Eurasian Journal of Analytical Chemistry
ISSN: 1306-3057 OPEN ACCESS 2019 14 (1): 91-102

Removal of COD and Ammoniacal Nitrogen in Leachate Using Rice Husk Ash as Adsorbent

K. Prasanna* and R. Annadurai

Received: 25 December 2018 ▪ Revised: 15 January 2019 ▪ Accepted: 02 February 2019

Abstract: Leachate generation inside Solid Waste Landfills and Dumpsite is regarded as a major threat to the environment that has to be managed utilizing proper disposal systems and waste management techniques. In this study, the leachate characteristics such as pH, Turbidity, EC, TDS, TSS, DO, BOD, COD and Ammoniacal Nitrogen were identified and the leachate was treated with rice husk ash to reduce the concentration of COD and Ammoniacal Nitrogen. The conditions such as contact time, adsorbent dosage and pH were varied to identify the maximum reduction in concentration. It was observed that the removal of COD and Ammoniacal Nitrogen was between 15.9 - 26.7% and 9.5 - 26.7% when varying adsorbent dosage. The reduction efficiency of COD and Ammoniacal Nitrogen was between 15.3 - 36.1 % and 20.2 - 30.8 % while varying the contact time. When the pH was adjusted the COD and Ammoniacal Nitrogen removal efficiency was 29.7 - 47.5% and 18.6 - 47.1 %. Hence, it is found that rice husk ash can be utilized as a low cost adsorbent which is said to be a feasible technique in treating the leachate.

INTRODUCTION

Population growth, coupled to changes in solid waste characteristics and amount produced per capita, is a matter for global concern, with available resources and energy on the brink of exhaustion [1-4]. Leachate is formed as a result of rainfall, surface run-off and seepage of groundwater that percolates through the landfill[5-8]. There are three classes of landfill leachate in terms of landfill age: the young, middle-age, and mature landfill leachate [9-10]. The reduction in concentrations of COD, BOD and ammonium compounds present inside leachate is an essential requirement before discharging it into rivers, lakes or water bodies.The treatment of leachate can be categorized into two main types such as physical (adsorption)/ chemical (coagulation, flocculation) and biological (using microbes) methods[11-15]. Biological process is conventionally preferred to physico-chemical methods but application of biological treatment alone does not fulfill the satisfactory requirement of effluent quality confirming to standard of regulatory board due to presence of many dissolved toxic constituents in leachate. Adsorption process is a conventional and economical process for treatment of dissolved toxic and organic matters [16-22].

Perungudi dumpsite situated at Chennai, TamilNadu lies on the southeast shoreline of India. Chennai is the fourth biggest city in India. Chennai city utilizes two main dumpsites for its solid waste disposal namely Perungudi located in the south and Kodungaiyurlocated in the north. Both the dumpsites are still in active phase. Solid Waste dumping at Chennai has been divided into two parts. The first eight zones in one part come under Kodungaiyur and remaining seven zones in another part which comes under Perungudi. ThePerungudi dumpsite has been in operation since 1987 with a total of 85 wards at present. It lies in the co-ordinates of 12.057’13.5”N & 80.014’05.8” E. The total population at Perungudi surrounding is estimated to be 43, 493 according to 2011 Census. The average waste disposed at the dumpsite is 3,917 tonnes/ day. A total area of 800 sections is available of which 380 sections have been utilized for dumping.The technique which is used for waste disposal inside the dumpsite is by leveling and open space dumping. The dumpsite is placed at 1.5 to 2.0 km from the west side of Buckingham canal and is situated within Pallikaranaimarshlands which extendup to a length of 10 km from north to south

K. Prasanna, Department of Civil Engineering, SRM Institute of Science and Technology, Kattankulathur, Kancheepuram Dist., Tamil Nadu, India. E-mail:prasanna.env@gmail.com
R. Annadurai, Department of Civil Engineering, SRM Institute of Science and Technology, Kattankulathur, Kancheepuram Dist., Tamil Nadu, India.

and for a width of 3 to 4 km from west to east making the dumpsite always surrounded by inactive and moving water. A Google Earth image of the dumpsite location is given in Figure 1.

Fig 1: Dumpsite location

MATERIALS AND METHODS

i. Characteristics of Rice-Husk Ash(R-HA)
ii. Identifying the characteristics of raw leachate
iii. Treating leachate with Rice-Husk Ash(R-HA)
iv. Identifying the characteristics of treated leachate

Collection of Leachate Samples

The leachate sample was collected in a 10litre can which was washed with water and dried in sunlight. The leachate was collected beside the boundary wall of the dumpsite where the leachate was stagnant. The collected leachate was refrigerated at 4ºC to inhibit any change in characteristics.The collected sample is shown in Fig. 2(a)

Preparation of Adsorbent

Raw rice husk was obtained commercially from Chromepet, Chennai, TamilNadu. It was then washed with distilled water to remove any impurities or dust present in it. It was then allowed to dry and crushed. The rice husk was then converted into Rice-Husk Ash(R-HA) by heating it in a muffle furnace at 150ºC for 24 hours. The rice husk ash is shown in Fig. 2 (b) and its characteristics are shown in Table 1.

Table1: Rice Husk Ash Characteristics

PARAMETERS	VALUES
pH	6.2
Moisture Content (%)	2.7
Density (g/cm^3)	1.15
Bulk Density (kg/m^3)	174

(a) (b)

Fig. 2: Materials (a)Leachate Sample and (b) Rice husk ash

RESULTS AND DISCUSSION

Leachate Characterization

The Leachate Sample I (LeS I), Leachate Sample II (LeS II) and Leachate Sample III (LeS III) collected from the dumpsite was characterized by laboratory analysis are shown in Table 2. The leachate characteristics are as follows:

Table 2: Characteristics of Leachate

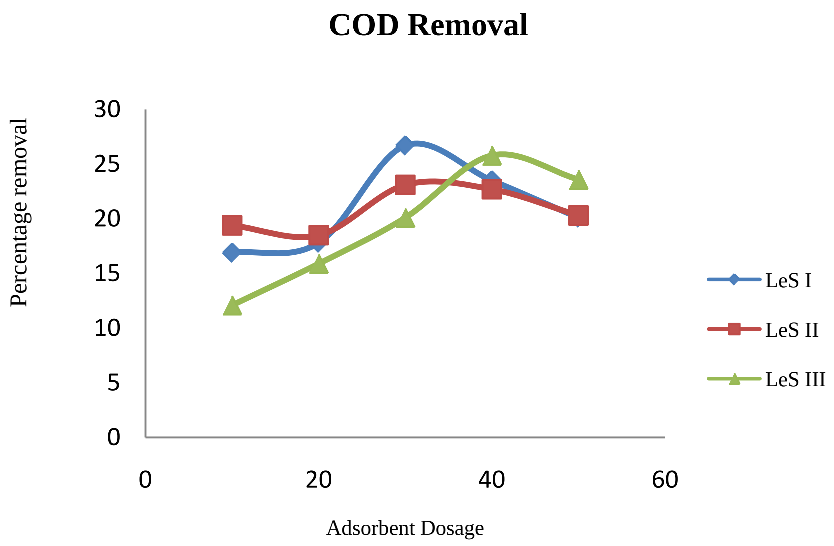
PARAMETERS	VALUES			UNIT	TESTING METHOD
	LeS I	LeS II	LeS III		
pH	7.9	6.1	5.7	-	pH meter
Odour	Foul smell	Foul smell	Foul smell	-	Physical sensation
Colour	Dark black	Dark Brown	Dark black	-	Physical appearance
Turbidity	4.64	5.41	4.18	NTU	Turbidity meter
Electrical Conductivity	14.6	10.1	17.2	µS/ cm	EC meter
Total Suspended Solids	371	295	284	mg/ l	Gravimetric method
Total Dissolved Solids	1016	1512	1197	mg/ l	TDS meter
Dissolved Oxygen	5.37	5.20	5.77	mg/ l	DO probe
Biochemical Oxygen Demand	272	191	255	mg/ l	BOD Incubator
Chemical Oxygen Demand	1352	2160	1309	mg/ l	Open reflux method
Ammoniacal nitrogen	740	683	715	mg/ l	Nesslerization method

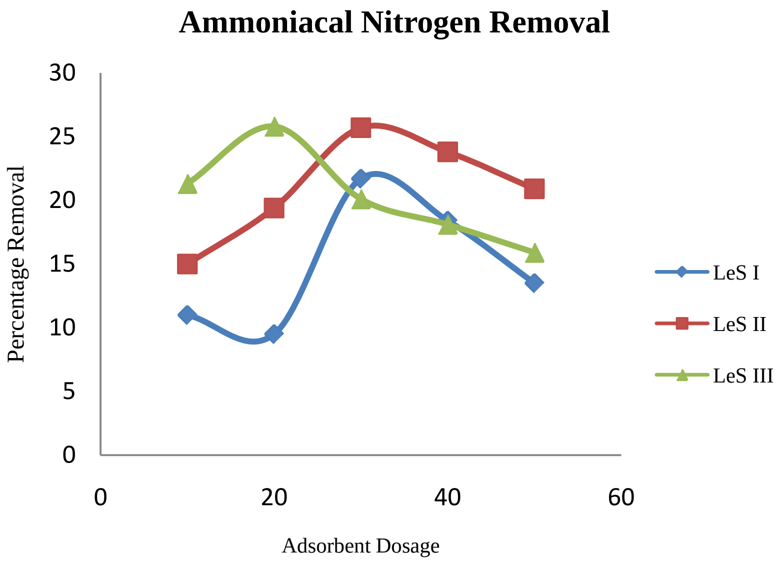
Effect of Adsorbent Dosage

100ml of Leachate Sample I (LeS I), Leachate Sample II (LeS II) and Leachate Sample III (LeS III) was taken respectively in five conical flasks each. The rice husk ash was added in dosages of 10, 20, 30, 40 and 50 g to each of the conical flasks containing the samples. The solution was then mixed well and strained with the help of a filter paper. The sample was then analyzed to find the dosage which has high removal efficiency. Table 3 represents the removal efficiency of COD was between 15.9 – 26.7% with the highest removal efficiency of 26.7%. The removal efficiency of Ammoniacal Nitrogen was between the ranges of 9.5% - 25.7% with the highest removal efficiencies of 25.7%. Figure.3 (a) and (b) shows the removal efficiency of COD and Ammoniacal Nitrogen respectively by varying the adsorbent dosage.

Table 3: Effect of Adsorbent Dosage

Adsorbent Dosage (g)	COD Removal (%)			Ammoniacal Nitrogen Removal (%)		
	LeS I	LeS II	LeS III	LeS I	LeS II	LeS III
10	16.9	19.4	12.1	11	15	21.3
20	17.8	18.5	15.9	9.5	19.4	25.8
30	26.7	23.1	20.1	21.7	25.7	20.1
40	23.5	22.7	25.8	18.4	23.8	18.1
50	20.1	20.3	23.6	13.5	20.9	15.9





(a) (b)

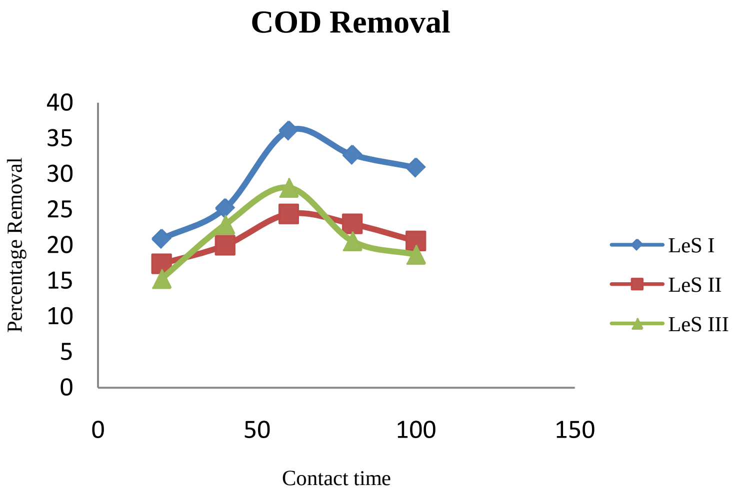
Fig 3: Adsorbent Dosage - (a) COD Removal (b) Ammoniacal Nitrogen Removal

Effect of Contact Time

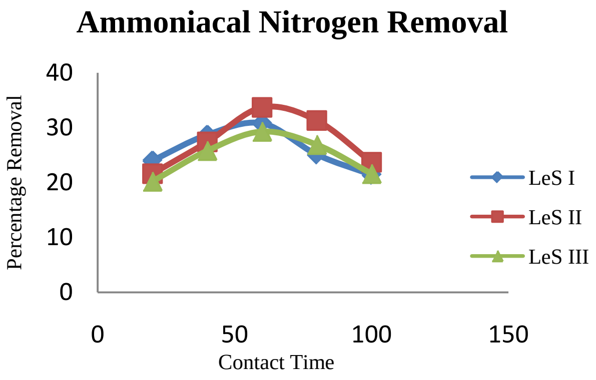
100ml of Leachate Sample I (LeS I), Leachate Sample II (LeS II) and Leachate Sample III (LeS III) was taken respectively in five conical flasks each. The rice husk ash was added in dosages of 30g to each of the conical flasks containing the samples. The solution was then mixed well for various contact periods of 20, 40, 60, 80 and 100 minutes respectively and strained with the help of a filter paper. The sample was then analyzed to find the dosage which has high removal efficiency. Table 4 presents the removal efficiency of COD was between 15.3 – 36.1% with the highest removal efficiency of 36.1%. The removal efficiency of Ammoniacal Nitrogen was between the ranges of 20.2 – 33.7% with the highest removal efficiency of 33.7%. Figure.4 (a)and (b) shows the removal efficiencies of COD and Ammoniacal Nitrogen respectively by varying the contact time.

Table 4: Effect of Contact Time

Contact Time (mins)	COD Removal (%)			Ammoniacal Nitrogen Removal (%)		
	LeS I	LeS II	LeS III	LeS I	LeS II	LeS III
20	20.9	17.4	15.3	24	21.6	20.2
40	25.2	20	22.9	28.7	27.4	25.8
60	36.1	24.4	28.1	30.8	33.7	29.3
80	32.7	23	20.6	25.1	31.3	26.9
100	30.9	20.6	18.7	21.4	23.7	21.6



(a)



(b)

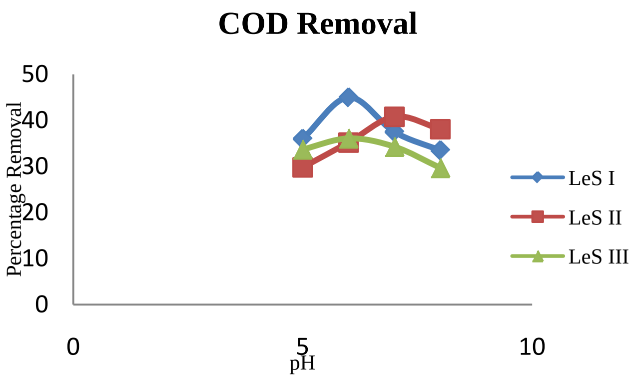
Fig 4: Contact Time -(a) COD Removal (b) Ammoniacal Nitrogen Removal

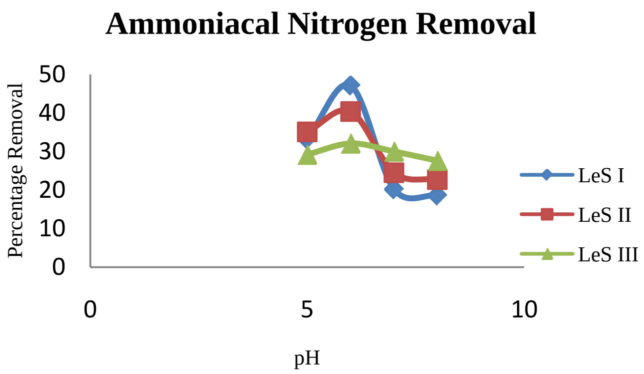
Effect of pH

100ml of Leachate Sample I (LeS I), Leachate Sample II (LeS II) and Leachate Sample III (LeS III) was taken respectively in five conical flasks each. The rice husk ash was added in dosages of 30g to each of the conical flasks containing the samples. The solution was then mixed well for a contact period of 60 minutes and strained with the help of a filter paper. The sample was then analyzed to find the dosage which has the highest removal efficiency. Table 5 shows the removal efficiency of COD was between 29.7 – 47.5% with the highest removal efficiency of 47.5%. The removal efficiency of Ammoniacal Nitrogen was between the ranges of 18.6 – 47.1%% with the highest removal efficiency of 41.7%. Figure 5(a) and (b) shows the removal efficiencies of COD and Ammoniacal Nitrogen respectively by varying the pH.

Table 5: Effect of pH

pH	COD Removal (%)			Ammoniacal Nitrogen Removal (%)		
	LeS I	LeS II	LeS III	LeS I	LeS II	LeS III
5	36	29.8	33.7	33.2	35.1	29.2
6	45	35.2	36.1	47.1	40.4	32.1
7	47.5	40.8	34.3	20.2	24.5	30
8	33.5	38.1	29.7	18.6	22.7	27.6





(a) (b)

Fig 5: pH - (a) COD Removal (b) Ammoniacal Nitrogen Removal

Adsorption Isotherm

The adsorption mechanism can be determined by estimating the equilibrium data (adsorption data)acquired from the experiment. The current study dealt using Langumuir and Freundlich isotherms to determine the adsorption data.

Langmuir Isotherm

The assumptions for Langmuir Isotherm model are:

i. Monolayer formation happens on the surface of the adsorbent.
ii. Surface of adsorbent is homogenous, possess identical and energetically equivalent adsorption site.

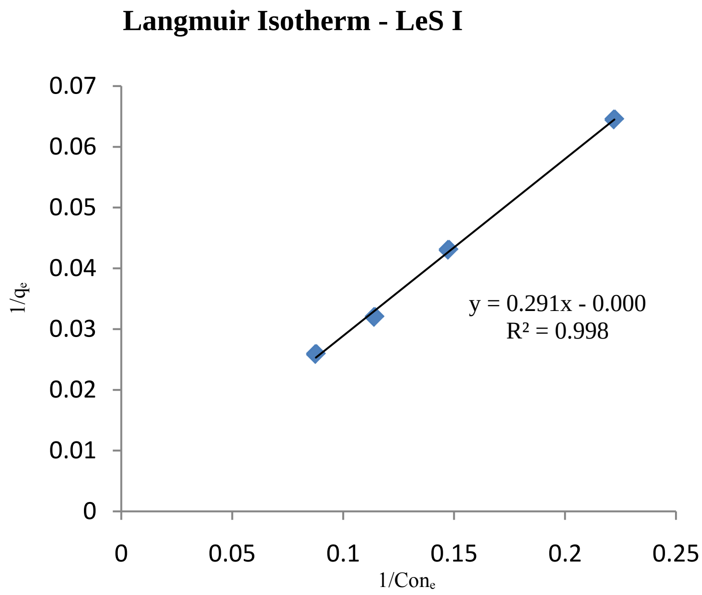
The Langmuir models is represented by the following equation,

$$\frac{1}{q_e} = \frac{1}{K_a qm}\frac{1}{C_e} + \frac{1}{qm}$$

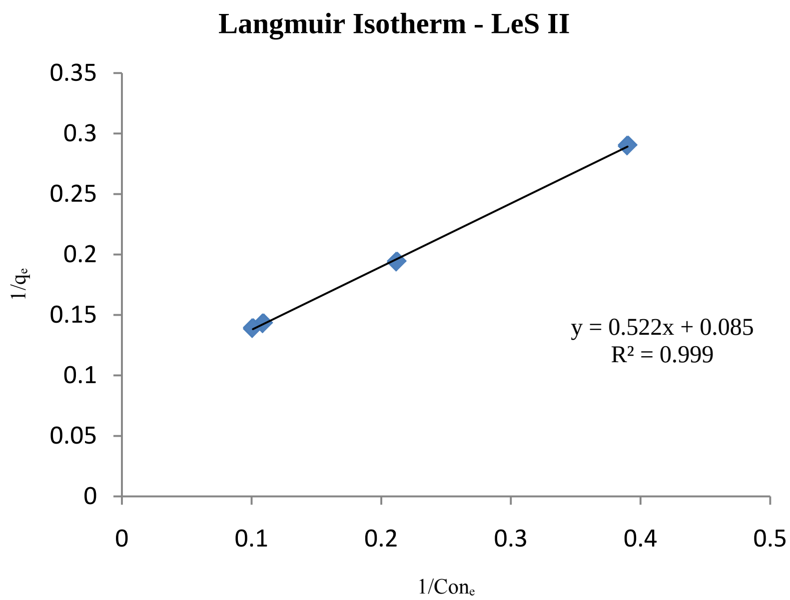
The Langmuir adsorption isotherm study for the removal of COD for three samples is represented graphically in Figures 6 (a), (b) and (c) and the readings are shown in Table 6. Similarly the Langmuir isotherm for Ammoniacal Nitrogen is given in Table 7 and Figures 7 (a), (b) and (c)respectively.

Table 6: Langmuir Isotherm for COD

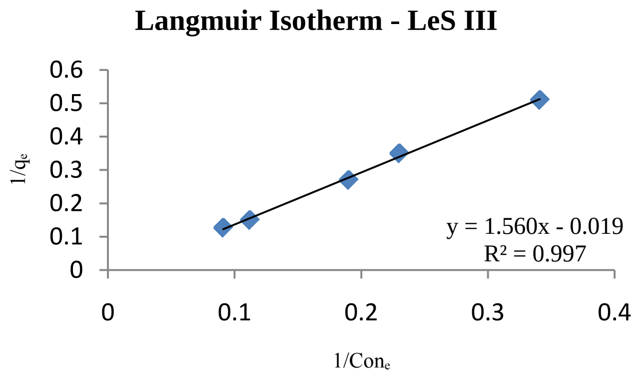
$1/Con_e$	$1/q_e$	$1/Con_e$	$1/q_e$	$1/Con_e$	$1/q_e$
LeS I		LeS II		LeS III	
0.454	0.128	0.554	0.4	0.341	0.51
0.222	0.064	0.39	0.29	0.23	0.35
0.147	0.043	0.212	0.194	0.112	0.15
0.114	0.032	0.109	0.143	0.19	0.27
0.087	0.025	0.101	0.139	0.091	0.127



(a)



(b)

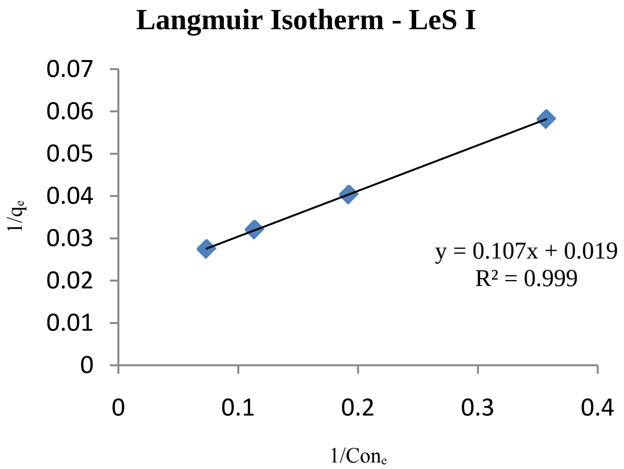


(c)

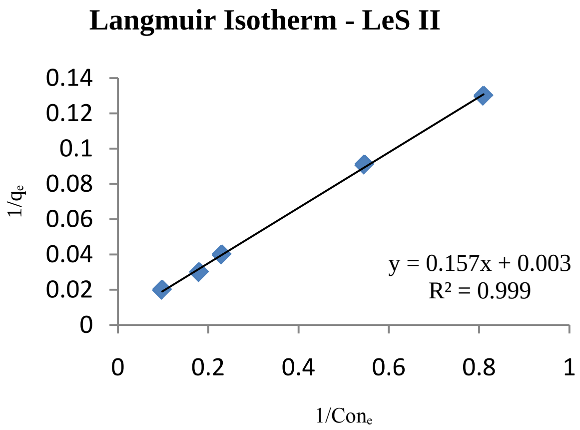
Fig 6: Langmuir Isotherm for COD – (a) LeS I (b) LeS II (c) LeS III

Table 7: Langmuir Isotherm for Ammoniacal Nitrogen

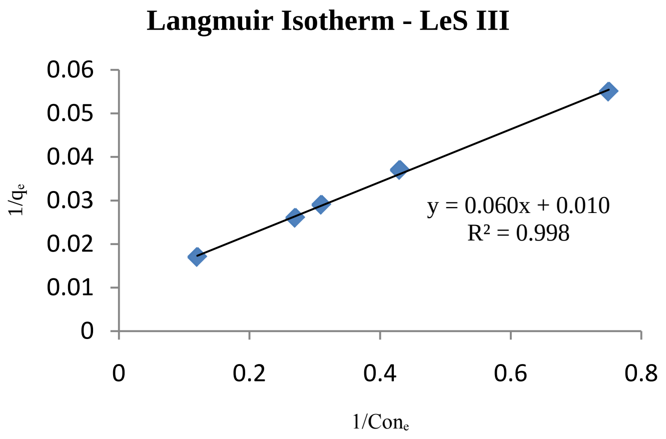
$1/Con_e$	$1/q_e$	$1/Con_e$	$1/q_e$	$1/Con_e$	$1/q_e$
LeS I		LeS II		LeS III	
0.909	0.112	0.81	0.13	0.75	0.0555
0.357	0.058	0.546	0.091	0.43	0.037
0.192	0.040	0.23	0.043	0.31	0.029
0.113	0.032	0.18	0.036	0.27	0.026
0.073	0.027	0.098	0.027	0.12	0.017



(a)



(b)



(c)

Fig 7: Langmuir Isotherm for Ammoniacal Nitrogen – (a) LeS I (b) LeS II (c) LeS III

Freundlich Isotherm

i. The Freundlich model is applicable to heterogeneous systems
ii. Formation of a multilayer.

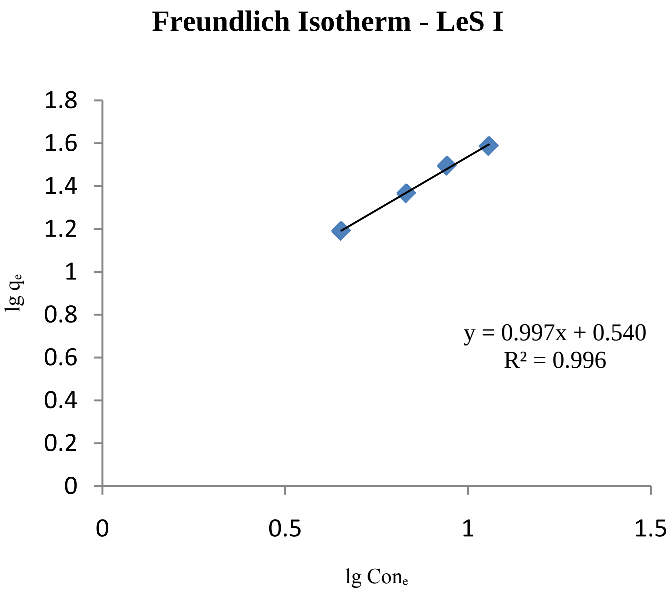
The freundlich adsorption isotherm is given by,

$$\log q_e = \log Kf + \frac{1}{n}\log C_e$$

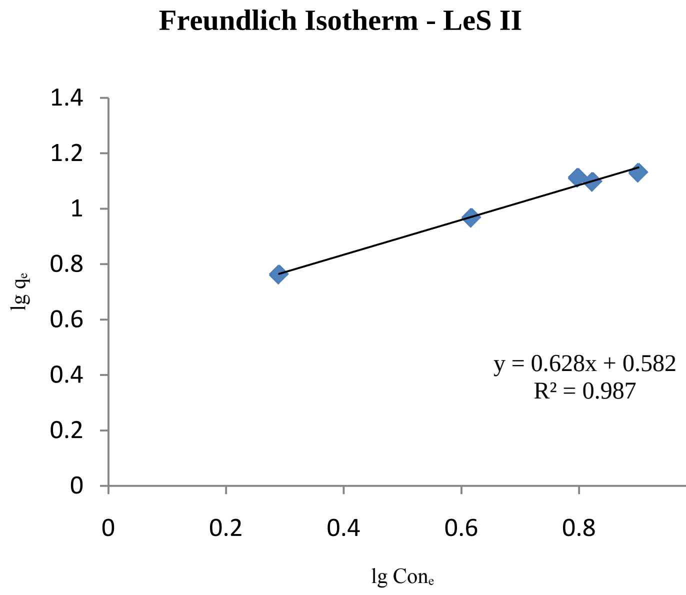
The Freundlich adsorption isotherm study for the removal of COD is represented graphically in Figures 8 (a), (b) and (c) and their corresponding readings are shown in Table 8. Similarly the Langmuir isotherm for Ammoniacal Nitrogen is given in Table 9 and Figures 9 (a), (b) and (c) respectively.

Table 8: Freundlich Isotherm for COD

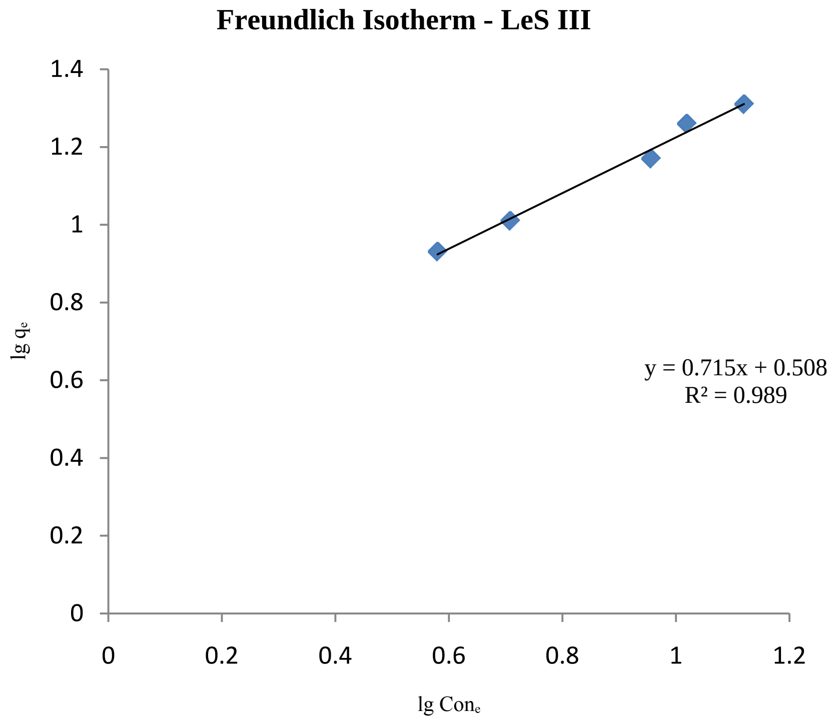
lgCon$_e$	**lg q$_e$**	**lgCon$_e$**	**lg q$_e$**	**lgCon$_e$**	**lg q$_e$**
LeS I		LeS II		LeS III	
0.342	0.892	0.29	0.762	0.58	0.931
0.653	1.190	0.617	0.967	0.708	1.01
0.831	1.365	0.798	1.112	0.956	1.17
0.942	1.494	0.823	1.097	1.019	1.26
1.056	1.586	0.901	1.13	1.12	1.31



(a)



(b)

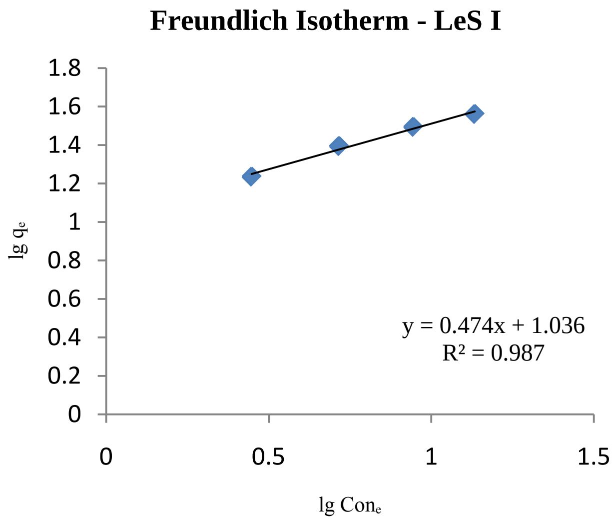


(c)

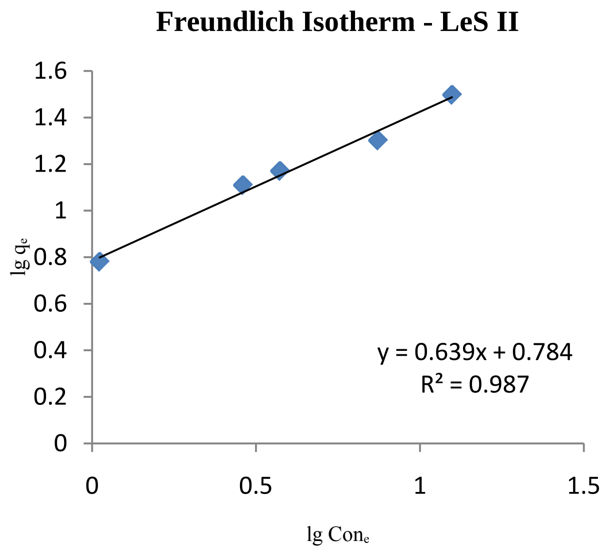
Fig 8: Freundlich Isotherm for COD – (a) LeS I (b) LeS II (c) LeS III

Table 9: Freundlich Isotherm for Ammoniacal Nitrogen

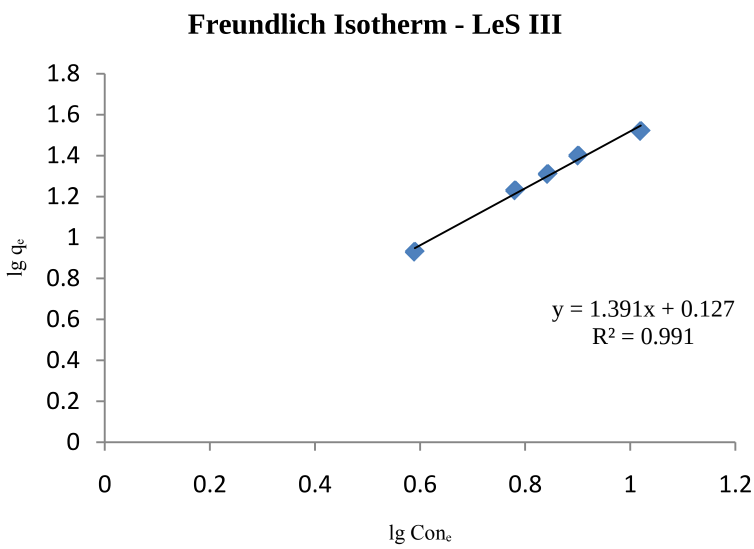
$lgCon_e$	$lg\ q_e$	$lgCon_e$	$lg\ q_e$	$lgCon_e$	$lg\ q_e$
LeS I		LeS II		LeS III	
0.041	0.949	0.023	0.78	0.59	0.93
0.447	1.235	0.46	1.109	0.781	1.23
0.716	1.394	0.573	1.17	0.843	1.31
0.944	1.494	0.872	1.301	0.901	1.4
1.133	1.561	1.098	1.497	1.02	1.52



(a)



(b)



(c)

Fig 9: Freundlich Isotherm for Ammoniacal Nitrogen – (a) LeS I (b) LeS II (c) LeS III

CONCLUSION

The feasibility of utilizing Rice-Husk Ash (R-HA) for the treatment of leachate for the reduction of COD and Ammoniacal Nitrogen was studied and evaluated using adsorption process. The optimum conditions such as adsorbent dosage, contact time and pH were varied. The present study showed that R-HA, a natural adsorbent is helpful in the treat leachate by a maximum removal efficiency of 47.1% for CODLeS I – 636mg/l, 38.1% for LeSII – 881mg/l, 472 mg/l and 47.1% for Ammoniacal Nitrogen LeS I – 348mg/l, 40.4% for LeS II – 275mg/l and 32.1% for LeSIII – 229mg/l. The adsorption process follows both Langmuir and Freundlich isotherms. It was found that maximum adsorption efficiency was obtained for adsorbent dosage of 30g, contact time of 60 minutes and pH 7 for COD and pH 6 for Ammoniacal Nitrogen.

CONFLICT OF INTEREST

The authors would like to declare that there are no conflicts of interest regarding the publication of this paper.

REFERENCES

[1] Martins, T. H., Souza, T. S., & Foresti, E. (2017). Ammonium removal from landfill leachate by Clinoptilolite adsorption followed by bioregeneration. *Journal of Environmental Chemical Engineering*, *5*(1), 63-68.

[2] Bernard, C., Colin, J. R., & Anne, L. D. D. (1997). Estimation of the hazard of landfills through toxicity testing of leachates: 2. Comparison of physico-chemical characteristics of landfill leachates with their toxicity determined with a battery of tests. *Chemosphere*, *35*(11), 2783-2796.

[3] Sanjay, M., Amit, D., & Mukherjee, S. N. (2013). Applications of adsorption process for treatment of landfill leachate. *Journal of Environmental Research And Development*, *8*(2).

[4] Raghab, S. M., El Meguid, A. M. A., & Hegazi, H. A. (2013). Treatment of leachate from municipal solid waste landfill. *HBRC journal*, *9*(2), 187-192.

[5] Parameswari, K., Mudgal, B. V., & Nelliyat, P. (2012). Evaluation of groundwater contamination and its impact: an interdisciplinary approach. *Environment, development and sustainability*, *14*(5), 725-744.

[6] Parameswari, K., & Mudgal, B. V. (2014). Geochemical investigation of groundwater contamination in Perungudi dumpsite, South India. *Arabian Journal of Geosciences*, *7*(4), 1363-1371.

[7] Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., & Moulin, P. (2008). Landfill leachate treatment: review and opportunity. *Journal of hazardous materials*, *150*(3), 468-493.

[8] Sivakumar, D., Murugan, N., Rajeshwaran, R., Shobana, T., Soundarya, C., & Vanitha, V. S. (2014). Role of rice husk silica powder for removing Cr (VI) in a tannery industry wastewater. *International Journal of ChemTech Research*, *6*(9), 4373-4378.

[9] Singh, S. R., & Singh, A. P. (2012). Treatment of water containg chromium (VI) using rice husk carbon as a newlow cost adsorbent. *International Journal of Environmental Research*, *6*(4), 917-924.

[10] Foo, K. Y., & Hameed, B. H. (2009). An overview of landfill leachate treatment via activated carbon adsorption process. *Journal of hazardous materials*, *171*(1-3), 54-60.

[11] Kaur, K., Mor, S., & Ravindra, K. (2016). Removal of chemical oxygen demand from landfill leachate using cow-dung ash as a low-cost adsorbent. *Journal of colloid and interface science*, *469*, 338-343.

[12] Halim, A. A., Abidin, N. N. Z., Awang, N., Ithnin, A., Othman, M. S., & Wahab, M. I. (2011). Ammonia and COD removal from synthetic leachate using rice husk composite adsorbent. *Journal of Urban and Environmental Engineering*, *5*(1), 24-31.

[13] Sivakumar, D. (2013). Adsorption study on municipal solid waste leachate using moringa oleifera seed. *International Journal of Environmental Science and Technology*, *10*(1), 113-124.

[14] Lim, P. E., Lim, S. P., Seng, C. E., & 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.

[15] Lim, H. K., Ismail, N., Abustan, I., Murshed, M. F., & Ahmad, A. (2012). Treatment of landfill leachate by using lateritic soil as a natural coagulant. *Journal of environmental management*, *112*, 353-359.

[16] Bhusari, A.A., & Bhusari, S. (2015). Investigation of feasibility of rice husk ash for effluent treatment of waste water: Adsorption & Comparative study. *International Journal of Emerging Trends in Engineering and Basic Sciences*, *2*(2), 177– 181.

[17] Maranon, E., Castrillon, L., Fernández-Nava, Y., Fernández-Méndez, A., & Fernández-Sánchez, A. (2010). Colour, turbidity and COD removal from old landfill leachate by coagulation-flocculation treatment. *Waste Management & Research*, *28*(8), 731-737.

[18] Agbugui, P.A., & Nwaedozie, J.M. (2015). Adsorption of Heavy Metals from Simulated Landfill Leachates unto Composite Mix of Agricultural Solid Wastes**.** *IOSR Journal of Applied Chemistry*, *8*(2), 49– 54.

[19] Daud, Z., Abubakar, M. H., Kadir, A. A., Latiff, A. A. A., Awang, H., Halim, A. A., & Marto, A. (2017). Adsorption studies of leachate on cockle shells. *International Journal of GEOMATE*, *12*(29), 46-52.

[20] Xue, Q., Li, J. S., Wang, P., Liu, L., & Li, Z. Z. (2014). Removal of heavy metals from landfill leachate using municipal solid waste incineration fly ash as adsorbent. *Clean–soil, air, water*, *42*(11), 1626-1631.

[21] Wu, J. J., Wu, C. C., Ma, H. W., & Chang, C. C. (2004). Treatment of landfill leachate by ozone-based advanced oxidation processes. *Chemosphere*, *54*(7), 997-1003.

[22] Prasanna, K., Annadurai, R., & Kumaran, P. V. (2018). Assessment of Heavy Metal Concentration Present In Subsurface Water Due to Solid Waste Dumping. *Journal of Engineering Science and Technology,* 13(11), 3632 – 3647.