Heterogeneous Photocatalytic Degradation of Naphthalene using Periwinkle Shell Ash: Effect of Operating Variables, Kinetic and Isotherm Study

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Abstract - This study investigated the potential use of low cost photocatalyst, Periwinkle shell ash (PSA) for the batch photocatalytic degradation of naphthalene in aqueous solutions. The effect of contact time, initial naphthalene concentration, PSA dosage, presence of electron accepting oxidant (H$_2$O$_2$), and the pH of solution on the percentage photodegradation of naphthalene determined. For the treatment conditions considered in this study, the optimum values were obtained to be: contact time, 210 minutes; initial naphthalene concentration, 25 mg/L; PSA dosage, 2 g; pH, 9. The addition of Hydrogen Peroxide (H$_2$O$_2$) enhanced the photodegradation process with almost 100 percent degradation achieved. The adsorption equilibrium data fitted well to the Langmuir isotherm equation ($R^2$=0.993) indicating monolayer type adsorption while the kinetics of the process was well described by the Langmuir-Hinshelwood kinetic model with high correlation coefficient value ($R^2$=0.998). This study has demonstrated that the low cost photocatalyst, PSA can be used for removal of naphthalene from aqueous solution. Also the kinetic information obtained can be used for designing treatment systems for naphthalene abatement.

INTRODUCTION

The scale of environmental pollution and particularly water pollution in the world today has prompted engineers and scientists to focus attention on cleaner and more environmentally friendly processes (Abdollahi et al., 2011). Naphthalene is an important polycyclic aromatic hydrocarbon (PAH) which enters the environment through various sources such as incomplete combustion of gasoline and diesel in internal combustion engines, combustion of coal and oil for power generation, wood burning, tobacco smoking, fumigants etc (Jia and Batterman, 2010; Li et al., 2010; Wilson et al., 2003). As a result of it relatively higher solubility compared to other PAHs, it can be readily mobilised into the aqueous phase through discharges from industrial and domestic effluents, leaks of PAHs containing materials, used oil, bilge water, runoff from paved roads, parking lots etc (Alamo-Nole et al., 2011; Lair et al., 2008).

Exposure to naphthalene is considered to be carcinogenic, toxic and mutagenic to humans with both acute and chronic effects on health; hence it has been listed as a priority environmental pollutant by many countries (ATSDR, 2005; Henner et al., 1997; Lair et al., 2008). Removal of naphthalene from aqueous solutions can be accomplished by various methods including electron beam irradiation (Cooper et al., 2002), biodegradation using surfactants (Liu et al., 1995), ozonolysis (Legube et al., 1986), adsorption using zeolites and activated carbon (Ania et al., 2007; Chang et al., 2004) and photocatalytic degradation using Titanium dioxide (TiO$_2$) and Zinc oxide (ZnO) (Lair et al., 2008; Zhou et al., 2012).

Photocatalysis is a promising technique for the degradation of organic pollutants in aqueous media. It is based on the surface activation of semiconductors notably ZnO and TiO$_2$ by ultraviolet (UV) radiation. Perhaps the most significant advantage of this technique is that it can be used to degrade most organic compounds which are not amenable to other conventional treatment processes. It is faster than most bioprocesses and cheaper than ozonolysis and radiation based processes as it can be carried out under direct sunlight, making it able to operate independent of any external power source (Lair et al., 2008).

Woo et al. (2009) studied the photocatalytic degradation of some PAHs namely naphthalene, acenaphthylene, phenanthrene, anthracene, and benzo[a]anthracene. These PAHs typically have low solubility in aqueous medium hence they investigated the effect of acetone on the photocatalytic degradation efficiency. They reported that addition of 16% acetone greatly enhanced the efficiency of the process with all of the PAHs degraded within a 24 hour period using TiO$_2$. Gautam et al. (2005) studied the photocatalytic degradation of 4-nitroaniline using solar and artificial UV radiation in the presence of TiO$_2$ suspensions in a batch and continuous annular reactor. They observed that catalyst loading, pH, initial concentration and the presence of anions influenced the rate of photocatalytic degradation. They further reported that P-Aminophenol, p-benzoquinone...
and hydroquinone were the intermediates during the degradation process. Wu et al. (2008) studied the photocatalytic degradation of terbufos in aqueous suspensions using TiO$_2$. They reported that various operational variables such as catalyst loading, pH, and the presence of anions affected the rate of degradation with about 99% of terbufos degraded within 90 minutes. Vasconcelos et al. (2009) reported results on the performance of heterogeneous photocatalytic degradation, photo-induced oxidation, ozonation and peroxone in degrading the fluoroquinolone antimicrobial ciprofloxacin (CIP) in a hospital effluent. They reported that both heterogeneous photocatalytic degradation and peroxone led to almost complete CIP degradation after one hour of treatment.

From these studies, it was observed that photocatalytic degradation is fast and efficient and conventional catalyst such as TiO$_2$ is typically used in the presence of UV light. The use of TiO$_2$ in photocatalysis is highly evident in degrading organic pollutants in wastewater, sludges and contaminated soils due to its high activity, stability under irradiation, reliability, low cost and availability (Ahmed et al., 2011). Despite these attractive characteristics, the commercial application of TiO$_2$ for the photocatalytic degradation of liquid wastes is limited by the recovery potential of the catalyst and economic viability of the process with respect to the efficiency in the use of radiation. As a result of these limitations, researchers have focused attention on the development of photocatalysts with better recovery and light absorption capacity. Hence, focus will be on replacement of the commercial catalysts with locally sourced catalysts such as periwinkle shell ash. Periwinkle shell is a waste product generated from the consumption.

Periwinkle, a small greenish-blue marine snail housed in a V shaped spiral shell. It is found in many coastal communities within Nigeria (Olutoge et al., 2012). After consumption of the edible part as sea food, the shell is typically disposed off as waste thereby constituting environmental problems. Although some research work have focused on utilising the shell as coarse aggregate in concrete, manufacture of building blocks, as paving of water logged areas e.t.c., yet a large amount of these shells are still disposed resulting in the need to find other means of improving upon the reuse capacity of these shells (Aku et al., 2012).

The aim of this study therefore is to evaluate the potential use of periwinkle shell ash (PSA) for the photocatalytic degradation of naphthalene in aqueous solution. The effects of factors such as contact time, initial naphthalene concentration, catalyst dosage, pH, and amount of oxidant (Hydrogen peroxide, H$_2$O$_2$) on the degradation process was investigated. The photocatalytic degradation of naphthalene was further evaluated by carrying out kinetic (pseudo-first-order, pseudo-second-order, intra particle diffusion and Langmuir-Hinshelwood models) and isotherm studies (using common isotherms such as Langmuir, and Freundlich isotherms).

### MATERIALS AND METHODS

#### Preparation and Characterisation of Adsorbent (Periwinkle shell ash)

Periwinkle shells were obtained from Evbuobanosa in Edo State of Nigeria. They were washed and dried in an oven at 110°C to constant mass, followed by crushing, then calcined at 600°C in a muffle furnace. The calcination was carried out in such a way that neither the fuel for heating nor the fire gases came in contact with the material that was being calcined. It was thereafter sieved to obtain fine particles (< 350Hm) of periwinkle shell ash (PSA). The prepared PSA was characterized by determining the composition using X-Ray Fluorescence (XRF) analysis. Complete mineralogical analysis was carried out by X-ray diffraction (XRD) to determine the ultimate elemental composition of the PSA using a Philips X-ray diffractometer (Aku et al., 2012). Fourier transform infrared spectrometry (FTIR) was also carried out on the PSA. The IR spectra of the PSA were recorded using Perkin Elmer spectrum 100 FT–IR spectrometer in the frequency range 4000 to 400 cm$^{-1}$, operating in ATR (attenuated total reflectance) mode. The surface structure and other properties of the PSA were evaluated by nitrogen adsorption method at -196°C (Aisien et al., 2013). Nitrogen adsorption isotherms were determined using an adsorption equipment (BET 624, Micro-meritics, Germany). The surface area of the PSA was determined using the standard BET equation. The bulk density of the PSA was determined following standard methods (APHA-AWWA-WPCF, 1989).

#### Preparation of Adsorbate

Analytical reagent grade naphthalene, provided by Griffin and George Ltd, Loughborough, England was used as the representative PAH. A stock solution of naphthalene was prepared by dissolving 1 g of naphthalene in 1L of a binary solution comprising 50 mL of methanol (British Drug Houses Ltd, England) and 950 mL of deionised water. Naphthalene is a hydrophobic compound with low solubility in water. The water-methanol solution was
used instead of pure deionised water to enhance the solubility of hydrophobic naphthalene (Agarry et al., 2013; Chang et al., 2004). Working solutions with different concentrations of naphthalene were prepared by appropriate dilutions of the stock solution with distilled water immediately prior to their use.

**Analysis of Naphthalene in Aqueous Solution**

A UV-Vis spectrophotometer (PG Instruments model T70) was used to determine the concentration of undegraded naphthalene in the aqueous medium at a wavelength of 226 nm. The pH of the aqueous medium was adjusted using 0.5 M HCl and 0.1 M NaOH solutions.

**Batch Study of the Photocatalytic Degradation of Naphthalene**

Batch photocatalytic degradation of naphthalene using PSA in the presence of UV radiation from sunlight was carried out in mechanically agitated 250 mL jacketed glass flasks with a working volume of 100 mL. Two grams (2 g) of PSA was added to the aqueous solution of naphthalene of the desired concentration. For all studies, the suspensions were magnetically stirred without any permanent air bubbling. The temperature was maintained at 20°C and monitored throughout the process (Lair et al., 2008). The effects of contact time, initial naphthalene concentration, PSA dosage, amount of oxidant and pH of solution on the degradation efficiency were investigated. At the end of each experiment the agitated solution mixture was filtered through a 0.45 μm membrane and the residual concentration of naphthalene was determined spectrophotometrically. The percentage photocatalytic degradation of naphthalene was calculated using the equation:

\[
\text{% Photodegradation} = \left(\frac{C_o - C_t}{C_o}\right) \times 100
\]

where \(C_o\) and \(C_t\) are the initial and the liquid-phase concentration of naphthalene at time \(t\), respectively.

**RESULTS AND DISCUSSION**

**Characterisation of PSA**

PSA is a very complex material in terms of chemical composition as it contains a lot of chemical compounds typically oxide of metals. The chemical composition of PSA as obtained from X-Ray Fluorescence (XRF) analysis is presented in Table 1

<table>
<thead>
<tr>
<th>Chemical Component</th>
<th>Composition (wt%)</th>
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<tbody>
<tr>
<td>MgO</td>
<td>1.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>33.2</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.0</td>
</tr>
<tr>
<td>MnO₂</td>
<td>1.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.2</td>
</tr>
<tr>
<td>CaO</td>
<td>41.3</td>
</tr>
<tr>
<td>CuO</td>
<td>1.03</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.38</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.02</td>
</tr>
<tr>
<td>on Ignition</td>
<td>1.8</td>
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The results of complete mineralogical analysis as carried out by X-ray diffraction (XRD) to determine the ultimate elemental composition of the PSA is presented in Table 2. The major constituent of the PSA used in this study was calcium oxide (CaO) which accounted for 41.3% of the weight of PSA characterised. This was followed by silica, aluminium oxide and Iron oxide which accounted for about 33.2, 9.2 and 5% respectively as shown in Table 1. Some other oxides such as K₂O, Na₂O, TiO₂ and MnO₂ were also found to be present in small amounts. XRD results obtained for ultimate elemental composition indicate that the major element found in PSA is iron (Fe) which accounted for about 19.2% of the weight of PSA characterised. This was followed by
Zinc (Zn) and Nickel (Ni) which accounted for about 16.5 and 9% respectively as shown in Table 2. Some of the oxides and elements presented in Tables 1 and 2 have been established to possess photocatalytic properties thus supporting the choice of PSA for this study.

Table 2: Ultimate elemental composition of PSA

<table>
<thead>
<tr>
<th>Chemical Component</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>19.20</td>
</tr>
<tr>
<td>Cr</td>
<td>6.30</td>
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<tr>
<td>V</td>
<td>1.50</td>
</tr>
<tr>
<td>Ni</td>
<td>9.00</td>
</tr>
<tr>
<td>Se</td>
<td>0.13</td>
</tr>
<tr>
<td>Pb</td>
<td>0.08</td>
</tr>
<tr>
<td>Al</td>
<td>12.30</td>
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<tr>
<td>Zn</td>
<td>16.50</td>
</tr>
<tr>
<td>Sn</td>
<td>8.00</td>
</tr>
<tr>
<td>Cd</td>
<td>0.05</td>
</tr>
<tr>
<td>Cu</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Table 3: Physical properties of PSA

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m²/g)</td>
<td>400</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>2940</td>
</tr>
<tr>
<td>Porosity (-)</td>
<td>0.004</td>
</tr>
</tbody>
</table>

The surface area, bulk density, and porosity of the PSA used in this study are presented in Table 3. The results presented in Tables 1, 2 and 3 are similar to those reported in the literature (Kosmatka et al., 2003; Owabor and Iyaomolere, 2013; Umoh and Olusola, 2012).

The pattern of naphthalene uptake by PSA may be attributed to the active groups and bonds present in the photocatalyst (Nagarajan et al., 2013). The result of FTIR analysis of the PSA in the range 350 to 4400 cm⁻¹ is shown in Figure 1. Peaks in the range of 3100 to 3500 cm⁻¹ is indicative of the presence of OH groups and the stretching of the N-H bond of the amino group (Park et al., 2005). Absorption bands in the range of 2700 to 1430 cm⁻¹ and 900 to 1380 cm⁻¹ are indicative of the presence of phenyl groups and the stretching of the C-O bond in carboxylic groups present in the PSA.

![FTIR spectra of periwinkle shell ash](image-url)
Effect of contact time on the photocatalytic degradation of naphthalene

The profile of time dependent study of photocatalytic degradation of naphthalene by PSA in the presence of UV from sunlight is shown in Figure 2. It can be observed from the Figure that the degradation process was rapid for the first 150 minutes as indicated by the steep increase in the percentage degradation of naphthalene. The rate of photocatalytic degradation continues to increase but less rapidly for the next 60 minutes and the profile levels off thereafter indicating that equilibrium has been reached. At equilibrium, all available active sites on the PSA particles are occupied by the naphthalene molecules which leads to saturation hence no noticeable increase in degradation is observed. The rapid rate of photodegradation observed at the initial stage of the process may be attributed to the abundant availability of active sites on the surface of the PSA. These sites are later occupied by the naphthalene molecule as the process progresses consequently leading to the slow degradation rate observed in the later part of the process (Amenaghawon et al., 2013; Mahvi et al., 2004). An equilibrium time of 100 minutes was reported by Woo et al. (2009) for the photocatalytic removal of naphthalene from aqueous solution using Titanium dioxide (TiO$_2$) in the presence of UV light. Abdollahi et al. (2011) reported an equilibrium contact time of 240 minutes for the photodegradation of m-cresol by Zinc Oxide using visible light irradiation.

Effect of initial naphthalene concentration on the photocatalytic degradation of naphthalene

The concentration of pollutant is a very important variable during any abatement process. The effect of the initial concentration of naphthalene on the photodegradation efficiency is presented in Figure 3. The results show that increasing the concentration of naphthalene resulted in a decrease in the percentage degradation of naphthalene by PSA. At an initial concentration of 25 mg/L, there was about 90% photodegradation of naphthalene while the photodegradation reduced to about 60% at an initial concentration of 150 mg/L$^{-1}$.

Fig. 2: Effect of contact time on the photocatalytic degradation of naphthalene by PSA (pH 9; PSA dose, 2 g; initial concentration, 25 mg$L^{-1}$; Temperature, 20°C)

Fig. 3: Effect of initial concentration on the photocatalytic degradation of naphthalene by PSA (pH 9; PSA dose, 2 g; Temperature, 20°C)
The trend observed can be explained by the fact that at high concentrations of naphthalene, the active sites on the PSA are occupied by the naphthalene molecules and its intermediates thereby leading to reduced generation of the electron-hole pair ($e^-h^+$) which consequently reduces the photodegradation efficiency (Abdollahi et al., 2011; Konstantinou and Albanis, 2004). Another reason could be that with every other variable held constant while the initial naphthalene concentration is increased, the amount of hydroxyl and oxygen ($\cdot$OH and $O_2^{2-}$) free radicals formed on the surface of the PSA is also constant. Hence the relative ratio of these radicals available for attacking the naphthalene molecules decreases and the photodegradation efficiency consequently decreases (Lathasree et al., 2004; Rana and Sharma, 2010).

**Effect of PSA dosage on the photocatalytic degradation of naphthalene**

The result of the investigation of the effect of PSA dosage on the photocatalytic degradation of naphthalene is presented in Figure 4. The percentage degradation of naphthalene initially increased with increase in PSA dosage up to a maximum value of about 90% at a PSA dosage of 2 g. Further increase in PSA dosage resulted in a decrease in the percentage degradation of naphthalene. The initial increase in percentage degradation of naphthalene observed could be attributed to the fact that increasing the amount of PSA increases the number of active sites on the PSA surface which in turn increases the number of free radicals ($\cdot$OH and $O_2^{2-}$) consequently leading to enhanced photodegradation of naphthalene (Inamdar and Singh, 2008). Furthermore, more of the naphthalene molecules were removed from the solution by adsorption as a result of the increase in the dosage of PSA.

![Fig. 4: Effect of PSA dosage on the photocatalytic degradation of naphthalene by PSA (pH 9; initial concentration, 25 mg L$^{-1}$; Temperature, 20°C)](image)

![Fig. 5: Effect of pH on the photocatalytic degradation of naphthalene by PSA (Initial concentration, 25 mg L$^{-1}$; PSA dose, 2 g; Temperature, 20°C)](image)
The decrease in photodegradation efficiency observed beyond the optimum PSA dosage might have been as a result of some factors. These factors include increased opacity of the aqueous medium and enhancement of the light reflectance as a result of the excess of PSA particles, agglomeration and sedimentation of the PSA particles is possible at high PSA dosage, thus making a fraction of the PSA surface inaccessible for radiation absorption and consequently resulting in a decrease in the degradation of the naphthalene molecules (Abdollahi et al., 2011; Konstantinou and Albanis, 2004; Rana and Sharma, 2010).

**Effect of pH on the photocatalytic degradation of naphthalene**

The effect of pH on the photocatalytic degradation of naphthalene by PSA is presented in Figure 5. The pH of the aqueous medium is important in that it controls the surface charge properties of the photocatalyst (Abdollahi et al., 2011). It also affects the production of hydroxyl radicals which are powerful oxidizing agents (Rana and Sharma, 2010). The percentage degradation of naphthalene initially increased with increase in pH up to a maximum value of about 92% at a pH of 9. Further increase in pH did not result in an increase in the percentage degradation of naphthalene. Similar observations have been reported by Qamar et al. (2005) for the photocatalysed degradation of two selected azo dye derivative in aqueous suspension as well as Abdollahi et al. (2011) for the photodegradation of m-cresol by Zinc Oxide under visible-light irradiation. The initial increase in percentage degradation of naphthalene observed could be attributed to the increase in the adsorption of naphthalene on the PSA surface which results from a decrease in the electrostatic repulsive forces and increased interaction between photocatalyst surface and naphthalene molecules (Kosmulski, 2006). Additionally, in alkaline solutions, the hydroxyl ions (OH\(^-\)) are readily generated. When a hole is generated by the photocatalyst, an electron is abstracted from the OH\(^-\) ions converting it into hydroxyl radicals (•OH) which are responsible for the photodegradation of naphthalene (Menkiti et al., 2009). However, beyond the pH value of 9, the photodegradation efficiency was observed to decrease. This could be attributed to the fact that at high pH values and consequently high hydroxyl ions (OH\(^-\)) concentrations, the rate at which the hydroxyl radicals (•OH) are used up is accelerated resulting in a decrease in the photodegradation efficiency (Abdollahi et al., 2011). In addition, the abundant hydroxyl ions (OH\(^-\)) generated at high pH values will compete with the electron rich naphthalene for adsorption on the PSA surface. The hydroxyl ions (OH\(^-\)) will make the PSA surface to be negatively charged and as a result, the approach of the naphthalene molecules to the PSA surface will be slowed because of the repulsive force between the hydroxyl ions (OH\(^-\)) and the naphthalene molecules thereby leading to a decrease in the photodegradation efficiency (Kothari et al., 2007).

**Effect of oxidant dosage on the photocatalytic degradation of naphthalene**

The effect of hydrogen peroxide (H\(_2\)O\(_2\)) on the photocatalytic degradation of naphthalene by PSA is illustrated in Figure 6. Generally, it can be observed that the percentage degradation of naphthalene increased with increase in the amount of oxidant used. Almost 100% degradation of naphthalene was recorded when 10 cm\(^3\) of hydrogen peroxide was used. The trend observed may be due to the oxidative effect of hydrogen peroxide. The effect of H\(_2\)O\(_2\) has been the subject of many studies and it has been established that it increases the photodegradation rates of organic pollutants (Hallam, 1992). Hydrogen peroxide which is an electron acceptor is known to generate hydroxyl radicals by the mechanisms shown in equation (2). H\(_2\)O\(_2\) is a better electron acceptor than molecular oxygen based on their respective one-electron reduction potentials.

\[
H_2O_2 + e^- \rightarrow OH^- + OH
\]  

(2)

Fig. 6: Effect of oxidant (H\(_2\)O\(_2\)) loading on the photocatalytic degradation of naphthalene by PSA (pH, 9; initial concentration, 25 mg/L PSA dose, 2 g; Temperature, 20°C)
The increase in percentage degradation of naphthalene observed when the amount of \( \text{H}_2\text{O}_2 \) was increased may be attributed to some factors which include the ability of \( \text{H}_2\text{O}_2 \) to remove the electrons trapped on the surface of the PSA thereby lowering the electron-hole recombination rate and consequently improving the utilisation of holes in the production of the hydroxyl radicals (•OH). In addition \( \text{H}_2\text{O}_2 \) can also cleave in the presence of UV radiation to directly produce the hydroxyl radicals (•OH). Lastly, rapid oxygen consumption or passive oxygen mass transfer in the liquid phase may result to that phase being depleted of oxygen, hence \( \text{H}_2\text{O}_2 \) addition alleviates this problem. The free radicals formed from the addition of \( \text{H}_2\text{O}_2 \) create a strong oxidation environment which favours the photocatalytic degradation of naphthalene.

**Kinetics of Photodegradation of Naphthalene**

The kinetics of photodegradation was studied for its important function in the treatment of naphthalene contaminated aqueous systems. Four kinetic models namely Lagergren pseudo first order, pseudo second-order, intra particle diffusion and Langmuir-Hinshelwood kinetic models were used to elucidate the mechanism of the degradation process.

**Pseudo-first order model**

The Lagergren pseudo first order kinetic model (Lagergren, 1898) has been widely used to describe the kinetics of heterogeneous treatment processes. It is expressed in its integrated linear form in Equation (3).

\[
\ln(q_e - q_t) = \ln(q_e - k_1 t)
\]  

(3)

where \( q_e \) and \( q_t \) (mg/g) are adsorption capacity at equilibrium and at time \( t \), respectively, \( k_1 \) is the rate constant of pseudo first order adsorption (min\(^{-1}\)). The values of \( \ln(q_e - q_t) \) were linearly correlated with \( t \). The plot of \( \ln(q_e - q_t) \) versus \( t \) resulted in a linear relationship from which \( k_1 \) and \( q_e \) was determined from the slope and intercept respectively as shown in Figure 7. The first order rate constants calculated from the plot are given in Table 4. A linear relationship observed in the semi-log plot is indicative of the applicability of the model and the first order of the process.

**Pseudo-second order model**

The pseudo-second order kinetic model which assumes that chemisorption is the rate determining step can be expressed in its integrated linear form as in Equation (4).

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t}
\]  

(4)

The initial adsorption rate, \( h \) (mg.g\(^{-1}\).min\(^{-1}\)) is expressed as follows:

\[
h = k_2 q_e^2
\]  

(5)

Where \( k_2 \) is the rate constant of the pseudo second order process (g.mg\(^{-1}\).min\(^{-1}\)). The plot of \( (t/q_t) \) and \( t \) of Equation (4) is shown in Figure 8. The kinetic constants calculated from the plot are shown in Table 4. It can be observed that the model did not fit the experimental data. This indicates that the model was not able to describe the mechanism of the process.
Intra particle diffusion model

The intra particle diffusion kinetic model (Weber and Morris, 1963) was fitted to the batch equilibrium data to elucidate the diffusion mechanism. The model equation is presented in Equation (6).

\[ q_t = k_p t^{1/2} + c \]  

(6)

Where \( K_p \) is the intra particle diffusion rate constant (mg g\(^{-1}\) min\(^{-1/2}\)) and \( c \) is an indication of boundary layer effect. The larger the intercept, the greater is the contribution of the surface sorption in the rate controlling step. The calculated values of the intra particle diffusion rate constant and the boundary layer thickness are presented in Table 4. The plot of \( q_t \) vs \( t^{1/2} \) as presented in Figure 9 indicates the existence (although not significant) of some boundary layer effect and further showed that intra particle diffusion was not the only rate limiting step.

Langmuir-Hinshelwood model

The Langmuir–Hinshelwood kinetic equation has been applied severally to the analysis of heterogeneous photocatalytic reactions (Bianco-Prevot et al., 2001; Houas et al., 2001; Lachheb et al., 2002; Stylidi et al., 2003).

\[ r = \frac{kC}{1 + KC} \]  

(7)

where \( r \) is the degradation rate of the pollutant (mg/L.min), \( C \) the concentration of the pollutant (mg/L), \( t \) the irradiation time, \( k \) the reaction rate constant (mg/L.min), and \( K \) is the adsorption coefficient of the pollutant (L/mg). The values of the calculated constants are presented in Table 4. A linear expression was obtained by plotting the reciprocal initial rate against the reciprocal initial concentration (Figure 10).
Fig. 9: Intra particle diffusion model fitted to batch equilibrium data for naphthalene photodegradation by PSA (pH, 9; initial concentration, 25 mgL$^{-1}$ PSA dose, 2 g; Temperature, 20°C)

Fig. 10: Langmuir-Hinshelwood model fitted to batch equilibrium data for naphthalene photodegradation by PSA (pH, 9; PSA dose, 2 g; Temperature, 20°C)

In conclusion, Table 4 shows that the tested kinetic models fitted well to the kinetic data with high correlation coefficients with the exception of the pseudo second order model. However, the Langmuir-Hinshelwood resulted in the best fit with highest correlation coefficient to describe the adsorption behaviour of naphthalene onto PSA.

Table 4: Kinetic constant parameter values for the photodegradation of naphthalene by PSA

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>Parameters</th>
<th>Values</th>
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<tbody>
<tr>
<td>Lagergren Pseudo First-Order</td>
<td>$k_i$ (min$^{-1}$)</td>
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</tr>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>1.116</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.972</td>
</tr>
<tr>
<td>Intra particle diffusion</td>
<td>$K_p$ (mg/g/min$^{1/2}$)</td>
<td>0.352</td>
</tr>
<tr>
<td></td>
<td>$C$ (mg/g)</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.986</td>
</tr>
<tr>
<td>Langmuir-Hinshelwood</td>
<td>$k$ (mgL$^{-1}$.min)</td>
<td>333.333</td>
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<td></td>
<td>$K$ (Lmg$^{-1}$)</td>
<td>0.00102</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.998</td>
</tr>
</tbody>
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**Isotherm Studies**

Isotherm studies were carried out to explore the relationship between naphthalene uptake ($q_e$) and its equilibrium concentration in the solution ($C_e$). Equilibrium data was analysed using adsorption isotherms which are helpful in determining the adsorption capacity of PSA for naphthalene. The Langmuir and Freundlich adsorption isotherm models were used to analyze the equilibrium data for the photodegradation of naphthalene.
using PSA. The curves of the related adsorption isotherms were regressed and parameters of the equations were thus obtained.

**Langmuir isotherm**

The Langmuir isotherm model (Langmuir, 1914) has been used empirically because it contains the two useful parameters \( q_o \) and \( K_L \), which reflect the two important characteristics of the sorption system. It assumes that the adsorption process is of the monolayer type which indicates that the adsorbate is adsorbed onto a surface with finite number of sites which are homogeneously distributed over the surface of the adsorbent (Agarry and Aremu, 2012). The Langmuir isotherm equation is given as:

\[
q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \tag{8}
\]

\( q_o \) is the maximum sorption capacity (mg/g) of the adsorbent while \( K_L \) is the sorption constant (L/mg) at a given temperature. The parameters of the Langmuir isotherm equation were obtained by fitting the equation directly to the equilibrium data using the non-linear curve fitting tool of MATLAB 7.0 software package. The shape obtained for the isotherm is shown in Figure 11. The values of the Langmuir isotherm parameters as well as the correlation coefficient \( R^2 \) of the Langmuir equation for the photodegradation of naphthalene by PSA are given in Table 6. The values of these parameters were close to those reported by Agarry et al. (2013) and Tsyntsarski et al. (2011) for the adsorption of naphthalene by spent tea leaves and activated carbon produced from biomass and coal wastes respectively.

The essential characteristics of the Langmuir isotherm model can also be explained in terms of a dimensionless constant referred to as the separation factor \( R_L \) defined in Equation (9) (Anirudhan and Radhakrishnan, 2008; Annadurai et al., 2007).

\[
R_L = \frac{q_o K_L C_e}{1 + K_L C_o} \tag{9}
\]

\( C_o \) is the initial concentration of naphthalene. The value of the separation factor determines the nature of adsorption as follows: \( R_L > 1 \) unfavourable, \( R_L = 1 \) linear, \( 0 < R_L < 1 \) favourable and \( R_L = 0 \) irreversible. For this study, the values of \( R_L \) given in Table 5 are between zero and one indicating that the adsorption was favourable.

<table>
<thead>
<tr>
<th>Initial concentration(mg/L)</th>
<th>( R_L ) Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.739</td>
</tr>
<tr>
<td>50</td>
<td>0.587</td>
</tr>
<tr>
<td>75</td>
<td>0.486</td>
</tr>
<tr>
<td>100</td>
<td>0.415</td>
</tr>
<tr>
<td>125</td>
<td>0.362</td>
</tr>
<tr>
<td>150</td>
<td>0.321</td>
</tr>
</tbody>
</table>

**Freundlich isotherm**

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

\[
q_e = K_f (C_e)^{1/n} \tag{10}
\]

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_o ) (mg/g)</td>
<td>( K_f ) (L/mg)</td>
</tr>
<tr>
<td>12.346</td>
<td>0.0141</td>
</tr>
</tbody>
</table>
Figure 11: Langmuir isotherm model fitted to batch equilibrium data for naphthalene photodegradation by PSA (pH, 9; PSA dose, 2 g; Temperature, 20°C)

Figure 12: Freundlich isotherm model fitted to batch equilibrium data for naphthalene photodegradation by PSA (pH, 9; PSA dose, 2 g; Temperature, 20°C)

The high values of the correlation coefficients as shown in Table 6 indicates that the data conformed well to both isotherm equations; however, a better fit resulted for the case of Langmuir isotherm equation as seen in the higher value of the correlation coefficient. Values of $K_f$ and $n$ have been reported by various researchers on adsorption of naphthalene. Pal (2012) reported $K_f$ and $n$ values of 0.3 and 1.12, 0.025 and 1.47 for the adsorption of naphthalene by sugarcane bagasse and rice husk respectively. Agarry et al. (2013) reported $K_f$ and $n$ values 2.44 and 1.85 respectively for the adsorption of naphthalene on spent tea leaves. Therefore the constants obtained in this study are comparable to those reported by previous researchers. The difference could be as a result of difference in the range of concentration, type of material used, pH, temperature and properties of the adsorbent such as functional groups present on the surface, surface area, pore structure, etc (Agarry and Aremu, 2012). The shape of the adsorption isotherm presented in Figure 11 indicates that it belongs to the L2 category of isotherm which is the Langmuir type of adsorption (Annadurai et al., 1997). Agarry and Aremu, (2012) reported that this type of isotherm is usually met with when the adsorbate is strongly attracted to the surface of the adsorbent.

**Intermediates of Naphthalene Degradation**

Determination of the some intermediate photoproducots of naphthalene photodegradation was carried out by GC-MS analysis. Results of the analyses revealed a series of peaks at different retention times. The degradation of naphthalene progressed through the formation of several intermediates as shown in Table 7. The most abundant of these was 2-formylcinnamaldehyde with a retention time of 21.1 minutes. This compound was also identified by other researchers as an intermediate degradation product of naphthalene (Lair et al., 2008; Pramauro et al., 1998). Aside from this, 5-Hydroxy-1,4- naphthoquinone, and naphthols were also present in high amounts (Hykrdová et al, 2002). Other compounds, 1,2-benzenedicarboxylic acid, phthalic acid, and 1,4-Naphthoquinone were also present though in smaller amounts.
Table 7: Reaction intermediates identified by GC-MS

<table>
<thead>
<tr>
<th>Degradation product</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Formylcinnamaldehyde</td>
<td>21.1</td>
</tr>
<tr>
<td>1-Naphthol</td>
<td>20.7</td>
</tr>
<tr>
<td>2-Naphthol</td>
<td>20.8</td>
</tr>
<tr>
<td>1,4-Naphthoquinone</td>
<td>19.4</td>
</tr>
<tr>
<td>5-Hydroxy-1,4-naphthoquinone</td>
<td>20.9</td>
</tr>
<tr>
<td>1,2-benzenedicarboxylic acid phthalic</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>21.0</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The batch photodegradation of naphthalene in aqueous medium using periwinkle shell ash in the presence of UV from sunlight was investigated. Photodegradation of naphthalene by PSA is influenced by factors such as contact time, initial naphthalene concentration, PSA dosage, presence of oxidant and solution pH. For the conditions considered in this study, the optimum values obtained are as follows: contact time, 210 minutes; initial naphthalene concentration, 25 mg/L; PSA dosage, 2 g; pH, 9. The addition of electron accepting oxidant (H\textsubscript{2}O\textsubscript{2}) enhanced the photodegradation process with almost 100 percent degradation achieved. The adsorption equilibrium data fitted well to the Langmuir isotherm equation indicating mono layer type adsorption while the kinetics of the process was well described by the Langmuir-Hinshelwood kinetic model with high correlation coefficient value. This study has demonstrated that the low cost photocatalyst, PSA from waste materials can be used for removal of naphthalene from aqueous solution. Also the kinetic information obtained can be used for designing economically viable treatment systems for naphthalene abatement.

REFERENCES

34. Li, Z., Mulholland, J.A., Romanoff, L.C., Pittman, E.N., Trinidad, D.A., Lewin, M.D. and Sjödin, A. (2010). Assessment of non-occupational exposure to polycyclic aromatic...


