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Photocatalytic decolourisation of industrial wastewater from a soft drink company

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Abstract

The photocatalytic decolourisation of industrial wastewater from a soft drink company was investigated. Four catalysts namely titanium dioxide (TiO_2), zinc oxide (ZnO), periwinkle shell ash (PSA) and snail shell ash (SSA) were evaluated for their potential use as photocatalysts for decolourisation of wastewater. Two sets of preliminary experiments were carried out, the first without light and the second in the presence of sunlight to determine the best catalyst for the study. Results of preliminary studies showed that PSA was best suited for the decolourisation of the wastewater samples hence it was chosen for further studies. The percent decolourisation was monitored spectrophotometrically by the measurement of absorbance at a wavelength of 201nm. The effect of catalyst dosage and oxidant (H_2O_2) loading on the degradation process was investigated. The percent decolourisation increased with increase in PSA dosage with a dosage of 12 g/L resulting in the maximum percent decolourisation of 62%. Addition of oxidant enhanced the photodegradation process with almost 100% decolourisation achieved. The degradation process conformed to a pseudo first order reaction and this was appropriately described by the Langmuir-Hinshelwood kinetic model.

Keywords: Photocatalytic decolourisation, wastewater, Periwinkle shell, Snail shell, Langmuir-Hinshelwood model

1. Introduction

Most beverage industries consume large quantities of water and produce large volumes of waste water from different steps in the production process. This wastewater which is often rich in colour contains a large proportion of residues and other chemicals that require proper treatment before being released into the environment (Guendy, 2009). Numerous studies focusing on the decolourisation of industrial wastewater have been carried out across the globe (Abdullah et al, 1990; Andreozzi et al, 1999; Attaia et al, 2008; Balanosky et al, 1999; Caliman et al, 2002). Amongst these is the use of photocatalysis in the treatment of industrial wastewater. The importance of photocatalytic decolourization of industrial wastewater has gained considerable attention in recent years. (Attaia et al, 2008; Caliman et al, 2002; Joshi et al, 2001). Recent studies show that heterogeneous photocatalysis using titanium dioxide and/or zinc oxide is the best method for use in the degradation of coloured organic chemicals (Alinsafi et al, 2007; Attaia et al, 2008; Joshi et al, 2001, Pekakis et al, 2006). Hussein et al. (2008) reported that titanium dioxide and zinc oxide have good photocatalytic properties and nominated both catalysts to be promising substrates for photodegradation of wastewater. Photocatalytic decolourisation shows a great potential in providing an alternative for better treatment of wastewater and consequent protection of the environment.

The removal of colour from wastewater is often more important than the removal of other organic colourless chemicals. Decolourisation of effluent from industries especially from textile dyeing and finishing industries is considered important because of aesthetic and environmental concern (Grzechulska and Morawski 2002). Nevertheless, not all treatment process based on decolourisation can be utilized for decontamination. The primary requirement of this process is that the

products of degradation should not be toxic or at least less toxic than the original compounds (Hussein et al, 2008).

The overall benefits of the decolourisation of industrial wastewater may include saving a huge amount of water especially from textile industries which has been regarded as chemical and water intensive (Attaia et al, 2008). The treated wastewater may be recycled and used in the same factory or utilized in other applications such agriculture where water quality is not of primal importance. This is considered to be an excellent means of saving huge amount of water especially in the countries which are affected by water deficiency.

This study aims to investigate the degradation of coloured matter in industrial wastewater obtained from a soft drinks company by utilizing photocatalytic decolourisation. The objectives include determining the best catalyst to use for the degradation process, investigating the effect of catalyst dosage and oxidant concentration on degradation and identifying the kinetics of the photocatalytic reaction.

2. Materials and Methods

2.1 Preparation and Characterisation of Catalysts

The photocatalysts employed in this study were titanium dioxide (TiO_2), zinc oxide (ZnO), Snail shell ash and Periwinkle shell ash. Titanium dioxide and zinc oxide were obtained from the Department of Chemical Engineering Laboratory, University of Benin, Benin City, Edo State, Nigeria. Snail shell and periwinkle shell were sourced locally. The shells 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 resulting mass of calcined shells was thereafter sieved to obtain fine particles (< 350µm) 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). The surface structure and other properties of the WTRG were evaluated by nitrogen adsorption method at -196ºC. Nitrogen adsorption isotherms were determined using an adsorption equipment (BET 624, Micro-meritics, Germany). The surface area of the WTRG was determined using the standard BET equation. The same procedure was applied for the characterisation of snail shell ash (SSA).

2.2 Industrial Wastewater

Industrial wastewater was obtained from a soft drink company in Benin City, Edo State, Nigeria. All other reagents used were of analytical grade. Table 1 shows the actual physico-chemical characteristics of the wastewater used in this study.

Table 1: Physico-chemical properties of wastewater

Parameter	Value
BOD	250 mg/L
COD	975 mg/L
TSS	130 mg/L
VSS	58 mg/L
pH	8.3
EC	5.7 mS/cm
Colour	10000 Pt-CoU

2.3 Photocatalytic Degradation Studies

All the photocatalytic degradation experiments were carried out under atmospheric conditions in a mechanically agitated Pyrex glass vessel under visible light. The sunlight was directed to the reaction vessel using a converging lens with a focal length of 14 cm. The sunlight experiments were carried out between 9:00 A.M to 2:30 P.M. on a sunny day. The light intensity was measured using UV-light intensity detector (Lutron UV-340), which was found to be in the range of 0.370 to 0.480 mW/cm^2. For each experiment, 2g of catalyst was added to the aqueous wastewater solution and the suspension was magnetically stirred without any permanent air bubbling. The temperature was maintained at 20 ^{o}C and monitored throughout the process (Lair et al, 2008). The study was also carried out in the absence of light and catalyst to check if there was any change in the decolourisation of the sample.

The effects of PSA dosage and amount of oxidant (H_2O_2) on the degradation efficiency were investigated. At the end of each experiment the agitated suspension mixture was filtered through a 0.45 µm membrane and the residual concentration of coloured matter in the wastewater sample was determined spectrophotometrically. The percent decolourisation which was used as an indication of degradation of the wastewater was calculated using Equation (1) (Janhavi and Singh 2008).

$$\text{Percent Decolourisation} = \left(1 - \frac{C_i}{C_o}\right) \times 100 \qquad (1)$$

C_o (mg/L) is the initial concentration before irradiation by sunlight and C_i (mg/L) is the instantaneous concentration in the sample at time *t*.

Preliminary studies were carried out to determine which of the catalysts would be more effective in the decolourisation of the wastewater. This was done by carrying out photocatalytic degradation experiments on the wastewater samples making use of fixed amounts of TiO_2, ZnO, periwinkle shell ash and snail shell ash.

3. Results and Discussion

3.1 Characterisation of Catalysts

The chemical composition of the catalysts (PSA and SSA) as obtained from X-Ray Fluorescence (XRF) analysis is presented in Table 2. The results of complete mineralogical analysis as carried out by X-ray diffraction (XRD) to determine the ultimate elemental composition of the catalysts is presented in Table 3. 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 3. Some other oxides such as K_2O, Na_2O, TiO_2 and MnO_2 were also found to be present in small amounts. For SSA, the major component was Fe_2O_3 which accounted for 36.4% of the weight of PSA characterised. 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 3. Some of the oxides and elements presented in Tables 2 and 3 have been established to possess photocatalytic properties thus supporting the choice of PSA for this study. For SSA, the major component was Zn which accounted for 19.68% of the weight of SSA characterised.

Table 2: Chemical composition of PSA and SSA

Chemical Component	PSA (wt %)	SSA (wt %)
MgO	1.2	0.3
SiO_2	33.2	21.3
ZnO	3.2	2.3
Fe_2O_3	5.0	36.4
MnO_2	1.0	2.1
Al_2O_3	9.2	11.2
CaO	41.3	9.3
CuO	1.3	1.3
K_2O	1.4	1.4
Na_2O	1.38	0.35
TiO_2	0.02	0.01

Table 3: Ultimate elemental composition of PSA and SSA

Chemical Component	PSA (wt %)	SSA (wt %)
Fe	19.20	16.44
Cr	6.30	5.83
V	1.50	2.10
Ni	9.00	7.86
Se	0.13	1.32
Pb	0.08	1.81
Al	12.30	11.30
Zn	16.50	19.68
Sn	8.00	10.21
Cd	0.05	1.05
Cu	2.40	1.40

Table 4: Physical properties of PSA and SSA

Property	PSA	SSA
Surface area (m^2/g)	400	339
Bulk density (kg/m^3)	2940	1894
Porosity (-)	0.004	0.023

The surface area, bulk density, and porosity of the PSA and SSA used in this study are presented in Table 4. The results presented in Tables 2, 3 and 4 are similar to those reported in the literature (Owabor and Iyaomolere, 2013; Umoh and Olusola, 2012).

3.2 Preliminary Studies

The results of preliminary studies on the photocatalytic decolourisation of industrial wastewater using TiO_2, ZnO, PSA and SSA are presented in Table 5. Table 5 compares the percent decolourisation of wastewater for all four catalysts both in the presence and absence of light. The results indicate that there was some level of decolourisation (although not very significant) observed in the absence of light. This might be attributed to the catalytic activity of the catalysts. The highest percent decolourisation in the absence of light was recorded when periwinkle shell ash was used. The percent decolourisation was significantly enhanced when the experiments were carried out in the presence of light as seen from the results in Table 5. The results also show that sunlight plays a significant role in the photodegradation process. Hussein et al. (2008) reported similar results when they combined sunlight with photocatalysts in the degradation of thymol blue. The efficiency of the catalyst under conditions of sunlight is related to the activation of its active sites by absorbed light (Zahraa et al, 2006).The highest percent decolourisation was recorded when periwinkle shell ash

was used in the presence of sunlight. This indicated that periwinkle shell ash performed best in the degradation of the industrial wastewater used in this study. Based on the results obtained, periwinkle shell ash was chosen for further investigations.

Table 5: Results of preliminary studies carried out in the absence and presence of light respectively

Catalyst	Percent Decolourisation	
	Without sunlight	With Sunlight
TiO_2	21.59	87.14
ZnO	7.87	63.73
Snail shell ash	9.04	77.53
Periwinkle shell ash	25.35	89.68

3.3 Effect of Catalyst Dosage

Fig. 1 shows the effect of catalyst (PSA) dosage on the degradation of industrial wastewater. It was observed that percent degradation increased with increase in catalyst dosage up to an optimum point. Further increase in catalyst dosage resulted in a decrease in the decolourisation of wastewater. The optimum dosage of catalyst was 12.5g/L. The initial increase in percent decolourisation could be attributed to the increase in the number of active sites on the PSA surface as a result of increased PSA dosage. By increasing the dosage of PSA, the number of free radicals (•OH and O_2^{2-}) in solution are also increased consequently leading to enhanced photodegradation of the wastewater sample (Inamdar and Singh, 2008). The decline in photodegradation later observed is readily explained by the fact that as the catalyst dosage is further increased beyond the optimum, the suspended particles of the PSA aggregate together and this reduces the amount of sunlight reaching the active sites of the catalyst and consequently, the rate of reaction decreases. Similar results were reported by Janhavi and Singh (2008) when they used photocatalytic degradation to treat effluent discharge from the dairy industry.

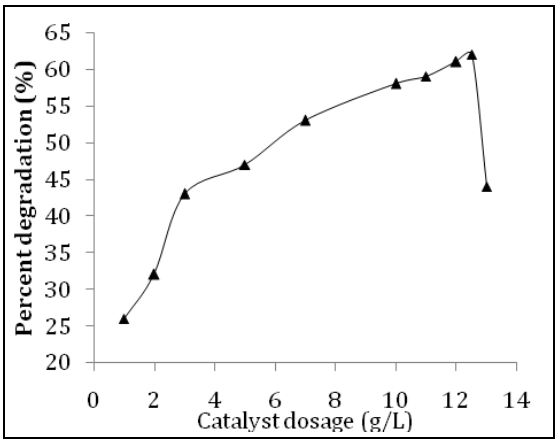

Fig. 1: Effect of catalyst dosage on percent degradation of wastewater

3.3 Effect of Oxidant Loading

Fig. 2 shows the effect of oxidant loading on the degradation of industrial wastewater. It was observed that a maximum decolourisation efficiency of 26% was obtained when the oxidant (H_2O_2) was used alone without the PSA catalyst. When the oxidant was combined with PSA in the presence of sunlight, the percentage decolourisation increased with increase in the amount of oxidant used. Almost 100% decolourisation of wastewater was recorded when 8 cm^3 of hydrogen peroxide was used indicating the efficacy of using an oxidant during photocatalytic degradation of coloured industrial wastewater. The trend observed may be due to the oxidative effect of hydrogen peroxide. Hydrogen peroxide is an electron acceptor which can generate hydroxyl radicals. The free radicals formed from the addition of H_2O_2 create a strong oxidation environment which favours the photocatalytic decolourisation process.

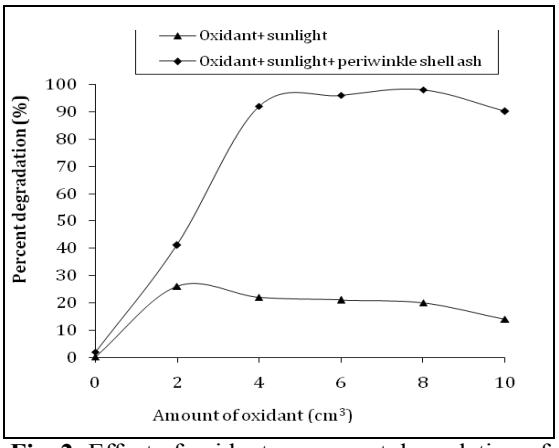

Fig. 2: Effect of oxidant on percent degradation of wastewater

3.4 Kinetic Model

The Langmuir- Hinshelwood kinetic model has been used to describe many photocatalytic reactions (Turchi and Ollis, 1989; Abdullah et al, 1990; Al-Ekabi and Serpone, 1989). The rate of reaction can be expressed as:

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \quad (2)$$

r is the rate of the reactant (mg/L min), C is the concentration of the reactant (mg/L), t the illumination time, k the reaction rate constant (mg/L min), and K is the adsorption coefficient of the reactant (L/mg). When the chemical concentration C is small, the above equation can be simplified to an apparent first-order equation

$$\ln \frac{C_o}{C_i} = kt \quad (3)$$

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

$$k = \frac{\ln C_o / C_i}{t} \quad (4)$$

A plot of ln C_o/C_i versus time results in a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k.

Fig. 3 shows a plot of ln C_o/C_i versus time at different volumes of wastewater. As shown in the Figure, the plot is fitted with a straight line using linear regression techniques. The slope corresponds to the apparent pseudo-first order reaction rate constant. The calculated rate constants and corresponding correlation constants are given in Table 6. The closeness of the correlation constants to unity indicates that the degradation process follows pseudo first-order kinetics and this is well represented by the Langmuir–Hinshelwood model. According to Rashed and El-Amin, (2007), first-order kinetics is appropriate for the entire concentration range up to a few mg/L and can be well fitted by this kinetic model.

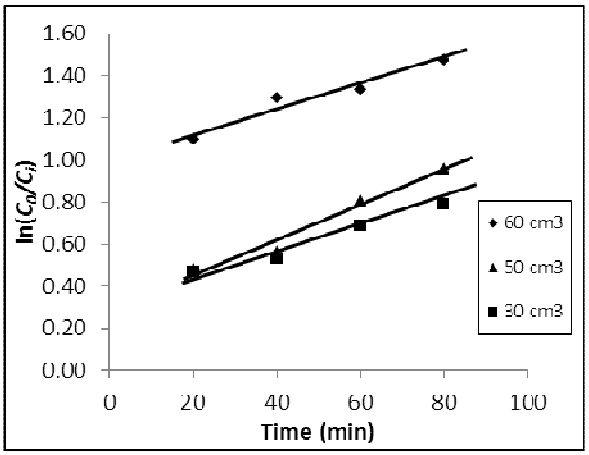

Fig. 3: Pseudo-first-order kinetics for photocatalytic degradation

Table 6: Rate constant for photocatalytic degradation of industrial wastewater

Volume of wastewater (cm^3)	Rate constant, k (per min)	Regression value (R^2)
30	0.0058	0.94
50	0.0084	0.97
60	0.0056	0.98

4. Conclusions

The photocatalytic decolourisation of industrial wastewater from a soft drink company was investigated in this study. The following conclusions can be drawn from this study.

- Solar irradiation has proved an efficient source of light for the decolourization of industrial wastewater.
- Photocatalytic decolourisation using periwinkle shell ash catalyst is efficient in decolourizing wastewater from a soft drinks company.
- Almost complete decolourisation (98%) is obtained in 60 min of solar irradiation when an oxidant is added to the catalyst "periwinkle shell".
- The photocatalytic decolourisation process proceeds as a pseudo-first order reaction and its kinetics is well represented by the Langmuir-Hinshelwood kinetic model.

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