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EMPIRICAL MODELLING OF BOD REDUCTION DURING TREATMENT OF LANDFILL LEACHATE USING SOLAR UV FACILITATED PHOTOCATALYTIC DEGRADATION

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ABSTRACT

The empirical modelling of the degradation of landfill leachate via heterogeneous photocatalytic degradation using zinc oxide (ZnO) in the presence of ultra violet (UV) radiation from sunlight was investigated in this study. Results obtained after characterising the raw leachate showed that its physico-chemical properties did not meet the requirements set by the Federal Environmental Protection Agency (FEPA) thus necessitating the need for the treatment. The reduction in the biochemical oxygen demand (BOD) of the leachate in the course of treatment was used to monitor the rate of degradation of the leachate. An empirical mathematical model was proposed to describe the rate of degradation and the kinetic parameters- degradation rate constant (k) and exponential order (α) were estimated in the course of validating the model. Model validation results show that the model was able to predict the experimental results to a high level of confidence indicating that there was a good fit between experimental and model predicted results. The BOD was observed to reduce in the course of treatment indicating a reduction in the organic pollutant load of the leachate. The final BOD of the treated leachate met the requirements of FEPA indicating that the treated leachate could be safely discharged into natural water bodies without fear of it causing any deleterious effect on the ecosystem.

1. INTRODUCTION

There has been a rapid increase in the generation of municipal and industrial solid wastes in recent years. This has coincided with the increase in global population and industrial activities recorded in the past couple of years (Renou et al., 2008). Sanitary landfills have been the widely accepted as the most economical way of solid waste disposal (Kurniawan et al, 2006). After landfilling, solid waste undergoes physico-chemical and biological changes and in the process, landfill leachate is generated as a result of water from precipitation, surface run-off, and infiltration or intrusion of groundwater percolating through the landfill (Di Palma et al., 2002).

It is well established that landfill leachate contains large quantities of toxic and recalcitrant constituents and it is usually characterised by water quality parameters such as BOD, COD, BOD/COD ratio, pH, suspended solids (SS), ammonium nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN) and heavy metals (Baderna et al., 2011). Biological treatment is the most common method for detoxifying landfill leachate as a result of its reliability, simplicity and high cost effectiveness (Wu et al., 2004). Even though this type of treatment has been reported to be effective in significantly reducing the BOD, COD, ammonia-nitrogen and heavy metal content of landfill leachate, it is however only effective for the treatment of young leachate which is readily biodegradable and not effective for leachate containing recalcitrant constituents (Deng and Englehardt, 2006). This has necessitated the need to search for other effective and efficient methods for the treatment of stabilised landfill leachate.

Heterogeneous photocatalytic degradation has been identified as a promising technique for the removal of most organic pollutants from liquid effluents (Aisien et al., 2014). The process is facilitated by semiconductor photocatalysts notably zinc oxide (ZnO) and titanium dioxide (TiO_2) which generate hydroxyl radicals when excited in the presence of UV radiation (Akyol and Bayramoglu 2008). The photocatalytic reaction takes place when the semiconductor particle absorbs a photon of light which is more energetic than its bandgap leading to the excitation of the electron from the valence band to the conduction band. An hole–electron pair is formed in the process and this initiates the oxidation of the pollutant (Matilainen and Sillanpää, 2010). The important advantage of this method is that it often results in complete mineralisation and degradation of most pollutants that are not readily amenable to other treatment processes. Furthermore, it is cheaper than most processes and it can be carried out under ambient conditions (Pare et al., 2009).

This study is an attempt to empirically model the degradation of the organic portion of the landfill leachate. Modelling of the process enables its representation in a mathematical sense. Simulation of the formulated model can be utilised in analysing the behaviour of the process, provision of insights into the mechanisms that drive the process, understanding the response of the process to changes in operating conditions, design of controllers and design of entirely new processes (Suja and Thyagarajan, 2009). This leads to vast improvements in process economics, design, operation and control (Lee et al, 1997). Model predictions also make it possible to identify optimal design and operational parameters and this consequently leads to the maximisation of the system's performance (Amenaghawon and Okieimen, 2012).

The current work deals with the use of solar UV assisted photocatalysis for the purpose of treating landfill leachate. A mathematical model of the degradation process was formulated and validated for the purpose of predicting the performance of the process. The scope of this study has been limited to purely empirical models which are derived from and based entirely on available data. In such a model, relationships between variables are derived by analysing the available data and selecting the mathematical form which is a compromise between accuracy of fit and simplicity.

2. MATERIALS AND METHODS

2.1. Leachate Collection and Characterisation

The raw leachate used in this study was collected from the Ikhueniro landfill located in the outskirts of Benin City, Edo State, Nigeria. After collection, the leachate was stored at 4 ºC to minimise any further change that could occur in its physico-chemical and biological properties until it was needed for use. The physico-chemical characteristics of the raw leachate were determined before the treatment process was commenced (Wu et al., 2004).

2.2. Photocatalyst

ZnO was used as the semiconductor photocatalyst in this study. It was procured from BDH Chemical Ltd, England.

2.3. Photocatalytic Degradation Studies

The method described in Aisien et al. (2013) was adopted for treating the leachate. All the photocatalytic degradation experiments were carried out under atmospheric conditions in mechanically agitated 1000 mL Erlenmeyer flasks with a working volume of 500 mL. The degradation reaction was facilitated by UV radiation from sunlight. A 14 cm focal length converging lens was used to direct the rays of sunlight onto the reaction vessel. The temperature was maintained at 32ºC. A control experiment was also carried out in the absence of light and catalyst to check if there was any change in the degradation of the leachate sample. At the end of each experiment the agitated suspension mixture was filtered using a 0.45 µm membrane and the resulting filtrate was analysed to determine the residual concentration of contaminants present in the sample.

2.4 Analytical methods

The pH of the samples was measured using an electronic pH meter (Fisher Accruement pH meter). The BOD, DO and turbidity of the leachate were determined according to standard methods (APHA, 2000).

3. RESULTS AND DISCUSSION

3.1. Characteristics of Raw Leachate

Table 1 shows the results of the characterisation of the raw leachate used in this study. It can be observed from the values of pH, DO, BOD and turbidity that the raw leachate can be classified as stabilised or old leachate according to the criteria outlined by Aziz et al. (2010). In addition, the level of pollution observed in the leachate as evident from the values of the physico-chemical properties of the leachate is such that it did not meet the requirements of BOD, DO and turbidity (<30 mg/L, >2mg/L and <10 NTU respectively) as prescribed by FEPA (FEPA 1997). This thus shows the need to treat the leachate before discharging it into natural water bodies.

Table 1: Characteristics of law leachate used in this study

Parameter	Value
pH	7.5
BOD (mg/L)	34
DO (mg/L)	0.4
Turbidity (NTU)	234
Pb (mg/L)	5.5
Cd (mg/L)	2
Ni (mg/L)	2

3.2. Experimental Results from Photodegradation Studies

Table 2 shows the variation of BOD of the leachate samples with time. The general trend observed shows that the BOD of the treated leachate decreased with increase in time showing that the organic content of the leachate was being degraded into less toxic forms.

Table 2: Experimental values of BOD with time

Time	BOD (mg/L)	
	Control	Treated
0	34	34
1	34	30.9
2	31	24.8
3	33	18.3
4	34	11.4
5	32	4.9

3.3. Empirical Model Formulation

For the current study, the degradation of leachate occurring in a batch system is represented as shown in Equation (1).

$$Raw\ Leachate \xrightarrow[Sunlight]{ZnO} Simple\ compounds \quad (1)$$

In formulating the model, the following assumptions were made:

i. The volume of the reactor is fixed
ii. No nuclear reaction occurs; hence rate of material generation is zero

iii. The system is isothermal
iv. The degradation rate can be likened to the rate of reaction from chemical kinetics
v. The reduction in the BOD of the leachate was likened to the disappearance of reactant from chemical kinetics
vi. The biodegradation rate was monitored by following the reduction in the BOD of leachate with time

The proposed model for describing the rate of degradation of the raw leachate is BOD dependent and is presented as a power law as shown Equation (2).

$$-\frac{d[BOD]}{dt} = k\ [BOD]^{\alpha} \tag{2}$$

The experimental data presented in Table 2 was fitted to various standard equation forms to determine the one that provided the best fit. The results of the fitting exercise are presented in Table 3.

Table 3: Empirical equations generated to represent the variation of BOD with time

Equation form	Equation	R^2
Linear	$BOD=-6.01t+37.75$	0.989
Polynomial	$BOD=-0.36t^2-4.21+34.55$	0.997
Exponential	$BOD=43.68exp(-0.37t)$	0.895

In the modeling of BOD, the second degree polynomial was adopted as the empirical equation to represent the variation of BOD with time. The second degree polynomial was chosen because it had the highest coefficient of determination (R^2 value). Hence the reduction in BOD with time which is an indication of degradation of the leachate is represented by Equation (3).

$$BOD=-0.36t^2-4.21+34.55 \tag{3}$$

Using Equation (3), values of BOD at different times during the treatment process were obtained as shown in Table 4. The relatively low values of the standard deviation obtained between the measured and calculated BOD values as shown in Table 4 shows the suitability of the second degree model for describing the variation of the BOD of the leachate with time.

Table 4: Comparison between measure and calculated values of BOD

Time (h)	$[BOD]_{measured}$	$[BOD]_{calculated}$	Standard Deviation
0	34.0	34.6	0.39
1	30.9	30.0	0.65
2	24.8	24.7	0.08
3	18.3	18.7	0.26
4	11.4	11.9	0.38
5	4.9	4.5	0.30

3.4. Model Validation

Model validation has to do with the estimation of model parameters by making use of the results of an experiment to validate the model (Amenaghawon and Obahiagbon 2013). An experimental validation of the proposed empirical model (i.e. Equation 2) was carried out by estimating the degradation rate constant *k* and the exponential order of the reaction *α*. The model was simulated and the result of the simulation was compared with experimental results to assess validity. Equation (2) was linearised by making use of the data presented in Table 2 to obtain the values of the degradation parameters. The linearisation was done by applying natural logarithm to the equation to obtain the following linearised form.

$$\ln(-r) = \ln(k) + \alpha \ln(BOD) \quad (4)$$

Where *r* represents the rate of biodegradation

$$r = \frac{d[BOD]}{dt} \quad (5)$$

The rate of degradation as indicated in Equation (5) was calculated from Equation (3) by simple differentiation. The logarithm of rate of degradation was then plotted against the logarithm of BOD to obtain a straight line from which the degradation parameters *k* and *α* were obtained from the intercept and slope respectively as shown in Fig. 1. The values of these parameters are presented in Table 5 alongside the R^2 value. The model had a high R^2 value as shown in Table 5. This shows that the model was able to adequately represent the relationship between the variables.

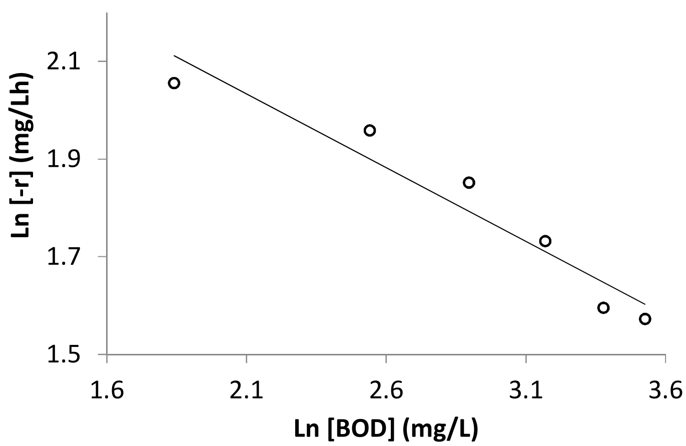

Figure 1: Linearisation of BOD rate equation

Table 5: Values of degradation parameters

Degradation rate constant, *k* (h^{-1})	Exponential order *α*	R^2
14.397	-0.302	0.926

Applying the values of the parameters presented in Table 5 to Equation (2) results in the empirical model describing the rate of degradation of the leachate sample in the course of treatment. This is shown in Equation (6).

$$-\frac{d[BOD]}{dt} = 14.397[BOD]^{-0.302} \tag{6}$$

The empirical model (Equation 6) was validated by using it to calculate the values of BOD at various times during treatment and comparing the results with those obtained during the actual experiments. The result is presented in Figure 2.

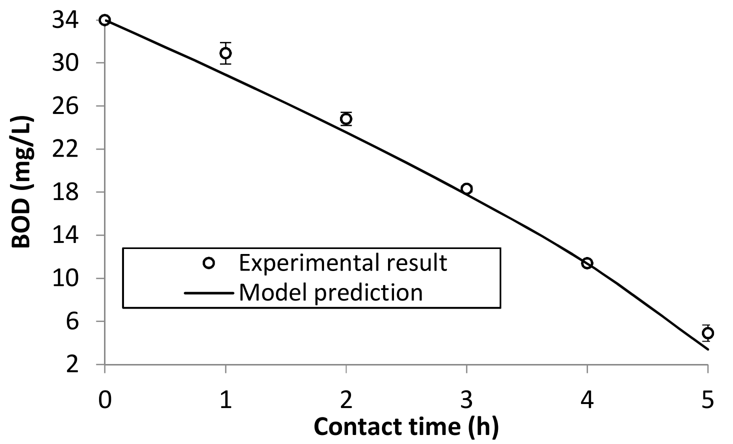

Figure 2: Comparison between experimental results and model prediction

Figure 2 shows the overlay plot of the BOD of the leachate in the course of treatment. The plot displays a comparison between the experimental results and those predicted by the empirical model in terms of trend and correlation. In terms of correlation, it is evident from the plot that the model was able to replicate the experimental values of the BOD to a high level of confidence. The standard deviation bars in the plot show the level of variation between the experimental results and those predicted by the model. The relatively small magnitude of the standard deviation bars shows that there was little variation between the experimental results and the model predicted results indicating that the experimental results were very similar to the model predicted results. This means that the model exhibited a good fit and correlation with the experimental data thus showing the validation of the model.

In terms of trend, the BOD of the treated leachate was observed to decrease with time as shown in Figure 2. The BOD is a largely accepted water quality indicating parameter and it measures the level of contamination and organic pollutant load of a water body (Samal et al., 2011). Hence, the reduction recorded in the BOD of the treated leachate as observed in Figure 2 could be attributed to a reduction in the organic pollutant load of the leachate. This process would have been facilitated by the hydroxyl radicals (OH•) released in solution which oxidize the pollutants into nontoxic forms. According to Aisien et al. (2015), the hydroxyl radicals are important species during photocatalytic degradation and they are the principal oxidants responsible for high degradation efficiency. In addition, the reduction in BOD could also have resulted from the activities of the indigenous microbes present in the leachate which converts the organic pollutants into less toxic substances such as CO_2, H_2O and many intermediates like organic acids, lipids, esters, complex alcohols and microbial proteins in form of enzymes (Obahiagbon et al., 2009). From Figure 2, it was observed that the greatest reduction in BOD (85.6%) was recorded after 5 hours of treatment. Similar results with respect to the reduction in BOD during treatment have been reported by previous researchers (Amenaghawon et al., 2013; Amenaghawon et al., 2014; Obahiagbon et al., 2009). The final BOD of the treated leachate met the specification of BOD set by the Federal Environmental Protection Agency (FEPA, 1997).

4. CONCLUSION

The empirical modelling of the degradation of landfill leachate using heterogeneous photocatalytic degradation was investigated in this study. The following conclusions can be drawn.

- The use of modelling tools to describe the trends in the degradation of landfill leachate has been demonstrated.
- The rate of degradation was accurately represented by a validated empirical model which was able to replicate the results of the experiment to a high level of confidence.
- Kinetic parameters indicating the rate of degradation can be estimated accurately using experimentally generated data.
- Increasing contact time favoured the treatment of the leachate as seen in the reduction (85.6%) in the value of the BOD

The final BOD of the treated leachate met the requirements of FEPA indicating that the treated leachate could be safely discharged into natural water bodies.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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