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Removal of Pb (II) from aqueous solution by using Natural plant material Cynodon dactylon

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ABSTRACT

The studies on adsorption of Pb (II) were conducted by varying various parameters such as contact time, pH, and amount of adsorbent, concentration of adsorbate, mesh size and temperature. The kinetics of adsorption of Pb (II) ion followed pseudo second order. Langmuir adsorption, Freundlich, Temkin, DKR, Harkin-jura, Redlich-peterson and Halsey isotherms were employed in order to evaluate the optimum adsorption capacity of the adsorbent. The adsorption capacity was found to be pH dependant. Cynodon dactylon was found to be very effective and reached equilibrium in 3 h (adsorbate concentration 150 mg l⁻¹). The rate constant has been calculated at 303, 313, 323 and 333K and the activation energy (E_a) was calculated using the Arrhenius equation. Thermodynamic parameters such as standard Gibbs energy (ΔG°) and heat of adsorption (ΔH°) were calculated. The ΔG° and ΔH° values for Pb (II) adsorption on the Cynodon dactylon showed the process to be endothermic in nature. The percentage of adsorption increased with decrease in pH and showed maximum removal of Pb (II) in the pH range 5 for an initial concentration of 10 mg l⁻¹.

Keywords: Equilibrium isotherm, Thermodynamic, Kinetic, Lead, adsorption, Freundlich, Gibb's free energy, activation energy, Cynodon dactylon.

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INTRODUCTION

Many industries, especially plating facilities and electronic manufacturing often lead to the containing of heavy metals in the effluent of wastewater which is the serious environmental problems. All heavy metals are toxic and non-biodegradable and should be separated from wastewater. There are several ways for separation heavy metals from wastewater such as chemical separation, filtration, membrane separation, electrochemical treatment, ion exchange, and adsorption [1-5]. All these methods, with the exception of adsorption are costly, have low output and are incapable of removing trace level of heavy metals from wastewater. Adsorption has been shown to be a feasible alternative method for removing heavy metals from wastewater. Several natural and synthetic hydrous solids have been investigated as adsorbent of heavy metals. Among these, metal oxides [6-8] and activated carbon [9, 10] are the most extensively employed, but the high cost of these materials limits their large "scale use for removal of metals [11]. Adsorbents can be used for water and wastewater treatment and indeed they are widely used due to their higher output and low costs [12-16]. Among current adsorbents, activated carbon is used in different industries, but it is not a selective adsorbent. Recently, a number of studies were carried out on low cost adsorbents from natural resources. The use of low cost adsorbent for heavy metals derived from natural resources has been reviewed by Baily, Olin, Bricka, and Adrian [17] and Babel and Kurniawan [18]. Such the low cost adsorbents are pineapple and paper waste sludges which are the biodegradable. Lead (Pb) is a highly toxic metal that is very poisonous for neurobehavioral development [19] and brain cell function [20] even in trace concentration (ppm) and therefore, before the disposal of lead containing industrial wastes their lead content should be eliminated. Many researches were published on removing of lead ions by different adsorbents such as natural and industrial materials, granular activated carbon, char, and chitosan. [21-23] In the present research, the herb *Cynodon dactylon* as adsorbents to remove lead from wastewater, the equilibrium and kinetic and thermodynamic studies have been studied.

MATERIALS AND METHOD

The pH was adjusted with a digital pH meter (Jenway Model 3320) using HCl (0.1 mol L⁻¹) and NaOH (0.1 mol L⁻¹). Lead (II) was estimated with a UV/VIS spectrophotometer (Labomed UVD 3500) at λ_{\max} 520 nm.

Preparation of adsorbent

Casuarina equisetifolia, collected from the Tranquebar coastal area, was crushed with laboratory-scale crushers, powdered with a disk pulverizer, and sieved to 0-63 mesh (ASTM). The powdered adsorbent was washed, dried at 105 °C for 10 h in an oven, and stored in high-density polythene (HDPE) bags. The proximate analysis of the coal was carried out by using standard methods (ASTM D 5142-90). Powdered adsorbent was soaked in HCl (0.1 mol L⁻¹) for 24 h, followed by filtering and washings with distilled water. Afterwards, it was dried in an oven at 105 °C for 10 h and stored in HDPE bags.

Chemicals

All chemicals used during experimental work were of analytical grade and were used as such without purification. Lead (II)(Fluka), HCl (E. Merck 11.6 M). Double distilled water was used for the preparation of all types of solution and dilution when required.

Instrumentation

Balance ER-120A (AND), Electric grinder (Kenwood), pH meter HANNA pH 211 (with glass electrode), UV/VIS spectrophotometer (Labomed, Inc. Spectro UV-Vis double beam UVD = 3500).

Standard Solutions

The stock Lead (II) solution was prepared by dissolving accurately analar grade of 1.5980g. of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) in 100ml. of deionised water. Dilute to 1 litre in a volumetric flask with deionised water. Form this stock solution, 10,20,30,40, 50 and 60 ppm solutions were prepared by diluting it suitably.

Adsorption Experiments

The adsorption studies were carried out at 30 ± 1 °C. pH of the solution was adjusted with 0.1 N HCl. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture were filtered and the remaining metal ion concentration were determined in the filtrate (Spectro UV-Vis Double Beam UVD- 3500, Labomed.Inco) at $\lambda_{\text{max}} = 520$ nm. The effect of various parameters on the rate of adsorption process were observed by varying mesh size of adsorbent, contact time t , initial concentration of metal ion C_0 , adsorbent amount , initial pH of solution and temperature. The solution volume (V) was kept constant 50 ml. The metal ion adsorption (%) at any instant of time was determined by the following equation:

$$\text{Metal ion adsorption (\%)} = (C_0 - C_e) \times 100 / C_0$$

Where C_0 is the initial concentration and C_e is the concentration of the metal ion at equilibrium. To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

Spectrophotometric Determination of Lead

Materials and instruments. The following materials were used: lead stock standard solution, 1000 ppm (analytical grade); chloroform (HPLC grade); dithizone (diphenylthiocarbazone, p.a. grade); diethyldithiocarbamic acid sodium salt (p.a. grade); hydroxylamine hydrochloride (p.a. grade); ammonium hydroxide (ACS reagent grade); nitric acid (ACS reagent grade); hydrogen

peroxide 35% (p.a. grade); and sulfuric acid (p.a. grade), Citric acid (reagent grade) and potassium cyanide (reagent grade). Deionized (DI) water was from a reverse osmosis system. All other chemicals, including hydrochloric acid, ethanol, phenol red, thymol blue, and so forth, either reagent or better grades. 1% HNO_3 , 1% HCl , and 3 N HCl were prepared by mixing appropriate amount of DI water and the concentrate HNO_3 and HCl , respectively.

Reagent preparations

First, we diluted the 1000 ppm of lead stock solution with 1% HNO_3 . Then a 0.003% dithizone extraction solution was made as follows: 30 mg dithizone were dissolved in 1000 ml of chloroform, and 5 ml of ethanol were added as a stabilizer. The solution was stored in a refrigerator. Each time before use, we washed a suitable volume of the dithizone solution with half of its volume of 1% HCl . After washing, the aqueous phase was discarded. We prepared a 0.001% standard dithizone solution by dissolving 10 mg of dithizone in 1000 ml of chloroform and storing it in a refrigerator.

To prepare the 30% ammonium citrate solution, we dissolved 60 g of citric acid in approximately 100 ml of DI water. Two drops of 0.1% phenol red in ethanol were added, and the pH was adjusted with ammonium hydroxide until the indicator turned from yellow to pink. Any lead present in the citric acid was removed by extracting the solution with 10 ml of 0.003% dithizone extraction solution. The extraction was repeated until the dithizone solution did not change color. The citrate solution was then diluted to 200 ml.

To prepare the 2% ammonium cyanide solution, we dissolved 2 g of potassium cyanide in 15 ml of ammonium hydroxide, then diluted it with DI water to 100 ml. For the 5% potassium cyanide solution, we dissolved 25 g of potassium cyanide in sufficient water to make 100 ml. We removed lead from this solution by repeated extracting with 10 ml of 0.003% dithizone extraction solution until the dithizone solution did not change color. We removed any remaining dithizone from the aqueous solution by extracting with 10 ml of chloroform and repeated this process three times. We then diluted the cyanide solution with DI water to 500 ml.

To prepare the 20% hydroxylamine hydrochloride solution, we dissolved 20 g of hydroxylamine hydrochloride in sufficient DI water to make ~60 ml. Five drops of 0.1% thymol blue in the ethanol solution were added, and the pH was adjusted with ammonium hydroxide until a yellow color appeared. We added and dissolved 0.4 g sodium diethyldithiocarbamate, and allowed it to stand for 5 min. The solution was extracted five times with successive 10 ml of chloroform. Drop by drop, we added 3 N hydrochloric acid until the solution became pink, and then diluted it to 100 ml with DI water.

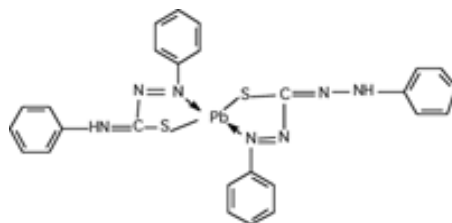


Fig 1a

All reagent solutions were kept in a refrigerator and were stable for at least four weeks.

Analytical procedure. In a weak alkaline solution, dithizone can form a stable complex with lead in a 2:1 ratio (Figure 1a). This complex has a maximum absorbance at 520 nm. To obtain reliable results, the key step was to quantitatively dissolve and then isolate lead from the sample. The optimized and validated analytical procedure follows.

Step 1. Into a 250-ml beaker, weigh an appropriate amount of samples containing $\leq 25 \mu\text{g}$ of lead, such as 1–2 g of inorganic sample, 5 g of a mixture sample of inorganic and organic, or 10 g of organic sample. Add 10 ml of 1:1 H_2SO_4 (1:1 of $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$, v/v) and a few glass beads into the beaker. Cover the beaker with a piece of watching glass and heat the beaker on a hot plate until the sample becomes brown or dark brown.

Step 2. Drop by drop carefully add H_2O_2 (35%), until the organic materials are completely destroyed, which is indicated by the solution becoming clear. For mineral-containing samples, some white residue will remain.

Step 3. For some samples of mixed organic and inorganic materials, $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$ may not be able to destroy the organic components completely. In this case, alternatively adding H_2O_2 and HNO_3 could speed the digestion. Wait for evolution of SO_3 smoke before switching solvents.

Step 4. For alkaline earth-salt samples such as dicalcium phosphate, H_2SO_4 should be avoided for digestion because it can form heavy precipitation with the metal ions and make the lead separation impossible. For these types of samples, neat nitric acid is sufficient.

Step 5. After sample digestion, let the solution cool to room temperature. Wash the beaker with approximately 10 ml of DI water. Heat the solution again until SO_3 smoke is evolved. Repeat the washing and heating one more time to remove any residual H_2O_2 . If H_2O_2 is not completely removed, it will fail the lead extraction separation.

Step 6. Add 10 ml of DI water to the sample beaker and stir to dissolve any water-soluble salt. Add 5 ml of 30% ammonium citrate solution, 2 ml of 20% hydroxylamine hydrochloride solution, and mix well. (Note: For alkaline earth-salt samples, do not add the 10 ml of DI water, instead add 20 ml of 30% ammonium citrate and 2 ml of 20% hydroxylamine hydrochloride solution, and mix well.)

Step 7. Add two drops of 0.1% phenol red in ethanol. Carefully adjust the pH with ammonium hydroxide until the solution changes colors from pink to yellow then back to pink again. Cool the solution to room temperature. Completely transfer the sample to a 125-ml separatory funnel for liquid–liquid extraction of the lead.

Step 8. Into the separatory funnel containing the sample solution, add 2 ml of 5% potassium cyanide solution and 5 ml of 0.003% dithizone extraction solution. Shake the separatory funnel for ~30 s, carefully releasing pressure from time to time. Drain the bottom dithizone phase to a 60-ml separatory funnel containing 20 ml of 1% HCl, which is used for back extraction of lead. Repeat the extraction three more times. Collect all the dithizone phases in the 60-ml separatory funnel. The original aqueous sample solution should be collected in a specific container for waste treatment.

Step 9. Shake the 60-ml separator funnel for 45 s to back-extract lead to the acidic aqueous phase. Drain the dithizone phase into a beaker containing 20 ml of DI water to recycle the dithizone solution.

Step 10. In the 60-ml separatory funnel, add 4 ml of 2% ammonium cyanide and 5 ml of 0.001% standard dithizone solution. Shake the separatory funnel for 45 s. Drain the dithizone solution into a 10-ml of centrifuge tube for the spectrophotometric determination of lead.

Step 11. To construct the standard calibration curve, extract lead standard solutions containing 0.0, 1.0, 5.0, 10.0, and 25 μg of lead in the same way as described in steps 6–10. Using chloroform as a reference, measure the absorbance of the solutions at 520 nm. Create a calibration curve from the measured results. The R^2 value should be .0.990.

Step 12. Measure the absorbance of the samples at 520 nm.

Isotherm studies

A series of experiments were carried out for isothermal and kinetic study of *Cynodon dactylon* adsorption of Lead (II) metal ion. Langmuir (eq :1) ,Freundlich(eq :2) ,Temkin(eq :3) ,Harkin-Jura (eq :4),Halsey(eq :5),Redlich-peterson(eq :6) and ,Dubinin-Kaganer-Radushkevich(DKR) (eq :7) were plotted by using standard straight-line equations and corresponding parameters were calculated from their respective graphs.

$$C_e/X = 1/K * K_L + C_e/ K \quad \text{-----} \quad (1)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad \text{-----} \quad (2)$$

$$q_e = K_T \ln C_e + b_T \quad \text{-----} \quad (3)$$

$$1/q_e^2 = B/A - 1/A \log C_e \quad \text{-----} \quad (4)$$

$$\ln q_e = 1/n \ln K - 1/n \ln C_e \quad \text{-----} \quad (5)$$

$$q_e = K_R C_e / (1+b_R C_e^\beta) \quad \text{-----} \quad (6)$$

$$\log q_e = \log X_m - \beta \epsilon^2 / 2.303 \text{ ----- (7)}$$

K (mg/g) : an indicator of the adsorption capacity, $1/n$ (mg/L): adsorption intensity, ϵ (the Polanyi potential) = $RT \ln (1 + 1/C_e)$, q_e : the amount of metal ions adsorbed per unit weight of *Cynodon dactylon* (mg/g), K' : constant related to the adsorption energy (mol²/KJ²), R : gas constant (kJ/K.mol), T : temperature (K), C_e is the equilibrium concentration of the adsorbate (mg/L) and X is the amount of adsorbate adsorbed (mg/g). K_L indicates monolayer adsorption capacity (mg/g), K is the Langmuir equation constant (L/mg), K_F and $1/n$ are constants for a given adsorbate and adsorbent at a particular temperature and b_T (KJ/mol) is adsorption potential of the adsorbent. K_T is the Temkin isotherm constant and $1/A$ is the external surface area for the Harkin –Jura isotherm. K_R , b_R , β are Redlich Peterson constants. X_m is maximum sorption capacity; β is mean sorption energy and ϵ sorption potential in DKR isotherms

RESULTS AND DISCUSSION

Characterization of adsorbent

The adsorbent analysis revealed that it had high moisture content and volatile matter. Ash content was also appreciable. Results are illustrated in Table 1. It was determined by proximate and ultimate analysis as follows:

Proximate analysis

Moisture

About 1g of finely powdered air-dried adsorbent sample is weighed and taken in a crucible. The crucible is placed inside an electric hot-air oven and heated at 100-105°C for 1 hour. It is then taken out, cooled in a desiccator and weighed. From this, the percentage of moisture can be calculated as follows:

$$\text{Percentage of moisture} = (\text{loss in weight of adsorbent} / \text{weight of air dried adsorbent taken}) * 100$$

Volatile matter

The crucible with moisture free adsorbent sample is covered with a lid and placed in an electric muffle furnace, heated at 905-945°C for seven minutes. It is then taken out, cooled in a desiccator and weighed. From this, the percentage of volatile matter can be calculated as follows:

$$\text{Percentage of volatile matter} = (\text{loss in weight of adsorbent} / \text{weight of dried adsorbent taken}) * 100$$

Ash content

The crucible with residual adsorbent sample is placed in an electric muffle furnace, heated without lid at 650-750°C for 30 minutes. It is then taken out, cooled in a desiccator and weighed. From this, the percentage of ash content can be calculated as follows:

$$\text{Percentage of ash} = (\text{weight of ash left} / \text{weight of dried adsorbent taken}) * 100$$

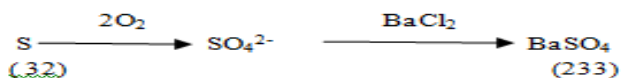
Fixed carbon

The fixed carbon content can be calculated from the following equation

$$\text{Percentage of} = 100 - \% \text{ of (moisture + volatile matter + ash)}$$

Ultimate analysis of Sulphur

A known quantity of adsorbent sample is burnt completely in a Bomb calorimeter. During this process sulphur is converted in sulphate, which is extracted with water. The extract is then treated with BaCl₂ solution so that sulphates are precipitated as BaSO₄. The precipitate is filtered, dried and weighed. From the weight of BaSO₄ obtained, the sulphur present in the adsorbent was calculated as follows.



$$\text{Percentage of sulphur in adsorbent} = (32 * \text{weight of BaSO}_4 \text{ obtained}) / (233 * \text{weight Of dried adsorbent taken})$$

Results are given in table: 1

Parameters	Moisture	Volatile matter	Ash	Fixed C	S	Heating value Btu/lb
Values	2.5%	10.13%	5.5%	75.11	1.2%	5.56%

Effect of initial pH

The acidity of solution pH is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. The uptake and percentage removal of Lead (II) from the aqueous solution are strongly affected by the pH of the solution as illustrated in Fig. 1a. The uptake of Lead (II) increases from 30.02% to 90.56% when the pH increases from pH 1 to pH 6. Lead (II) sorption is noted to increase significantly 90.56% adsorption capacity at pH 6. After that the capacity of adsorption decreases slightly in pH range of 7 to 9. The minimum adsorption observed at low pH (pH 1) may be due to the fact that the

higher concentration and higher mobility of H⁺ ions present favoured the preferential adsorption of hydrogen ions compared to Lead (II) ions [24]. It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H⁺), thereby preventing the metal ions from approaching the binding sites of the sorbent [25]. This means that at higher H⁺ concentration, the biosorbent surface becomes more positively charged such that the attraction

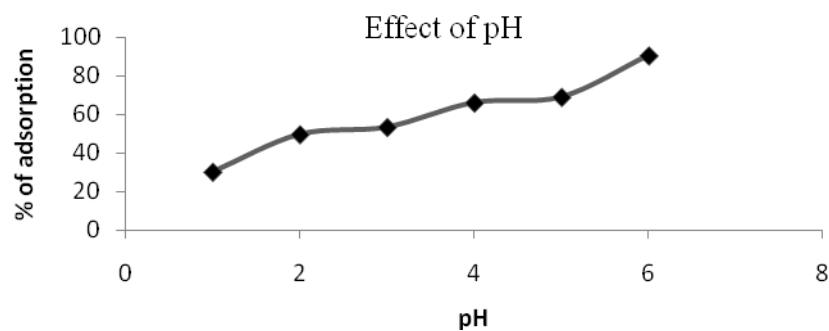


Fig 1b

between biomass and metal cations is reduced [26]. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater Lead (II) removal. It is commonly agreed that the sorption of metal cations increases with increasing pH (Fig 1) as the metal ionic species become less stable in the solution. However, at higher pH values (pH 7, pH 8 and pH 9) there is a decrease in the adsorption capacity. This is due to the occurrence of Lead (II) precipitation. At pH 7 there are three species present in solution as suggested by Elliot and Huang. [27], Pb²⁺ in very small quantities and Pb(OH)⁺ and Pb(OH)₂ in large quantities. Three species are adsorbed at the surface of adsorbent by ion exchange mechanism with the functional groups present in adsorbent or by hydrogen bonding.

Effect of adsorbent dosage

The adsorbent dosage is another important parameter, which influences the extent of metal uptake from the solution and thus the effect as shown in Fig. 2. It was evident that the amount of metal uptake increases from 66.63% with 50mg adsorbent up to 94.00% with 200mg adsorbent. Prior to that, it is apparent that the percent removal of Lead (II) increases as the adsorbent dosage increases from 50mg up to 200mg due to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is plausible that with higher dosage of adsorbent there would be greater availability of exchangeable sites from metal ions [28]. Besides, Fourest and Roux [29] suggested that the reduction in adsorbent dosage in the suspension at a given metal concentration enhances the metal/adsorbent ratio, and thus increases the metal uptake per unit adsorbent, as long as the latter is not saturated. Similar observation has been reported by Mashitah et al [30] for the adsorption of Lead (II) ions onto Pycnoporou sanguineus biomass. However, in some cases, the adsorption capacity decreased sharply with the increasing of adsorbent dosage these results may due to the overlapping of the adsorption sites as a result of

overcrowding of adsorbent particles [31]. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from metal [32].

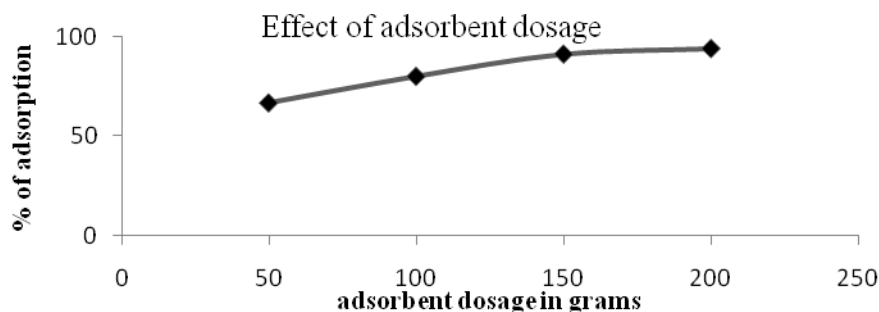


Fig 2

Effect of initial adsorbate concentration

Figure 3 show that adsorption capacity decreases from 90.12% to 64.12% as the metal concentration increases from 10 to 60 mg/L. The trend is that of the result of the progressive decrease in the electrostatic interaction between the Lead (II) ions and the adsorbent active sites. Moreover, this can be explained by the fact that less adsorption sites were being covered as the metal ions concentration decreases [33]. Besides, lower initial concentrations lead to an increase in the affinity of the Lead (II) ions towards the active sites [34]. The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species at lower concentrations [35]. Similar results were observed by Han et al. [36] for the adsorption of Lead (II) on chaff.

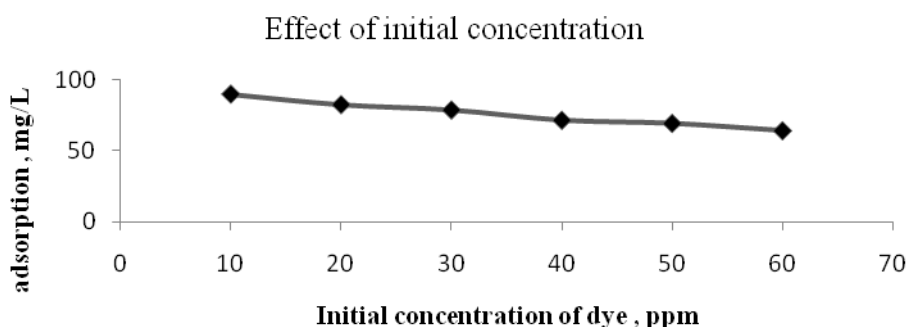


Fig 3

Effect of Mesh Size

The effect of adsorbent's mesh size was studied in the range of 0-200 microns mesh size (0-63, 63-125, 125-200) for checking the maximum adsorption of Lead (II), and the smallest mesh size (0-63) was shown to be best for adsorption, as particles with smallest size presents a larger surface area and the results are shown in Fig. 4. Mesh size is inversely related with

particle size. As the mesh size is larger, the size of particle is accordingly decreased which results in more surface area available for adsorption.

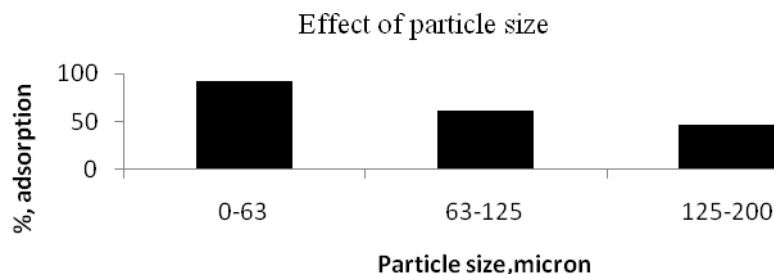


Fig 4

Effect of Temperature

Temperature has an important effect on the rate of adsorption. The percentage of Lead (II) adsorption was studied as a function of temperature in the range of 30-60 °C. The results obtained were present in Fig. 5. It was observed that adsorption yield increase with increase in temperature. The minimum adsorption was 90.1 % at 30 °C and maximum adsorption was 97.13 % at 60 °C for 25 ppm initial concentration of metal ion solution. The increase in adsorption at high temperature because molecules move with great speed and strong interaction was available for metal ion anions with adsorbent material.

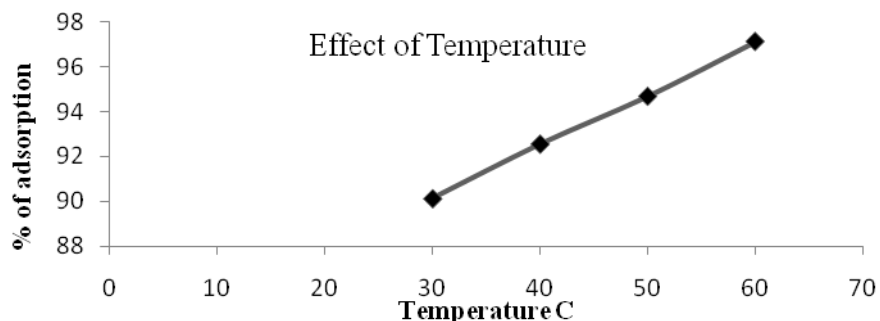


Fig 5

Adsorption isotherm

Isotherm parameters, evaluated from the linear plots of equations (1-7) are illustrated in Table 2a, 2b and 2c,(Fig:6-12).The K_L value for the Langmuir isotherm, ie. 2.7027mg/g, indicated the high adsorption capacity of biosorbent toward chromium adsorption. The R^2 (correlation coefficient) value 0.978 indicated that the Langmuir isotherm is good for explaining the Lead (II) adsorption. The R^2 value calculated for the Freundlich isotherm was found to be 0.995, indicating that the experimental data can be explained by the Freundlich isotherm. The K_f (ultimate adsorption capacity) value as calculated from the Freundlich isotherm was 3.069.The Temkin equation was also good to explain

the experimental data ,with an R^2 value 0.966.bT (heat of sorption) was calculated from the Tempkin plot as 2.333 KJ/mol ,indicating moderately strong cohesive forces between Lead (II) and biosorbent. A value less than 8 indicates a weak interaction between the adsorbent and adsorbate .The Harkin –Jura expression of the value of the correlation coefficient was 0.905,providing good suitability for the experimental data of Lead (II) on Cynodon dactylon . Halsey’s expression of the value of the correlation coefficient was 0.995, providing a better fit for the experimental data of Lead (II)on Cynodon dactylon. The Harkin-Jura and Halsey equations were more suitable to explain the multi layer adsorption of the adsorbate on adsorbent (Oladoja et al., 2008)37. The R^2 value calculated for the Redlich-peterson isotherm was found to be 0.994, indicating that the experimental data can be explained by the Redlich-peterson isotherm. The β value as calculated from this isotherm was 0.523. The R^2 value calculated for the DKR isotherm was found to be 0.930, indicating that the experimental data can be explained by the DKR isotherm poorly. The β value as calculated from this isotherm was 1.586.

c0	%	ce	c0-ce	qe	ka	Ka C0	ce/qe	Logce
10	90.12	0.988	9.01	3.00	3.0405	30.4049	0.3289	-0.0052
20	82.65	3.47	16.53	5.51	1.5879	31.7579	0.6298	0.5403
30	78.87	6.339	23.66	7.89	1.2442	37.3261	0.8037	0.8020
40	71.59	11.36	28.64	9.55	0.8400	33.5985	1.1905	1.0555
50	69.31	15.35	34.66	11.55	0.7528	37.6398	1.3284	1.1860
60	64.12	21.53	38.47	12.82	0.5957	35.7414	1.6787	1.3330

Table 2a

log qe	log ce/qe*-1	ce β	1/ce+1	ϵ^2	1/qe 2
0.4777	0.4829	0.993706	2.0121	3.1056	0.110815
0.7412	0.2008	1.916868	1.2882	0.4074	0.032938
0.8969	0.0949	2.626981	1.1578	0.1363	0.016076
0.9798	-0.0757	3.564863	1.0880	0.0452	0.010975
1.0626	-0.1233	4.171197	1.0652	0.0253	0.007494
1.1080	-0.2250	4.979216	1.0465	0.0131	0.006081

Table 2b

Langmuir parameters	$K_L = 2.7027$	$q_0 = 15.873$	$b_L = 0.1702$	$R^2 = 0.978$
Freundlich parameter	$K_F = 3.069$	$n = 2.1008$		$R^2 = 0.995$
Dubinin-kaganer-Radushkevich parameters	$\beta = 1.586$	$b = 0.698$	$q_0 = 4.988$	$R^2 = 0.93$
Redlich peterson parameters	$\beta = 0.523$	$K_R = 3.1152$	$b_R = 0.0124$	$R^2 = 0.994$
Tempkin parameters	$k_T = 7.394$	$b_T = 2.333$		$R^2 = 0.966$
Harkin-jura parameters	$A = 31.25$	$B = 1.468$		$R^2 = 0.905$
Halsey parameters	$n = 2.10084$	$K = 2.7818$		$R^2 = 0.995$

Table 2c

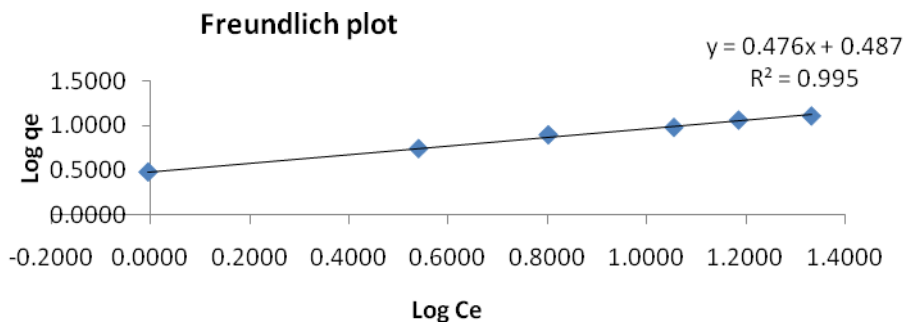


Fig 6

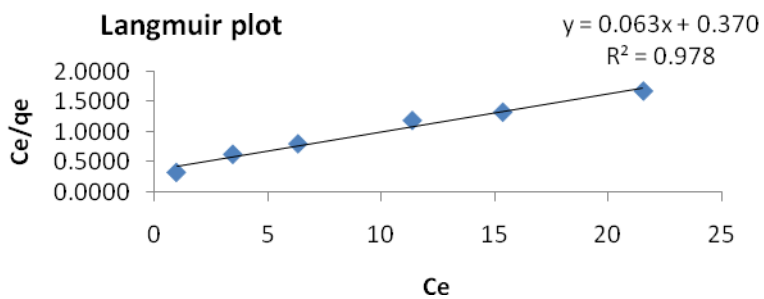


Fig7

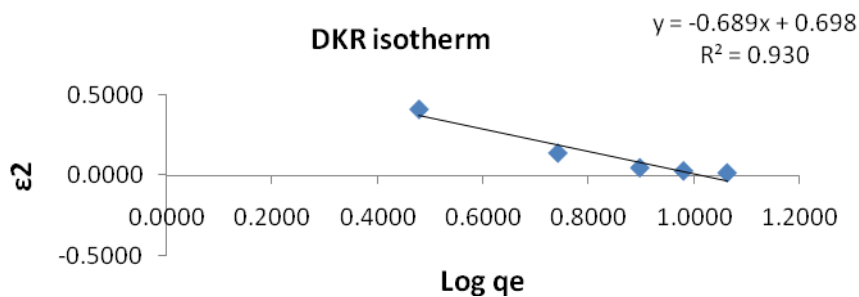


Fig 8

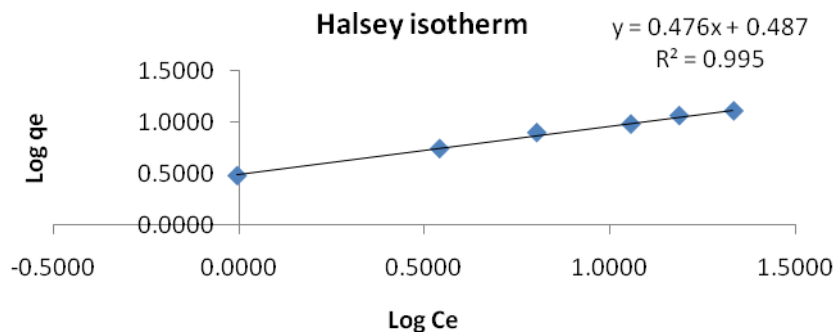


Fig 9

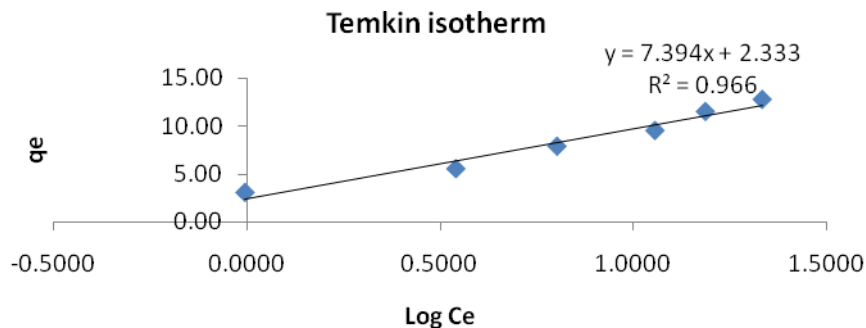


Fig 10

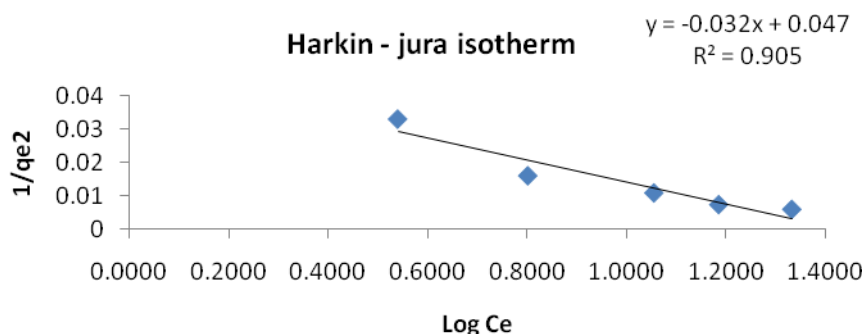


Fig 11

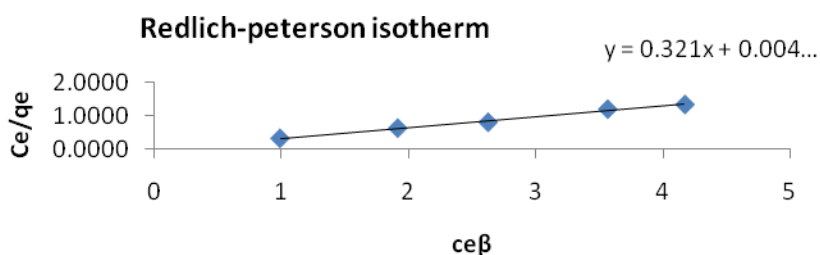


Fig 12

Thermodynamic parameters

Thermodynamic parameters such as standard Gibbs free energy (ΔG^0), Enthalpy (ΔH^0) and entropy (ΔS^0) were also calculated using equations 8 and 9 and the results obtained are illustrated in table-3a,3b (Fig:13).

$$\Delta G^0 = -RT \ln K \quad \text{-----} 8$$

$$\ln K_c = (\Delta S^0/R) - (\Delta H^0/RT) \quad \text{-----} 9$$

Here, K denotes the distribution coefficient for the adsorption. R is the universal constant and T is the absolute temperature in Kelvin. The negative value of the ΔG^0 at the studied temperature range indicated that the sorption of Lead (II) on sorbent was

thermodynamically feasible and spontaneous. The increase in the value of ΔG^0 with temperature further showed the increase in feasibility of sorption at the elevated temperature for Cynodon dactylon. In other words, sorption is endothermic in nature. The positive value of ΔH^0 for cynodon dactylon showed that the sorption was endothermic. The positive value of ΔS^0 showed an increased randomness at the solid Lead (II) solution interface during the adsorption of Lead (II), reflecting the affinity of cynodon dactylon for Lead (II).

T,K	c0	%	ce	c0-ce	ka
303.15	50	90.1	4.95	45.05	3.03367
313.15	50	92.54	3.73	46.27	4.134942
323.15	50	94.68	2.66	47.34	5.932331
333.15	50	97.13	1.435	48.565	11.28107

Table 3a

ΔG^0	ΔH^0	ΔS^0	Log 10 Ka	1/T
-2797.06	25.4657	65.10028	0.481968	0.003299
-3695.64			0.616469	0.003193
-4783.39			0.773225	0.003095
-6711.6			1.05235	0.003002

Table 3b

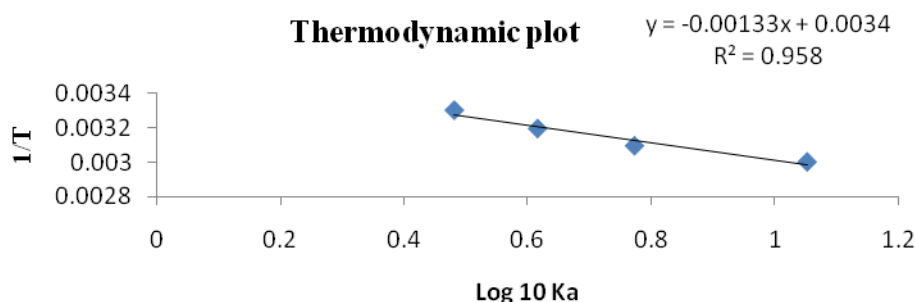


Fig 13

Arrhenius equation

Activation energies for adsorption of Lead (II) on adsorbent was calculated using the Arrhenius equation (eq10), plotted in Fig 14 and tabulated in table 4. The activation energy obtained (Table 4) in this case, indicate that physical forces are involved in the sorption mechanism and sorption feasibility.

Arrhenius equation

$$\text{Log } K = \text{Log } A - (E_A / 2.303 \text{ RT}) \text{ ----- } 10$$

Ea	Log A	R2
35.92004	6.635	0.958

Table 4

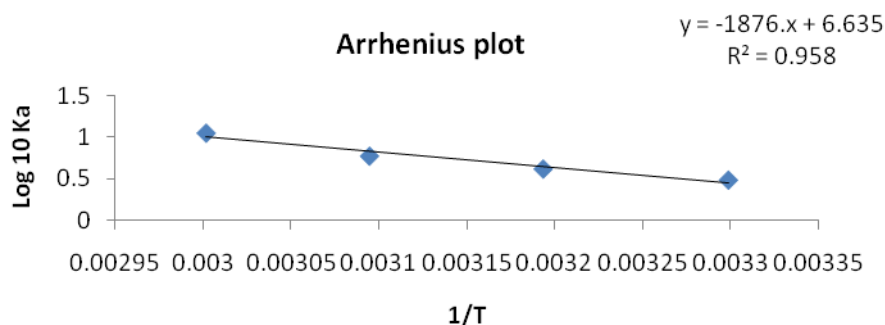


Fig 14

Kinetic study

A linear trace for the plot of $\log (q_e - q)$ Vs time (Fig:15-18) shows that the adsorption kinetics follow pseudo second order kinetics' additionally pseudo first order, intra particle diffusion and Elovich model of kinetics were verified. (Tables 5a, 5b, 5c)

First order equation

$$\log (q_e - q_t) = \log q_e - (K_1 t / 2.303) \text{ ----- 11}$$

Second order equation

$$t/q_t = 1/n + t/q_e^2 \text{ ----- 12}$$

Intra particle diffusion equation

$$q_t = K_{pt} t^{1/2} + C \text{ ----- 13}$$

Elovich model equation

$$q_t = \alpha + \beta \ln t \text{ ----- 14}$$

Time,min	%	C0	Ce	ct=C0-Ce	qt	t/qt
30	74.15	10	2.6	7.415	2.472	12.138
60	77.96	10	2.2	7.796	2.599	23.089
90	81	10	1.9	8.1	2.700	33.333
120	88.1	10	1.2	8.81	2.937	40.863
150	92.45	10	0.8	9.245	3.082	48.675
180	94.33	10	0.6	9.433	3.144	57.246

Table 5a

qe-qt	Log (qe-qt)	t1/2	1/qt	1/t	Ln t
0.983	-0.0072992	5.477226	0.404585	0.033333	3.401197
0.856	-0.0673572	7.745967	0.384813	0.016667	4.094345
0.755	-0.122053	9.486833	0.37037	0.011111	4.49981
0.518	-0.2853909	10.95445	0.340522	0.008333	4.787492
0.373	-0.4279032	12.24745	0.3245	0.006667	5.010635
0.311	-0.5077053	13.41641	0.318032	0.005556	5.192957

Table 5b

I Order	K1 = 0.0069	qe = 1.1479	R2=0.969
II Order	K2 = 0.0177	qe = 3.3898	R2=0.994
Intra particle diffusion	Kp = 0.091	C = 1.922	R2=0.915
Elovich model	$\beta = 0.393$	$\alpha = 1.051$	R2=0.964

Table 5c

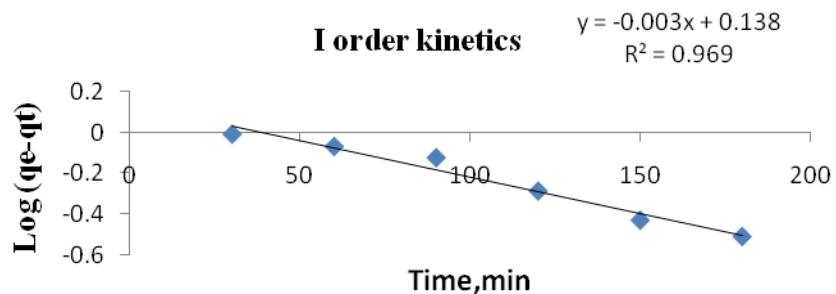


Fig 15

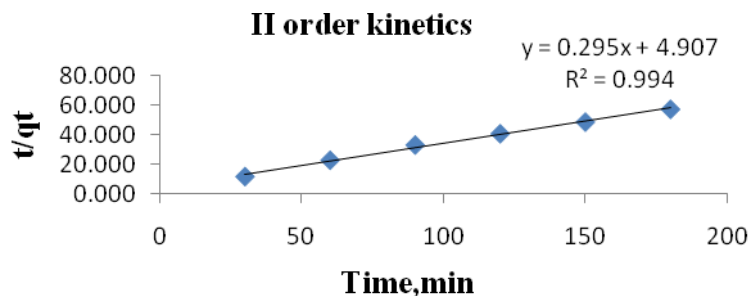


Fig 16

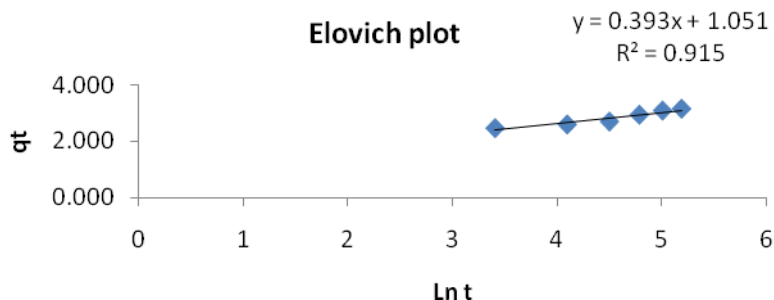


Fig 17

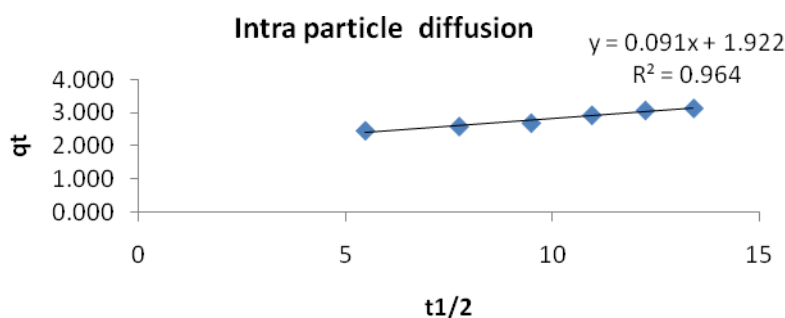


Fig 18

FT-IR studies

The action of oxidizing Oxygen on the surface of the carbonaceous precursor causes formation of surface oxides. Their structure have not been investigated completely because of the greater number of possible surface groups. The most common Oxygen groups on the surface are carboxylic, lactonic and phenolic. These groups have acidic character, which can be relatively easily determined by titration methods that are based on titrations using bases of different strengths. The method of Boehm has been followed to find the density of functional groups present on the carbon surface. FT-IR (JASCO FTIR-3500) spectra of the activated carbon samples before and after adsorptions are shown in the figures(19 &20) respectively. The spectra provide the evidences for the presence of surface groups on the adsorbent's surface as established by Boehm titrations. Notable differences among them are the peak intensities. The carbons have marked differences in the intensities of nearly all the absorption bands, reflecting that the density of corresponding functional groups differ a lot. The intense broad band between 3100 and 3500 cm^{-1} are connected with $\nu(\text{O-H})$. The O-H groups are likely associated by means of hydrogen bonds. The band of non bonded hydroxyl groupings, besides being a sharp band is usually located above 3500 cm^{-1} . The band in the range below 3849.96 and 3962 cm^{-1} were assigned by Zawadzki to Hydrogen bonds of type $(\text{H}_2\text{O}-\text{H}-\text{OH}_2)^+$ with protons of acidic groups. Intense bands at 2285 cm^{-1} indicates C-H stretching from CH_2 groups. The bands around 1620 cm^{-1} are ascribable to $\nu(\text{C=O})$ vibration in configurations such as lactones, quinone and COOH groups. Their intensity denotes a low concentration of surface C=O groups in adsorbent. According to correlation charts, Band at 1620 cm^{-1} are due to asymmetric and

symmetric ν (COO⁻) vibrations are skeletal C=C aromatic vibrations. The band at 1200cm⁻¹ is associated with phenolic OH groups and to OH groups in aliphatic carbons respectively. It could also be due to -SO₃H groups because of sulphuric acid treatment. The bands at 875.95 and 588.76 cm⁻¹ are due to COO and C-O-H groups respectively. After adsorption some peaks is vanished due to desorption in to adsorbate and few peaks are slightly shifted to higher or lower wave numbers due to electrostatic forces. There are no new peaks after adsorption confirmed absence of formation of new compounds shown in the table 6.

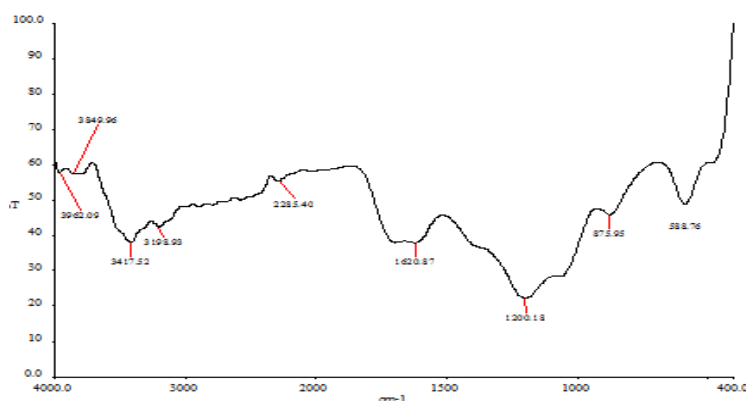


Fig 19

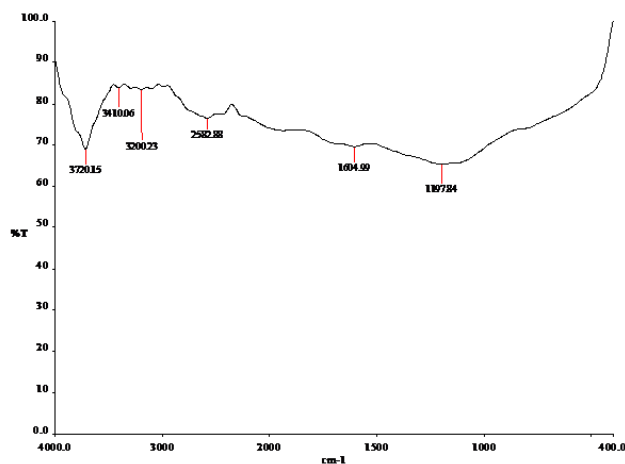


Fig 20

Wave number,cm-1	Functional group
Before ads	
588.76	COO
875.95	C_O_H
1200.18	Lactonic groups
1620.87	Skeletal C=C aromatic
2285.40	C-H &CH ₂
3198.93	V(O-H) vibrations, Hydrogen bonds

3417.52	V(O-H) vibrations, Hydrogen bonds
3849.96	V(O-H) vibrations, Hydrogen bonds
3962.09	V(O-H) vibrations, Hydrogen bonds

Table 6

CONCLUSION

The study indicates that activated carbon prepared from *Cynodon dactylon* could be used as an effective adsorbent material for the treatment of Lead in aqueous wastewater. The adsorption of Lead on activated carbon is found to be pH, initial concentration and dose dependent. The optimum conditions of Lead uptake obtained from this study are: pH 6.0, initial concentration 10 mg/L and biomass loading of 150mg. In addition, the correlation of Langmuir adsorption isotherm fits the experimental data most accurately. It was determined that the maximum adsorption capacity is 94 %. The material is not only economical, but also is an agricultural waste product. Hence activated carbon derived from *Cynodon dactylon* would be useful for the economic treatment of wastewater containing Lead metal ions. There are peaks after adsorption confirmed adsorption Pb (II) on adsorbent surface.

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