Nat. Volatiles & Essent. Oils, 2021; 8(5): 10443-10449

NVEO
Natural Volatiles & Essential Oils

Leachate Treatment by *Parkia Speciosa* (Petai) pods derived Activated Carbon

Vivek Laishram[1*], Potsangbam Albino Kumar[2]

[1,2]Department of Civil Engineering, National Institute of Technology Manipur- 795004

Abstract

This study focuses on the employment of a waste derived Parkia Speciosa (Petai) pods activated carbon (PPAC) synthesized with 30% H_3P0_4 at an impregnation ratio of 1:1 for organic ions (COD) uptake from landfill leachate collected from Lamdeng Solid Waste Management Plant, Imphal, Manipur which was pretreated in the previous part of this study. To study the sorption mechanism and rate controlling steps, intra-particle diffusion, Elovich model and non-linear Langmuir and Fruendlich isotherm models were used to test the adsorption data. The adsorption equilibrium was practically reached at 90 min contact time yielding 93% COD removal at an optimum dose of 11g/L PPAC in the previous part of the study. The adsorption kinetic studies revealed that the correlation coefficients (R^2) for Elovich model was 0.953 as compared to 0.847 for diffusion model signifying the better fit of the adsorption kinetics data on Elovich model. In the previous part of this study, the linearized Langmuir model fitted better yielding a higher R^2 value of 0.998 as compared to 0.497 for the linearized Freundlich isotherm model with lesser Chi-square (χ^2) of 0.56 for Langmuir's isotherm against that of 13.87 for Fruendlich. However, in this part of the study also, the modeling results revealed that the non-linearized Langmuir model (R^2=0.971) even fitted the data better than non-linearized Fruendlich model (R^2=0.891) with χ^2 value of 0.94 and 4.65 for Langmuir and Fruendlich isotherm respectively. From the observations, the organic ions mainly COD is adsorbed on PPAC (q_{max}=180.65mg/g), the surface of which is mostly homogeneous. Monolayer adsorption occurs without lateral interactions between the adsorbed molecules suggesting the nature of adsorption to be predominantly chemical adsorption.

Keywords: Activated Carbon, Adsorption, COD, Landfill leachate, Parkia Speciosa

Introduction

The major environmental issues faced by people with the process of urbanization and industrialization are the rapid generation of solid waste. In Imphal city, the disposal of solid waste is a serious issue. Due to the rapid growth in population, the quantity of solid waste has come in abundance. The municipal solid waste (MSW) generates leachate which contains biodegradable organic matter, heavy metals and inorganic salts in enormous quantities. Leachate affects living organisms and ecosystems by causing soil, air, surface water and groundwater pollution [1] [2]. The treatment methods used for leachate generally involves a combination of appropriate techniques because it cannot be treated efficiently by using only a single technique due to its refractory nature. The coupling of the biological and physico-chemical processes leads to more efficient treatment and have been reported as an effective treatment for leachate [3]. The pre-treatment of stabilized leachate from Imphal city, India by coagulation-flocculation

has been presented in our previous part of this study [4]. Low cost waste derived activated carbon (AC) has gained interest in the last decades due to its efficiency in treating wastewater and potential for the minimum generation of agro-residues [5]. Owing to these issues and search for sustainable alternatives for leachate treatment, the pre-treated stabilized leachate obtained after coagulation-flocculation in the previous part of this study [4] is further explored by adsorption on PPAC, the kinetics and isotherm analysis of which is mainly discussed in the part of this study.

Material and Methods

Synthesis and characterization of pretreated leachate and adsorbent

The waste derived PPAC was synthesized by impregnating 100 g of crushed petai pods with 167 ml of 30% phosphoric acid solution (activating agent) at a mass impregnation ratio of 1:1 for 24 hours and then

carbonizing the impregnated petai pods at 400°C for a duration of 30 minutes in a muffle furnace. The activated PPAC was then rinsed repeatedly for residue removal and oven dried at 100^0C. The final PPAC was then sieved using a 125µ sieve and stored in desiccators for further use in adsorption experiments. The effluent COD concentration was as high as 1280 mg/L after pretreatment with alum in our previous study [4]. Similar studies were also reported with pretreated stabilized leachate yielding 1560 mg/L using alum as coagulant [6]. Surface analysis using Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDAX) were investigated using Zeiss Sigma-300 Model. Surface area, pore volume of adsorbent were evaluated using Quantachrome operated Nova Station–A-BET analyzer and pore dimensions was determined using the Brunauer-Emmett-Teller (BET) method [7].

Adsorption experiments

For the equilibrium study, the batch experiments were conducted by the addition of appropriate amount of PPAC to a series of 1L pretreated leachate samples using a Phipps and Bird Jar Test Apparatus (PB – 600). After being agitated for 3 hours at 300 rpm, 30 min settling time was given and the supernatant was filtered using Whatman No.47 filter paper and the equilibrium COD concentrations (Ce, mg COD/L) in the filtrates were analyzed by closed reflux method. Adsorbate (COD) uptake at equilibrium (qe, mg COD/g) was calculated from Eqn. (1):

$$q_e = \frac{C_o - C_e}{m} V \qquad (1)$$

where, C_o= initial concentration, V = volume of pretreated leachate sample in L and m = mass of PPAC in g.

Adsorption Kinetics and Isotherms

The adsorption data was studied by the application of two adsorption kinetics models namely Elovich model [8] and diffusion model [9]. After attainment of equilibrium conditions, non linearized form of Langmuir [10] and Freundlich [11] isotherms were employed to understand the adsorbate molecules distribution. The non–linear regression involves the error distributions between the calculated and predicted values based on the convergence data and were used for analyzing the adsorption processes [12].

Table 1. Porosity structures of PPAC

Properties	**Activation (400 ^{0}C)**
BET Surface Area (m^2/g)	239.13
Pore Diameter (nm)	3.218
Pore Volume (cc/g)	0.072
Pores Surface Area (m^2/g)	79.32
Micropore Volume (cc/g)	0.035
Micropore Area (m^2/g)	101.18
External Surface Area (m^2/g)	136.62

Results and Discussion

Characterization of PPAC

PPAC when activated at 400 ^{0}C gives BET surface area of 239.13 m^2/g corresponding to 3.218 nm pore diameter and 0.072 cc/g pore volume (Table I). Similar studies were also reported with BET surface areas of 188-300 m²/g at 350-400°C activating temperatures [6]. SEM image before PPAC adsorption (Fig.1) have a smooth and uniform micro porous structure favourable for the uptake of organic ions from leachate whereas after adsorption (Fig.2) most of the available pores are filled with the ions in leachate leading to the saturation of PPAC. EDAX analysis gives the elemental compositions of PPAC before and after adsorption which corresponds to the peak on the EDAX image [Fig.3(a), (b)] confirming the adsorption of ions onto PPAC which was in the range of 0.20 – 4.12 keV in the EDAX spectra.

Adsorption kinetics

The study of adsorption kinetics on COD removal by PPAC was conducted with pretreated leachate COD of 1280 mg/L using 8 g/L adsorbent dose at optimum pH 2. Kinetics of adsorption gives the rate of uptake amount of ions or adsorbed from the solution [12]. The kinetics data was analyzed first by Elovich model which is represented by Eqn. (2):

$$q_t = \frac{1}{\beta}\ln(\alpha\,\beta) + \beta\,\ln(t) \qquad (2)$$

where, q_t (mg/g) is the adsorbed amount at time t, α (mg/g min) is the initial sorption rate and β (g/mg) is the desorption constant. From Fig. 4, it can be observed that the correlation coefficient (R^2) value is

Figure 1. PPAC before adsorption

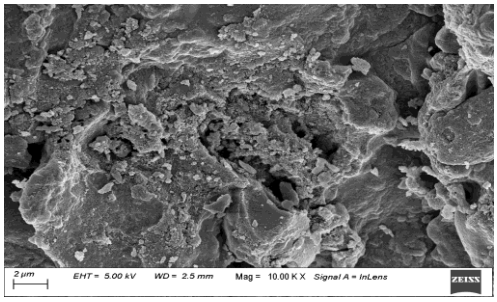


Figure 2. PPAC after adsorption

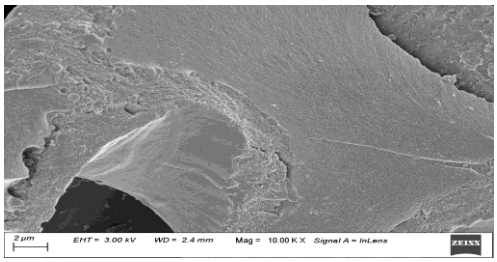
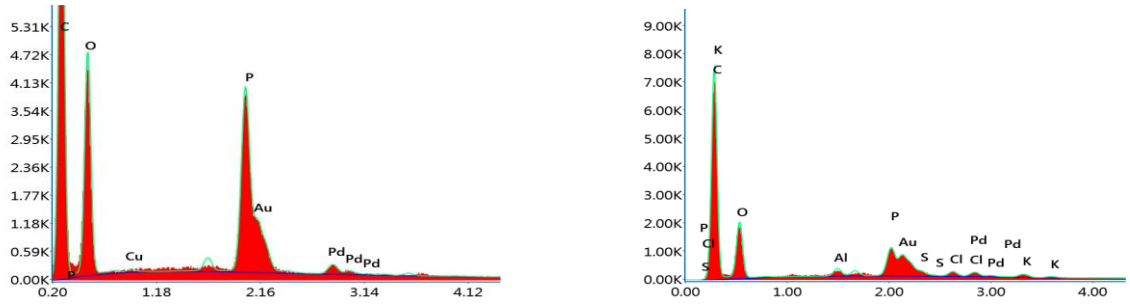


Figure 3. EDAX spectra of PPAC (a) before and (b) after adsorption



(a) **(b)**

above 0.95 suggesting that the adsorption kinetics data obeys the Elovich model. The evaluated value of α and β for Elovich model are shown in Table II for comparison with that of the Diffusion model coefficients.

To analyze the rate-controlling factors of adsorption, the kinetic data was also treated with diffusion model given by Eqn. (3):

$$q_t = K_d\, t^{1/2} + C \qquad (3)$$

where q_t (mg/g) is the amount of adsorbed ions at time t, K_d (mg/g $min^{1/2}$) is the diffusion rate constant

Figure 4. Elovich kinetics model for COD adsorption

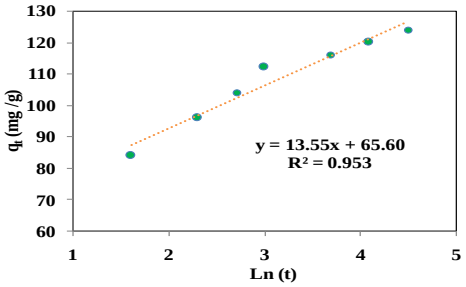
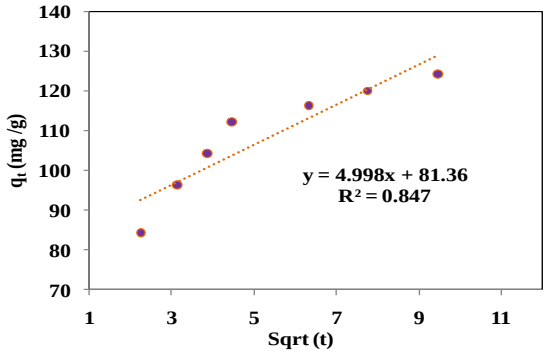


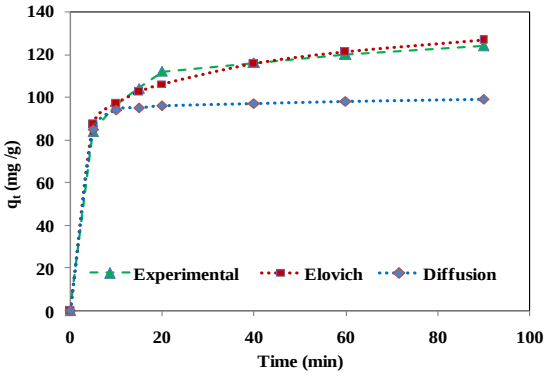
Figure 5. Diffusion model for COD adsorption



and C (mg/g) is the diffusion constant [9]. The value of K_d and C were given by slope and the intercept of the linear plot of $t^{½}$ vs. q_t respectively. From Fig.5, it was observed that the kinetics data did not obey diffusion model as the R^2 value was less than 0.95. The evaluated coefficients of diffusion model K_d and C are shown in Table 2.

For comparison between Elovich and Diffusion model, the predicted q_t values are plotted against the experimental q_t values. In Fig. 6, the predicted q_t values of Elovich model are observed to be much closer to the experimental q_t values than that of Diffusion suggesting a better fit on Elovich model.

Figure 6. Experimental Vs. Predicted qt for Elovich and Diffusion models



The experimental and predicted q_t values were also compared through evaluated errors using the Chi-square equation given by Eqn. (4):

$$\chi^2 = \Sigma \frac{(q_t(exp.) - q_t(pred.))^2}{q_t(exp.)} \qquad (4)$$

where, q_t (exp.) and q_t (pred.) are the experimental and the predicted amount of ions adsorbed per gram of adsorbent at time t. The evaluated χ2 values for both Elovich and Diffusion were shown in Table II. The χ2 value for Elovich is 0.75 against very high value of 6.63 for Diffusion model indicating insignificant error for Elovich model. The kinetics data of COD adsorption on PPAC can thus be well explained by Elovich model.

Table 2 Elovich and Diffusion parameters

ELOVICH			
R^2	**α (mg/g min)**	**β (g/mg)**	**χ2**
0.953	9.35	13.55	0.75
DIFFUSION			
R^2	**k_d (mg/g $min^{1/2}$)**	**C (mg/g)**	**χ2**
0.847	4.99	81.36	6.63

Adsorption isotherm studies

The non-linear form of Langmuir (Eqn.5) and Fruendlich (Eqn.6) isotherms were applied to the adsorption data after the kinetics study which are given by:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \qquad (5)$$

$$q_e = K_f C_e^{1/n} \qquad (6)$$

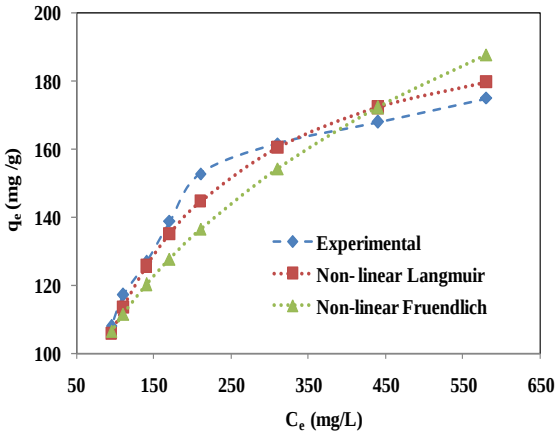
where, q_{max} is the maximum adsorptive capacity (mg/g), b is the Langmuir adsorption constant (L/mg), Freundlich coefficient K_f represents an indicator of adsorption capacity, 1/n indicates the adsorption intensity, while its reciprocal n represents the affinity factor for the Freundlich model [13]. As shown in

Table III, the non-linear Langmuir isotherm model correlates to the activated carbon adsorption yielding R^2 of 0.971 as compared to R^2 of 0.891 for non-linear Fruendlich isotherm. Also for better comparison between the two isotherm models, the predicted q_e values are plotted against the experimental q_e values. From Fig.7, it can be observed that the predicted q_e values of non-linear Langmuir isotherm are closer to the experimental q_e values than that of the predicted q_e values of non-linear Fruendlich isotherm. Also, when the experimental and predicted q_e values were compared using Chi-square and standard error (SE), lesser χ^2 and standard error of 0.94 and 5.99 respectively were observed for Langmuir isotherm against that of 4. 65 and 11.58 respectively for Freundlich isotherm suggesting the better fit of COD adsorption onto PPAC by Langmuir's isotherm model. This finding indicated the homogenous surface of PPAC with adsorption of organic ions (COD) occurring through monolayer adsorption on the surface of PPAC with no interaction of adsorbed neighboring ions with each other.

Table 3. Regression data of Non-linear Langmuir and Fruendlich isotherm models

Non-linear Langmuir isotherm	**q_{max} (mg/g)**	**b (L/mg)**	**R^2**	**χ^2**	**SE**
	180.65	0.0108	0.971	0.94	5.99
Non-linear Freundlich isotherm	**K_f (L/g)**	**1/n**	**R^2**	**χ^2**	**SE**
	25.36	3.17	0.891	4.65	11.58

Figure 7. Experimental Vs. Predicted q_e for non-linear Langmuir and Fruendlich isotherm models



Conclusion

This part of the study revealed that the kinetics data of the adsorption of organic ions (mainly COD) by PPAC from pretreated landfill leachate can be described by Elovich model (R^2 = 0.953) with predicted amounts of ions adsorbed much closer to experimental values and also with insignificant χ2 error of 0.75. After the attainment of equilibrium conditions, the isotherm data fitted well to the non linearlized Langmuir model (R^2 = 0.971) with χ2 error of 0.94 yielding a maximum adsorption capacity of 180.65 mg COD/g. Both the kinetics and isotherm study revealed that, the adsorption of organic ions (COD) on PPAC

was predominantly due to chemical adsorption with almost insignificant amount of physical adsorption or diffusion

REFERENCES

1. Tatsi, A. I. Zouboulis, K. A. Matis, "Coagulation–flocculation pretreatment of sanitary landfill leachates", Chemosphere, vol. 53, pp.737–744, April 2003.
2. Z. Zhang, Z.P. Wang, Y.J. Lin, N.S. Deng, T. Tao, K. Zhuo, "Landfill leachate treatment by a coagulation–photooxidation process", J. Hazard. Mater., vol. B95, pp.153–159, 2002.
3. X. Wang, S Chen, X. Gu and K Wang, "Pilot study on the advanced treatment of landfill leachate using a combined coagulation, fenton oxidation and biological aerated filter process", Waste Management, vol.29, no.4, pp.1354-1358, Dec. 2008.
4. V. Laishram and P. A. Kumar, "Reduction of COD and turbidity in leachates through coagulation-adsorption" J. Indian Chem. Soc., vol. 97,no.10b, pp.1-10, 2020.
5. Y. Guo, D. A. Rockstraw, "Activated carbons prepared from rice hull by one-step phosphoric acid activation", Microporous and Mesoporous Materials, vol 100, no.1, pp.12-19, Nov 2006.
6. R. Gandhimathi, N. J. Durai, P. V. Nidheesh, S. T. Ramesh and S. Kanmani, "Use of combined coagulation-adsorption process as pretreatment of landfill leachate", Iranian J. of Environ. Health Sci. & Engg., pp.10-24, 2013.
7. Reffas, V. Bernardet, B. David, L. Reinert, M. B. Lehocine, M. Dubois, N. Batisse and L. Duclaux, "Carbons prepared from coffee grounds by H3PO4 activation: Characterization and adsorption of methylene blue and Nylosan Red N-2RBL", J. Hazard. Mater. vol. 175, pp. 779–788, Oct. 2009.
8. D. L. Sparks, "Kinetics of reaction in pure and mixed systems, in Soil Physical Chemistry", Edited by Sparks, CRC Press, Boca Raton, Florida, 1986.
9. T. E. Hristova, "Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones", Bulgarian Chemical Communications, vol. 43, no. 3, pp. 370 – 377, 2011.
10. S. Jiang, T. Yu, R. Xia, X. Wang and M. Gao, "Realization of super high adsorption capability of 2D δ-MnO2 /GO through intra-particle diffusion", Materials Chem. and Phy., vol. 232, pp. 374–381, May 2019.
11. K. Pirzadeh and A. A. Ghoreyshi, "Phenol removal from aqueous phase by adsorption on activated carbon prepared from paper mill sludge", Desalin. Water Treat., vol.52, pp.6505–6518, Oct. 2014.
12. J. Luna, L. Montes, S. M. Vargas,"Linear and nonlinear kinetic and isotherm adsorption models for arsenic removal by manganese ferrite nanoparticles", SN Applied Sciences, vol.1, pp. 950, July 2019.
13. S. Elabbas, L. Mandi, F. Berrekhis, M. N. Pons, J. P. Leclerc and N. Ouazzani, "Removal of Cr(III) from chrome tanning wastewater by adsorption using two natural carbonaceous materials: Eggshell and powdered marble", J. of Environ. Manage., vol.166, pp. 589-595.