THERMODYNAMIC STUDY OF SOLUOS DUMPSITE LEACHATE TREATMENT USING AGRICULTURAL WASTE AS BIOSORBENT

***[1]Salami, L.,[2] Alfred, E.A. and [2]Olakanmi, O.S.**

[1]Environmental Engineering Research Unit, Department of Chemical Engineering, Lagos State University, Epe, Lagos State, Nigeria

[2]Department of Chemical Engineering, Lagos State University, Epe, Lagos State, Nigeria

***Corresponding author:** SalamiLukumon@yahoo.com; Lukumon.salami@Lasu.edu.ng

ABSTRACT

Thermodynamic plays a very vital role in the treatment of leachate as it gives an insight of the nature of the adsorption process. The aim of this work was to study the thermodynamic of Lagos dumpsite leachate using agricultural waste as biosorbent with a view to establish the nature of the adsorption process. *Musa sapientum* peels collected from a local market in Epe area of Lagos State were used to produce biosorbent. Thermodynamic adsorption process was carried out at various temperatures using the prepared biosorbent for the treatement of leachate collected Lagos dumpsite. The results obtained revealed that the percentage removal of total dissolved solids (TDS) from the leachate was directly proportional to temperature. The percentage removal of 76.89 and 62.92 were obtained at temperature 303 and 423 K respectively. The values of Gibb's free energy (0*G*D) also followed the same tread of direct proportionality with temperatures. The 0*G*Dvalues obtained ranged between 2.772 and 6.236 KJ/mol which revealed the removal of TDS from Lagos dumpsite leachate using *Musa sapientum* peels biosorbent was non spontaneous and endergonic in nature. Enthalpy (0*H*D) value of – 5.873 KJ/mol was obtained which implied the adsorption process was exothermic. Entropy (0*S*D) value of – 28.589 J/mol.K was also obtained which indicated that the randomness at the biosorbent and leachate interface decreased. It was concluded that the established thermodynamic parameters in this work can be used to navigate the design of the adsorption process of treatment of Lagos dumpsite leachate using *Musa sapientum* peels as biosorbent.

Keywords: Biosorbent, dumpsite, study, thermodynamic and treatment.

1. INTRODUCTION

The use of open dumpsite for disposal of solid wastes in major cities of Nigeria in recent time has been a concern especially in Lagos State, the most populous city in Nigeria. Leachates are generated from the solid wastes as a result of infiltration of precipitation through the wastes which leads to extraction of water soluble compounds and particulate matter of the solid waste (Aziz *et al*., 2017 and Salami and Susu, 2019). The treatment of leachates from dumpsites is a global concern and is very vital in order to avert contamination of surface and groundwater, vegetation and soil which can lead to adverse health and environmental problems. One major way of treating leachates is the use of activated carbons produced from agricultural wastes because of their relative low cost , easy to produce and they are eco – friendly.

Numerous works have been carried out on the treatment of leachates by researchers (Enenebeaku *et al*., 2015; Nnaemeka *et al*., 2019; Lim *et al*., 2010; Aziz *et al*.,2011; Olafadehan *et al*., 2018; Kalderis *et al*., 2008; Ab Ghani *et al*., 2017; Foo *et al*., 2013; Hur and Kim, 2000; Zajc *et al*., 2004; Dabrowski, 2001; Aghamohammadi *et al*., 2007; Liyan *et al*., 2009; Yahya *et al*., 2017; El – Sayed *et al*., 2020 and Mohammed, 2021). Enenebeaku *et al*. (2015) worked on adsorptive removal of methylene blue from aqueous solution using agricultural wastes. The work revealed that raw corn cob powder can be effectively used as low cost and efficient biosorbent without any pretreatment and modification for the treatment of dye effluents. Alaa El – Din *et al*. (2018) studied the removal of oil spill from seawater polluted by crude oil using banana peels. The study showed that as temperature increased, the percentage removal of oil spill from the polluted seawtaer decreased.

Nnaemeka *et al*. (2019) investigated the thermodynamic of adsorption of copper (ii) and lead (ii) ions using raw maize cob. The investigation indicated trhat the adsorption of lead ion was spontaneous and

exothermic in nature while that of copper (ii) uions was also spontaneous but endothermic in nature. El – Sayed *et al*. (2020) analysed the bio – sorption of tennary treatment using eggshell wastes. The analysis revealed that eggshell wastes can simultaneously remove $co^{3+,}$ $Zn^{2+,}$ Hg^{2+} and Pb^{2+} from effluent and the process was spontaneous and endothermic in nature. Mohammed (2021) carried out a review on the removal of lead ions from municipal wastewater (leachate) using agricultural wastes. The review presented various agricultural wastes which had been used fro removal of lead ions from wastewater. The agricultural wastes include cocoa shells, rice husk, peat, banana peel, hyacinth roots, coconut shell and sugarcane bagasse.

It is evident from the available literature that the thermodynamic study of treatment of Lagos dumpsite leachate especially in therm of TDS using *Musa sapientum* peels biosorbent has not been given adequate attention. Therefore the aim of this work is to carry out the thermodynamic study for treatment of Lagos dumpsite leachate using *Musa sapientum* peels biosorbent. The thermodynamic of the adsorption when established will help to comprehend wholly the nature of the adsorption process which justifies this work. It is also imperative that the thermodynamic study of Lagos dumpsite leachate using *Musa sapientum* peels biosorbent is carried out in order to make available fundamental thermodynamic data base which can be used by environmental engineers, chemical engineers, mechanical engineers, chemists and other users of such materials who might work on treatment of Lagos dumpsite leachates which further justifies and shows the contribution of this work.

2. METHODOLOGY

2.1 Preparation of Adsorbent

Muse sapientum peels were collected from a local market in Epe area of Lagos State, Nigeria. The peels were washed with water to remove any unwanted materials. The peels sample were carbonised in a furnace at 600^{o}C for a duration of 1 hr. The char product from the furnace was quenchehed with cold water in order to cool after which it was tranferred into the oven for further drying at 110^{o}C. The impregnation of the activated carbon was done with tetraoxosulphate (vi) (H_2SO_4) (10 % by weight) followed by heating in the absence of air. The obtained moist paste was charged into the furnace and heated for 1 hr at a temperature of 110^{o}C until a constant weight of activated carbon was obtained. The chemical activation was carried out to remove the tar in the pores of the activated carbon. The activated carbon was then rinsed thoroughly with distilled water to remove the remaining H_2SO_4. The activated carbon was then dried in an oven at a temperature of 110^{o}C for 3 hrs. The refined activated carbon was crushed with the aid of a mortar to size of 100 mesh.

2.2 Thermodynamic of Adsorption Process

100 ml of leachate collected from Soluos dumpsite in Lagos State, Nigeria, having a pH of 7.2 was measured into 250 ml conical flasks containing 1 g each of the prepared biosorbent. The mixture was agitated with a shaker at 150 rpm for 2 hrs after which it was left undisturbed for 20 mins and then filtered. The concentration of the total dissolved solid (TDS) in the filtrate was determined at 30 £ T £ 150^{o}C using the standard methods prescribed by American Public Health Association (1994) for the examination of water and wastewater. The percentage removal,q and adsorption capacity values at equilibrium, q_e are determined using Equations 1 – 2 respectively (Olafadehan, 2021).

$$\theta = \left(\frac{C_o - C_i}{C_o}\right) X\ 100 \qquad (1)$$

$$q_e = \left(\frac{C_o - C_e}{m}\right)V \qquad (2)$$

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.

3. RESULTS AND DISCUSSION

The effect of temperature on the percentage removal of TDS from dumpsite leachates using biosorbent is necessary and this was done before investigationg the thermodynamic of the adsorption process. Temperature changes can imply two different effects on the process of adsorption. Before equilibrium is achieved, temperature changes alter adsorption rate but when equilibrium is achieved, it alters the position of equilibrium adsorption of the adsorbent for a particular adsorbate (Olafadehan, 2021). The graph of percentage removal against temperature at a pH of 7.2, adsorbent dosage of 1 g/100 ml and agitation speed of 150 rpm is presented in Figure 1. In Figure 1, as the temperature increased, the percentage removal of TDS from Lagos dumpsite leachate decreased. At temperature of 303 K, the percentage removal of TDS was 76.89 while it was 62.93 percent at a temperature of 423 K. the percentage removal of TDS on the produced biosorbent decreased due to adsorption which has initially taken place on the adsorbent (Zubair *et al*., 2008). The low percentage removal of TDS at higher temperatures may be as a result of destruction of active binding sites (Witek – Krowiak *et al*., 2011).

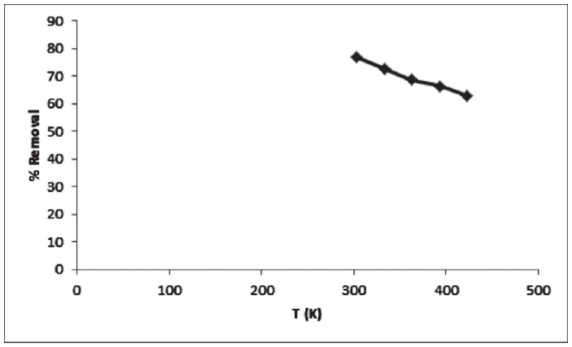

Fig.1. A graph of % removal against temperature at pH = 7.2, adsorbent dosage = 1 g/100ml and agitation speed = 150 rpm.

Having carried out the temperature dependence of TDS removal from Lagos dumpsite leachate using *Musa sapientum* peels biosorbent, the thermodynamic parameters of the process were computed in order to comprehend wholly the nature of the adsorption process. Equation (3) was used to determine the thermodynamic equilibrium constant, K_c (Olafadehan *et al*., 2018).

$$qe = Kecc \quad (3)$$

The ΔG^o was calculated using Equation (4) (Alshabane *et al*., 2013 and Donghee *et al*., 2010)

$$\Delta G^O = -RT \ln Kc \quad (4)$$

where R is the gas constant (8.314 J/mol.K) and T is the absolute temperature. The Von't Hoff model presented in Equation (5) was used to compute the ΔH^o and ΔS^o (Patil *et al*., 2011).

$$\ln Kc = \frac{\Delta S^o}{R} \text{ and } \frac{\Delta H^o}{RT} \quad (5)$$

A plot of ln Kc against was made as shown in Figure 2. The slope was used to calculate ΔH^o and the intercept on y axis was used to determine ΔS^o. Table 1 shows the thermodynamic parameters for Lagos dumpsite leachate treatment using *Musa sapientum* peels biosorbent.

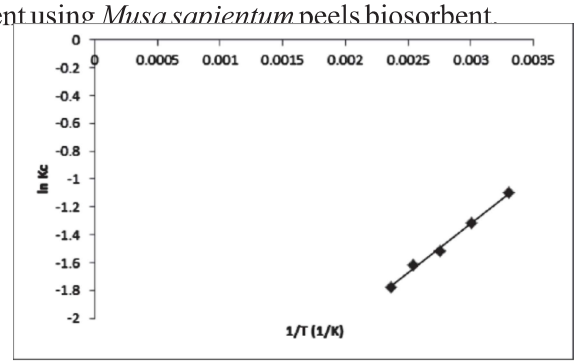

Fig. 2. Van't Hoff plot for treatment of Lagos dumpsite leachate using Musa sapientum peel at pH = 7.2, adsorbent dosage = 1 g/100ml and agitation speed = 150 rpm.

Table 1. Thermodynamic parameters for leachate treatment using *Musa sapientum* peel.

Temperature (K)	ΔG (KJ/mol)
303	2.772
333	3.651
363	4.576
393	5.283
423	6.236
ΔH (KJ/m	- 5.873
ΔS(KJ/mol.K)	- 0.028.589

The value of ΔG^o was used to determine the spontaneity of the adsorption process. If ΔG^o values were all negative at all temperatures, the adsorption process was spontaneous while its positive values indicated non spontaneity of the adsorption process (Olafedehan, 2021). The adsorption process is then described as endergonic and exergonic for positive and negative values of ΔG^o respectively. In this work, the ΔG^o values varied between 2.772 and 6.236 KJ/mol. The ΔG^o values were directly proportional to temperature that is as temperature increased, ΔG^o value decreased and vice versa. All the ΔG^o values were positive at all temperatures investigated which implied that the removal of TDS from Lagos dumpsite leachate using *Musa sapientum* peels biosorbent was non spontaneous and endergonic in nature.

The work of Olafadehan *et al*. (2018) on removal of zinc (ii) ion from industrial wastewater using composite biosorbent prepared from walnut also showed positive values for ΔG^o for all temperatures investigated. It can be deduced that removal of zinc (ii) ion from industrial wastewater and removal TDS from Lagos dumpsite leachate followed similar adsorption process. However, the work of El – Sayed *et al*. (2020) on biosorption for tennary effluent using eggshell wastes and the work of Enenebeaku *et al*. (2015) on adsorptive removal of methyl blue from aqueous solution using agricultural waste showed negative values of ΔG^o for all temperatures considered. This revealed that agricultural wastes used as biosorbent behavior differently and have different thermodynamic nature.

The value of ΔH^o was used to determine whether the adsorption process was exothermic or endothermic. A positive value of ΔH^o implies endothermic process while a negative value means the process is exothermic. The ΔH^o value obtained in this work was – 5.873 KJ/mol which indicated that the treatment of Lagos dumpsite leachate using *Musa sapientum* peels biosorbent was an exothermic process. ΔS^o value was used to determine the degree of randomness at the solid and solution interface (Alshabanat *et al*., 2013 and Ahmed and Kumar, 2010). The negative value of ΔS^o means that randomness at solid and solution interface decreases as a result of adsorbate adsorption on the adsorbent and conversely for positive value of ΔS^o. The ΔS^o obtained in this work was – 28.589 J/mol.K which revealed that the randomness at the *Musa sapientum* biosorbent and leachate interface decreased. The established thermodynamic parameters can be used to navigate the design of the adsorption process of treatment of Lagos dumpsite leachate using *Musa sapientum* peels as biosorbent.

REFERENCES

Ab Ghani, Z., Yusoff, M.S., Zaman, N.Q., Zamir, M.F.M.A. and Andas, J. (2017). Optimization of preparation conditions for activated carbon from banana pseudo – stem using response surface methodology on removal of colour and COD from landfill leachate. Waste Management, 62: 177 – 187.

Aghamohammadi, N., Abdul Aziz, H., Isa, M.H. and Zinatizadeh, A.A. (2007). Powdered activated carbon augmented activated sludge process for treatment of semi – aerobic landfill leachate using response surface methodology. Bioresource Technology, 98(18): 3570 – 3578.

Ahmad, R. and Kumar, R. (2010). Adsorptive removal of Congo re dye from aqueous solution using bael shell carbon. Applied Surface Scinece, 257: 1628 – 1633.

Alaa El – Din, G., Amer, A.A., Malsh, G. and Hussein, M. (2018). Study on the use of banana peels for oil spill removal. Alexandria Engineering Journal, 57: 2061 – 2068.

Alshabanet, M., Alsenani, G. and Almufarij, R. (2013). Removal of crystal violet dye from aqueous solution onto date palm fiber by adsorption technique. Journal of Chemistry, 1 – 6.

American Public Health Association, APHA (1994). Standard methods for examination of water and wastewater, Wastington.

Aziz, S.O., Aziz, H.A., Yusoff, M.S. and bashir, M. (2011). Landfill leachate treatment using powdered activated carbon augmented sequencing batch reactor (SBR) process: Optimization by response surface methodology. Journal of Hazardous Materials, 189 (1 - 2): 404 – 413.

Aziz, H.A., Alias, S., Adlan, M.N., Faridahj, A.H. and Zahari, M.S. (2007). Colour removal from landfill leachate by coagulation and flocculation processes. Bioresources Technology, 98(1): 218 – 220.

Dabrowski, A. (2001). Adsorption from theory to practice. Advances in Colloid and Interface Science, 93(1 - 3): 135 – 224.

Donghee, P., Yeoung – sang, Y. and Jong, M.P. (2010). The past, present and future trends of biosorption. Biotechnology and bioprocessing Engineering, 15: 86 – 102.

El – Sayed, R.E.H., Merit, R., Fatma, E.F. and Khalek, M.A.A. (2020). Bio – sorption for tannery effluent treatment using eggshell wastes: kinetics, isotherm and thermodynamic study. Egyptian Journal of Petroleum, 29: 273 – 278.

Enenebeaku, K.C., Okorocha, J.N. and Akalezi, O.C. (2015). Adsorption removal of methylene blue from aqueous solution using agricultural waste. American Journal of Chemistry and Materia;ls Science, 2(3): 14 – 25.

Foo, k., Lee, L. and Hameed, B. (2013). Preparation of bananafrond activated carbon by microwave induced activation for the removal of boron and total iron from landfill leachate. Chemical Engineering Journal, 223: 604 – 610.

Hur, J.M. and Kim, S.H. (2000). Combined adsorption and chemical precipitation process for pretreatment or post treatment of landfill leachate. Korean Journal of Chemicak Engineering, 17(4): 433 – 437.

Kalderis, D., Koutoulakis, D., Paraskeva, P., Diamodopoulos, E., Otal, E., Del Valle, J.O. and Fernandez – Pereira, C. (2008). Adsorption of polluting substances on activated carbon prepared from rice husk and sugarcane bagasse. Chemical Engineering Journal, 144(1): 42 – 50.

Lim, P.E., Lim, S.P., Seng, C.E. and Noor, A.M. (2010). Treatment of landfill leachate in sequencing batch reactor supplemented with activated rice husk as adsorbent. Chemical Engineering Journal, 159 (1- 3): 123 – 128.

Liyan, S., Youcai, Z., Weimin, S. and Ziyang, J. (2009). Hydrophobic organic chemicals removal from biologically treated landfill leachate by powdered activated carbon, granular activated carbon and bimimetic fat cell. Journal of Hazardous Materials, 163(2 - 3): 1084 – 1089.

Mohammed, J.A.A. (2021). Utilization of conventional treatments and agricultural wastes as low – cost adsorbents for removal of lead ions from wastewater. UKH Journal of Science and Engineering, 5(1): 1 – 17.

Nnaemeka, J.O., Enyinnaya, P.N., Ikechukwu, O.A., Maureen, O.C., Basil, N.A. and Chijioke, E.O. (2019). Adsorption of selected heavy metals using agricultural wastes: Equilibrum, kinetic and thermodynamic studies. American Journal of Engineering Research, 8(12): 761 – 87.

Olafadehan, O.A., Akpo, O.Y., Enemuo, O., Amoo, K.O. and Abatan, O.G. (2018). Equilibrum, kinetic and thermodynamic studies of biosorption of zinc ions from industrial wastewater using derived

composite biosorbents from walnut shell. African Journal of Environmental Science and Technology, 12(9): 335 – 350.

Olafadehan, O.A. (2021). Fundamentals of adsorption processes. LAP Lamber Academic Publishing, Mauritius.

Patil, S., Renukdas, S., and Patel, N. (2011). Removal of methylene blue, a basic dye from aqueous solutions by adsorption using teak tree (Tectonagradnic) bark powder. International Journal of Environmental Science, 1 (5): 711 – 726.

Salami, L. and Susu, A.A. (2019). A comprehensive study of leachate characteristics from three Soluos dumpsites in Igando area of Lagos State, Nigeria. Greener Journal of Environmental Management and Safety, 8(1): 1 – 14.

Witek – Krowiak, A., Szafran, R.G. and Modelski, S. (2011). Biosorption of heavy metal from aqueous solution onto peanut shell as a low cost biosorbent, Desalination, 265: 126 – 134.

Yahya, M.I., Mohammed – Dabo, I.A., Ahmed, A.S. and Olawale, A.S. (2017). Adsorption removal of lead from aqueous solution using raw and modified shea butter cake. Journal of the Nigerian Society of Chemical Engineers, 32(1): 25 – 33.

Zubair, A., Bhatti, H.N., Hanif, M.A. and Shafqat, F. (2008). Kinetic and equilibrium modeling for Cr (iii) and Cr (vi) removal from aqueous solution by Citrus reticulate waste biomass. Water, Air and Soil pollution, 191: 305 – 318.