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Kinetic and Sorption Modellingof Photocatalytic Removal of Pb(II) In Paint EffluentUsing TiO_2 Under Solar Irradiation

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Abstract

The kinetics and sorption modeling of photocatalytic removal of lead ion (Pb^{2+}) in paint effluent using titanium dioxide (TiO_2) was studied. The process was carried out in a batch system at different contact time and catalyst dosage under solar irradiation; and the residual metal ion in the solution was determined using atomic absorption spectrophotometer (AAS). The results showed that about 96% removal efficiency was achieved at optimum catalyst dosage of 1g/L, and the process attained equilibrium at 140 minutes. Pseudo-first order model with a rate constant of 0.0194min^{-1}showed sufficient description of the kinetics of the process; and intraparticle diffusion modelrevealed that the uptake of Pb^{2+} was more of the film diffusion than the intraparticle diffusion. Langmuir isotherm with a regression value, R^2(0.931)and adsorption capacity (1.56L/mg)best described the sorption of Pb^{2+} onto TiO_2. Meanwhile, the heat of sorption (+3.2015 KJ/mol) obtained from Temkin isotherm indicates that the process was exothermic.

Keywords: Adsorption capacity, lead, exothermic, film diffusion, solar irradiation.

1.0 Introduction

Industrial effluent is a complex mixture of several classes of pollutants including synthetic chemicals of various description, hydrocarbons and heavy metals [1]. Paint and textile industries release effluents that can be in the form of solid, liquid or gaseous organic or inorganic substances. In the three forms of pollutants, the liquid effluent is the most significant and abundant[2]. Most industries discharge their untreated effluents through drains or canals into the nearest water body such as streams[3],while some others release their effluents into vegetation leading to a high bioaccumulation in the plants or soil [4]. Most industrial effluents contain high concentration of potentially mutagenic heavy metals, and it has been reported that heavy metals are among the most toxic and environmentally dangerous pollutants [5]. Quite a number of toxic heavy metals such as Lead (Pb), Chromium (Cr), Cadmium (Cd), Manganese (Mn), Copper (Cu), Zinc (Zn) etc. are present in paint effluent [6, 4]. Lead is a toxic substance, however some of its compounds are used as colour pigments and drying agent to improve luster in house-hood paints.The impact of lead in industrial effluents on aquatic and terrestrial ecosystems has drawn a lot of attention worldwide because of its overwhelming environmental significance [7]. Conventional methods for the removal of metal ion include adsorption, ion exchange, extraction etc. However, the use of adsorption techniques can only remove the metal ion from one site of the environment to another.

Heterogeneous photocatalysis facilitated by UV irradiated semiconductor oxide such as TiO_2has been identified as a promising technique for the oxidation of organic and inorganic contaminants in liquid effluent [8]. The photocatalysis initiated by solar energy in the presence of a stable metal oxide as catalyst has been studied extensively[9].On the absorption of photonenergy (*hv*) equal or greater than the band gap energy of the semiconductor (3.2 eV for anatase), an electron (e^-) is excitedfrom the valence band (VB) to the conduction band (CB)of the semiconductor. Simultaneously, an electron vacancy or a positively charged hole (h^+) is created in the VB. The semiconductor then exhibits a void energy region in which no energy levels are available to promote the recombination of $e^-$and h^+ produced by photo-activation in the solid [10].A simplified mechanism for the photo-activation of a semiconductor catalyst is presented in Figure1. Ultraviolet (UV) or near-ultraviolet photons (λ< 387 nm) are typically required for this kind of reaction[11].The valence band h^+ is strongly oxidizing, and the conduction band $e^-$is strongly reducing. At the external surface, the excited electron and the hole can take part in

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redox reactions with adsorbed species such as water. Generally, the h^+oxidizes water to hydroxyl radicals ($OH^{\cdot}$) which subsequently initiate a chain of reactions leading to the oxidation of pollutant, or it can be combined with the electron from a donor species, depending on the mechanism of the photoreaction. Similarly, the electron can be donated to an electron acceptor such as an oxygen molecule leading to formation of superoxide radical ($O_2^{\cdot-}$) or a metal ion with a redox potential more positive than the band gap of the photocatalyst. The hydroxyl radical ($OH^{\cdot}$) was proposed to be the primary oxidant in the photocatalytic system[12].Lead (II) ionis oxidized to its higher valence state which is practically insoluble in aqueous solution and is thus filtered off. The electron-transfer process is more efficient if the species are pre-adsorbed on the surface of the catalyst[10].

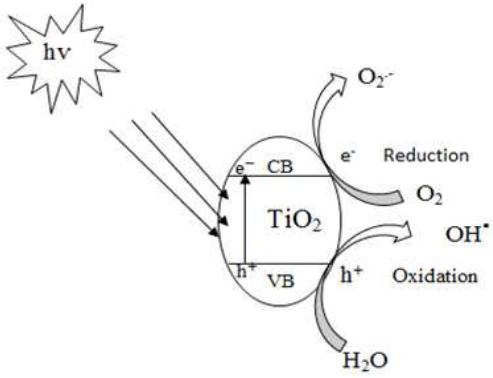

Figure 1:*A simplified mechanism for the photo-catalytic removal of* Pb^{2+} [13]

Simple chemical equations for the photocatalytic reaction of lead (II) ion to lead (IV) oxide are as follows;

$$TiO_2 + hv \rightarrow e^- + h^+ \quad (1)$$

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

$$Pb^{2+} \rightarrow Pb^{4+} + 2e^- (E^o = -0.67V) \quad (3)$$

$$Pb^{4+} + 2OH^{\cdot} \rightarrow PbO_2 + 2H^+ \quad (4)$$

As a result of the toxic nature of lead to organisms in the environment, it is necessary to carry out a thorough assessment of lead content in paint effluent,andthen reducethe concentration to acceptable level before discharge into the environment.Therefore, this study was focused on the photocatalytic removal of Pb^{2+} in paint effluent using titanium dioxide as catalyst under the sun. Lead and Cadmium have been removed by photocatalytic process using TiO_2 irradiated by artificial UV-lamp [14], while chromium (IV) has been removed by carbon modified (CM)-n-TiO_2 nanoparticls under solar irradiation [13].

2.0 Methodology

2.1 Materials

Paint effluent, reddish in colour, was collected from a small-scale paint producer in Benin City. The sample was stored in a clean plastic can and kept in a refrigerator at 4^{o}C. The pH of the effluent was measured, and the effluent was used in all experimentswithout further dilution. Anatase form of TiO_2, a product of BDH chemical Ltd, England with an average particle size of 21 nm and surface area (BET) of 50±15m^2/g was used as catalyst.

2.2 Photocatalytic Studies

The photocatalytic removal of $Pb^{2+}$was conducted in a batch system.A certain volume (200ml) of paint effluent was measured into different conical flasks(500ml) containing 0.05g, 0.1g, 0.15g, 0.2g, 0.25gof TiO_2, and control (no catalyst).The flasks were placed on a flat orbital shaker(Optima OS-752 model) operated at a speed of 120 rpm for continuous shaking under the sun (temperature, 32±2^{o}C) for 3hours.The experiment was repeated in the laboratory using air bath shaker (Model THZ-82)without sunlight; the conical flasks were wrapped with aluminium foil to prevent penetration of UV rays[15]. Samples were collected from each flask at predetermined time to evaluate the effect of irradiation time and catalyst dosage, the samples were filtered using fine crystalline filter paper (whatman number 42). The filtered samples wereanalysed using AAS (Solar 969 model, Unicam series). The percentage removal efficiency of pb^{2+} was obtained from the equation:

$$\%\, Removal = \frac{C_i - C_f}{C_i} \times 100 \quad (5)$$

$C_i$and C_f are the initial and final concentration of Pb^{2+}in solution.

2.3 Kinetic Model Equations

The experimental data were subjected to kinetic models such as pseudo-first order, pseudo second order and intra-particle diffusion models, to determine the kinetic parameters and rate-limiting step of the process.

Pseudo-first order kinetic equation

$$\frac{d_q}{d_t} = K_1(q_e - q_t) \quad (6)$$

Where, q_e and $q_t$are the amounts of Pb^{2+}removedat equilibrium and time t, respectively per unit mass of the catalyst (mg/g); and K_1 is the pseudo first-order rate constant. After integration and applying boundary conditions t = 0 to t = t and q_t = 0 to $q_t = q_t$equation (6) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (7)$$

The plot of log $(q_e - q_t)$againstt gives a linear relationship whereK_1 and $q_e$were determined from the slope and intercept of the plot, respectively [16, 17].

Pseudo-second order kinetic equation

The pseudo second-order adsorption kinetic rate equation is expressed as:

$$\frac{d_q}{d_t} = K_2(q_e - q_t)^2 \quad (8)$$

K_2 is the rate constant of pseudo second-order adsorption (g/mg.min). Linearizing equation (8) for the boundary conditions t = 0 to t = t and q_t = 0 to $q_t = q_t$, becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \quad (9)$$

Further rearrangement of equation (9) gives the following:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e}t \quad (10)$$

and$h = K_2 q^2$, where h is the initial rate of sorption (mg/g)

The plot of t/q_t against t yield a straight line whereK_2 can be calculated [16, 17]

Intra particle diffusion-controlled sorption

To investigate the internal diffusion mechanism during photocatalytic process, the intra-particle diffusion equation has been used, considering that adsorption is usually controlled by an external film resistanceand internal or intra-particle diffusion [18]. For adsorption onto spherical particles with constant diffusion coefficient, Crank [19] proposed the following equation:

$$q_t = K_{id} t^{0.5} \quad (11)$$

The coefficient $k_{id}$is determined from the linear plot of *qt* versus (time)$^{0.5}$. Good linearization of data is normally observed for the initial phase of reaction in accordance with expected behavior if intra particle diffusion is rate limiting [20]. The intra particle diffusion plot of q_t versus $t^{0.5}$should be linear. If the plot is not completely linear, and do not pass through the origin, then the intra particle diffusion cannotbe the only mechanism involved [21]. According to previous work [22], if the intra-particle diffusion plot does not pass through the origin, then equation (11) becomes:

$$q_t = K_{id} t^{0.5} + C_{id} \quad (12)$$

Where C_{id} is intra particle diffusion constant or intercept of the line (mg/g). It is directly proportional to the boundary layer. Apart from the linearity of the intra particle diffusion plot, the sorption mechanism assumes intra particle diffusion if the following are met:

i. High coefficient of determination (R^2) to ascertain applicability
ii. Straight line which passes through the origin
iii. Intercept $C_{id} < 0$.

Deviation from (ii) and (iii) above shows that the mode of transport is affected by more than one process [22].

2.4 Adsorption Isotherms

Adsorption isotherms relate the concentration of solute on the surface of the adsorbent to the concentration of the solute in the fluid with which the adsorbent is in contact. For single metal adsorption, Langmuir, Freundlich and Temkin isotherm modelswere used toestablishthe adsorption isothermsof photocatalytic removal of Pb^{2+}.

Freundlich Isotherm

Freundlich isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface [23]. The experimental data often fit to the empirical equation as shown:

$$q_e = K_f C_e^{1/n} \quad (13)$$

The constants associated with the Freundlich isotherm model are sorption capacity (K_f) and sorption intensity $(1/n)$. These parameters provide an indication for the capacity of the adsorbent/adsorbate system and favourability of the isotherm, respectively.C_e is the equilibrium concentration of adsorbate (mg/L), and q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

Linearizing equation (13), we have:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (14)$$

The slope, 1/n ranges from 0 and 1, it is also a measure of surface heterogeneity. The system become more heterogeneous as the value gets closer to zero [24]. If 1/n is equal to 1, then the partition between the two phases are independent of the concentration. If value of 1/n is below one, it indicates a normal adsorption. On the other hand, 1/n above one indicates cooperative adsorption [25, 26].

Langmuir isotherm

This isotherm describes quantitatively, the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir model represents the equilibrium distribution of adsorbate between the solid and liquid phases [27]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir proposed the following equation:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (15)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (15) into linear form

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad (16)$$

Where; C_e is the equilibrium concentration of adsorbate (mg/L).

q_e is the amount of metal adsorbed per gram by the adsorbent at equilibrium (mg/g).

Q_o is maximum monolayer coverage capacity (mg/g).

$K_L$is Langmuir isotherm constant (L/mg). The values of Q_o and K_L were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$[28].

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant, also referred to as separation factor [29].

$$R_L = \frac{1}{1 + (K_L C_0)} \quad (17)$$

where C_o is initial concentration.

The value of R_L indicates the shape of the isotherm to be linear (R_L=1), unfavourabe (R_L>1), irreversible (R_L=0) and favourable (0< R_L<1) [30].

Temkin isotherm model

Temkin model was used to test the adsorption potential of TiO_2. The model takes into account the effect of indirect adsorbent/adsorbate interaction on the adsorption process; and it is assumed that the heat of adsorption (ΔH_{ads}) of all molecules in the layer decreased linearly by increasing the coverage area [30]. The simplest form of Temkin isotherm is given as follows:

$$q_e = \frac{RT}{b_T}\ln(K_T C_e) \quad (18)$$

The linear form of equation (18) is given as follows:

$$q_e = \frac{RT}{b_T} ln K_T + \frac{RT}{b_T} ln C_e \quad (19)$$

where, *R* is gas constant (0.008314 KJ/mol.K), T is the absolute temperature (K), $1/b_T$ is the Temkin constant related to the heat of sorption (KJ/mol) which indicates the adsorption potentials of the adsorbent, and K_T (L/g) is Temkin constant related to adsorption capacity.

3.0 Results and Discussion

3.1 Assessment of Concentration of Lead in Paint Effluent

The pH and the initial concentration of Pb^{2+} were determined in the paint effluent. The effluent has a pH value of 6.7 and Pb^{2+} content of 3.796mg/L. This concentration of $Pb^{2+}$is outsidethe recommended acceptable discharge limit of < 1.0mg/Lset by the Federal Environment Protection Agency of Nigeria [31]. This is an indication that the effluent was highly contaminated with Pb^{2+} and the disposal of such effluent without treatment will pose an adverse lead poisoning to both terrestrial and aquatic organisms in the environment.

3.2 Effect of Catalyst Dosage

The effect of catalyst (TiO_2) dosage on the photocatalytic removal of Pb^{2+}ion in paint effluent is shown in Figure 2. The catalyst (TiO_2) dosage was varied from 0.25g/Lto 1.25g/L. The result shows that the percentage removal of Pb^{2+} increased

with increasing catalyst dose up to an optimum point and then decreased. From the result, it was observed that the percentage removal increased from 70% to 96% as the catalyst concentration increases from 0.25g/Lto 1.0g/L, and further increase of the catalyst concentration to 1.25g/L, the percentage removal decreased to 93%. Thus, 1.0g/L was the optimum catalyst concentration for the process.An optimum TiO_2 dosage of 0.9g/L has been reported in literature for the removal of lead and cadmium with UV-lamp irradiated photocatalytic process [14]. The initial increase in percentage removal could be due to the increase in the number of active sites on the catalyst surface as a result of increased catalyst dosage. Increasing the dosage of catalyst, the number of free radical ($OH^{\bullet}$) in solution were also increased consequently leading to enhanced photo-oxidation of the substrate in the effluent sample. The decreased in photo-oxidation as the catalyst concentrationwas increased beyond the optimum dosage could be attributed to the suspended particles of the catalyst which aggregate together and then reduced the amount of sunlight reaching the active sites of the catalyst and consequently, the rate of reaction decreases. This is in conformity with the report from literature[32].

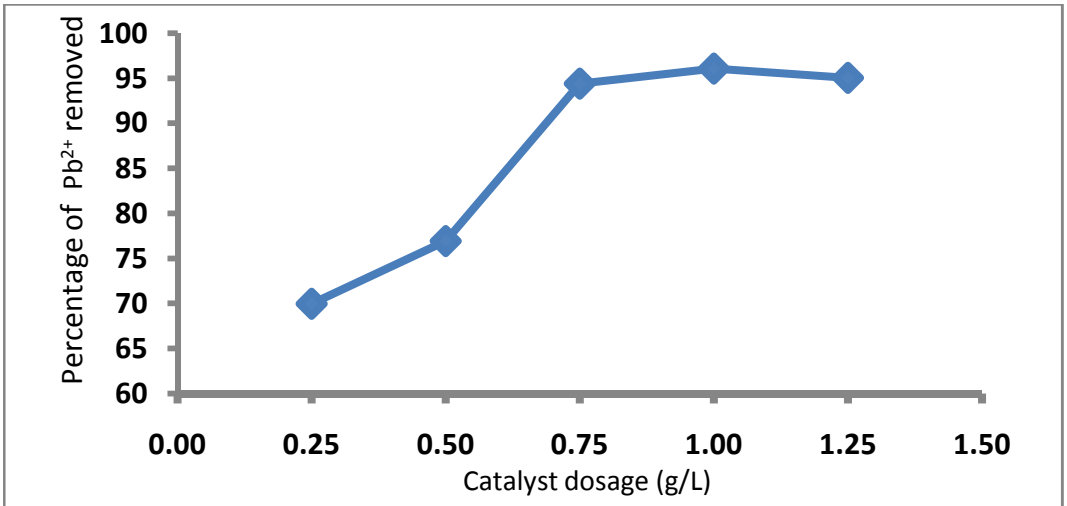

Figure 2: Effect of catalyst dosage on the photocatalytic removal of Pb^{2+}

3.3 Effect of Irradiation Time

The effect of irradiation time on the photocatalytic removal of $Pb^{2+}$was investigated. Figure 3 clearly shows that sampling was carried out at an interval of 20 minutes for 3 hours. From the result, it was observed that the rate of Pb^{2+}removal was rapidin the first 60 minutes; it then became slower and almost constant at 140 minutes for all the catalyst concentration tested. At this point, the process was said to have reached equilibrium.The amount of Pb^{2+} removed at equilibrium was 75%, 81%, 92%, 96% and 95% for 0.25g/L, 0.5g/L, 0.75g/L, 1g/L and 1.25g/L respectively. Greater photon was absorbed by the catalyst at elongated irradiation time; however at equilibrium, the formation of lead oxide in the solution could impede the penetration of the photon energy thereby limiting the generation of hydroxyl radical. Secondly, the active sites of the catalyst would have been completely filled by the substrate and became saturated. This is in agreement with other reports in literature [33].

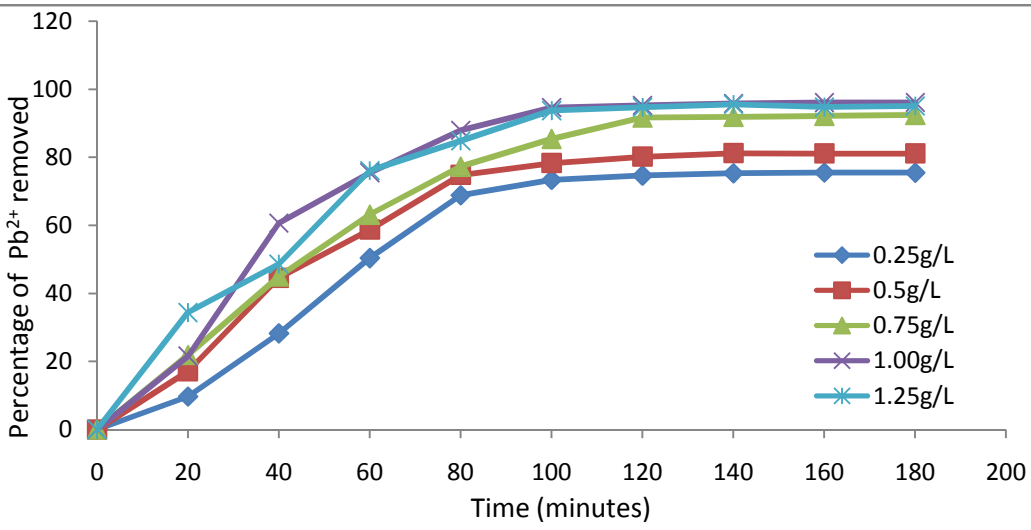

Figure 3: Effect of irradiation time on photocatalytic removal of Pb^{2+}

3.4 Effect of TiO_2 and UV Irradiation

Control experiments were carried out to investigate the effects of sunlight and catalyst on the removal of Pb^{2+}. As one set of experiment was carried out under the sun but without catalyst, another set was done with a concentration of 1.0mg/L TiO_2 in the laboratory without sunlight (dark experiment). The results of the control experiments in comparison with the one carried out in the presence of catalyst and sunlight are shown in Figure 4. From the result, it was deduced that sunlight and catalyst played prominent roles in the photocatalytic oxidation process,about 58 % removal of Pb^{2+} was obtained at the dark (adsorption) experiment as against 96% with sunlight and catalyst, while no significant amount of $Pb^{2+}$was removed with sunlight alone. This is in agreement with previous studies which reported that photocatalysis is initiated by photon energy (UV rays) in the presence of a stable metal oxide as catalyst for the degradation of organic and inorganic compounds[8, 9].

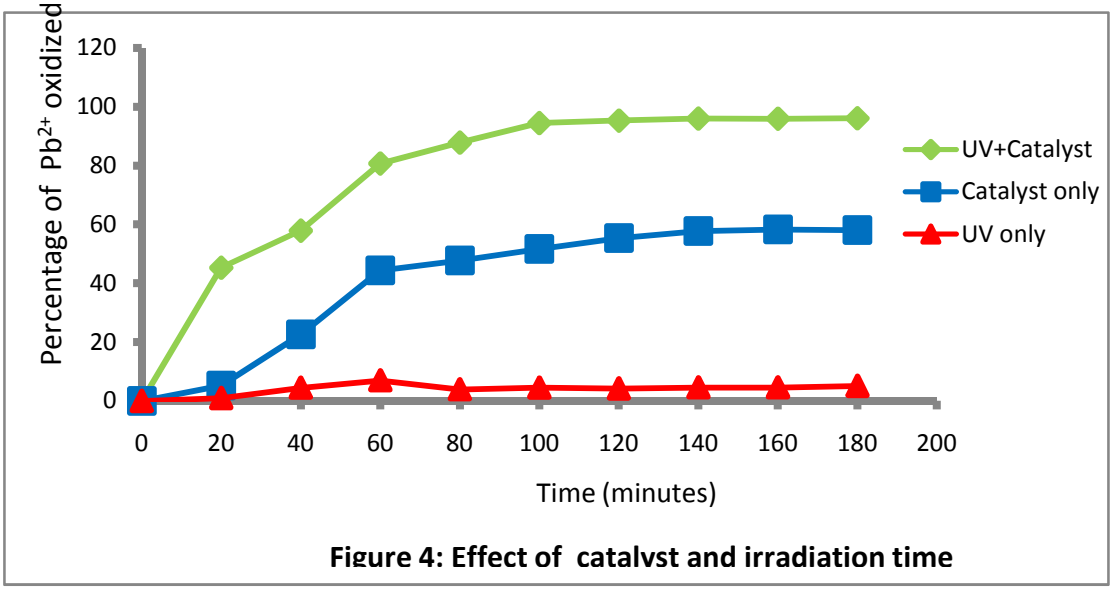

Figure 4: Effect of catalyst and irradiation time

3.5 Kinetic Models

Thelinear plotsof the kinetic modelsfor the photocatalytic process are presented in Figures 5 and 6 for pseudofirst-order and pseudo second-order models, respectively. The rate constants and other parameters were calculated and presented in Table 1. The coefficient of determination (R^2)and the kinetic rate constants values revealed that the process fitted more to the pseudo first-order model than pseudo second-order model. For the optimum catalytic dosage of 1g/L, the rate constant (k_1) of

0.0194min^{-1} and $R^2$of 0.9539 were obtained for pseudo-first order kinetic model while pseudo second-order models had rate constant (k_2) of 1.4 x 10^{-2}g/mg.min and $R^2$of 0.8157. The R^2 represents the percent of the data closest to the line of best fit. R^2 for pseudo first order is 0.9539 which means that 95.39% of the total variation of data in y-axis can be explained by the linear relationship between y and x, that is, only 4.61% remains unexplained. In addition to the good linear model fit, the reaction rate constant suggested that photocatalytic removal of Pb^{2+} followed pseudo first-order kinetics and that Pb^{2+}were adsorbed onto the TiO_2 surface via chemical interaction. In another work, the pseudo first-order model was also found applicable when the photocatalytic properties of ZnO nanocrystal were investigated in the oxidation of insecticide diazion [33].

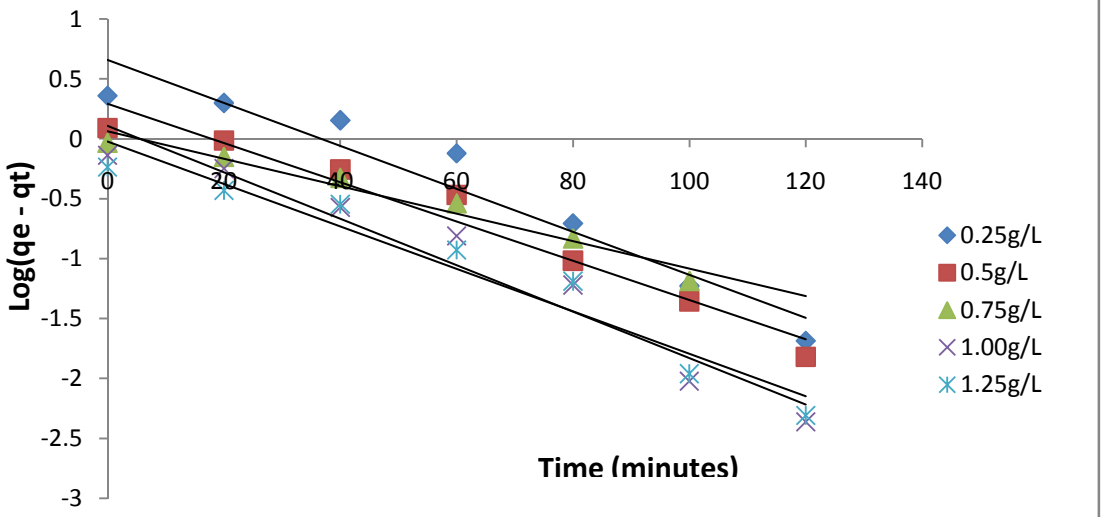

Figure 5: Pseudo-first order kinetic model for photocatalytic removal of Pb^{2+}

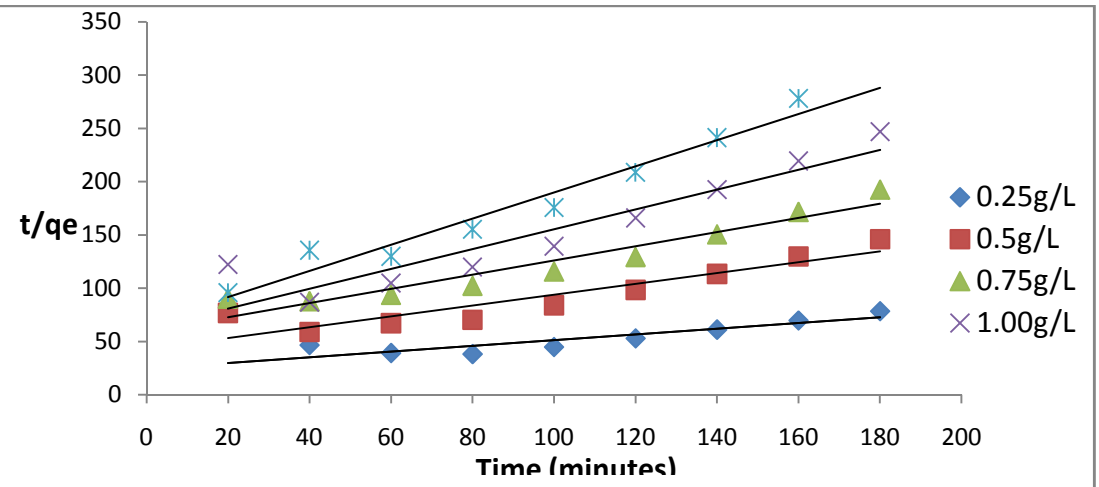

Figure 6: Pseudo-second order kinetic model for photocatalytic removalof Pb^{2+}

The intra-particle diffusion often plays important role in adsorption process especially for porous adsorbent.It is a transport process involving movement of species from the bulk of the solution to the solid phase [34]. Thekinetics data from this study were fitted into intra-particle diffusion model using equation (11). A linear plot of qt versus the square root of the time, gives the rate constant (slope of the plot). A non-regression coefficient plot gives a 3-phase plot viz. the initial (linear), second and third phases [22]. The linear stage corresponding to fast uptake of sorbate; and if the line in the initial stage does not pass through the origin, it denotes that uptake is dominated by film diffusion than it does for the intraparticle diffusion process. In the second stage, sorbate adsorption speeds up reflecting nonconsecutive diffusion of sorbate molecules into the micropores of the sorbent; and in the third phase, diffusion remains fairly constant when the pore volume is exhausted [35]. The linear

plot is shown in Figure 7. It comprises the initial phase of 60 minutes of the photocatalytic reaction. The intra-particle diffusion constants were calculated from the slopes of the linear plot and shown in Table 1. The regression lines in Figure 7 did not pass through the origin, and an intercept C_{id} was provided. This is an indication of the role of other rate-limiting steps of the process other than the intra particle diffusion.In addition, theK_{id}values are greater than 0, both intra-particle diffusion and external mass transfer (film diffusion) are considered as rate limiting steps. The value of C_{id} provides information related to the thickness of the boundary layer; and it is directly proportional to the boundary layer[20].

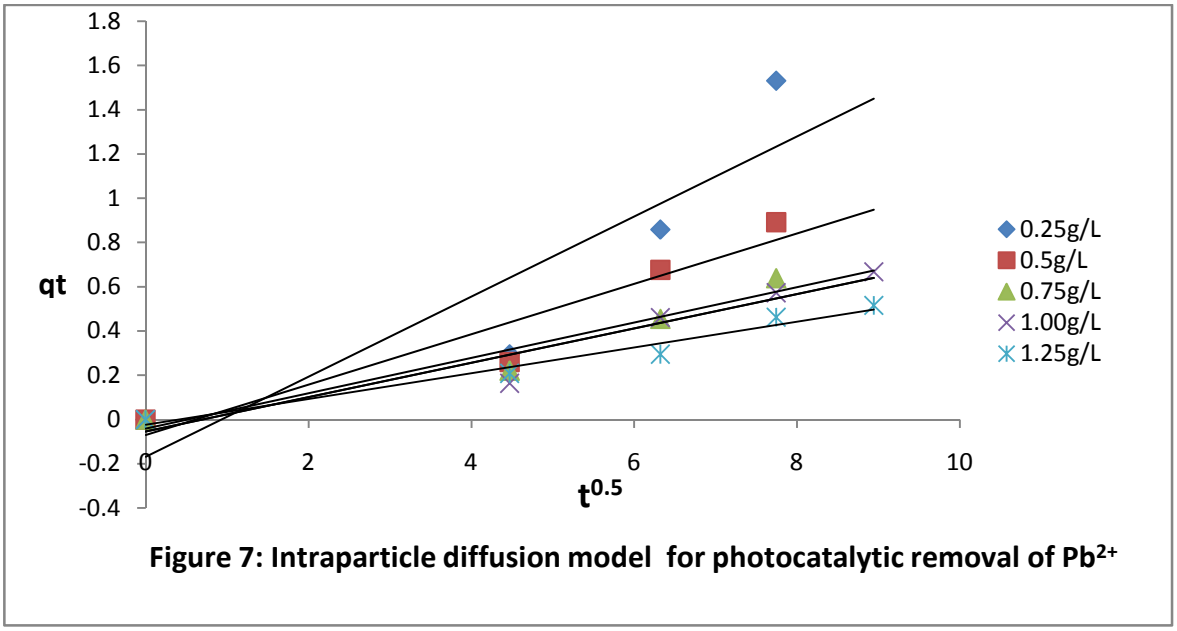

Figure 7: Intraparticle diffusion model for photocatalytic removal of Pb^{2+}

Table 1: kinetic parameters for photocatalytic removal of Pb^{2+}inpaint effluent

Catalyst dosage (g/L)	Pseudo-first order		Pseudo-second order		Intra-particle diffusion		
	K_1 (min^{-1})	R^2	K_2 (g/mg.min)	R^2	K_{int} (g/mg.$min^{0.5}$)	C_{id} (mg/g)	R^2
0.25	0.0179	0.9295	2.99E-3	0.8108	0.1810	-0.1683	0.8165
0.50	0.0164	0.9695	5.98E-3	0.8510	0.1138	-0.0704	0.9091
0.75	0.0120	0.9653	7.48E-3	0.9248	0.0799	-0.0415	0.9374
1-00	0.0194	0.9539	1.4E-2	0.8157	0.0777	-0.0545	0.9318
1.25	0.0177	0.9599	2.2E-2	0.9597	0.0582	-0.0236	0.9389

3.6 Adsorption Isotherms

Following the mechanism of heterogeneous photocatalysis, the substrate is pre-adsorbed on the surface of the catalyst prior to the UV illumination [36]. The data obtained from this study were fitted to Freundlich, Langmuir and Temkin isotherm models; and the linear plots are shown in Figures 8, 9 and 10, respectively. The isotherm parameters and correlation coefficients are presented in Table 2. Langmuir isotherm with a regression value, $R^2$of 0.931 and sorption capacity of 1.56L/mg gave thebest description for the adsorption of Pb^{2+} on TiO_2. Langmuir isotherm was also reported in literature to have well described the photocatalytic decolourisation of acid orange 7 in aqueous solution [37]. The R_L value of0.5814 was obtained in this study; thus the values of $R_L$between 0 and 1 indicate favourable adsorption [30]. Though the value of R^2

(0.903) obtained from the Freundlich model was lower than the R^2value in Langmuir, 1/n (adsorption strength)was 0.7015 whichindicates favourability of the adsorption process [24]. The parameters K_T and b_T of the Temkin model were obtained at305K; $b_T$referred to as the heat of sorption gave a positive value of 3.2015 KJ/mol indicating that the adsorption process was exothermic. This is in conformity with literature [38].

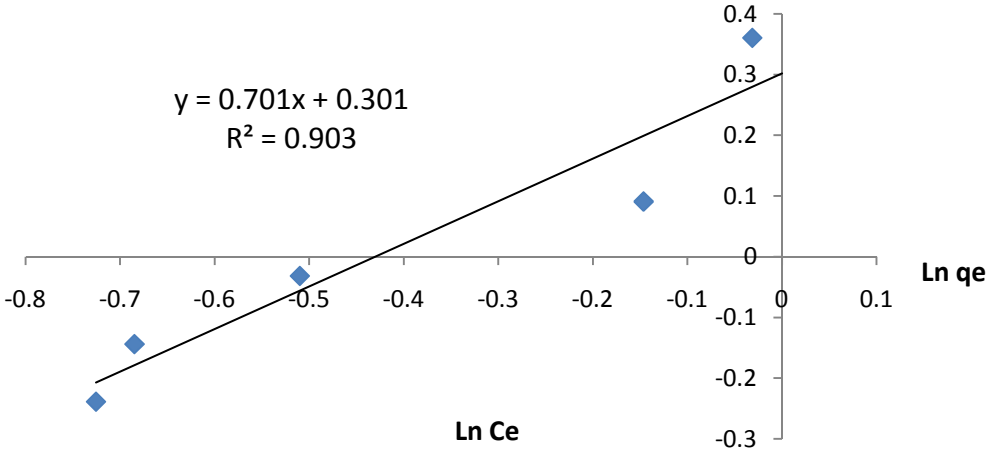

Figure 8: Freudlich sorption isotherm for photocatalytic removal of Pb^{2+}

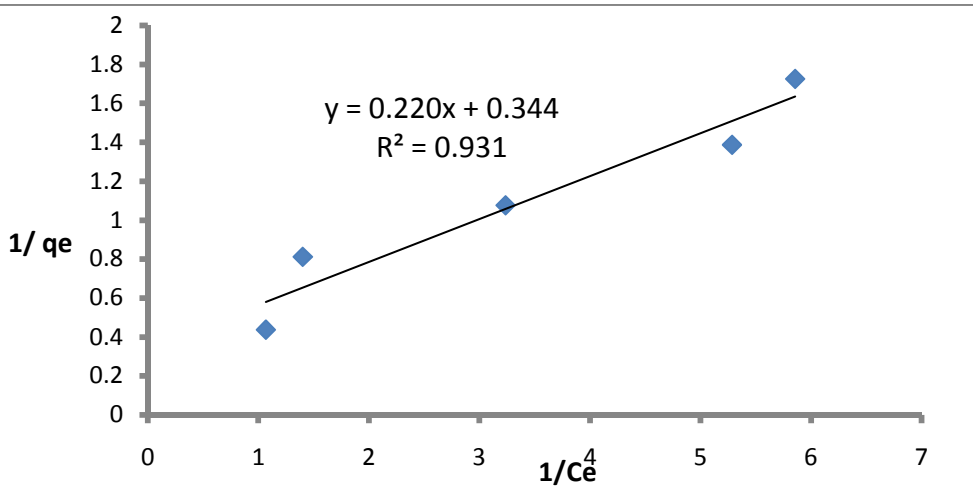

Figure 9: Langmuir sorption isotherm for photocatalytic removal of Pb^{2+}

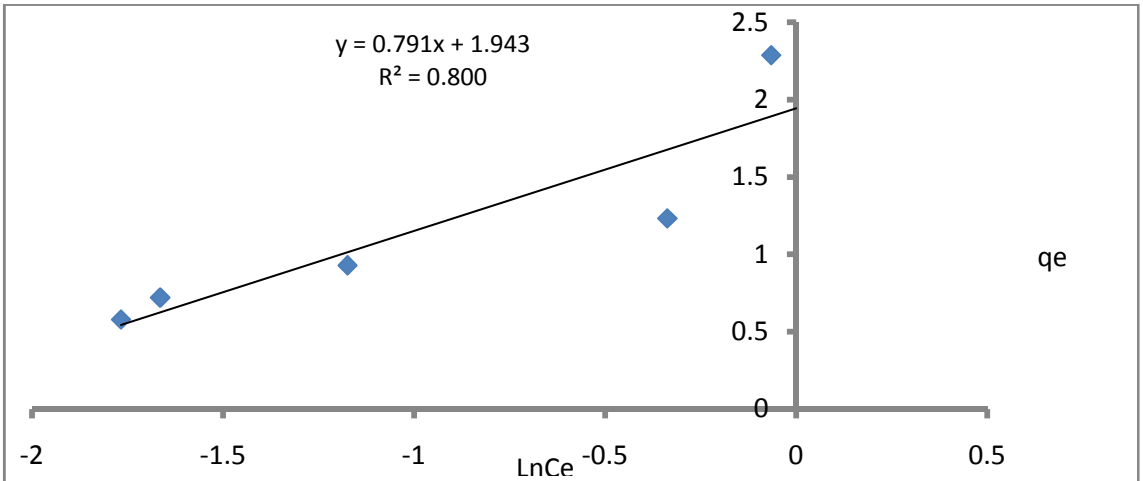

Figure 10: Temkin sorption isotherm for photocatalytic removal of Pb^{2+}

Table 2: Adsorption isotherm parameters for photocatalytic removal of Pb^{2+}inpaint effluent

Langmuir			**Freundlich**				**Temkim**		
K_L (L/mg)	R^2	R_L	K_f(mg/g)	R^2	1/n	n	K_T L/mg	b_T (kJ/mol)	R^2
1.56	0.931	0.1445	1.35	0.903	0.7015	1.43	11.65	3.2015	0.8003

4.0 Conclusion

This study has shown that effluentfrom local paint manufacturing industry containsPb^{2+}concentration of 3.796mg/Lwhich is well abovethe recommended acceptable discharge limit of < 1.0mg/Lset by FEPA. Thesunlight facilitated photocatalytic process for the removal of Pb^{2+} from aqueous solutionwas subjected to kinetic and sorption models. The pseudo-first order model gave the best description of the kinetic mechanismwhile the equilibrium data was best fitted toLangmuir isotherm. The rate constant and adsorption capacity based on pseudo-first order and Langmuir models were 0.0194min^{-1} and 1.56L/mg, respectively. The adsorption process is exothermic as the heat of sorption (3.2015) obtained from Temkim isotherm was greater than zero.It was shownin this work that sunlight facilitated photocatalytic process had an optimum TiO_2 dosage of 1g/L for effectiveremoval ofPb^{2+} from aqueous solution as against 0.9g/L with artificial UV-lamp induced photocatalysis reported in literature.

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