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PHOTOCATALYTIC DECOLOURISATION OF WASTEWATER FROM PAINT INDUSTRY USING SOLAR-IRRADIATED TITANIUM OXIDE CATALYST

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Abstract

Photocatalysis is a reliable and low-cost energy technology adopted for the abatement of environmental pollutions. In this study, the photocatalytic decolourisation of wastewater from paint industry was investigated in a batch process. Solar-irradiated titanium oxide (TiO_2) was used as photocatalyst. The experiment was carried out in two sets, first, with sunlight and secondly without the sunlight. The effect of catalyst dosage on the decolourisation process was also investigated. The residual colour in the wastewater was measured in a uv/vis spectrophotometer at a wavelength of 552nm. Results of these studies showed a decolourisation efficiency of 98.6% under the sunlight and 59.8% without sun light at optimum catalyst dosage of 1% (w/v).The photocatalytic decolourisation process was adequately fitted to the Langmuir-Hinshelwood kinetic model with a coefficient of determination (R^2) of 0.9699.The kinetics and adsorption rate constants obtained are0.0788 mg/dm^3.min and 0.1260 dm^3/mg respectively. The results indicate that $TiO_2$is an excellent solar-aided catalyst for the purification of wastewater in the environment.

Keywords: Photocatalysis, titanium oxide, decolourisation, Langmuir-Hinshelwood model, and solar-irradiation

1.0 Introduction

Paint manufacturing industry has a wide spectrum of operations ranging from small-scale units that use traditional manufacturing process, to the very large integrated industries using modern equipment and machineries. The paint industry requires great amount of chemical pigments, soluble in water and organic solvents, for its operations[1].Pigments commonly used in the paint industry include red oxide, cadmium red, saturn red, barium yellow, naples yellow, chrome green, emerald green, olympian green, cobalt blue etc. Red oxide is known as one of the single largest chemicals used in paint industry as paint primer; it isa multi-component substance comprising a complex mix of individual substances with different physico-chemical properties. Its chemical composition shows high percentage of iron oxide (Fe_2O_3), which imparts its unique red colour. Effluent generated from paint industry contain highly toxic chemical substances (inorganic and organic) which cumulate to biorefractory compounds such as Chemical oxygen demand (COD), Biochemical oxygen demand (BOD) and Total organic compound (TOC)that are harmful to the aquatic ecosystem and contaminates the food chain. Paint effluent also has adverse effects on human; it irritates the eyes, skin, and the respiratory organs, and it can contribute to muscle weakness, kidney and liver damages [2]. Based on the adverse effects of paint effluent on the environment, spillages or uncontrolled discharges into watercourses must be immediately alerted to the Environmental Agency or other appropriate regulatory body.

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Although, many conventional treatment techniques such as adsorption, membrane filtration, coagulation-flocculation, biodegradation, phytoremediation are widely used to remove colour from industrial wastewater; these methods are either expensive, inefficient or take considerable time[3]. In recent years, advanced oxidation technologies (AOTs) have been found as an efficient method for the treatment of organic and other pollutants in aqueous system [4].AOTs can be divided into catalytic and non-catalytic applications as shown in Figure 1

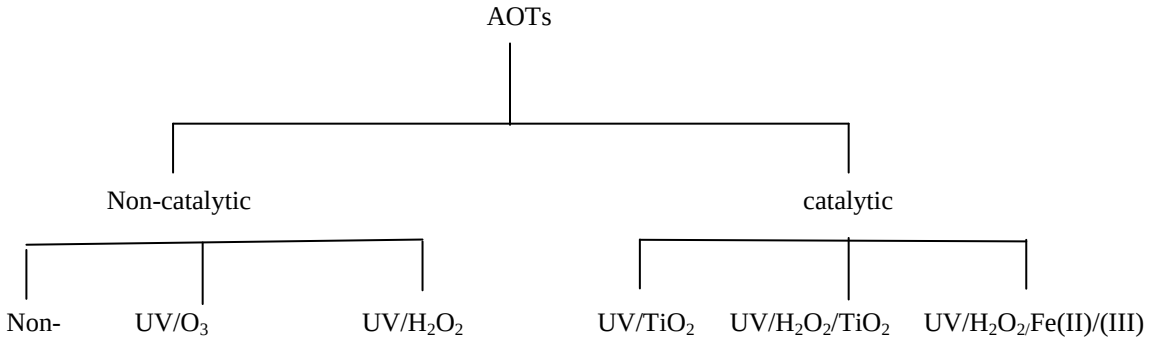

Figure 1: Subdivisions of Advanced Oxidation Technology[4].

Thermal plasma

The purpose of AOTs is to generate a powerful oxidants, the hydroxyl radical (•OH), from oxidizing agents such as ozone, hydrogen peroxide and metal oxide catalyst using ultraviolet light (UV) from natural (sunlight) or artificial energy sources. The UV in natural sunlight represents only 5%–8% of the solar spectrum at sea level[5].

The •OH is capable of oxidising organic contaminants in water and gas streams to form water and carbon (IV) oxide. Photocatalysis using a metal oxide as catalyst is a low-cost technology that has been widely used by many researchers for the removal of various types of dye from polluted water [6,7,8,9].A wide range of metal oxide semiconductors used for photocatalysis are shown in Table 1. Many studies have reported that titanium oxide or zinc oxide photocatalyst is the best method for the degradation of coloured organic chemicals in aqueous solution because they have the best photocatalytic properties [9,10,11]. TO_2 semiconductor exists in three crystalline forms; these area natase, rutile, brookite. Anatase and rutile are the common forms of the semiconductor; the former is the most effective in wastewater treatment. The band gap energies are 3.2 eV for anatase and 3.0 eV for rutile but the oxidative processes are similar. Anatase TiO_2 is of special interest since it can use natural (solar) UV radiation; this is because it has an appropriate energetic separation between its valence and conduction bands, which can be surpassed by the energy of a solar photon. [12].

Table 1: Band gap energy of some common semiconductorsused in photocatalysis [12]

Semiconductor	Band gap(eV)	Band gapWavelength (nm)
TiO_2 (rutile)	3.0	413
TiO_2 (anatase)	3.2	387
SnO_2	3.9	318
ZnO	3.2	387
ZnS	3.7	335
CdS	2.5	496

The general reaction mechanism of a metal oxide semiconductor involves several steps such as electron-hole pair production, recombination of electron pair, and chemical reaction. A semiconductor is a material that has an electrical conductivity between that of a conductor and an insulator. At low temperatures, pure semiconductors behave like insulators, but under higher temperatures or light or with the addition of impurities, however, the conductivity of semiconductors can be increased, reaching levels that may approach those of metals. The molecular orbit of semiconductor has a band structure, and the bands of interest in photocatalys is are the occupied valence band (V_B) and the unoccupied conduction band (C_B), separated by an energy distance referred to as the band gap (E_{bg}).

The band gap is related to the wavelength (λ) of the radiation by the Planck's equation:

$$\lambda = \frac{hc}{E_{bg}} \qquad (1)$$

where*h* is the Planck's constant and *c* is the speed of light.

When the photocatalyst is irradiated with photons of energy equal to or more than the band gap energy of the photocatalyst, the electrons (e^-) are excited from the valence band (V_B) to the conduction band (C_B) with the simultaneous creation of holes (h^+) in the V_B. (h^+ is imaginary positively charged particle). The positive hole and the excited electron either recombine or become involved in redox reactions with adsorbed groupsof chemical in the following ways: [13].

$TiO_2 + hv \rightarrow e^- + h^+$ (2)

Where hv is the photon energy essential to transfer the electron from $V_B$valence band to C_B. The electrons generated through irradiation could be trapped by oxygen (O_2) absorbed on the photocatalyst surface to give superoxide radical ($O_2^{\cdot-}$) as shown in equation (3);

$e^- + O_2 \rightarrow O_2^{\cdot-}$ (3)

The photocatalyticdecolourization of iron oxide (Fe_2O_3)in wastewater occurs when the electron in the conduction band reacts with $Fe^{+3}$to give Fe^{+2} according to equation (4):

$e^- + F^{3+} \rightarrow F^{2+}$ (4)

Consequently, $O_2^{\cdot-}$ could react with water molecule(H_2O) to produced hydro-peroxyl radical ($HO_2^{\cdot}$) and hydroxyl radical ($HO^{\cdot}$) which are strong oxidizing agents to decompose any organic molecules in the wastewater.

$O_2^{\cdot-} + H_2O \rightarrow HO_2^{\cdot} + HO^{\cdot}$ (5)

$HO_2^{\cdot}$will also react with Fe^{+3} to produce FeO as shown in the following equation:

$F^{3+} + HO_2^{\cdot} \rightarrow FeO + OH^+$ (6)

Simultaneously, the photo-induced holes could be trapped by surface hydroxyl groups on the photocatalyst surface to give hydroxyl radicals.

$h^+ + OH^- \rightarrow HO^{\cdot}$ (7)

$h^+ + H_2O \rightarrow HO^{\cdot} + H^+$ (8)

Finally, the organic pollutant will be oxidized to yield carbon dioxide and water as follow:

$OH^{\cdot} + pollutant + O_2 \rightarrow CO_2 + H_2O$ (9)

2.0 Materials and Methods

2.1 Material

Paint effluent was obtained from a paint manufacturing company in Benin City, Edo State, Nigeria. The sample was stored in a clean plastic jar with a screw cap, and kept in a refrigerator for a day prior to the commencement of the experiment. Anatase form of TiO_2 was used as catalyst in this study. It is a product of BDH chemical Ltd, England with an average particle size of 21 nm and surface area (BET) of 50±15m^2/g. Iron (III) Oxide (Fe_2O_3) was used for the standard curve.

2.2 Calibration curve

In order to determine the wavelength for red oxide absorption, a spectrum scanning for iron (III) oxide solution was carried out using UV/VIS spectrophotometer(PG Instrument- T70). The maximum absorbance was recorded at 552 nm. To determine the concentration of the red oxide after treatment, a calibration curve was drawn by measuring the absorbance of iron (III) Oxide solution of known concentrations[14].

2.3 Photocatalytic decolourisation

The photocatalytic studies were conducted in a batch system at atmospheric condition. For the effect of sunlight experiment, 2g of TiO_2 was mixed with 200 cm^3 in 500cm^3 Erlenmeyer flask shaken on a flat orbital shaker (Optima OS-752). The experiment was conducted between the hours of 12 noon and 3 pm outside the laboratory directly under the sun as a source of UV rays in a sunny day. The temperature was intermittently measured throughout the experiment, and an average temperature of 32±3^oC was measured. Samples were withdrawn at an interval of 20 minutes using 10 cm^3 syringe, the sample was centrifuged and filtered through a what mann No 42 filter paper. The residual colour was measured in a UV/VIS spectrophotometer at 552 nm. The experiment without light was carried out in the laboratory by wrapping the Erlenmeyer flask with aluminium foil paper to screen out any penetration of UV rays [15, 16].

The effect of catalyst dosage was performed by adding 0.5g, 1g, 1.5g, 2g, 2.5g of $TiO_2$to a set of five Erlenmeyer flasks containing 200 cm^3 of paint effluent. The flasks were agitated continuously under the sun for 3hours.Samples were collected from each flask at predetermined time to evaluate the residual colour. The percentage of declourisation was calculated using the following equation:

$$\%\ decolourisation = \frac{C_o - C_t}{C_o} \times 100 \quad (10)$$

whereC_o (mg/dm^3) is the initial concentration of red oxide in paint effluent and C_t (mg/dm^3) is the concentration in the sample at time t.

3.0 Results and Discussion

3.1 Studies on the effect of TiO_2 and sunlight irradiation

Two sets of experiments were carried out to investigate the effects of sunlight and catalyst on the decolourisation of red oxide. One set of the experiments was performed with catalystinthe laboratory without sunlight (dark experiment), and the other was done under the sunlight. Decolourisation efficiency of 59.8% was achieved without sunlight, which indicates that only adsorption process occurred. Meanwhile, 98% decolourisation was obtained with catalyst in the presence of sunlight. The plot of the data obtained from experiments with and without sunlight are shown in Figure 2. From the result, it was shown that sunlight played significant roles in the photocatalytic decolourisation of paint effluent. The efficiency of the catalyst in presence of sunlight is related to the activation of its active sites by absorbed light [17]

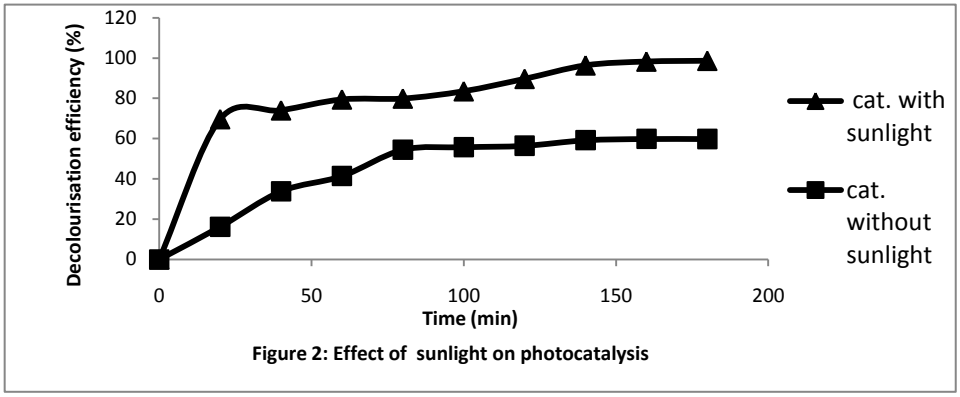

Figure 2: Effect of sunlight on photocatalysis

3.2 Effect of Catalyst Dosage

The catalyst dosage was varied from 0.25%– 1.25%to determine the optimum dosage. Figure 3 shows the effect of TiO_2dosage on the decolourisation of paint wastewater. It was observed that the percentage decolourisation increased from 74 to 98% as the catalyst dosage increases from 0.25% to 1%. Further increase in catalyst dosage to 1.25% resulted in a slight decrease in the decolourisation of wastewater. This indicates that the optimum dosage of catalyst was 1% (w/v). The initial increase in percentage decolourisation may be attributed to the increase in the active sites on the surface of the catalyst because of increased in TiO_2catalyst. When the dosage of TiO_2 is increased, the number of hydroxyl and superoxide radicals in the aqueous solution are increased, thereby leading to higher reduction of the iron (III) to iron (II) in the solution which will in turn reduce the colour of the wastewater. The decrease in decolourisation observed when the catalyst was increased above the optimum dosage can be result from the fact that the particle of the catalyst aggregate together which reduces the amount of sunlight reaching the active sites of the catalyst and consequently, reducing the amount of electron released[6, 8, 17].

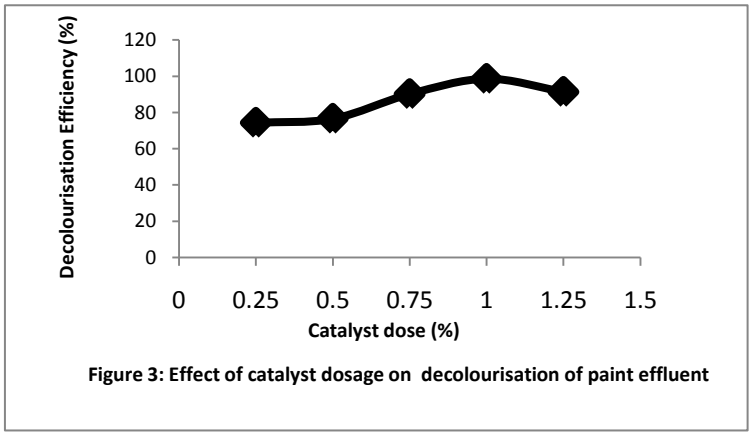

Figure 3: Effect of catalyst dosage on decolourisation of paint effluent

3.3 Kinetic Model

The experimental data obtained from the kinetics experiment were subjected to Langmuir–Hinshelwood kinetics models. This model developed by Turchi and Ollis [18] accommodates reactions and adsorption, which occur at the solid–liquid interface.

$$r = \frac{-dC}{dt} = \frac{k_r K_e C}{1 + K_e C} \qquad (11)$$

where$r$ is the rate of the reactant (mg/dm^3 min), C is the concentration of the reactant (mg/dm^3), t the irradiation time,k_r the reaction rate constant (mg/dm^{3}min), and K_e is the adsorption coefficient of the reactant (dm^3/mg). Equation (11) can be linearized to give

$$\frac{1}{r} = \frac{1}{k_r K_e}\frac{1}{C} + \frac{1}{K_e} \qquad (12)$$

A plot of $\frac{1}{r}$ against $\frac{1}{C}$ is shown in Figure 4 and the values of the k_r andK_e are presented in Table 3.

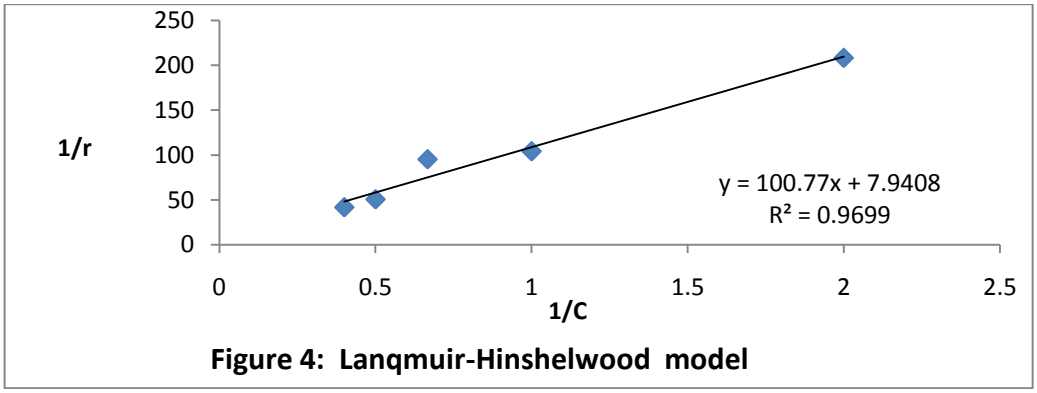

Figure 4: Lanqmuir-Hinshelwood model

When the solute concentration C is low, Langmuir–Hinshelwood equation is reduced to an apparent first-order equation as follow:

$$In\left(\frac{C_O}{C_i}\right) = kKt = kt \qquad (13)$$

In a plot of $In\left(\frac{C_O}{C_i}\right)$versus time at different catalyst dosage, the slope of the linear regression gives the apparent first-order rate constant. The kinetics data were also fitted to apparent second order equation. From the results, it was ascertained that the data fitted better to the pseudo first order because, the coefficient of determination (R^2) tends more to unity. The closeness of the R^2 to unity indicates a good fitness[8, 17].To investigate the internal diffusion mechanism during photocatalyticdecolourisation of red oxide, the intra-particle diffusion equation was used as follow:

$$q_t = K_{id}t^{0.5} \qquad (14)$$

The intra-particle diffusion plot of q_t versus $t^{0.5}$should be linear, and the coefficient (k_{id})was determined from the linear plot. Good linearization of data is observed if intra-particle diffusion is the rate limiting[19]. If the plot is not linear, and do not pass through the origin, then the intra particle diffusion shows that the mode of transport is affected by more than one process.Then equation (14) becomes:

$$q_t = K_{id}t^{0.5} + C_{id} \qquad (15)$$

whereC_{id}(intercept of the line) is intra particle diffusion constant(mg/g) which is directly proportional to the boundary layer[20]. The calculated rate constants and corresponding correlation constants obtained from the intra particle plot in Figure 5are given in Table 2.

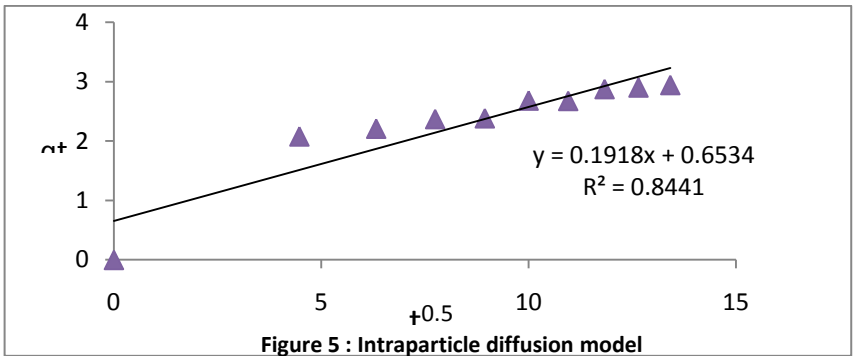

Figure 5 : Intraparticle diffusion model

Table 2:Langmuir-Hinshelwood model parameters

MODEL	PARAMETER	VALUE
Langmuir-Hinshelwood	K_e(dm^3/mg)	0.1260
	k_r (mg/dm^3.min)	0.0788
	R^2	0.9699
Intra particle diffusion	K_{int}(mg/g.min$^{0.5}$)	0.1918
	C_{id} (mg/g)	0.6534
	R^2	0.8441

Table 3: Kinetics parameter obtained from first and second order kinetic models

Catalyst dose (%)	Pseudo-first order		Pseudo-second order	
	K_1 (min^{-1})	R^2	K_2 (mg/g.min)	R^2
0.25	0.0219	0.7374	0.0216	0.8955
0.5	0.0222	0.8853	0.063	0.6905
0.75	0.016	0.8518	0.061	0.8642
1.0	0.0229	0.9163	0.094	0.601
1.25	0.022	0.8400	0.0371	0.6926

Conclusion

The photocatalytic decolourisation of paint effluent by sunlight-irradiated TiO_2 was investigated using two sets of experiments, and the following conclusions were drawn from this study. A very high decolourisation efficiency (98.6%) was achieved in 3 hours at an optimum catalyst dosage of 1% (w/v) under the sunlight. Meanwhile, about 59% decolourisation efficiency was obtained in the experiment carried out without sunlight.The kinetics of the photocatalytic process was described by the Langmuir-Hinshelwood (LH) kinetic model with the kinetic and adsorption rate constants as 0.1260 mg/L.min and 0.0788 L/mg respectively. Solar irradiated TiO_2 has proven as an effective means of decolourising industrial effluent.

Recommendation

Ultra-Violet (UV) rays in natural sunlight represents only 5%–8% of the solar spectrum at sea level and this provides a limitation for proper illumination of the catalysts in order to achieve a complete degradation of organic compounds in a short time. In order to surpass this limitation, a UV rays concentrator should be employed to increase intensity of the rays especially for field work.

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