\, \frac{Co}{Ct} = k_1t$		**Pseudo second order** $-r = KC^2 \frac{1}{Ct} - \frac{1}{Co} = K_1t$	
Conc. (mg/L)	**K_1 X 10^{-3}**	**r^2**	**K_2 X 10^{-3}**	**r^2**
50	4.0	0.983	8 E - 05	0.464
100	4.0	0.980	6 E - 05	0.782
150	4.0	0.981	5 E - 05	0.746
200	3.0	0.979	4E - 05	0.779
250	3.0	0.980	3 E - 05	0.867
300	1.0	0.982	1 E - 05	0.915

Table 1 shows the linear regression analysis of the kinetics of ethylbenzene degradation using photocatalysis. The results were used to analyse the rate of adsorption and possible adsorption mechanism of ethylbenzene onto TiO_2 catalyst using Pseudo-first order and second order models. From the table above, it can be observed that K for the first order is almost constant with a regression range of 0.979-0.983, while that of the second order ranges from 0.465-0.915. Hence, the photodegradation of ethylbenzene follows Pseudo-first order, which gives a better regression.

4. Conclusions

Photocatalysis is a promising technique for the degradation of various hazardous chemicals that are present in industrial wastewater using TiO_2 as photocatalyst, and it mineralize the organic contaminants into final end product. The removal rate of ethylbenzene depends on the light source, light intensity and other factors. It has been found that the result obtained in solar light are effective for the degradation of ethylbenzene in the presence of TiO_2, with optimum catalyst dose of 2g/l, pH 6.0, and optimum condition for degradation of ethylbenzene concentration is 100mg/l. The photocatalytic degradation of ethylbenzene using TiO_2 catalyst under solar irradiation follows Pseudo-first order kinetics, and this well presented by the Langmuir-Hinshelwood model. Hence, it can be concluded from the observations that solar photocatalysis can be suitably and cost effectively employed for the degradation of organic compounds.

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