



# Photocatalytic Degradation of Chlorobenzene in Aqueous Solutions—Comparison of $\text{TiO}_2$ with Periwinkle and Snail Shells' Powder as Photo Catalyst

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## Authors' contributions

Author NI wrote the procedure, carried out the experimental works and the UV analysis as part of his M. Eng. research work under the direct supervision of authors KMO and FAA. Author KMO wrote the introduction and discussed the results. All authors read and approved the final manuscript.

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## ABSTRACT

**Aim:** The goal of the study is to determine the efficiency of periwinkle shell powder and snail shell powder – two locally prepared photocatalysts in comparison with  $\text{TiO}_2$  in the treatment of wastewater polluted with chlorobenzene.

**Place and Duration of Study:** The present study was conducted between January and October 2011 at the Department of Chemical Engineering, University of Benin-Nigeria as part of a Master of Engineering Degree research project.

**Methodology:** The obtained periwinkle (PSA) and snail (SSA) shells were crushed to powder, sieved and then analysed for the functional group (especially the transition metals) using Fourier Transform Infra-red (FTIR) analysis. The catalytic activity of the unmodified PSA, SSA as well as their modification with  $\text{H}_2\text{O}_2$  were then compared with commercial grade  $\text{TiO}_2$  (Degussa P25) for the degradation of chlorobenzene in wastewater both under laboratory condition (dark) and solar irradiation using sets of special boron-silica glass reactors. UV/VIS spectrophotometer model T70 installed with

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printer was used for the determination of chlorobenzene concentration while BET surface area of the catalysts was determined by means of nitrogen adsorption/desorption isotherm.

**Results:** The result show that the photocatalytic activity of pure PSA and SSA were very poor when compared with TiO<sub>2</sub>. However, PSA and SSA modified with H<sub>2</sub>O<sub>2</sub> showed greater promise as their degradation efficiency increased by 87.98% and 41.72% respectively.

**Conclusion:** PSA and SSA cannot be used as photocatalyst for the degradation of organic pollutants in aqueous solution without being modified or doped with appropriate metal or non metal dopants.

*Keywords: Photocatalysts; periwinkle shell; snail shell; titanium dioxide; chlorobenzene; Degradation.*

## 1. INTRODUCTION

Environmental pollution due to anthropogenic factors has been a serious global problem since the dawn of the industrial revolution. Industrial wastes, some of which are highly toxic are daily discharged into the environment [1,2]. The oil industry in Nigeria is the worst culprit, discarding tons of toxic wastes into the atmosphere, hydrosphere and lithosphere on a continuous basis [3]. In addition to the large scale pollution caused by oil exploitation and production, the use of halogenated organic compounds as raw material for the manufacture of different industrial compounds such as drugs, dyes pesticides and solvents results in major environmental pollution to the atmosphere and the hydrosphere in particular.

Halogenated organic compounds are compounds containing a carbon directly linked with the halogen atom. Halogenated hydrocarbons and their derivatives are stable compounds, generally colourless and pleasantly smelling and with a markedly low chemical reactivity [2]. In addition, they have low volatility and are relatively more water soluble and hence are often found in aqueous media such as industrial wastewater [4]. These properties make halogenated organic compounds long lasting, non-biodegradable and non-photodegradable. One of such compounds, chlorobenzene - a chlorinated derivative of benzene had been listed as priority pollutant [5,6]. The ability of chlorobenzene to undergo wide variety of chemical reactions makes its application as reactants in numerous chemical and allied industries imperative. Chlorobenzene is used principally as chemical intermediate in the production of chemicals such as nitrochlorobenzenes and diphenyl oxide. These chemicals are subsequently used in the production of herbicides, dyestuffs, solvents, pesticides, and rubber chemicals among others [6].

The wide application of chlorobenzene based raw materials in the chemical and allied industries have resulted in the contamination of air, soil, surface water and underground water with chlorobenzene and other halogenated compounds thereby exposing humans and animals to serious health hazards. Contamination resulting from halogenated organic compounds such as chlorobenzene has been reported to cause irritation, pulmonary edema as well as inflammation of the respiratory tract in addition to liver damage and other neurological effects [7]. Based on the acute negative effects of chlorobenzene and its derivatives on humans and animals and considering their high solubility in water, it becomes necessary to device appropriate technology for the effective removal of these toxic pollutants from fresh water bodies and wastewater. Various methods have been developed for the detoxification of water contaminated with chlorobenzene and its derivatives. Many of these

methods are aimed at converting the toxic chlorobenzene and its derivatives into their non-toxic compounds [2]. Amongst these methods, photochemical processes have been found to be the most effective if the chlorinated compounds are present in the water effluent in low concentrations [8,9]. Heterogeneous photocatalytic oxidation is a photochemical process involving chemical reactions in the presence of semiconductors and light.

Heterogeneous photocatalytic oxidation process employs suitable semi-conductors as catalysts and ultraviolet light (UV) light. Thus it is based on the direct or indirect absorption of photons from UV or visible light by a semiconductor oxide that possesses the appropriate energy gap i.e. energy equal to or greater than the band gap of the semiconductor resulting in the production of electron hole ( $e^-/h^+$ ) pairs (or conduction band and valence band) during photocatalytic reaction [10]. Here, the semiconductor oxide used can behave as either electron donor or acceptor for molecules in contact with the semiconductor. The electron hole can recombine, releasing the absorbed light energy as heat without chemical reaction. Alternatively they can participate in redox reactions with absorbed species since the valence band hole are strongly oxidizing while the conduction band are strongly reducing. The excited electron can participate in redox reactions with water, hydroxyl ion ( $OH^-$ ), organic compounds on the semiconductor surface resulting in mineralization of the target pollutant [11]. Heterogeneous photocatalytic oxidation process had been found to be very effective in the degradation and conversion of persistent organic pollutants such as chlorobenzene to a more biologically degradable and less toxic substances. This reaction generates hydroxyl radicals under normal conditions with the production of end products such as  $CO_2$  and  $H_2O$  [12,13,14].

Among the common semiconductors in use,  $TiO_2$  and  $ZnO$  had proved to be of widespread environmental applications. Though  $ZnO$  as a photocatalyst exhibits unique physical and chemical characteristics such as wide band gap (3.2 eV) as well as large excitation binding energy (60 meV) at room temperature and radiation hardness, its use is restricted because it easily dissolves in acidic solutions [15]. The use of  $TiO_2$  in photocatalysis is highly favoured in detoxifying organic waste from wastewater, sludges and contaminated soils due to its high activity, low cost and availability. Other factors that enhance  $TiO_2$  photocatalytic activity are its specific surface area, the adsorption affinity and capacity for organic contaminants, electron-hole recombination process in the bulk and on the surface of the catalyst as well as the intensity and spectral distribution of the illuminating light [16,17]. Other factors include the catalyst crystal morphology, intrinsic solid state effects, stoichiometry of the catalyst oxide, concentration of the pollutant and pH [18,19].

However, despite the above characteristics of  $TiO_2$ , its commercial application in photocatalysis for treatment of aqueous wastes is limited by both the recovery of the catalyst after reaction and the economic feasibility of the process itself conditioned by the efficiency in the use of radiation. The energy used by this oxidation process at a wavelength less than 400nm is also very low (just about 4% of the solar spectrum). Based on these shortcomings, some researchers have developed supported photocatalysts with suitable recovery and optimal light absorption properties [20,21]. The use of dyes and porphyrins to enhance the efficiency of the solar spectrum to initiate the detoxification chemistry had also proved to be relatively effective [22]. Extension of the photocatalytic properties of  $TiO_2$  by regenerative photosensitization by means of  $H_2O_2$ , Fenton reagents, suspended bimetal nanoparticles as well as adsorbed coordination metal complexes have been proposed by many researchers [2,4,23,24,25,26]. In this study the effectiveness of two locally developed catalysts (periwinkle shells and snail shells) in their pure state as well as their modification with  $H_2O_2$

are compared with  $\text{TiO}_2$  (Degussa P25) - a widely used commercial grade catalyst in detoxifying effluent water polluted with chlorobenzene.

## **2. MATERIALS AND METHODS**

### **2.1 Materials**

The following were used for the experiments: Snail shells (SSA) and periwinkle shells (PSA) purchased from an open market in Warri in Delta State of Nigeria, P25 titanium dioxide ( $\text{TiO}_2$ ) was procured from BDH Chemical Ltd, Pools. England. Mortar and pestle for crushing the PSA and SSA were purchased from a local market in Benin City, Edo State of Nigeria. UV/VIS spectrophotometer model T70 installed with printer was used for the determination of chlorobenzene (CB) concentration, while Fourier Transformed Infra-red (FTIR) spectrometer model 8300 was used to determine the functional groups of the SSA and PSA. Air bath shaker THZ-82 and orbital shaker model OS-752 Optima, were used in shaking samples for adsorption experiments

### **2.2 Experimental Procedure**

#### **2.2.1 Preparation and characterization of periwinkle and snail shell powder**

100g each of SSA and PSA were washed and dried in an oven at  $110^\circ\text{C}$  to constant mass. The dried SSA and PSA were crushed using a mortar and pestle and then activated at  $600^\circ\text{C}$  in a muffle furnace. The grinded shells was sieved to obtain fine particle size ( $< 350\mu\text{m}$ ). The periwinkle shell ashes were tagged PSA while the snail shell ashes were tagged SSA. The prepared ashes were then characterized by analyzing for the elemental compositions (especially the transition elements) using Fourier Transform Infra-red (FTIR) analysis. The specific surface area of all the catalysts used in the study ( $\text{TiO}_2$  (Degussa P 25), SSA, PSA as well as SSA and PSA modified with  $\text{H}_2\text{O}_2$ ) was determined using the Brunauer, Emmett and Teller (BET) method based on nitrogen adsorption/desorption isotherm at 77K with a NOVA 1000 series analyzer in line with the standard procedure [27].

#### **2.2.2 Preparation of standard solutions**

Stock solution (500 mg/l) of chlorobenzene with 1:1 ratio of chlorobenzene-methanol solution was prepared with distilled water with the pH adjusted using 0.5M HCl and 0.1M NaOH solutions. Varying concentration of chlorobenzene solution was prepared from the stock using varied dilution ratio.

#### **2.2.3 Chlorobenzene adsorption studies**


The study was carried out using 50 ml of 500 mg/l chlorobenzene (CB) solution placed in five sets of boron-silica glass column reactors. To the five sets of reactors were added 2g each of  $\text{TiO}_2$ , PSA, SSA, as well as SSA and PSA mixed with 1 ml each of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The experiment was first conducted in the laboratory without light source (dark) and then repeated under sunlight. The CB removal efficiency was monitored at 30 minutes interval for 4 hours for both dark and sunlight irradiation. Samples were taken in triplicate through a syringe, filtered and analysed by means of a spectrophotometer that measures the absorbance of the CB in the solution at a wavelength of 258 nm. The absorbance which was consequently converted to concentration using a calibration chart


was used to calculate the CB removal efficiency. The effects of catalyst dosage, initial substrate concentration, pH variation as well as time variation were also determine to ascertain their optimum values.

### 3. RESULTS AND DISCUSSION

#### 3.1 Elemental Analysis of PSA and SSA

The results of the FTIR analysis of PSA and SSA (FT-IR spectra for the ashes are shown in the appendix) show the various functional groups present in the respective shell ashes indicated by the FTIR peaks. The corresponding functional groups for PSA were; alcohol (O-

H), carboxylic acids (-COOH), anhydride (C=O), amides (-CONH<sub>2</sub>), aromatic ring , nitro groups (N=O), alkene (=C-H), alkyl halide (-C-Cl), nitro- amines (N-H Bond). Functional

groups of the SSA were; Aldehydes (R-CHO), Carbonyl (C=O), aromatic ring , nitro group (N=O), amines-Secondary (N-H Bond), alcohol (C-OH), alkene (=C-H), alky halide (-C-Cl). Das et al. [28] reported that the presence of these functional groups enhances adsorption of the substrate to the adsorbent and that carboxyl and amino acid groups are very important moieties involved in binding process. The presence of these groups in PSA and SSA show that these ashes can be used effectively as catalysts in photocatalytic degradation of priority pollutants such as chlorobenzene present in wastewater and other water bodies.

The various metals present in PSA and SSA, whose oxides have some photo-catalytic properties that can enhance photo-degradation of organic pollutants, is shown in Table 1.

**Table 1. The results for the elemental analysis of PSA and SSA (Authors' analysis)**

PARAMETER	PSA (µg/g)	SSA (µg/g)
Iron (Fe)	21.2	20.5
Chromium (Cr)	6.3	7
Vanadium (V)	1.5	2.5
Nickel (Ni)	9	10.5
Selenium (Se)	0.125	0.075
Lead (Pb)	0.075	0.125
Aluminum (Al)	12.3	11.0
Zinc (Zn)	18.5	16.5
Tin (Sn)	8.0	7.0
Cadmium (Cd)	0.05	0.08
Copper (Cu)	4.4	1.8
Asenium (As)	ND	ND

ND = Not detected

#### 3.2 BET Surface Area Analysis

The results of the surface area analysis is shown in Table 2

**Table 2. Specific surface area of the photo catalysts used in this study**

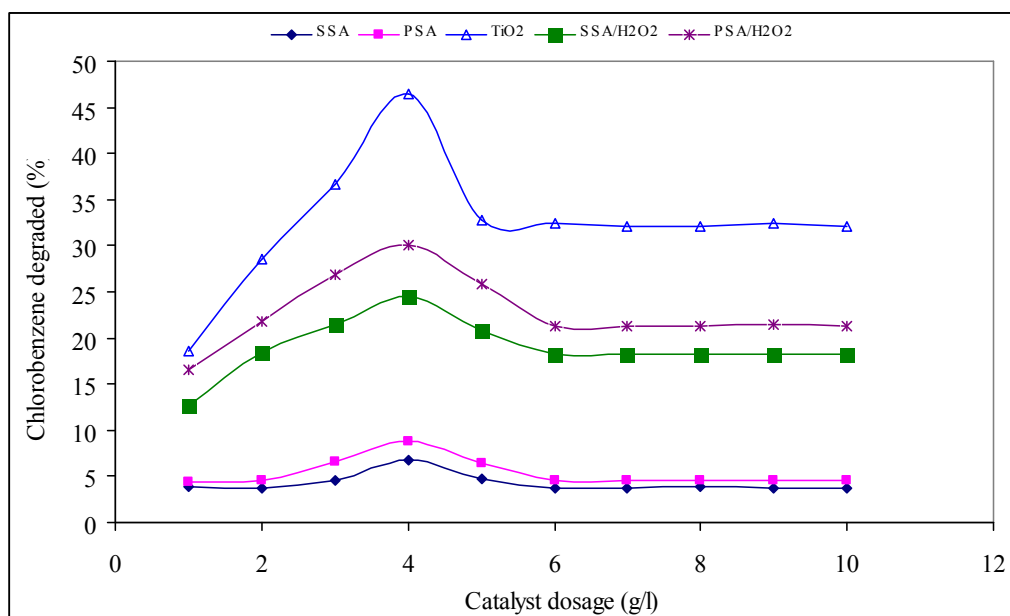
Catalyst	Specific surface area (m <sup>2</sup> /g)
TiO <sub>2</sub> (Degussa P25)	52
SSA	16
PSA	21
SSA/H <sub>2</sub> O <sub>2</sub>	29
PSA/H <sub>2</sub> O <sub>2</sub>	38

### 3.3 Optimization of Reaction Conditions

Series of experiments were conducted under sunlight irradiation to determine the optimum reaction conditions for maximum chlorobenzene degradation using both TiO<sub>2</sub> and the locally developed photocatalysts as well as their modifications. The optimum reaction conditions determined were: catalyst dosage, pH, initial substrate concentration and reaction time.

#### 3.3.1 Effect of catalyst dosage

One of the important parameters that have a strong influence on the degradation kinetics of chlorobenzene solution is the catalyst dosage. In order to optimize the required dosage of tested catalysts, experiments were conducted with varying dosage of the five catalyst samples used in this comparative study. The catalyst doses were varied from 1g to 10g. The results of the experiments is as presented in Fig. 3.1



**Fig. 3.1 Effects catalyst dosage on the photocatalytic degradation of chlorobenzene using different photocatalysts**

As can be observed from the results presented in the figure above, the percentage chlorobenzene removed increased as the catalyst dosage increases from 1 to 4 g/l for all

catalysts. At 4 g/l of catalyst dose, maximum degradation was observed for all the catalysts. The degradation rate dropped from 46.4% at 4 g/l catalyst dose to 32.8% at 5 g/l catalyst dose and remained relatively constant at this rate as catalyst dosage increases to 10 g/l for TiO<sub>2</sub>. For PSA, SSA as well as PSA and SSA modified with H<sub>2</sub>O<sub>2</sub>, the degradation rate decreased gradually from maximum values of 8.8%, 6.8%, 30.1% and 24.5% respectively at catalyst dosage of 4 g/l to 4.64%, 3.82%, 21.26% and 18.24% respectively at catalyst dosage of 6 g/l and remained relatively constant at these values as catalyst dosage increases to 10 g/l. From these results, 4 g/l was adopted as the optimum catalyst dosage for the photocatalytic experiments for all the catalysts.

The accelerated degradation experienced for all the catalysts as catalyst dosage increased from 1 to 4 g/l can be attributed to larger amount of photons adsorbed on the catalyst surface. However, as the catalyst loading increases the agglomeration and sedimentation of the catalysts makes a fraction of the catalysts inaccessible to absorbing chlorobenzene or absorbing radiation with consequent decrease in active sites available to the catalytic reaction. Studies had indicated that catalyst dosage administered above the optimum dose results in decreased degradation rate [29]. This observation is in agreement with the results of the present study. Generally, 4 g/l had been found to be the desired optimum catalyst dose for maximum degradation rate of most pollutants in wastewater [13,30]

### 3.3.2 Effect of pH Variation

pH plays an important role in photocatalytic oxidation of aqueous pollutants because it affects the production of hydroxyl radicals which are powerful oxidizing agent. In order to optimize the pH of the CB degradation process, experiments were conducted with varying pH at a fixed catalyst dosage of 4 g/l and initial substrate concentration of 100 mg/l. The results is presented in Fig. 3.2

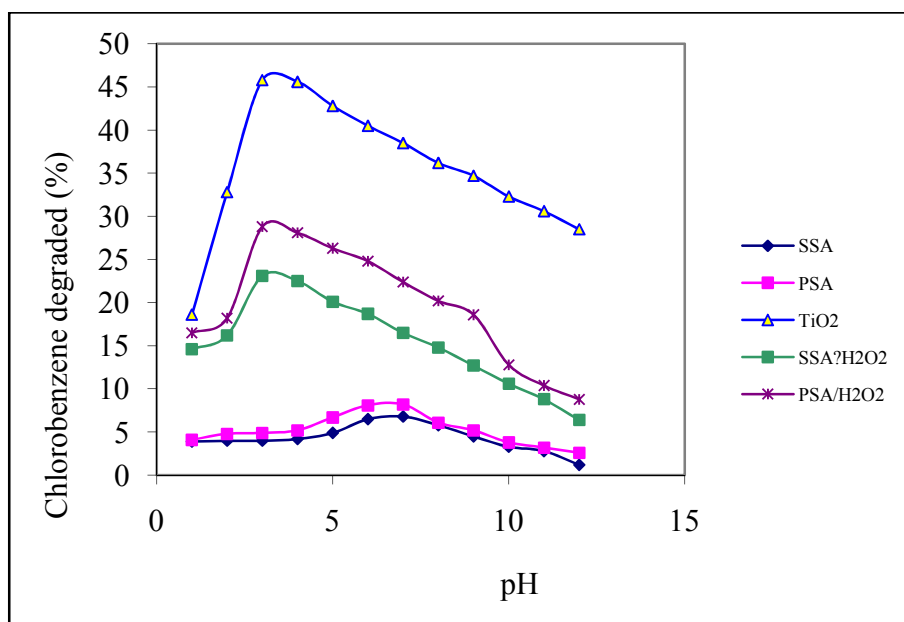
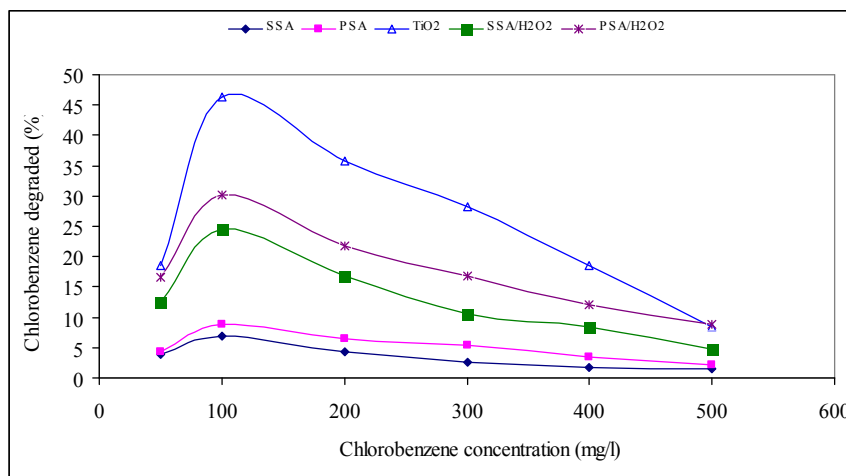


Fig. 3.2 Effects of pH variation on the photocatalytic degradation of chlorobenzene using different photocatalysts

The maximum degradation of chlorobenzene of 45.8% was obtained at a pH of 3 using TiO<sub>2</sub>. The same pH of 3 also gave maximum degradation with PSA and SSA doped with H<sub>2</sub>O<sub>2</sub>. However, maximum degradation rate of 8.2 and 6.8% were obtained at a pH of 6.8 and 7.2 for PSA and SSA used in their pure state. The role of initial pH in photocatalytic reactions is well known. It has a great effect on the electrostatic charge of the photocatalyst surface, which determines the catalyst-OH<sub>2</sub><sup>+</sup> groups. In the case of TiO<sub>2</sub> the adsorption of organic substrate with functional group like SO<sub>3</sub>H which are dissociated in aqueous media on the TiO<sub>2</sub> surface coupled with the reactivity of TiO<sub>2</sub> itself may be responsible for the acidic nature of the reaction. However, the basic nature of the pure powders of SSA and PSA may be responsible for their low photodegradation activities. The pH of these powders became normalized to 3 after the addition of H<sub>2</sub>O<sub>2</sub> which made the initial solution acidic thereby enhancing the photodegradation efficiency. The pH of the effluent after photocatalytic treatment with PSA and SSA doped with H<sub>2</sub>O<sub>2</sub> as well as TiO<sub>2</sub> was 7.38 which are biologically suitable for discharge into water body. Based on this result, pH of 3 was taken as the optimum pH for the reactions.

### 3.3.3 Effect of initial substrate concentration

The initial concentration of the pollutant in the solution to be detoxified is an important parameter to consider. As a result of this, the initial substrate concentration was optimized by varying the concentration of chlorobenzene between 50 and 500 mg/l at a catalyst dosage of 4 g/l and pH of 3. The results are presented in Fig. 3.3



**Fig. 3.3 Effects of initial substrate concentration on the photocatalytic degradation of chlorobenzene using different photocatalysts**

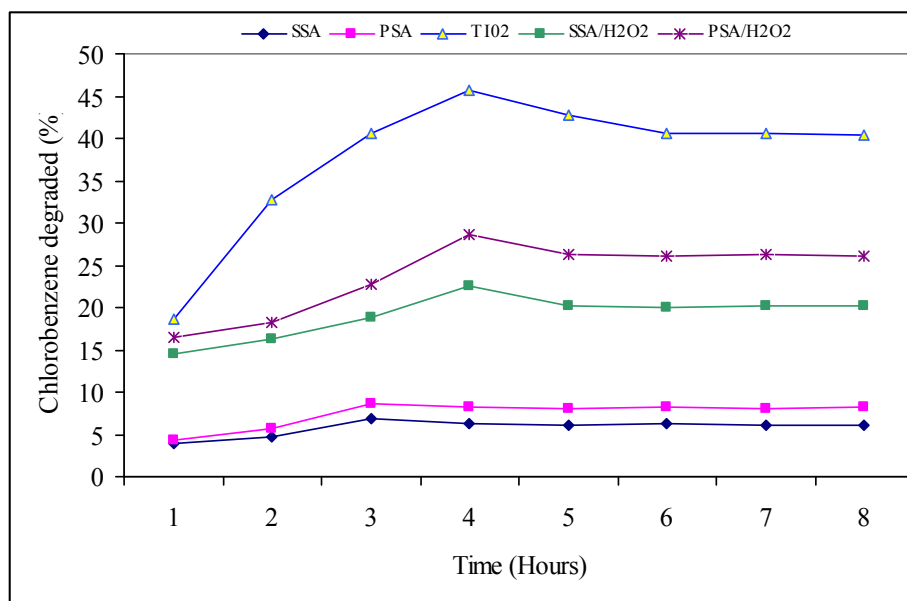
As can be seen from the figure, percentage chlorobenzene removed from the solution increased steadily from initial substrate concentration of 50 mg/l to 100 mg/l for all catalysts. As the substrate concentration increases beyond 100 mg/l, the percentage degradation decreases. This phenomenon may be as a result of the increase in the extent of adsorption on the catalyst surface as the substrate concentration increases resulting in reduced activity of the catalyst. It had been reported that at lower substrate concentration, the degradation rate is proportional to the concentration [31]. As the concentration increases beyond the optimum, the reaction is limited by diffusion to the semi-conductor surface leading to pseudo



first order kinetics. Similar observations has also made by others working on the photocatalytic degradation of 4-fluorophenol, phenol and m-nitrophenol as well as acid blue 80 using  $\text{TiO}_2$  and ZnO under solar irradiation [32,33,34].

### 3.3.4 Effect of time variation

The effect of time on the degradation of chlorobenzene under solar irradiation for  $\text{TiO}_2$ , PSA, SSA as well as PSA and SSA doped with 1 ml of  $\text{H}_2\text{O}_2$  (1% v/v) is presented in Figure 3.4



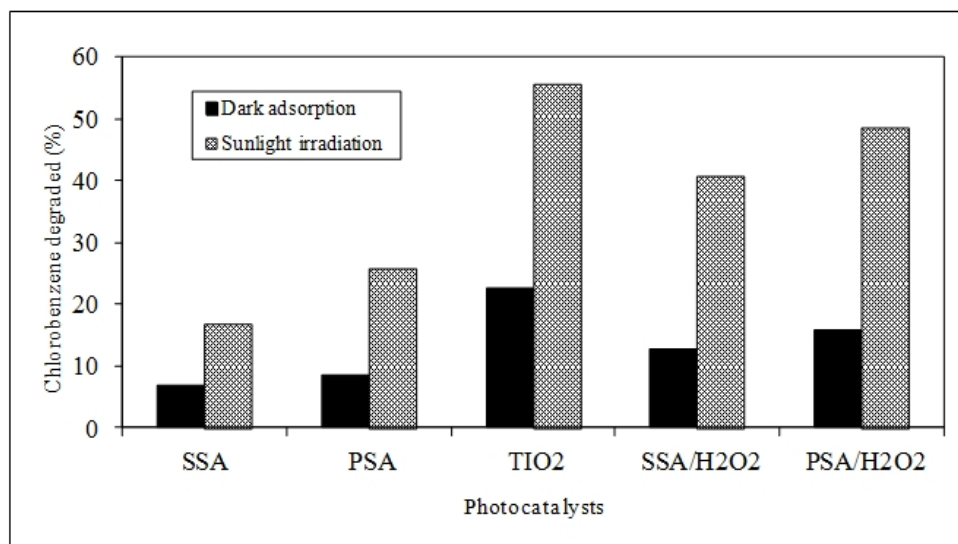
**Fig. 3.4 Effects of time variation on the photocatalytic degradation of chlorobenzene using different photocatalysts**

As observed from the Figure, the degradation rate with  $\text{TiO}_2$  photocatalyst increases steadily from 18.6 to 45.6% between 1 and 4 hours of reaction. As time increases beyond 4 hours, the degradation rate starts decreasing and remained relatively constant at about 40.5%. This gives the optimum reaction time of chlorobenzene degradation using  $\text{TiO}_2$  as 4 hours. SSA and PSA doped with 1 ml of  $\text{H}_2\text{O}_2$  (1% v/v) also exhibited similar trend with the same optimum time. However, the degradation rate with SSA and PSA used in their pure form only increased marginally from 3.9 to 6.8% and 4.4 to 8.6% between the first hour and 3 hours of reaction before decreasing to 6.2% and 8.2% respectively and remained relatively constant as time increases. It was therefore, concluded that the optimum reaction time for the developed SSA and PSA powders was 3 hours. The brevity of these powders reaction time may not be unrelated to their poor photocatalytic activity as we will see later in this discussion. The reaction time of 4 hours for  $\text{TiO}_2$  and  $\text{H}_2\text{O}_2$  modified SSA and PSA agrees with the results of earlier workers [13,35]

### 3.4 Chlorobenzene Degradation Study

After optimizing the operating conditions, degradation experiments were then conducted under laboratory condition (dark) and under sunlight irradiation using the optimum conditions

determined above. The results are as presented in Fig. 3.5. As shown in the Figure, TiO<sub>2</sub> photocatalyst degraded 22.4% and 55.6% of chlorobenzene in the dark and sunlight irradiation respectively, PSA degraded 8.6 and 25.8% while SSA degraded the least percentages (6.5 and 16.8 %) of chlorobenzene after 4 hours reaction time in each case. The high degradation rate of chlorobenzene under solar irradiation in the presence of TiO<sub>2</sub> is expected since TiO<sub>2</sub> had been found to be a highly effective photocatalyst for the degradation of priority pollutants in wastewater. This effectiveness is as a result of the high oxidizing power of the holes in the TiO<sub>2</sub> valence band enabling it to convert any organic

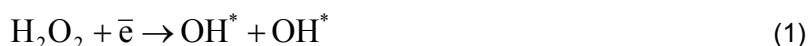


**Fig. 3.5 Percentage chlorobenzene degraded by the various photocatalysts used in the study**

species to CO<sub>2</sub>, water and mineral acids (such as HCl). These holes, however, are photogenerated and this explains why the degradation rate in the dark is quite low. The mechanisms of reactions involved are extensively discussed elsewhere [2]. Comparing the photocatalytic activity of TiO<sub>2</sub> (P25) with other photocatalysts in the degradation of methyl orange (MO), TiO<sub>2</sub> was found to be more effective than the other photocatalysts [28]. This was attributed to the crystalline composition of rutile and anatase which are the constituents of P25 TiO<sub>2</sub>, since the smaller band gap of rutile absorbs the photons and generates electron-hole pairs and then electron transfer takes place from the rutile conduction band to electron traps in anatase phase. As a result recombination is inhibited thus allowing the hole to move to the surface of the particle and react.

From Fig. 3.5, it is observed that the locally formulated catalyst powders (SSA and PSA) are poor photocatalysts in their pure state. However, PSA exhibits greater potential than SSA. This may be as a result of the presence of higher quantities of elemental transition metals such as tin (Sn), iron (Fe), copper (Cu) as well as zinc (Zn) in PSA powders when compared to SSA. Pure titania nanotubes doped with these metals had been found to enhance its photocatalytic efficiency [26,29]. The high concentrations of these transition metals in PSA may not be unrelated with the aquatic origin of the base material – periwinkles.

The difference in the photocatalytic activity of TiO<sub>2</sub> when compared to SSA, PSA and their modifications may likely be related to the variations in the BET (Brunauer, Emmet and Teller) surface area, impurities as well as existence of structural defects into crystalline framework or density of hydroxyl groups in the catalyst surface. The BET analysis of the catalysts shows that TiO<sub>2</sub> has the highest specific surface area of 52 m<sup>2</sup>/g, with the highest photocatalytic activity while SSA has the least specific surface area (16 m<sup>2</sup>/g) exhibiting the lowest photocatalytic efficiency (Table 2). It had been noted that a catalytic material with a high surface area exhibit the highest photocatalytic efficiency [11]. This is because high specific surface area gives rise to greater concentration of active sites which leads to higher reactivity. The high specific surface area of TiO<sub>2</sub> when compared with SSA and PSA may be as a result of its finer nature, since the smaller the particle size of a catalytic material, the larger its surface area and the higher its activity due to the greater absorbance of the pollutant on the catalyst surface. The two locally prepared catalyst powders (SSA and PSA) have bigger particles than TiO<sub>2</sub> and hence their low specific surface area and hence low activity. However, the surface area of these powders increased with the addition of H<sub>2</sub>O<sub>2</sub> with attendant increase in activity as Fig. 3.5 shows. This phenomenon may be as a result of initial breaking down of the powders' particle by the introduced H<sub>2</sub>O<sub>2</sub> thereby reducing the particle size of the powders leading to an increase in their surface area with increased activity. Various studies have shown that the photo catalytic degradation of water effluent pollutants can be enhanced by addition of H<sub>2</sub>O<sub>2</sub> because it is a better electron acceptor than oxygen. Reaction of H<sub>2</sub>O<sub>2</sub> with the substrate allows the formation of complexes (OH radicals) on the surface of the catalysts which shift the spectrum towards the visible region since the photo catalyst and H<sub>2</sub>O<sub>2</sub> do not absorb in this region [10, 36]. The decomposition of the H<sub>2</sub>O<sub>2</sub> for the formation of radicals during the degradation process can be represented as [10, 37]:



We believe this phenomenon is responsible for the increased photocatalytic activity of PSA in the presence of H<sub>2</sub>O<sub>2</sub> because the radicals (OH) produced by the H<sub>2</sub>O<sub>2</sub> (oxidant) attacks the chlorobenzene to initiate oxidation. Caution should however be exercised on the amount of H<sub>2</sub>O<sub>2</sub> to be added to the catalysts since high levels of H<sub>2</sub>O<sub>2</sub> inhibits the reaction kinetics. H<sub>2</sub>O<sub>2</sub> concentration of between 0.7–1.0 ml had been observed to be the optimum amount for maximum degradation [23]. Beyond the optimum H<sub>2</sub>O<sub>2</sub> amount, the degradation rate remained virtually constant. According to the authors, this may be due to the fact that the surface of the semiconductor catalyst is completely covered by H<sub>2</sub>O<sub>2</sub> molecules and as a result further amount of H<sub>2</sub>O<sub>2</sub> will remain in the bulk of the solution with no effect on the reaction rate. This explains why only 1 ml of H<sub>2</sub>O<sub>2</sub> (i.e. 1% v/v) was used throughout this study.

Though, photocatalytic activity is affected by the external area of the catalysts, the activity of the photocatalysts is not a function of surface area alone. Heat treatment of the photocatalysts had also been found to affect the photocatalytic activity significantly as the particle size of the photocatalysts increase with increasing temperature [38,39]

#### 4. CONCLUSION

The formulated PSA and SSA are poor photocatalyst in their pure unmodified state; however their photocatalytic activity can be enhanced by the addition of H<sub>2</sub>O<sub>2</sub> in moderation. PSA had better potential than SSA as it has higher content of transition metals probably acquired from

its aquatic origin. Other than the basic pH shown by PSA and SSA, other optimum conditions are the same as for TiO<sub>2</sub> and other known photocatalysts.

## **COMPETING INTEREST**

Authors have declared that no competing Interests Exists.

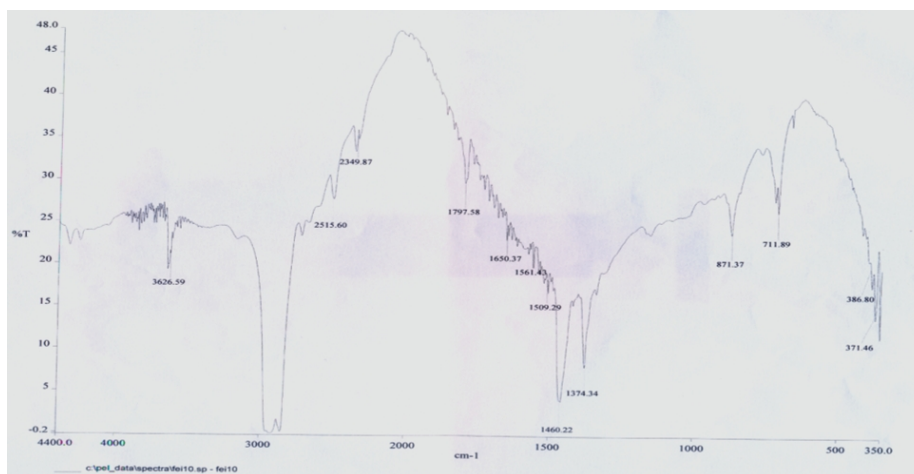
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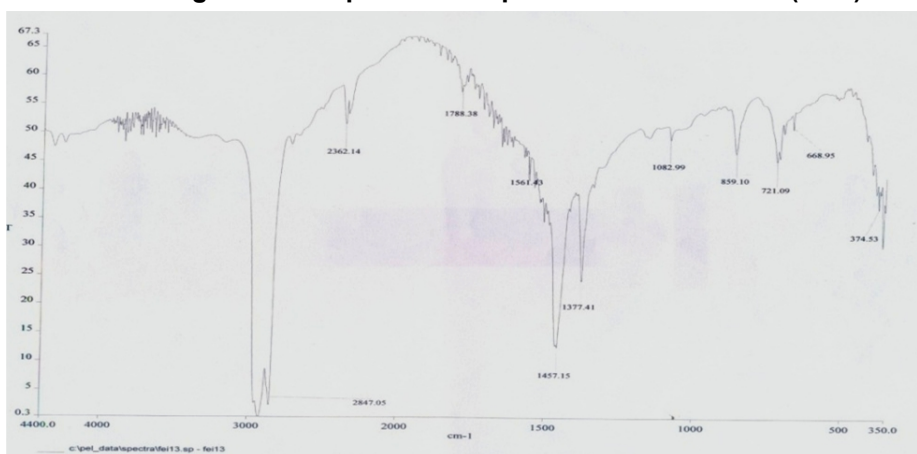
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## APPENDIX



**Fig. A1 FTIR spectrum for periwinkle shell ashes (PSA)**



**Fig. A2 FTIR spectrum for snail shell ashes (SSA)**

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