ADSORPTION STUDY OF SOLUOS DUMPSITE LEACHATE TREATMENT USING MUSA SAPIENTUM PEELS AS BIOSORBENT

ABSTRACT

Dumpsite leachate has the potential to pollute ground and surface water as well as vegetation within the vicinity of the dumpsite. Its treatment therefore needs adequate attention. The aim of this work is to study the adsorption of Soluos dumpsite leachate treatment using Musa sapientum peel as biosorbent with a view of establishing the adsorption isotherm model. Musa sapientum peels sourced from Ayetoro market in Epe area of Lagos State, Nigeria were used to prepare the adsorbent. Batch adsorption was carried out with various dosage of the prepared absorbent in leachate collected from Lagos dumpsite. The adsorption data obtained were fitted into Linear, Freundlich, Langmuir, Temkin and Hasley isotherm models. The results showed that the concentration of total dissolved solids (TDS) in the dumpsite leachate decreased as the adsorbent dosage increased. At adsorbent dosage of 10 g/L, the concentration of TDS in the leachate was 485.7 mg/L which was less than the 500 mg/L stipulated by National Environmental Standard and Regulatory Agency (NAESRA) for the discharge of wastewater. The coefficient of determination (R²) values for Linear, Freundlich and Hasley, Langmuir and Temkin isotherm models were 0.9944, 0.9936, 0.8562 and 0.9723 respectively. Linear isotherm model was jettisoned because the plot did not pass through the origin and Freundlich isotherm model was ignored as a result of N value which was less than unity hence Hasley isotherm model was adopted in this work. A good correlation existed between the experimental and predicted values, having a R² value of 0.9965 which further validated the Hasley isotherm model as the best adsorption model for the treatment of Lagos dumpsite leachate using Musa sapientum peel as biosorbent. It was concluded that *Musa sapientum* peel as biosorbent can be used for treatment of Lagos dumpsite leachate.

Keywords: Adsorption, biosorbent, leachate, total dissolved solids and treatment.

1. INTRODUCTION

When precipitation falls on wastes within the dumpsite or landfil site, it extracts the soluble components of the wastes to form leachate. Leachate is a dark liquid which emits a strong odour (Norashiddin et al., 2019). It consists various pollutants such as heavy metals, organic substances, ammonia and inorganic salts (Uygur and Kargi, 2004; Renou *et al.*, 2008; Aziz *et al.*, 2009 and Foul *et al.*, 2009). The leachate percolates through the soil matrix and pollutes the groundwater. It also pollutes surface water and affects vegetation. This makes it necessary for the leachate to be treated in order to avert the inherent dangers it poses.

Bioremediation is one way of treating leachate. It is a mean of destroying or rendering harmless various pollutants using natural biological activity. It involves the use of low – cost and low technological techniques (Akinyemi *et al.*, 2019). Various types of agricultural wastes such as coffee, palm shell, bagasse, coconut shell, banana psedo – stem, rice husks and the host of others have been used in the treatment of landfill leachates (Mohan and Singh, 2002; Lim, *et al.*, 2009; Halm *et al.*, 2010 and Ching *et al.*, 2011). It has been reported in the literature that the functional groups like hydroxyl, carbonxyl, thio and amino, phosphate present on the walls of agricultural wastes biomass play a very vital role for binding of contaminants which result in the treatment of landfill leachate (Kumar *et al.*, 2011 and Deshmukh *et al.*, 2017).

Extensive works have been done on the treatment of leachates by scholars (Hur and Kim, 2000; Dabrowski, 2001; Zajc *et al.*, 2004; Aghamohammadi *et al.*, 2007; Kalderis *et al.*, 2008; Liyan *et al.*, 2009; Lim *et al.*, 2010; Aziz *et al.*,2011; Foo *et al.*, 2013; Ab Ghani *et al.*, 2017; and Yahya *et al.*, 2017). Kaideris *et al.* (2008) worked on adsorption of polluting substances on activated carbon prepared from rice husk and suger cane bagasse. The work revealed 70 and 60 percent

removal of chemical oxygen demand (COD) and colour respectively. Aziz *et al.* (2011) carried out landfill leachate treatment using powdered activated carbon augmented sequencing batch reactor process. It was shown that 64.1, 71.2 and 81.4 percent removal of COD, colour and ammoniacal nitrogen were achieved. Foo *et al.* (2013) used banana frond activated carbon prepared by microwave induced activation to remove boron from landfill leachate. 92.73 percent of the boron were removed from the leachate. Ab Ghani *et al.* (2017) investigated the optimization of preparation conditions for activated carbon from banana pseudo – stem using response surface methodology on the removal of colour and COD from landfill leachate. The investigation showed that 91.2 and 83 percent removal of colour and COD respectively.

Rodrigo *et al.* (2019) research on landfill leachate treatment using activated carbon obtained from coffee waste. The research revealed that the ammonia adsorption data obtained were successfully modelled by Freundlich isotherm. It is evident from the myraid of literature that works on removal of TDS especially from Soluos dumpsite leachates are very scarce. Therefore the aim of this work is to study the tretment of Soluos dumpsite leachate using *Musa sapientum* peels as biosorbent with a view of establishing the adsorption isotherm model which provides useful information on the adsorption capacity of the biosorbent. The adsorption model is an important tool for predicting the design of adsorption batch reactor. The treatment of Lagos dumpsite leachate will minimise the inherent dangers pose by the leachate which justifies the work.

Muse sapientum peels were chosen for the treatment of Lagos dumpsite leachate because of the presence of free hydroxyl group of polymeric compounds such as lignin or pectin that contain the functional groups of alcohols, phenols and carboxylic acids and the N – H bending vibration of primary amines in the walls of the *Muse sapientum* peels agricultural waste as established in the work of DesMukh *et al.* (2017).

2. METHODOLOGY

2.1 Preparation of Adsorbent

Muse sapientum peels were sourced from Ayetoro market in Epe area of Lagos State, Nigeria. The peels were cleaned with water to remove any undesrable materials. The peels sample were carbonised in a furnace at a temperature of 600° C for a duration of 1 hr. The char product from the furnace was quencehed with cold water at -4° C in order to cool and then transferred into the oven for further drying at 110° C. The activated carbon was washed with tetraoxosulphate (vi) (H₂SO₄) (10 % by weight) followed by heating in the absence of air. The resultant moist paste was charged into the furnace and heated for 1 hr at a temperature of 110° C until a constant weight of activated carbon was achieved. The chemical activation was carried out to remove the tar in the pores of the activated carbon. The activated carbon was rinsed thoroughly with distilled water to remove the remaining H₂SO₄. The activated carbon was then dried in an oven at a temperature of 110° C for 3 hrs. The produced activated carbon was crushed with a mortar to size of 100° mesh.

2.2 Batch Adsorption

The method of Olafadehan et al. (2012) was adopted with a little modification. Batch adsorption equilibrum studies were carried out using the produced activated carbon of different known masses. Each mass was placed in 250 ml Erlenmeyer flask each containing 100 ml of leachate collected from Soluos dumpsite in Lagos State, Nigeria having a pH of 7.2. The flasks were agitated continuously at agitation speed of 150 rpm for 2 hrs by which equilibrum must have occured. The resultant mixture was filtered and the concentrations of TDS in the filtrates were determined as compared to COD in the work of Olafadehan et al. (2012). The concentrations of the TDS were determined according to the standard methods for examination of water and waste

water as prescribed by American Public Health Association (APHA, 1994). The adsorption capacity values at equilibrum, q_e [=] mg/g, were evaluated using Equation (1).

$$q_e = \left(\frac{c_o - c_e}{m}\right) V = \frac{X}{M} \tag{1}$$

Where c_o is the initial adsorbate concentration [=] mg/L and c_e is the adsorbate concentration at equilibrium [=] mg/L, m is the mass of adsorbent [=] g, V is the volume of aqueous solution (the leachate in contact with the adsorbent) [=] L, X the change in initial concentration and equilibrium concentration [=] mg/L and M is the carbon dosage [=] g/L.

3. RESULTS AND DISCUSSION

The analysis of batch adsorption equilibrium data for Lagos dumpsite leachate sample using *Musa sapientum* peel activated carbon at temperature of 30°C is presented in Table 1. The concentration of TDS in the dumpsite leachate decreased as the adsorbent dosage increased. At adsorbent dosage of 10 g/L, the concentration of TDS in the leachate was 485.7 mg/L which was less than the 500 mg/L stipulated by NAESRA for the discharge of wastewater.

Table 1. Analysis of batch adsorption equilibrium data for Lagos dumpsite leachate sample using Musa sapientum peel activated carbon at temperature of 30°C

| Activated carbon dosage | vated carbon dosage Activated carbon dosage, | | X (mg/L) |
|-------------------------|--|--------|----------|
| (g/100 ml) | M (g/L) | | |
| 0 | 0 | 2101.7 | - |
| 0.2 | 2 | 1100 | 1001.7 |
| 0.4 | 4 | 811 | 1290.7 |
| 0.6 | 6 | 632 | 1469.7 |

| 0.8 | 8 | 529 | 1572.7 |
|-----|----|-------|--------|
| 1.0 | 10 | 485.7 | 1616 |

Table 1. Analysis of batch adsorption equilibrium data for Lagos dumpsite leachate sample using *Musa sapientum* peel activated carbon at temperature of 30°C. (Continuation)

| $q_e = (X/M), (mg/g)$ | ln c _e | ln q _e | C_e/q_e (g/L) |
|-----------------------|-------------------|-------------------|-----------------|
| - | - | - | - |
| 500.85 | 7.003 | 6.2163 | 2.196 |
| 322.675 | 6.698 | 5.777 | 2.513 |
| 244.95 | 6.449 | 5.5011 | 2.580 |
| 196.588 | 6.271 | 5.281 | 2.691 |
| 161.6 | 6.186 | 5.085 | 3.006 |
| | | | |

Sorption equilibrium data generated in the treatment of Lagos dumpsite leachate were tested with different adsorption isotherm model given in Equations 2, 3, 5, 12 and 13.

• 1 - p Henry law: The one – parameter (1 - p) Henry law also known as linear adsorption isotherm is used to describe adsorptions at relative low pressure (Olafadehan, 2021). It is of the form shown in Equation (2) for liquid – phase adsorption.

$$q_e = k_H^{\gamma} c_e \tag{2}$$

Where k_H is the Henry law constant which was determined by plotting q_e against c_e . If a straight line passing through the origin was obtained with regression coefficient (\mathbb{R}^2) very close to unity, it means the isotherm model can be used to correlate the experimental data.

• 2 – p Freundlich isotherm: The two – parameter (2 - p) Freundlich isotherm describes adsorption on heterogeneous surfaces or surfaces supporting sites of varied affinities (Olafadehan, 2021). It also illustrates a multilayer adsorption which assumes the stronger binding sites are occupied first and the binding strength decreases with increasing degree of adsorption (Ewecharoen *et al.*, 2008). The Freundlich isotherm is presented in Equation (3).

$$q_e = k_F c_e^{\frac{1}{N}} \tag{3}$$

Where k_F is a constant which indicates the Freundlich adsorption capacity and parameter, N, characterizes the homogeneity of the system. Taking the logarithm of Equation (3) yields:

$$\ln q_e = \ln k_F + \frac{1}{N} \ln c_e \tag{4}$$

The Freundlich rate coefficient, N and k_F were evaluated from the slope and intercept on q_e axis respectively when $\ln q_e$ was plotted against $\ln c_e$. If a straight line is obtained having a very high \mathbb{R}^2 close to unity. Freundlich isotherm can be used to correlate the adsorption data of a system provided $N \succ 1$. The adsorption is considered favourable provided $0 \prec \frac{1}{N} \prec 1$ which indicates chemisorption and taken as unfavourable when $\frac{1}{N} \succ 1$.

• 2 – p Langmuir isotherm: The 2 – p Langmuir isotherm describes the monolayer adsorption on a solid surface where all sites are equivalent and independent. For liquid phase adsorption, the model is given as shown in Equation (5) (Olafadehan, 2021).

$$q_e = \frac{q_{\text{max}} K_L c_e}{1 + K_L c_e} \tag{5}$$

Where q_{max} is the Langmuir constant related to the adsorption capacity (maximum adsorption capacity for solid phase loading) [=] mg/g and K_L is the energy constant related to the heat of adsorption [=] dm³/mg. The various linear forms of Equation (5) are presented in Equations (6) – (10).

$$\frac{1}{q_e} = \frac{1}{K_L q_{\text{max}}} \frac{1}{c_e} + \frac{1}{q_{\text{max}}}$$
 (6)

$$\frac{c_e}{q_e} = \frac{1}{q_{\text{max}}} c_e + \frac{1}{K_L q_{\text{max}}} \tag{7}$$

$$q_e = \frac{1}{K_L} \frac{q_e}{c_e} + q_{\text{max}} \tag{8}$$

$$\frac{q_e}{c_e} = -K_L q_e + K_L q_{\text{max}} \tag{9}$$

$$\frac{1}{c_e} = -K_L q_{\text{max}} \frac{1}{q_e} - K_L \tag{10}$$

The plot of Langmuir isotherm model was generated with the use of Equation (7) since it has been established in the work of Olafadehan *et al.* (2018) that Equations (6) – (10) gave almost the results. Hall *et al.* (1966) and Malik (2004) descibed the important characteristics of Langmuir isotherm using a dimensionless constant, R_L , also known as separation factor or equivalent parameter and is given by Equation (11).

$$R_{L} = \frac{1}{1 + K_{L} c_{o}} \tag{11}$$

Where c_o is the initial concentration of adsorbate. Zhai *et al.* (2004) showed that R_L is an indication of the shape of the isotherm thus $R_L \prec 0$, $0 \prec R_L \prec 1$, $R_L = 1$ and $R_L \succ 1$ represent irreversible, favourable, linear and unfavourable isotherm respectively.

• 2 – p Temkin isotherm: The 2 – p Temkin isotherm reveals the effects of indirect adsorbent – adsorbate interactions on the adsorption process. For liquid phase adsorption, the Timkin isotherm model is shown in Equation (12).

$$q_e = \frac{RT}{b_T} \ln\left(A_T c_e\right) = \frac{RT}{b_T} \left(\ln A_T + \ln c_e\right) \tag{12}$$

Where b_T is the Temkin constant, which is related to the heat of adsorption [=] J/mol, A_T is the Temkin isotherm constant [=] L/g. A plot of q_e against lnc_e gives a straight line with slope equals $\frac{RT}{b_T}$ and intercept on q_e axis equals $\frac{RT}{b_T} \ln A_T$. These make the b_T and A_T to be determined at the adsorption isotherm.

• Hasley isotherm: This is important in the evaluation of multilayer adsorption at a relatively large distance from the surface (Ayawei, 2015). The isotherm is presented in Equation (13) and when linearised yields Equation (14).

$$q_e = (K_H c_e)^{\frac{1}{n_H}} \tag{13}$$

$$\ln q_e = \frac{1}{n_H} \ln K_H + \frac{1}{n_H} \ln c_e \tag{14}$$

Where K_H and n_H are the Hasley isotherm constants. A plot of $\ln q_e$ against $\ln c_e$ was made. This would yield a straight line graph with slope equivalent to $\frac{1}{n_H}$ hence n_H and K_H can be determined.

Table 2 shows isotherm parameters for the batch adsorption equilibrium data while Table 3 reveals the experimental (actual) and predicted values as well as percentage difference for Freundlich and Hasley isotherm models.

Table 2.Isotherm parameters for batch adsorption equilibrium data

| Isotherm | Parameters | Value |
|------------|------------|---------|
| Linear | R^2 | 0.9944 |
| | k_H | 0.536 |
| Freundlich | R^2 | 0.9936 |
| | N | 0.7551 |
| | k_F | 0.0467 |
| Langmuir | R^2 | 0.8562 |
| | q_{max} | -909 |
| | K_L | 0.0003 |
| | R_L | 0.593 |
| Timkin | R^2 | 0.9723 |
| | b_T | 6.253 |
| | A_T | 519.569 |
| Hasley | R^2 | 0.9936 |
| | n_H | 0.7551 |
| | K_H | 0.0989 |
| | | |

Table 3. Actual and predicted values as well as percentage differences for Freundlich and Hasley isotherm models

| M | $q_e (\mathrm{mg/g})$ | Freundlich model | | Hasley model | |
|-------|------------------------|--------------------------|--------------|--------------------------|--------------|
| (g/L) | | q_e (Predicted) (mg/g) | % difference | q_e (Predicted) (mg/g) | % difference |
| 2 | 500.85 | 497.775 | 0.614 | 497.80 | 0.609 |
| 4 | 322.675 | 332.455 | - 3.031 | 332.472 | - 3.036 |
| 6 | 244.95 | 238.95 | 0.0124 | 2.445 | 2.445 |
| 8 | 196.588 | 188.795 | 0.04 | 3.96 | 3.96 |
| 1.0 | 161.61 | 168.606 | - 0.043 | - 4.34 | - 4.34 |

Figures 1-4 depict the Linear, Freundlich and Hasley, Langmuir and Temkin isotherm models respectively for the treatment of Lagos dumpsite leachate while Figure 5 reveals the correlation between the predicted and actual values for Hasley isotherm model.

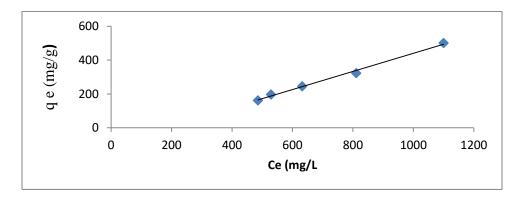


Fig.1. Linear isotherm plot for treatment of Soluos dumpsite leachate.

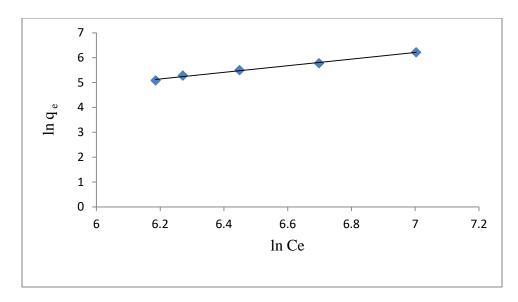


Fig.2. Freundlich and Hasley isotherms plot for treatment of Soluos dumpsite leachate.

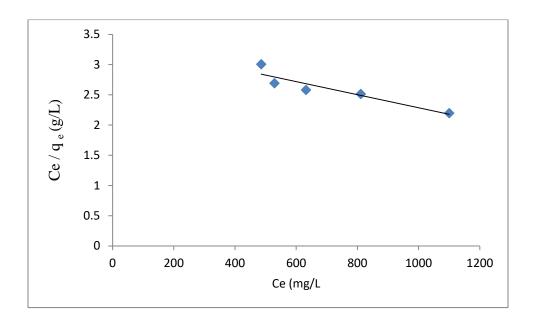


Fig.3. Langmuir isotherm plot for treatment of Soluos dumpsite leachate.

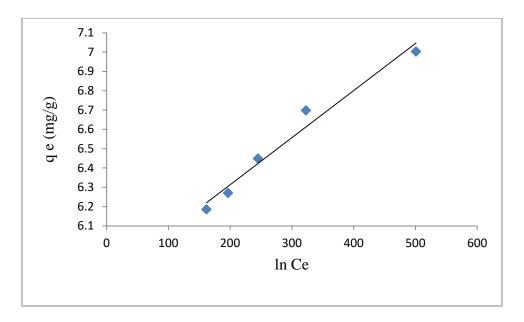


Fig.4. Timkin isotherm plot for treatment of Soluos dumpsite leachate.

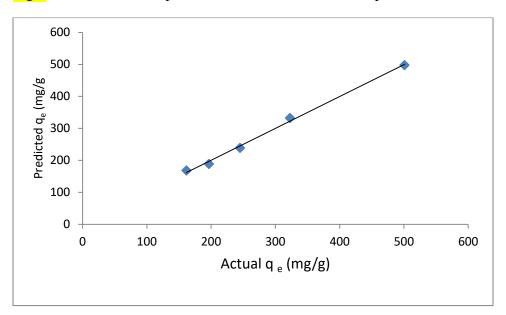


Fig.5. A graph of predicted against actual values for Hasley isotherm model

The R^2 value for linear, Freundlich and Hasley, Langmuir and Temkin isotherm models were 0.9944, 0.9936, 0.8562 and 0.9723 respectively. The closer the R^2 value to unity, the better the fitness of the experimental data to the isotherm model. Linear isotherm model has the highest R^2 value followed by Freundlich and Hasley isotherm models which have the same R^2 value 0.9936. For the linear isotherm model to be chosen based on its R^2 value, the plot of q_e against c_e must

pass through the origin which in this case, did not hence the linear isotherm model was jettison. The isotherm parameters of Freundlich and Hasley were substituted into the models which were then used to predict the experimental data. The percentage difference in absolute term between the experimental and predicted data for Freundlich and Hasley isotherm models ranged between 0.0124 and 3.031 and between 0.609 and 4.34 respectively which indicated Freundlich isotherm model was better in term of percentage difference between the experimental and the predicted data. However, for the Freundlich isotherm model to represent adsorption data, the value of N must be greater than unity and in this case, the value of N was 0.7551 which was less than unity hence Freundlich isotherm model was ignored and Hasley isotherm model was adopted as the isotherm model for the treatment of Soluos dumpsite leachate using Musa sapientum peel as biosorbent. A good correlation existed between the predicted and actual values as shown in Figure 5 for Hasley isotherm model, having a R² value of 0.9965. This further validated that the Hasley isotherm model correlated the experiment data obtained for the treatment of Soluos dumpsite leachate using Musa sapientum peel as biosorbent. Hasley isotherm model has also been applied to the removal of lead (11) from aqueous solution using shell carbon prepared by KOH (Song et al., 2013). The Hasley model fitted the experimental data with a high R² value, which was attributed to the heterogeneous distribution of active sites and multilayer adsorption of the shell carbon (Ayawei, 2015).

4. CONCLUSION

The equilibrium adsorption study of treatment of Lagos dumpsite leachate with a view of establishing the adsorption isotherm model which provides useful information on the adsorption capacity of the adsorbent has been carried out. The concentration of TDS in the dumpsite leachate decreased as the adsorbent dosage increased. At adsorbent dosage of 10 g/L, the concentration of TDS in the leachate was 485.7 mg/L which was less than the 500 mg/L

stipulated by NAESRA for the discharge of wastewater. Linear isotherm model has R² value of 0.9944 which was greater than the R² value of Hasley isotherm model but it was jettison because the plot did not pass through the origin. Hasley and Freundlich isotherm models have the same R² values but Freundlich isotherm model was ignored as a result of N value which was less than unity hence Hasley isotherm model was adopted to have fitted the adsorption data exceedingly well. A good correlation existed between the experimental and the predicted values, having a R² value of 0.9965 which further validated the Hasley isotherm model as the best adsorption model for the treatment of Soluos dumpsite leachate using *Musa sapientum* peel as biosorbent. Hence *Musa sapientum* as biosorbent can be used for treatment of Lagos dumpsite leachate.

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