Study on Landfill Leachate Treatment by Corncob Derived Activated Carbon: A Kinetic and Isotherm Study

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Abstract--- The present study aims to investigate adsorption of organic ions mainly COD from pretreated stabilized landfill leachate from Manipur, India. Corncob was utilized to synthesize a waste derived Corncob activated carbon (CCAC) and it was employed as a bio-adsorbent in batch mode in this study. For effective adsorption of organic ions, the chemical modification of CCAC was functionalized through treatment with phosphoric acid (H_3PO_4), in order to induce more number of –OH groups onto the adsorbent surface. The physico chemical properties of the prepared bio-carbon were characterized by their adsorptive nature towards zero point charge to estimate their surface charge density. CCAC was analyzed for morphological and surface characterization by various methods including, Field emission scanning electron microscopy (FESEM), Energy Dispersive X-Ray Analysis (EDAX), Brunauer-Emmett-Teller (BET) surface area. The impacts of adsorption processes such as initial pH, contact time and dose of adsorbent were considered to evaluate the performance of CCAC. CCAC showed maximum COD removal of 88.75% within 120 min contact time, at optimum pH 2. Adsorption kinetics was able to explain by Lagregren's pseudo-second-order equation suggesting behavior of chemical adsorption of COD on CCAC. Isotherm studies on the adsorption of COD on CCAC can be explained by Langmuir model that revealed the maximum monolayer coverage of 71.7 mg COD/g CCAC.

Index Terms— Adsorption, Bio-adsorbent, Corncob activated carbon (CCAC), Landfill Leachate

I. INTRODUCTION

The municipal solid waste (MSW) landfill site generates leachate which is very toxic and contaminates the surface and groundwater through soil percolation [1]. Very high quantities of biodegradable organic matter, heavy metals and inorganic salts [2] are present in leachate which affects living organisms and ecosystems. The specific composition of leachate establish its relative treatability and it may be classified as: (i) Leachate combined with domestic sewage and treated in municipal wastewater treatment plant (ii) Leachate biodegradation either through aerobic or anaerobic processes and (iii) Chemical/physical processes techniques [3]. 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 [4]. Our previous study [5] has already presented the pre-treatment part of stabilized leachate from Imphal city, India by coagulation-flocculation which resulted in the reduction of turbidity, COD and total iron of 70.93%, 55.55% and 40.08% respectively. The synthesis of activated carbon (AC) from many agricultural by-products has been widely increased in the last decades due to its potential for the minimum generation of agro-residues [6]. These adsorbents are generally low cost and being renewable allows their reuse. While recent studies have established the feasibility of agricultural residues-based adsorbents, effective landfill leachate treatment with COD below the permissible limit of 100 mg/L by these activated carbons is less reported. 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 [5] is further treated in this part of the study to remove organics mainly COD. The present study deals with the adsorption of the COD using Corncob activated carbon (CCAC).

II. MATERIAL AND METHODS

A. Leachate sample collection

Initially, stabilized leachate samples were collected once every two weeks from July 2019 to January 2020 from the sanitary landfill site of Lamdeng Khunnou Solid Waste Management Plant, Manipur, India (24º84'24.7704" N, 93º53' 23.9244" E). The samples were stored in 20 L clean polypropylene containers at 4ºC to abstain from the microbial activity that may change the characteristics of the leachate.

B. Synthesis of adsorbent

In this study, activated carbons derived from corncob (CCAC) were prepared in line with a reported method of activation [7], [8]. The corncob was first crushed using a miller and passed through a 300µ sieve before impregnation. The sample was then impregnated with 30% phosphoric acid solution (activating agent). 167 mL of 30% phosphoric acid was employed for the impregnation of 100 g crushed corncob with a mass ratio of 1:1 and shaken for about 5 minutes and kept for 24 hours to achieve homogeneity. The precursor was then put into a quartz crucible, heated in the muffle furnace at 300°C and 400°C for duration of 30 minutes each. After adequate carbonization, the activated product was cooled down to room temperature and then washed with distilled water repeatedly to remove residues and dried in an oven at 100^0C. CCAC was finally sieved again using 125µ sieve and stored in the desiccators for further use.

C. Characterization

Surface morphology of the adsorbent using Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray Analysis (EDAX) were investigated using Zeiss Sigma-300 Model. Surface area, pore volume of the adsorbent, CCAC were evaluated using Quantachrome operated Nova Station–A-BET analyzer and pore diameter was determined using the Brunauer- Emmett-Teller (BET) method [9].

D. Determination of pHpzc

The zero point of charges (pH_{ZPC}) is described as the pH where the net charge of absorbent's surface is equal to zero. The solid addition method [10] was used for the calculation of pH_{pzc} using 100 ml solution of 0.01M NaCl and boiled to get rid of CO_2. The pH ranges from 2–12 and were adjusted using HCl and NaOH (0.1N) after which, 0.5g of CCAC were immersed in a series of conical flasks containing the solution of different pH. After 24 hours, the final pH of suspensions was determined and the initial pH was then plotted against the difference between the initial and final pH.

E. Adsorption experiments

The effects of pH (2-12), contact time (5, 10, 20, 40, 60, 90,120, 150, 180 minutes) and adsorbent dose (9 – 18 g/L) on the removal of COD were studied. The batch adsorption experiments were conducted by the addition of appropriate amount of CCAC to a series of 1L pretreated leachate samples using a Phipps and Bird Jar Test Apparatus (PB – 600) for 3 hours at 300 rpm. After 30 min settling time, the adsorbed supernatant was withdrawn from the beakers, filtered using Whatman No. 47 filter paper and analyzed.

All the analyses in this study were conducted in triplicates until concordant values were obtained. If the standard deviation of the values were more than 5, the values were discarded and the experiments were re-performed again. The percentage of COD removal was calculated as:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

Where, C_o = initial concentration and C_e = final concentrations of COD in mg/L.

And the equilibrium adsorption capacity is calculated as:

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

Where, q_e = adsorption capacity at equilibrium in mg/L, V = volume of pretreated leachate sample in L, m = mass of CCAC in g

F. Analysis of Adsorption

Different models have been used in kinetic studies – Lagargren's nonlinear and linear pseudo-first-order equations (3) & (4) [11], Lagargren's nonlinear and linear pseudo-second-order equations (5) & (6) [12].

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (3)$$

$$Ln(q_e - q_t) = Lnq_e - k_1 t \qquad (4)$$

$$q_t = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)} \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

where, q_t and q_e are the adsorption amount at any instant of time (mg/g) and at equilibrium time respectively, k_1 and k_2 are the adsorption rate constant of pseudo-first-order equation (L/min) and pseudo-second-order equation (g/mg/min) respectively. For isotherm studies, the most commonly applied Langmuir and Freundlich models are employed. Langmuir (7) and Freundlich isotherms (8) were employed in the study and are expressed by [13] [14]:

$$q_e = \frac{q_{max} b C_e}{(1 + b C_e)} \qquad (7)$$

The acceptability of the isotherm equations was evaluated with respect to the correlation coefficients R^2, estimated from linear regression of the adsorption data. The Langmuir and Freundlich isotherm models are applied in their respective linearised equation forms (9) and (10) respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}} \qquad (9)$$

$$Log q_e = Log K_f + \frac{1}{n} Log C_e \qquad (10)$$

Where, C_e = equilibrium concentration in mg/L, b = Langmuir adsorption capacity constant, q_{max} = maximum

adsorption capacity in mg/g, K_f = Freundlich capacity factor and n = Freundlich's intensity/affinity factor.

III. RESULTS AND DISCUSSION

#### A. Characterization of pre-treated stabilized leachate

The effluent COD concentration is as high as 1280 mg/L after pretreatment with alum in our previous study [5] and other parameters detected in the pretreated leachate are presented in Table I. Similar studies were also reported with pretreated stabilized leachate yielding 1560 mg/L using alum as coagulant [15].

B. BET, SEM and EDAX Analysis of CCAC

From Table II, it can be observed that with the increase in temperature from 300 - 400^{0}C, the pore diameter increase from 2.86-3.12 resulting in an increase of 9.1% and the corresponding pore volume increased from 0.036-0.043 resulting in overall increase of 19.4%. All the surface parameters increased significantly which will enhance the adsorption and thus activation temperature of 400^{0}C is considered as the most suitable condition for this adsorption study. Similar studies were also reported with BET surface areas of 188-300 m²/g at 350-400°C activating temperatures [16]. CCAC before adsorption (Fig.1) have a smooth and uniform micro porous structure whereas after adsorption (Fig.2) most of the available pores are filled with ions in the leachate leading to the saturation of CCAC. The peak on the EDAX image (Fig.3, 4) confirms the adsorption of ions onto CCAC which was in the range of 0.20 – 4.12 keV in the EDAX spectra.

C. Point of zero charge (pHpzc)

The point at which the curve cuts the X-axis is the pH_{ZPC} of the adsorbent and is found to be 5 (Fig. 5). Therefore at pH below 5, the surface charge of PPAC will be positive and encourage binding of anions whereas cations ions will bind predominantly at pH above 5.
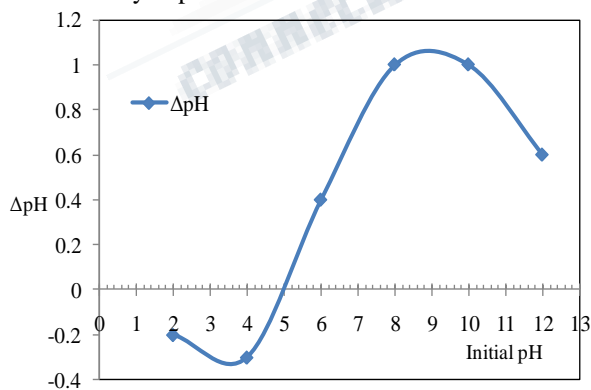
Fig. 5: Point of zero charge for CCAC

D. Effect of pH on COD removal

The effect of pH for was evaluated at a pH ranging from 2-12 using a random CCAC dose of 10g/L as shown in Fig. 6. It was seen that the maximun removal of COD were found at pH of 2. COD removal of 28.75% coresponding to 73.6 mg/g adsorption were obtained at a solution of pH 12 which increases to a maximum COD removal of 66.25% and 169.6 mg/g adsorption capacity at pH 2. A similar trend of decreasing the COD removal from 59% at pH 4 to 47.6% at pH 12 using palm bark powder was reported [17]. CCAC also exhibited a positive surface charge at acidic pH as its pH_{ZPC} was 5 favoring anionic organic molecules such as aromatic carboxylic acids and hydrocarbons and phenolic compounds etc. in leachate [18]. At basic pH, the surface of CCAC attained a negative charge thus repelling the organic molecules present in leachate and yielded lesser COD removal.
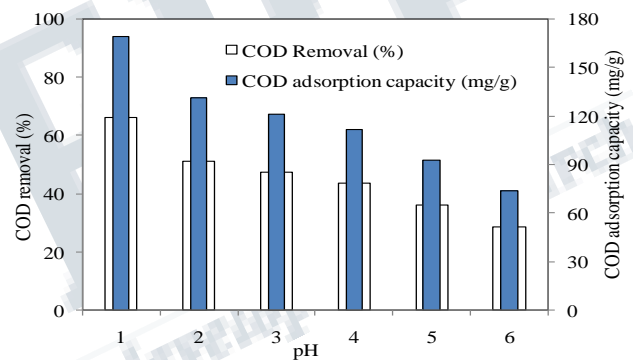
Fig.6: Effect of pH on COD removal by CCAC

E. Effect of contact time on COD removal

The effect of contact time was analysed at the optimum pH of 2 using a mass loading of 10 g/L with different time intervals varying from 5-180 minutes as shown graphically in Fig.7.

Table I: Physico-chemical characteristics of raw and pre-treated stabilized leachate from Lamdeng landfill

Sl.	Parameters	Stabilized leachate	Pre-treated Stabilized leachate	Permissible Limit CPCB, 2017
1	pH	8.01	3.8	5.5 – 9
2	Conductivity, ms/cm	6.55	10.40	-
3	Turbidity, NTU	161	46.8	300
4	Total Dissolved Solids, mg/L	4388	5110	1200
5	COD, mg/L	2880	1280	100
6	BOD_5, mg/L	420	196	50
7	BOD_5/COD	0.14	0.15	-

Table II: Porosity structures of CCAC activated at 300°C and 400°C

Properties	Activation Temperature (^{0}C)	
	300	400
BET Surface Area (m^2/g)	151.20	192.86
Pore Diameter (nm)	2.86	3.12
Pore Volume (cc/g)	0.036	0.043
Pores Surface Area (m^2/g)	41.05	62.25
Micropore Volume (cc/g)	0.023	0.031
Micropore Area (m^2/g)	79.54	92.13
External Surface Area (m^2/g)	68.27	100.05
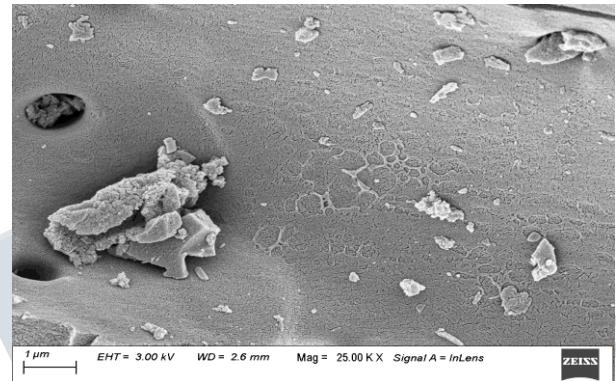
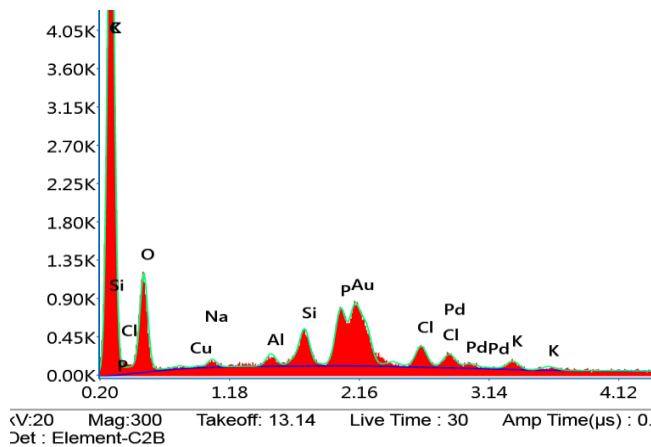**Fig.2: CCAC after adsorption**
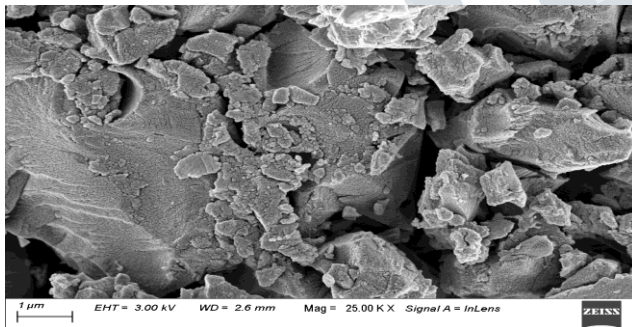
Fig.1: CCAC before adsorption
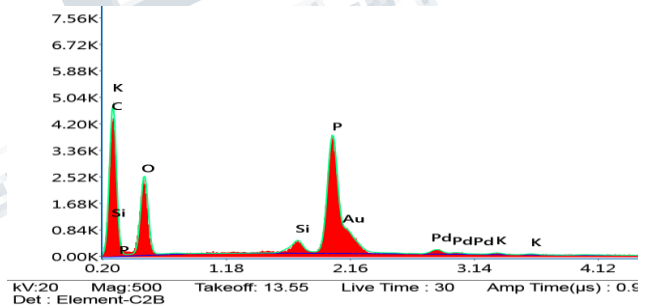
Fig. 3: EDAX spectra of CCAC before adsorption

Table III: Composition of CCAC before adsorption

Element	Weight %	Atomic %	Error %
C	52.23	64.14	8.23
O	34.32	31.64	10.73
Si	0.65	0.34	7.85
P	7.10	3.38	3.61
Pd	0.62	0.09	16.01
k	0.12	0.04	34.14
Au	4.97	0.37	17.45

Table IV: Composition of CCAC after adsorption

Element	Weight %	Atomic %	Error %
C	65.80	77.91	6.90
O	21.75	19.33	12.40
Na	0.63	0.39	19.65
Al	0.37	0.19	12.57
Si	0.86	0.44	7.31
P	1.50	0.69	5.55
Cl	0.66	0.26	11.59
Pd	0.71	0.10	14.84
K	0.30	0.11	15.76
Cu	0.29	0.07	28.51
Au	7.13	0.51	18.49

Fig. 4: EDAX spectra of CCAC after adsorption

It was found that rapid adsorption occurs during the first 20 minutes and then gradually approaches towards equilibrium at 120 minutes. A COD adsorption capacity of 65.6 mg/g was attained during the first 20 minutes of adsorption corresponding to 51.25% COD removal which further reached the equilibrium with COD adsorption capacity of 84.8 mg/g yielding 66.25% COD removal. This phenomenon of adsorption gradually slowing down after the first 20 min is due to the sudden reduction in adsorption sites available on the surface of CCAC, which in turn suggests that the adsorption process occurred via film diffusion [19].
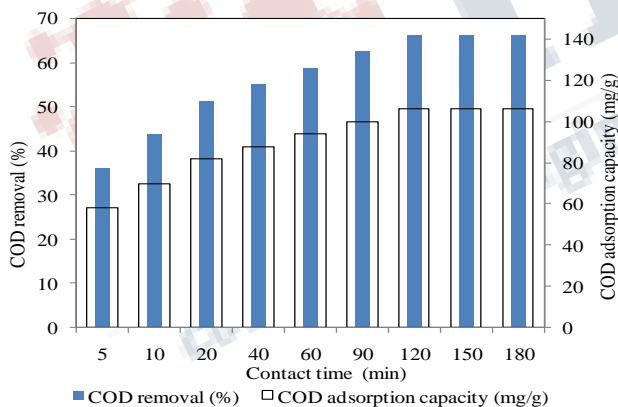

Fig.7: Contact time interference on COD removal

F. Adsorption kinetics

The adsorption kinetics was investigated by fitting the experimental data with pseudo-first-order and pseudo second-order models. From Fig. 8 and Fig .9, it can be observed that the adsoption data fitted well with the pseudo-second-order model as compared to pseudo-first-order. The Correlation coefficient R^2 for the second-order equation is 0.996 and is much higher than that of pseudo-

first-order first order with 0.903. From Table V, it is observed that the predicted pseudo-second-order q_e is 90.9 mg/g which is very close to the actual q_e of 84.8 mg/g as compared to that of 78.3 mg/g for the pseudo-first-order equation. This confirms the fixing of COD adsorption on CCAC to pseudo-second-order and specifies that the chemical interactions or bond formation between the CCAC and the leachate compounds (formation of covalent bonds) [20] is one of its mechanisms.
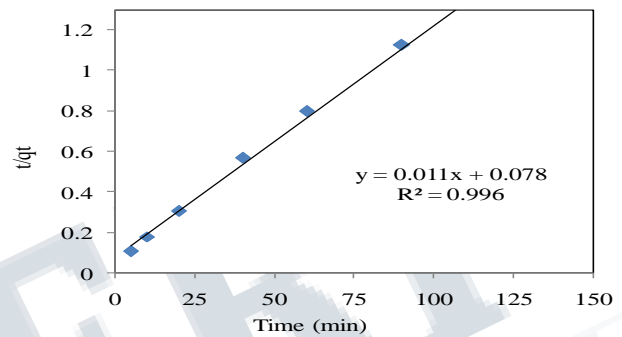
Fig.9: Lagergren Pseudo-second order

### G. Effect of dose of adsorbent on COD removal

The effect of dose of adsorbent on the percentage removal of COD at pH 2 is shown in Fig. 10. It can be seen that the COD percentage removal increased with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose of the adsorbent [21]. While adsorbent dose increases from 9 to 16 g/L, the COD removal increased 55% to 88.75% while the COD adsoprtion capacity reduced from 78.22 mg/g at 9 g/L to 71 mg/g at 16 g/L CCAC. This can be explaining due to the fact that, with an increase in CCAC dose, more unoccupied active sites for COD adsorption are still unused and available [21]. As insignificant COD removal was observed after the CCAC dose of 16 g/L, it is considered as the optimal CCAC dose in this study.
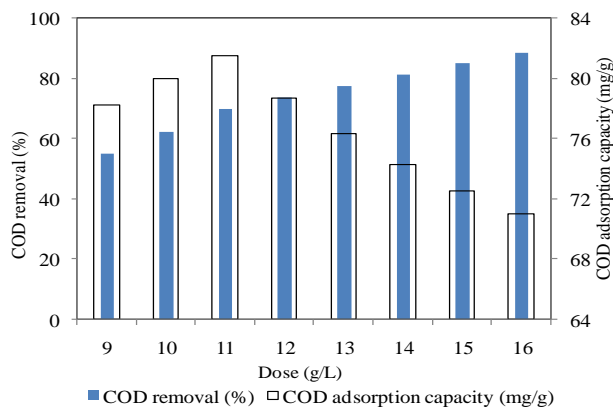
Fig.10: Influence of CCAC dosage on COD removal

Table V: Fitting parameters of two kinetics models

| $q_{e, exp}$ (mg/g)	Pseudo 1st order			Pseudo 2nd order		
	K_1	R^2	$q_{e, cal}$ (mg/g)	K_2	R^2	$q_{e, cal}$ (mg/g)
84.8	0.004	0.903	78.33	0.0015	0.996	90.91
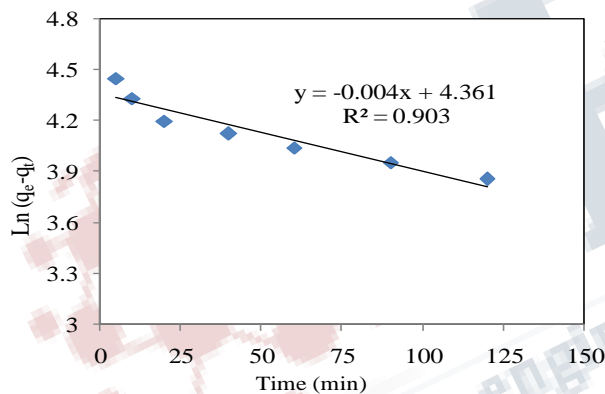
Fig.8: Lagergren Pseudo-first order

H. Adsorption isotherm studies

Table VI shows the experimental adsorption data fitted by the Langmuir and Freundlich isotherms models. As shown in Table VI, the Langmuir model fitted very well with the activated carbon adsorption with R^2 of 0.996 as compared to R^2 of 0.780 for fruendlich isotherm. Also, when the experimental and predicted q_e values were compared using Chi-square, lesser λ^2 of 0.25 for Langmuir's isotherm against that of 0.29 for Freundlich suggests the better fit of COD adsorption onto PPAC by Langmuir's model. This finding indicates the homogenous surface of CCAC with adsorption of leachate occurred through the formation of monolayer coverage on the surface of CCAC and no adsorbed neighboring ions interacted with each other [22].
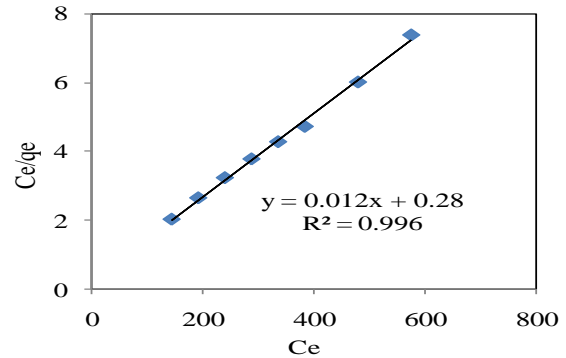
Fig.11: Langmuir isotherm model for COD removal
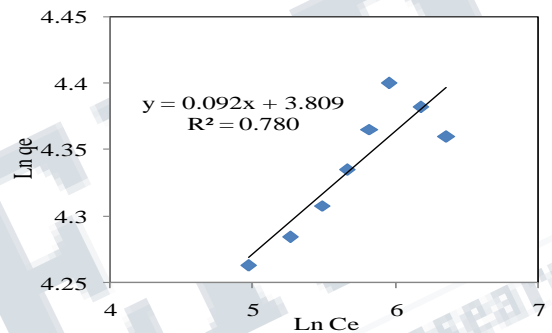
Fig.12: Fruendlich isotherm model for COD removal

Table VI: Regression data of Langmuir and Freundlich isotherm models

Langmuir isotherm	q_{max} (mg/g)	b	R^2	λ^2
	71.7	0.0043	0.996	0.252
Freundlich isotherm	K_f	1/n	R^2	λ^2
	45.11	0.092	0.780	0.289

IV. CONCLUSIONS

In this current study, CCAC was successfully used for COD removal from pre-treated stabilized leachate. The studies also indicated that CCAC can be considered as an efficient, eco-friendly, cost effective, easily available and waste derived natural adsorbent for the removal of organic ions mainly COD from pre-treated stabilized leachate. The optimum pH for organic ion adsorption mainly COD on adsorbent synthesized from Corncob was observed at acidic pH 2. The optimum adsorption contact time for CCAC was 120 minutes and the optimum dose of CCAC was found to be 16 g/L with COD removal of 88.75% yielding 71.7 mg/g maximum adsorption capacity. The adsption data fitted well with the pseudo-second-order model (R^2 = 0.996) as compared to pseudo-first-order (R^2 = 0.903). The isotherm study confirms the applicability of the Langmuir model by

comparing the correlation coefficient (R^2) and chi-square value of 0.996 and 0.25 respectively with that of Freundlich's model with the corresponding value of 0.780 and 0.29. With the formation of monolayer coverage, the maximum adsorption capacity is evaluated as 71.7 mg COD/g CCAC yielding COD effluent of 144 mg/L only which is very close to the permissible limit.

Conflict of interest

The authors hereby declared there is no conflict of interest for this manuscript.

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