COD Removal from Municipal Leachate using Cow Dung Ash

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Abstract— *Chemical oxygen demand (COD) of municipal leachate is one of the most important parameter that effect the environment. In this present investigation cow dung ash was used as the biosorbent in treating leachate. Various parameter variations were investigated during the study was dosage, contact time, mixing speed and pH. The result depicted that about 63% removal efficiency of COD was obtained for cow dung ash at constant dosage 0.6 gm, constant contact time 45min, and constant speed 150rpm and optimum pH of 6. The turbidity removal was about 65% at constant dosage of 0.6gm, constant contact time of 45min and an optimum speed of 150rpm. The result obtained for cow dung ash was then compared with one of the chemical adsorbent and the chemical adsorbent used was powdered activated carbon (PAC). Adsorption isotherm model study was conducted using both Langmuir and Freunlich isotherms. Both isotherms indicated good correlation with the data obtained from the experimental study. Langmuir isotherm was best fitted model because it possess highest value for the regression coefficient, R2 =0.943 at 303.15K. Surface morphological studies were done using FTIR and SEM which indicated good results such as good pore structures which cause high adsorption. Hence it is possible to use cow dung as a suitable biosorbent in treating municipal leachate and thereby reducing the use of chemicals which further effects the environment.*

Keywords— Bio Adsorbents, Cow Dung Ash, Powdered Activated Carbon, Cost Effective, Efficient

I. INTRODUCTION

About 95% of municipal solid waste produced in the world are directly discharges and buried in the landfill. Landfill is widely accepted method for the disposal of waste because of its cost effectiveness, simple operations during the process of burying the waste and also because of its capability to deal with huge amount of waste [1]. But one of the serious threat while talking about the landfill are the production of hazardous landfill leachate which is a dark brown colour liquor that are generally formed by the infiltration of rain water through the waste. This may cause serious environmental hazards because this leachate may further penetrate through the soil and it may cause serious pollutions to the surrounding water wells and aquifers [2]. More over ot may also possess vary bad odour which may be due to the percolation of water through the mixture of both organic and inorganic chemicals that are present in the waste [3].

Lechate generally characterized by the presence of high concentration of BOD, COD, ammonical nitrogen, heavy metals etc. COD at high concentration also possess great health risk and serious environmental problems. Also stabilised landfill leachate contains humid and fulvic substances that are difficult to remove by conventional treatment technologies. In many cases activated carbon plays a major role in treating such stabilized landfill leachate [4]. Large surface area of activated carbon along with numerous micro pores with favourable pore size distribution contributes to high adsorption efficiency for the activated carbon. But the main disadvantage of using such chemically activated carbon is the high cost in its manufacture [5]. Many researches are going on for the development of cost effective adsorbent for the treatment of landfill leachate. Various bio adsorbents that are derived from the agricultural waste also plays important role for the treatment of waste water which reduces the cost of treatment and it also reduce the negative impact to the environment [6].

Numerous studies reported that the waste stabilization proceeds in five sequential as well as distinct phases. From one phase to another the rate and characteristic of leachate and gas that are produced from the landfill varies from one phase to another also the microbial activities that are taking place from one phase to another also varies [7]. The final phase of the landfill is subjected to various factors such as physical, chemical and biological, age of the landfill, characteristics of the landfill waste, operational management controls along with site specific external conditions [8]. Constituents which are primarily organic in nature tends to decompose over time at a much faster rate while the inorganic constituent will remain over a long period of time even after the stabilization occur[9]. Different types of conservative consistent are heavy metal chloride and sulphide which remain stabilized in the landfill for a long period of time. Metals are usually precipitated in the landfill sometimes even in higher concentrations [10].

Leachate quality have been reported to show wide variability because it has been reported that the leachate obtained from the unlined landfill has erroneously low in concentration because of the dilution that may be cause from the ground water and also due to other sampling errors [11]. Hence prediction of leachate characteristics has become a difficult task. From various studies and researches it has been resulted that leachate recirculation tends to control waste decomposition and make the leachate characteristics more predictable [12].

In this present study cow dung ash is evaluated for its effectiveness in treating municipal leachate. The removal efficacy of the pollutants are also studied by using isotherm models

II. OBJECTIVES

The objectives of this study were
1) To characterize the leachate
2) To plot the adsorption isotherms of cow dung ash
3) To test the efficiency of cow dung ash
4) To compare the results with one of the chemical adsorbent such as powdered activated carbon

III. MATERIALS AND METHODS

A. *Cow Dung Ash*

Cow dung is an eco-friendly material that can be used as natural fertilizers that contain large quantity of constituents that are essential for the growth of plants. Cow dung ash is also being investigated for its use in the field of adsorption. It is one of the easily available material. In the present study Cow dung was collected from the nearby farm and it was dried under the sunlight for about 2 weeks and then it was oven dried at 500^0C for about 2 hours. The ash obtained then sieved through 90 micron sieve to obtain uniform particle size.

Fig. 1: Cow dung ash

B. Powdered Activated Carbon (PAC)

Activated carbon is usually produced from substance that contains high amount of carbonaceous material. Those substances may include coconut shell, nut shell, coal, peat, wood, lignite etc. [13]. activated carbon is also referred as activated charcoal because it offers low volume pores which in turns increase the surface area available for adsorption.[14] Powdered activated carbon was purchased from the nearby store and it was stored in an air tight container for the further analysis[15].

Fig. 2: Powdered Activated Carbon

C. Mucipal Leachate Sampling

About 20L of leachate was collected from the Attingal municipality. It was collected in a plastic container and stored in refrigerator at a temperature in the range of 4^0C. All the characterization study was done using standard methodology mentioned in APHA.

D. Surface Morphology

Cow dung was collected from nearby farm and it was dried under sunlight for about 2 weeks. After that complete combustion of cow dung cake will be carried out using oven for the collection of ash. The ash obtained will be then sieved using 90 micron sieve to obtain uniform particle size.

The material study of the cow dung ash was done using FTIR and SEM. The chemical characterization for the determination of functional groups that are present in the bio adsorbent was found by using potassium bromide pellet as blank which contains about 5% of carbon. Also the spectra was obtained between 400 to 4000cm^{-1}

E. Batch Experiments

Batch experiments were carried out to identify the optimum operation conditions. The experiments were done at room temperature in 100ml Erlenmeyer flask. The parameter variations selected was pH, dosage, contact time, mixing speed. The volume of leachate used was 50ml during each experiment. The dosage selected was in the range of 0.2g, 0.4g, 0.6g, 0.8g, 1g during first experiment under varying dosage. The second parameter variation was contact time, during that experiment various contact time in the range of 15min, 30min, 45min and 60min was provided with a fixed dose of adsorbent. The effect of agitating speed was also investigated with constant dosage and contact time. Here the agitation speed selected was in the range of 50rpm, 100rpm, 150rpm, and 200rpm. The last parameter variation provided was pH which was in the range of 2, 4, 6, 8, 10 and the experiment was conducted at constant dosage, contact time as well as mixing speed. pH variations was obtained by using the solutions of NaOH(0.1N) and HCl(0.1N) respectively. These experiments were carried to get the adsorption isotherms and to find the effect of these parameters in COD removal. After certain interval of time supernatant was collected and the corresponding COD removal was calculated using reflux titrimetry method

Fig. 3: Batch Adsorption

The efficiency of the adsorption experiment was calculated using the equation given below,

- Efficiency (%) = $\{ [C_0 - C_f].100 \}/C_0$
- C_0- initial concentration of the leachate
- C_f- final concentration of the leachate

F. Equilibrium Study

The kinetic study of adsorption for cow dung ash was done. Both Langmuir and Freundlich isotherms were plotted to determine the equilibrium characteristics of the adsorption.

For Langmuir isotherm the equation used was:

$$C_e/q_e = C_e/q_m + 1/(q_m b)$$

Where q_e – equilibrium adsorption capacity (mg/g)

C_e – equilibrium concentration of adsorbate (mg/L)

q_m – Maximum amount of adsorbate per unit weight of adsorbent (mg/g)

b – Langmuir constant related to binding site affinity with adsorbate (L/mg)

For Freundlich isotherm the equation used was:

$$q_e = K_f + (1/n)\log C_e$$

Where K_f – Freundlich constant, n - Constant related to adsorption intensity.

IV. Results and Discussion

A. Leachate Characteristics

The initial characteristic of leachate was carried and the pH of the leachate was slightly acidic in nature. Other physico-chemical characteristic obtained is given in the table.

Parameters	Values
Electrical Conductivity(mS/cm)	19.3
pH	5.28
Turbidity(NTU)	227.9
COD (mg/l)	44800
Total Solids(mg/l)	23170
Total Dissolved Solids(mg/l)	15170
Total Suspended Solids (mg/l)	7840

Table 1: Characterization of Leachate

B. Effect of Dosage

Dosage is an important factor that affects the rate of removal of COD from the leachate. From the test conducted the optimum Cod reduction was obtained at a dosage of 0.6gm for cow dung ash. About 61% removal efficiency of COD was obtained. For powdered activated carbon (PAC) an optimum COD removal was obtained at 0.8gm and the removal efficiency was 83%. Turbidity reduction was also analyzed for cow dung ash was 64.5%. Percent turbidity reduction of PAC was about 80%. The adsorption rate increases at first this may be due to the increase in surface area of adsorbent. After optimum range COD removal efficiency was reduced this may be due to the fact that increase in the adsorbent dose beyond the limit cause the surface of adsorbent site to undergo overlapping which may occur due to the overcrowding of the adsorbent particle. As a result the available surface area of adsorbent decreases which further decreases the removal rate per unit adsorbent.

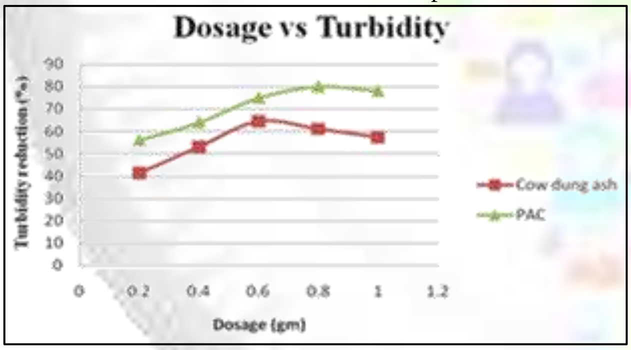

Fig. 4: Optimum dosage for the reduction of turbidity

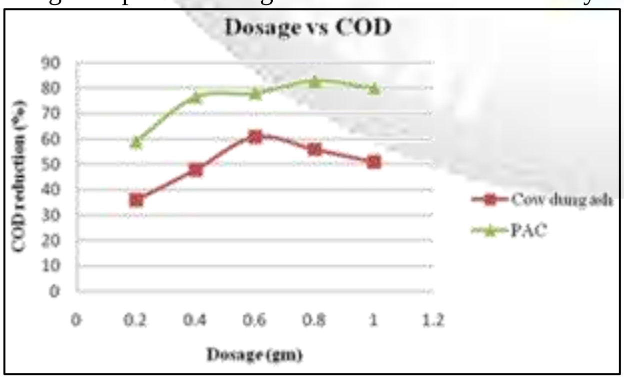

Fig. 5: Optimum dosage for the reduction of COD

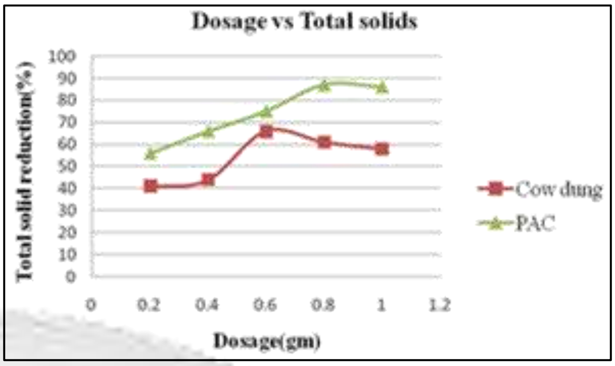

Fig. 6: Variation of Total solid with respect to dosage

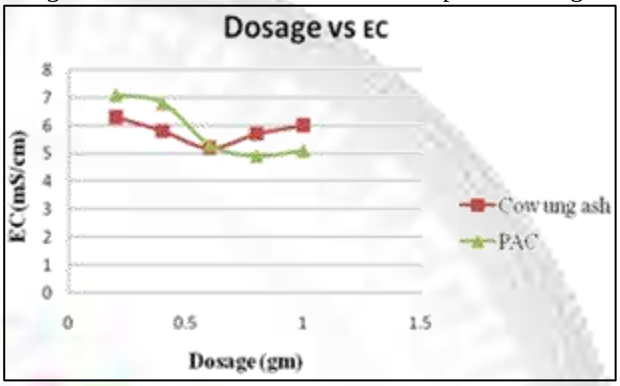

Fig. 7: Variation of EC with respect to dosage

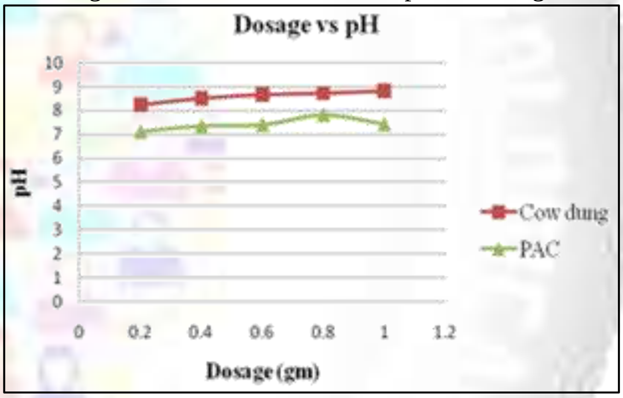

Fig. 8: Variation of pH with respect to dosage

C. Effect of Contact Time

Contact time is also another important parameter for the treatment of leachate. Optimum contact time can be defined as the time at which the process of adsorption attains the state of equilibrium. From the study it was obtained that for cow dung ash the COD reduction was about 61% under an optimum contact time of 45min along with turbidity reduction of about 64%. The experimental study under PAC reported that about 82% of COD removal efficacy with 85% reduction in turbidity at an optimum contact time of 30min was obtained.

The formation of monolayer cover over the surface of the adsorbate is indicated by smooth and independent nature of the curve. From the study conducted it was found that the adsorption rate increases with the time and after the optimum time the rate either remained constant or decreased which may be due to the development of equilibrium condition.

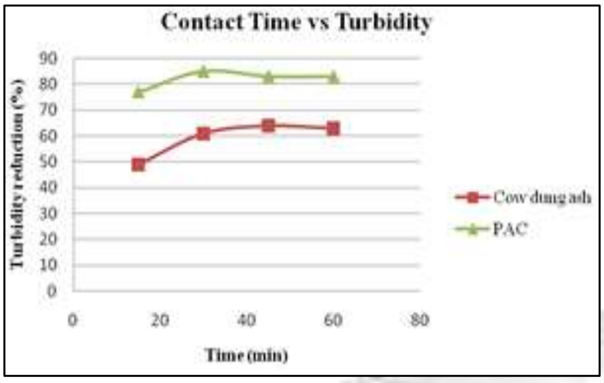

Fig. 9: Optimum time for the reduction of turbidity

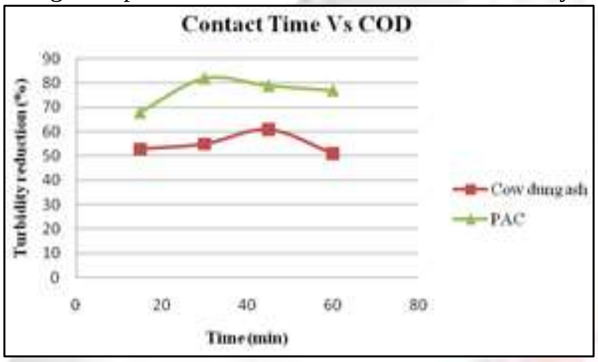

Fig. 10: Optimum time for the reduction of COD

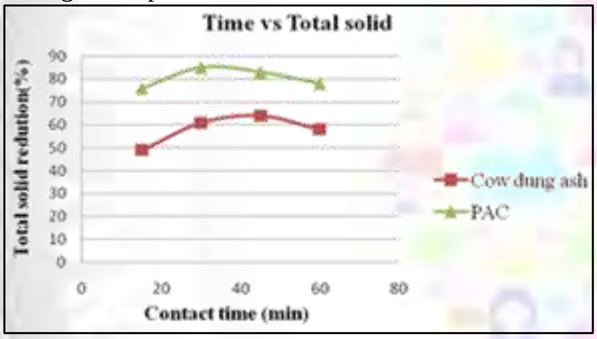

Fig. 11: Variation of Total solid with respect to time

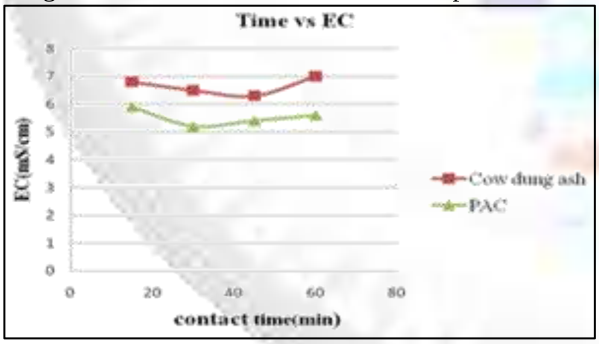

Fig. 12: Variation of EC with respect to time

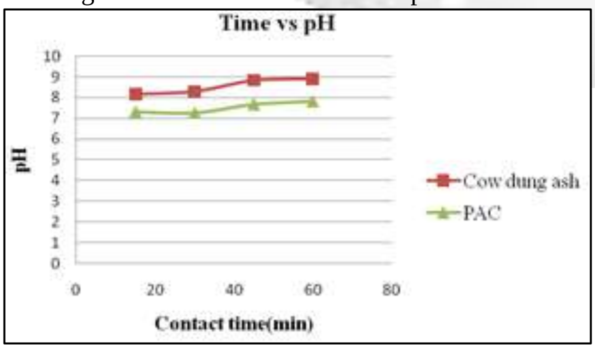

Fig. 13: Variation of pH with respect to time

D. Effect of Mixing Speed

Another parameter similar to contact time is the mixing speed that has certain effect on the COD reduction of leachate. From the study conducted it was obtained that for for cow dung ash the COD reduction was about 62% along with turbidity reduction of about 65% at an optimum mixing speed of about150rpm. The test result for PAC depicted about 80% reduction at same mixing speed along with 86% reduction in turbidity. From the experimental run it was clear that adsorption rate increased with increase in the agitation speed but further agitation above 150rpm showed a decreasing trend in the rate of adsorption. The main reason behind increase in the rate of COD reduction with increase in speed is due to the fact that the initial kinetic energy of the adsorbent as well as the molecule of the leachate increases as the mixing speed increase. As a result this may increase the interaction between the molecules and the adsorbent up to the state of equilibrium. After equilibrium the rate of adsorption decreases even with increase in the shaking speed which may be due to the extremely high kinetic energy of the molecule and the adsorbent which in turns limits their interaction.

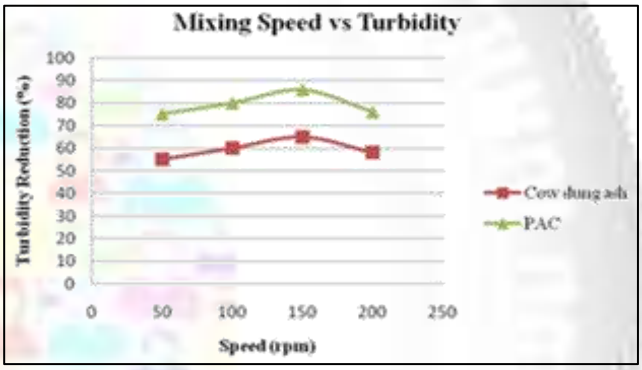

Fig. 14: Optimum speed for the reduction of turbidity

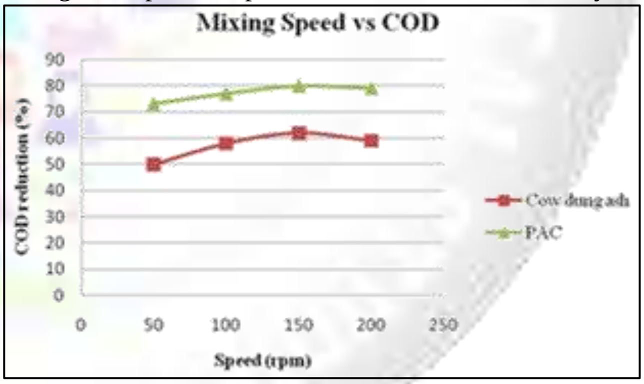

Fig. 15: Optimum speed for the reduction of COD

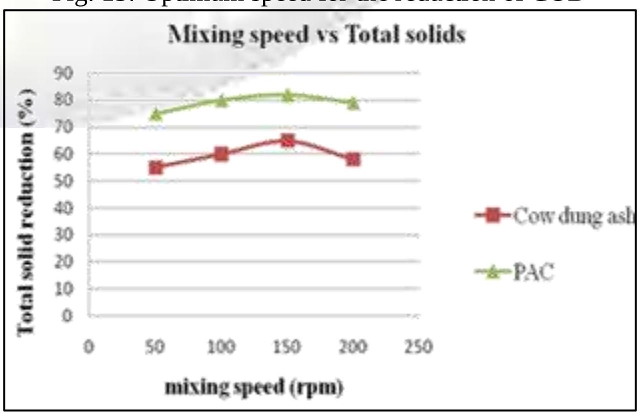

Fig. 16: Variation of Total solid with respect to speed

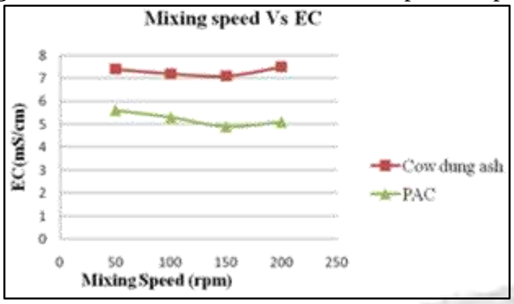

Fig. 17: Variation of EC with respect to speed

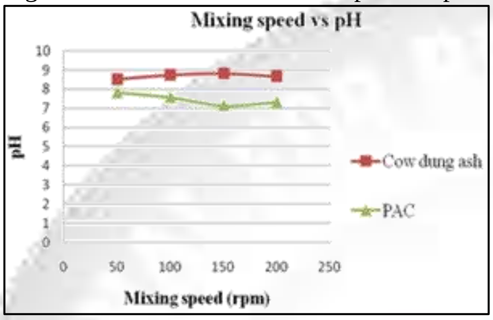

Fig. 18: Variation of pH with respect to speed

E. *Effect of pH*

The effect of pH on COD reduction was studied by adjusting the pH of leachate using NaOH(0.1N) and HCl(0.1N). pH was adjusted in the range of 2 to 10. For the study conducted using cow dung ash the result obtained was that about 63% of COD removal along with 59.1% reduction in turbidity at an optimum pH of about 6. The study performed under PAC result observed was about 88% removal of COD with 85% reduction in turbidity at an optimum pH in the range of 4. When the pH of the solution increases the site that poses negative charge undergo a great increase in number while the positive charge decreases. This causes an increase in force of attraction between the charged particles. As a result adsorption increases up to the state of equilibrium. Beyond equilibrium even with the increase in pH above 6 may cause the dissociation between the boundary of solid and liquid due to the interaction of acid and base.

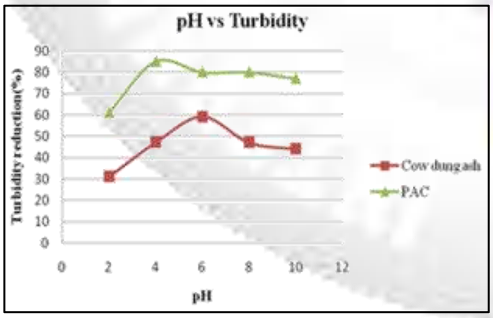

Fig. 19: Optimum pH for the reduction of turbidity

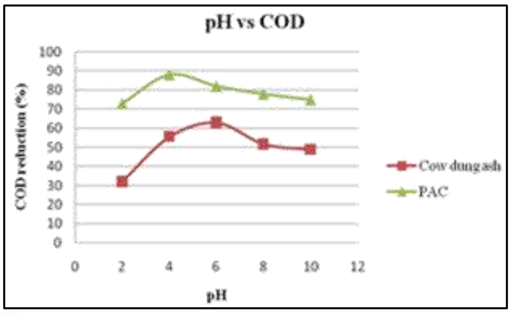

Fig. 20: Optimum speed for the reduction of COD

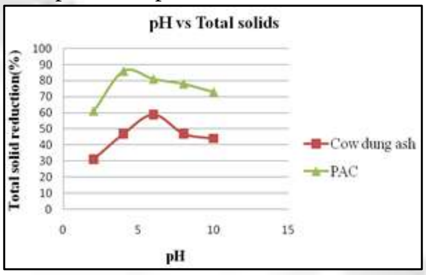

Fig. 21: Variation of Total solid with respect to pH

Adsorbents	Langmuir isotherm			Freundlich isotherm		
	q_m	b	R^2	k	n	R^2
Cow Dung Ash	125	-0.00007	0.940	0.86	0.99	0.931
PAC	500	-0.0006	0.997	0.00049	4.5	0.979

Table 2: Adsorption Isotherm Constants and Coefficients at 293.15k

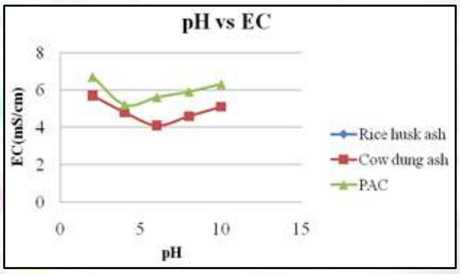

Fig. 22: Variation of EC with respect to pH

F. *Adsorption isotherm at 293.15k*

The model study conducted at 293.15K indicated that the reduction of COD from municipal leachate is best fitted to Langmuir adsorption model because it gives highest value for R2. From the result it is clear that the maximum adsorption capacity, qm for the cow dung ash was about 125L/mg. The value of qm obtained for PAC was about 500L/mg which had very high adsorptive capacity.

The difference in the adsorptive capacity may be due to the difference in the cation exchange mechanism during the process of adsorption. It can be observed that both the isotherm models have linear plots but by comparing two it is clear that the best fit is Langmuir adsorption

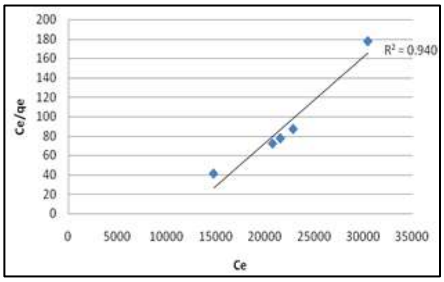

Fig. 23: Langmuir isotherm model for cow dung ash

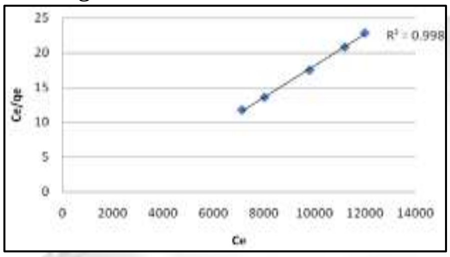

Fig. 24: Langmuir isotherm model for PAC

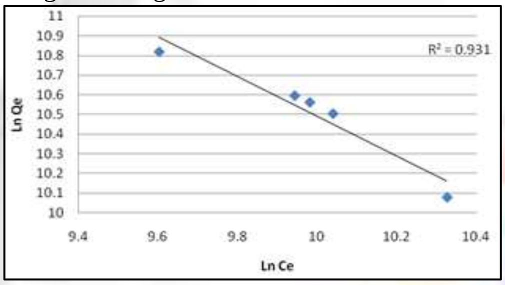

Fig. 25: Freundlich adsorption isotherm of cow dung ash

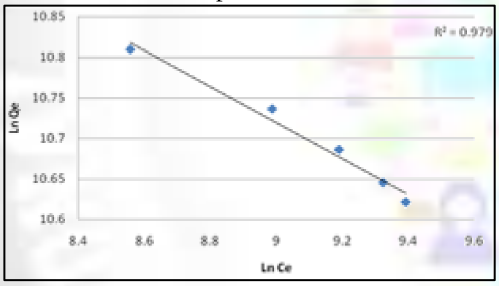

Fig. 26: Freundlich adsorption isotherm of PAC

G. *Adsorption isotherm at 303.15k*

The model study conducted at 303.15K indicated that COD reduction is best fitted to Langmuir adsorption model because it gives highest value for R^2. Also the maximum adsorption capacity, q_m for cow dung ash was about 100L/mg. Both Langmuir and Freundlich isotherm poses good values for R^2 on comparing Langmuir isotherm have the maximum values for R2 at both temperatures.

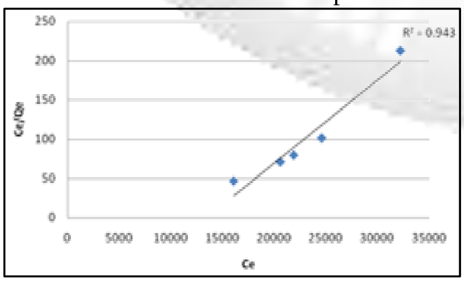

Fig. 27: Langmuir isotherm model for cow dung ash

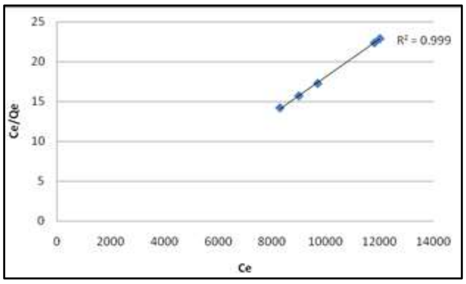

Fig. 28: Langmuir isotherm model for PAC

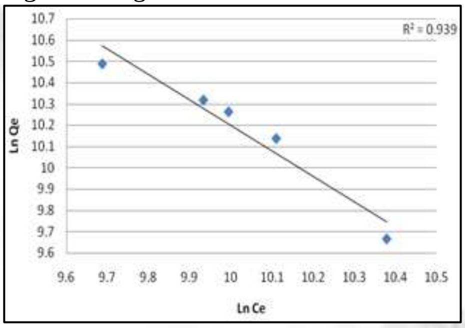

Fig. 29: Freundlich adsorption isotherm of cow dung ash

Adsorbents	Langmuir isotherm			Freundlich isotherm		
	q_m	b	R^2	k	n	R^2
Cow dung ash	100	-0.00007	0.943	3.9	0.84	0.939
PAC	500	-0.00036	0.999	0.00064	3.4	0.997

Table 3: Adsorption Isotherm Constants and Coefficient at 303.15k

H. *Adsorption Kinetics*

Adsorption kinetic study gives an idea about the type of most efficient adsorption system. It helps us to understand the changes in the adsorption with respect to time. Here both first order and second order kinetic study was done. The equation used for pseudo first order was,

$$Ln\ (q_e-q_t) = Ln\ q_e - k_1t$$

Where, q_e – amount of adsorbate adsorbed at equilibrium (mg/g)

q_t – amount of adsorbate adsorbed at time t (mg/g)

k_1 – rate constant of first order model (min^{-1})

t – time (min)

Usually the pseudo first order cannot be used for describing the kinetics study. In this present investigation also pseudo first order doesn't gives good result. As a result pseudo second order model study was done which indicated good result and it expressed a better fit. The equation used for pseudo second order is given below:

$$t/q_t = (1/k_2q_e^2) + (1/q_e)t$$

Where, k_2 – pseudo second order rate constant (min^{-1})

The result obtained for pseudo second order represented good correlation with the set of experimental data. Also it possessed high value for regression coefficient with linear plots which indicates that the mechanism of adsorption involved is chemisorptions. The value of R^2 obtained for pseudo second order was 0.969 and 0.993 for cow dung ash and PAC respectively.

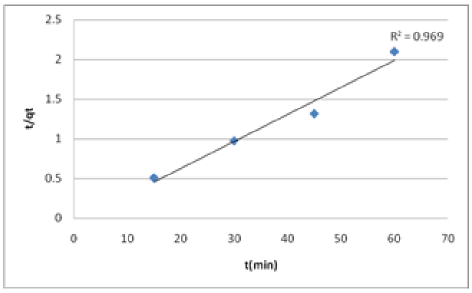

Fig. 30: Pseudo second order kinetic of cow dung ash

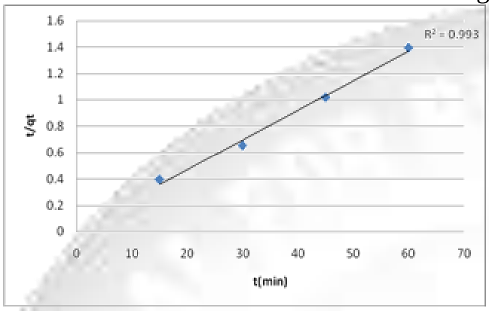

Fig. 31: Pseudo second order kinetic of PAC

Adsorbents	Pseudo second order kinetic equation			
	$q_{e\ cal}$	$q_{e\ exp}$	K	R^2
Cow dung ash	29.41	30.87	0.02	0.969
PAC	45.45	46	0.02	0.993

Table 4: Pseudo Second Order Parameters and Coefficients for various Adsorbents

I. Surface Morphology

Morphology of adsorbent using FTIR and SEM was done. FTIR or Fourier Transform Infrared Spectroscopy is a technique which gives an idea about the type of functional group present in the sample. The mechanism involved in this spectroscopy is that IR radiation is passed through the sample, during which some of the radiation is passed or transmitted by the sample which further gives a molecular spectrum. The spectrum that is obtained further represents the transmission, thus generating molecular information of the given sample. From the result obtained for cow dung ash the maximum peak was obtained at a band width of 668.36cm^{-1} which indicated the presence of C=C cyclic alkenes groups.

V. Conclusion

From the study conducted the maximum removal efficiency of COD using cow dung ash was 63% at optimum dosage of 0.6gm, optimum contact time of 45min, optimum mixing speed of 150rpm and at an optimum pH of 6. The turbidity removal was about 65% at constant dosage of 0.6gm, constant contact time of 45min and an optimum speed of 150rpm. The result obtained for the treatment of leachate using chemical adsorbent such as powdered activated carbon was about 88% COD removal at optimum dosage of 0.8gm, optimum contact time of 30min, optimum mixing speed of 150rpm and at an optimum pH of 4. The turbidity removal was about 86% at constant dosage of 0.8gm, constant contact time of 30min and an optimum speed of 150rpm. Hence cow dung ash can is used as suitable bio adsorbent for the treatment of municipal leachate for the reduction of COD and other organic contaminant thus safe guard the environment. Based on the adsorption study COD reduction is best fit to Langmuir isotherm because it gives highest value for R^2 model this signifies that the adsorption process that occurred was monolayer adsorption. This may be due to the fact that there occurred specific bonding between the surface of both adsorbate and adsorbent. Also from the FTIR study it is clear that due to the presence of functional groups C=C caused the greater reduction in COD during the process of adsorption. The COD removal efficiency of cow dung ash is low as compared to the commercially available activated carbon but on comparing it with cost effectiveness it may be useful for the treatment of leachate as well as for safe guard the environment

Acknowledgment

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