INTERNATIONAL JOURNAL FOR INNOVATIVE RESEARCH IN MULTIDISCIPLINARY FIELD
ISSN: 2455-0620 [Impact Factor: 6.719]
Monthly, Peer-Reviewed, Refereed, Indexed Journal with IC Value : 86.87
Volume - 8, Issue - 10, October - 2022 Publication Date: 15/10/2022

DOIs:10.2015/IJIRMF/202210003 --:-- Research Article

Optimization of Adsorption Condition for Lead Ions Removal Using Food Waste

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Abstract: Environmental pollution point of view, the discharge of industrial effluent in natural aquatic system create threat to aquatic life as contain heavy metals. The effluents therefore need treatments to remove those heavy metals. Adsorption process in optimized condition is known to be very effective in heavy metals removal. It's possible to obtained economically cheap adsorbent, if prepared from food industry waste. *Cajanus cajan*huskwhich is waste from Indian pulse processing industries), can be exploited for said the purpose. The present research work was therefore planned to exploit *Cajanus cajan*husk as adsorbent in optimised condition of adsorption in removing dangerous heavy metal Lead (Pb^{++} ions). To prepare adsorbent in laboratory from *Cajanus cajan*husk, the huskswere carbonized in muffle furnacein an airtight container for 1 hour at 500 ^{0}C. The optimum adsorption condition for the Pb^{++} ions from its solution was obtained in batch study (100 ml 50 ppm Pb^{++} ions solution). The pH condition was optimized by conducting batch study at 2, 3, 4, 5, 6, 7, 8, 9 and 10 pH.The speed of agitation changed from 50-250 rpm (50, 100, 150 200 and 250 revolution per minute)in the optimization of agitation speed. The altering temperature 60 ^{0}C, 50 ^{0}C, 40 ^{0}C, 30 ^{0}C, 20 ^{0}C and 10 ^{0}C were used in the study to optimize temperature of adsorption. Adsorbent dose 0.1 to 2 gm (0.1 gm, 0.2 gm, 0.4 gm, 0.8 gm, 1.2 gm, 1.6 gm, 1.8 gm and 2.0 gm)were used to optimize dose of adsorbent. The adsorption condition optimization study ended with contact time optimization by varying adsorption time from 0.5 hours to 4 hours (0.5-hour, 1 hour, 1.5-hour, 2.0-hour, 2.5-hour, 3.0-hour, 3.5 hour and 4.0 hour). Thermodynamic studies were carried out using adsorption data of temperature optimization. The work conclude that the adsorbent prepared from *Cajanus cajan*husk by their carbonization had capability to remove lead ions. The optimum conditions at which the prepared adsorbent removed 100 % Pb^{++} from its 100 ml, 50 ppm solution were agitation speed 150 rpm, pH 6.0, temperature 60 ^{0}C, contact time 3 hr., and adsorbent dose 2 gm. The thermodynamic study revealed all the thermodynamic parameter that is Standard enthalpy change Gibb's free energyandentropy change were positive and hence concluded that the Pb^{++}adsorption from its aqueous solution by prepared adsorbent wasnonspontaneous, endothermic, and favourable for entropy.

Key Words: *Cajanus cajan husk, Adsorption, Lead, Optimization, Thermodynamic.*

1. INTRODUCTION :

Heavy metals in excess amount are poisonous to all the kind of living system including human being. The wastewater created due to various chemical processes used in industries contain huge quantity of heavy metals like lead, arsenic, zinc, chromium ect.[1]. As the waste effluent from the industries contain all these heavy metals, there discharge in natural aquatic system produce threat to all the form of aquatic life (aquatic plants and animal). The discharge of effluent that contain heavy metals in aquatic systems thus create pollution in aquatic system and lead to environmental degradation[2]. Therefore, the direct disposal of industrial waste loaded with heavy metal ions is not recommended from environment safety point of view. The provision must be made to remove the heavy metal ions to the safer limit from the industrial effluent before putting in the natural aquatic systems [3]. The industrial effluents therefore need treatments to remove those heavy metals for their safe disposal. One of the efficienttreatmentsto remove metal ions is Adsorption[4]. In adsorption process the adsorbate molecules/ atoms/ ions are get deposited on the solid surface of adsorbent. Various types of adsorbents have been prepared from various sources. Economy point of view the food

industry waste is good as easily available at nominal cost in abundant quantity. Another reason for considering food waste as source of adsorption is that they have good property for binding metals ions. Particularly the food waste coming from agricultural commodities processing contain compounds like carbohydrates, fibres, proteins, sugar etc., which carries different types of functional groups that can complexing the metal ions by forming bonds with them[5]. India is mainly agricultural country and food processing industries in India mainly process agricultural produce as raw material. Pulses are one of the important agricultural crops in India and India is topmost producer of *Cajanus cajan*, a pulse used to produce Tur Dal. In India Dal particularly Tur Dal is important part of almost all the India meals [6]. The large numbers of *Cajanus cajan* pulse processing industries are available in India to cater the needs of Tur Dal. The processing of *Cajanus cajan*howeverproduce low-cost by-product or waste *Cajanus cajan*husk. As these husks are plant origin, it's obvious will have good potential for adsorbing metal ions[7]. The effectiveness of these husk can be further improved if the condition for adsorbing metal ions is optimized. The optimization of adsorption condition is essential for using these husks for their better utilization for the purpose of metal ions adsorption.
The aim of the present research work was to exploit *Cajanus cajan*husk as adsorbent in optimised condition of adsorption in removing dangerous heavy metal Lead (Pb^{++} ions).

2. MATERIALS AND METHODS :

Lead nitrate was used to prepare standard Lead ions solution (50 ppm). The *Cajanus cajan*husk were obtained from Niki Agro Products Pvt. Ltd, Jalgaon. Adsorbent from *Cajanus cajan*husk was prepared as per the method described by Parate and Talib (2014)by carbonizing the huskin an airtight container at 500 ^{0}C for 1 hours using muffle furnace[8].The Lead ions concentrationswereanalysed using AAS (Atomic Absorption Spectrophotometer) of ELICO Ltd. (SL 176).

2.1Optimization of Adsorption Condition

In the study of optimization of various parameters of lead adsorption, the batch study was carried out keeping particle size of adsorbent (0.25-0.15 mm), initial concentration of Pb solution (50 ppm), volume of Pb solution (100 ml), and 4 hr. contact time for each batch. The pH condition was optimized by conducting batch study at 2, 3, 4, 5, 6, 7, 8, 9 and 10 pH.The speed of agitation changed to50, 100, 150 200 and 250 revolution per minutein the optimization of agitation speed. The temperature 60 ^{0}C, 50 ^{0}C, 40 ^{0}C, 30 ^{0}C, 20 ^{0}C and 10 ^{0}C were used to optimize adsorption temperature. Adsorbent dose 0.1 to 2 gm (0.1 gm, 0.2 gm, 0.4 gm, 0.8 gm, 1.2 gm, 1.6 gm, 1.8 gm and 2.0 gm) were used to optimize the dose of adsorbent. The adsorption condition optimization study ended with contact time optimization by varying adsorption time from 0.5 hours to 4 hours (0.5-hour, 1 hour, 1.5-hour, 2.0-hour, 2.5-hour, 3.0-hour, 3.5 hour and 4.0 hour).

The Lead ions removal % was calculated after each batch run as follows:

$$\%.\text{Removal} = \left\{ \frac{C_i - C_e}{C_i} \right\} x\,100$$

Were,
$C_i$is Lead ions initial concentration and Ce is Lead ions equilibrium/ finalconcentration in mg/ L[9].

Theq_e that is capacity of adsorption was calculatedin mg/ gm by the following formula:

$$q_e = V\frac{(C_i - C_e)}{W}$$

Where, $C_i$is initial concentration of Lead ions and Ce is final or equilibrium concentration of Lead ion in mg/L, V is the volume of the solution in L and W is the mass of the Adsorbate in gm[10].

2.2 Thermodynamic studies:

Thermodynamic aspect of adsorption was studiedfrom the temperature optimization adsorption data gainedby estimating the standard ΔH^0 (enthalpy change), Gibb's free energy (ΔG^0), and ΔS^0 (entropy change).

The ΔG^0 in J/mol was obtained using K_C (constant of thermodynamic equilibrium)as perequation below:

$$\Delta G^0 = -RT \ln K_C$$

Where, T is temperature (Kelvin) and R= 8.314 J/mol K (ideal gas constant)

The K_C is related to C_∂ and C_e by following equation:

$$K_C = C_\partial / C_e$$

Were,

C_∂= mg of Lead ions adsorbed per litre
C_e= equilibrium concentration of Lead ions solution (mg/L)

Following relation wasused in the study to calculate C_∂

$$C_\partial = C_i - C_e$$

Were,

C_i= Lead ions initial concentration in mg/L
C_e= Lead ions Equilibrium concentration of in mg/L.

According to Van't Hoff equation ΔG^0 is related to ΔH^0 and ΔS^0 by the following relation:

$$\ln K_C = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

The slope and intercept of the plot of $\ln K_C$vs 1/T was used to calculate ΔH^0 and ΔS^0 [11].

3. RESULTS AND DISCUSSIONS :

3.1 Results of Optimization of Adsorption Parameters

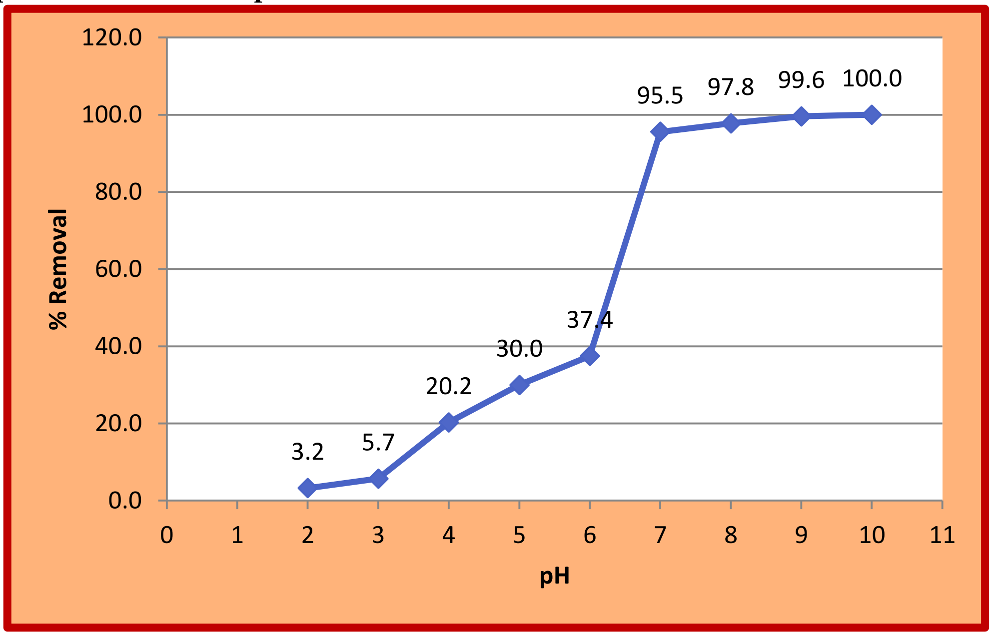

Fig. 1: Optimization of pH for Lead Adsorption by Cajanus Cajan Hush Adsorbent

The effect of pH on Pb^{++} ions adsorption by Cajanus cajan husk adsorbent is shown in Figure 1. At low pH the adsorption (Pb^{++} ions)wasfound to be low and as the pH increased the adsorption also increasedup to pH 6. As the pH increased beyond 6, the sudden increase in % removal of Pb^{++} ions were observed. Some precipitation was also observed in lead solution, which was of lead hydroxide[12, 13]. It was concluded thatthe removal of Pb^{++} ions above pH 6 was not due to adsorption but because of precipitation of lead ions into lead hydroxide. Keeping in view adsorption and precipitation, the adsorption pH was optimized as 6.

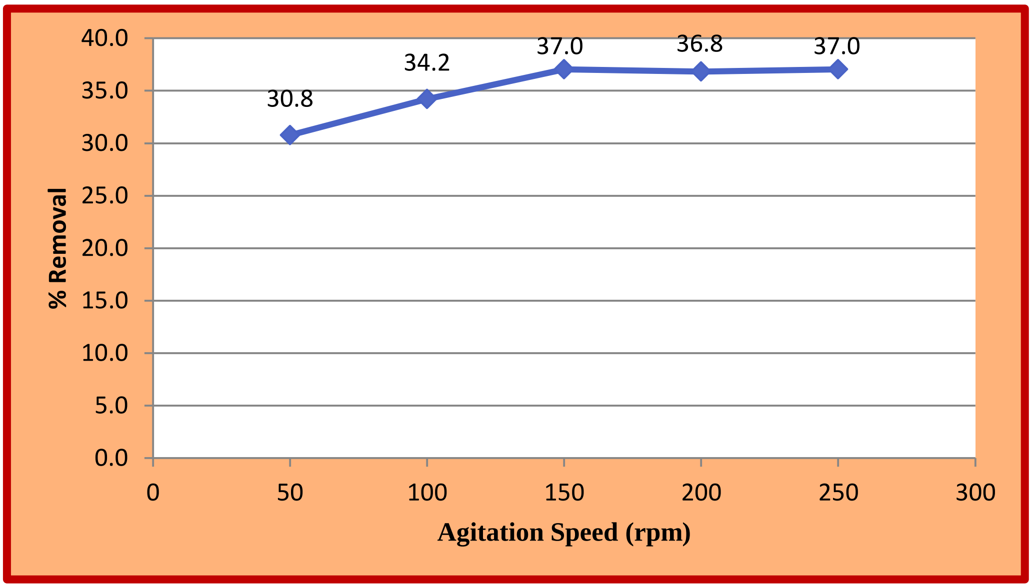

Fig. 2: Optimization of Agitation Speed for Lead Adsorption by Cajanus Cajan Hush Adsorbent

Figure 2 is showing the impact of agitation speed on adsorption (Pb^{++} ions) by Cajanus cajan husk adsorbent. It can be observed that at low rpm the adsorption was also low and as the rpm of agitation increased up to 150 rpm the adsorption also increased.The increasing agitation speed increases migration of adsorbate towards adsorbent surface and that lead to increase in adsorption [14]. Beyond 150 rpm, no significant adsorption observed.The agitation speed hence optimized as 150 rpm.

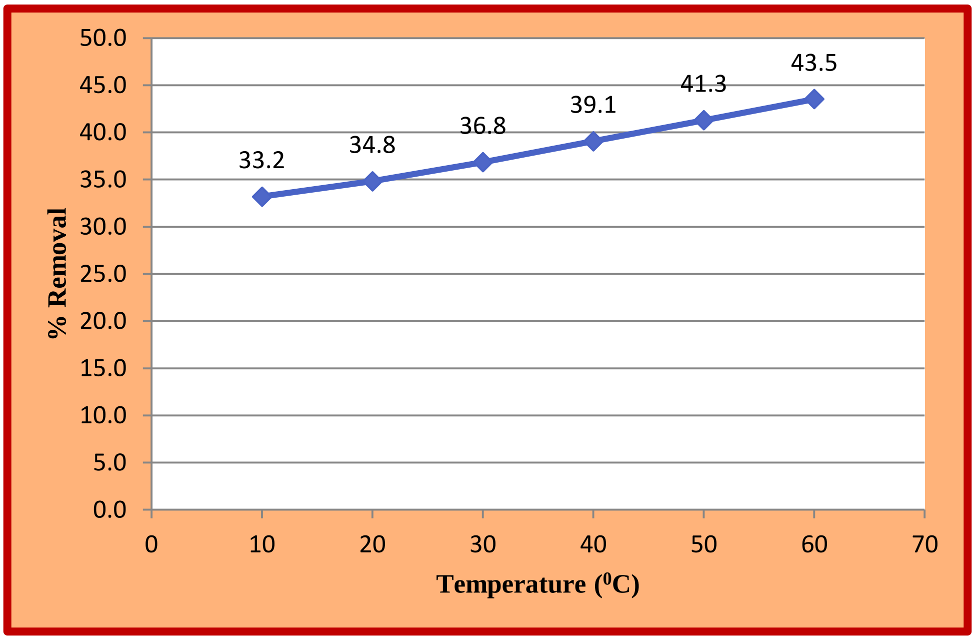

Fig. 3: Optimization of Temperature for Lead Adsorption by Cajanus Cajan Hush Adsorbent

Figure 3 is displaying the temperature effect of on Pb^{++} ions adsorption by Cajanus cajan husk adsorbent. The adsorption was less at low temperature and high at high temperature. As the temperature increased from low to high the % Lead ions removal also increased. It was concluded that lead ions adsorption on Cajanus cajan husk adsorbent surface was endothermic in nature. The reason behind the said observation may be the breaking of some internal bond in adsorbent structure and the formation of some new bonding sites on adsorbent surface[15]. The temperature of adsorption was thus optimized as 60 ^{0}C.

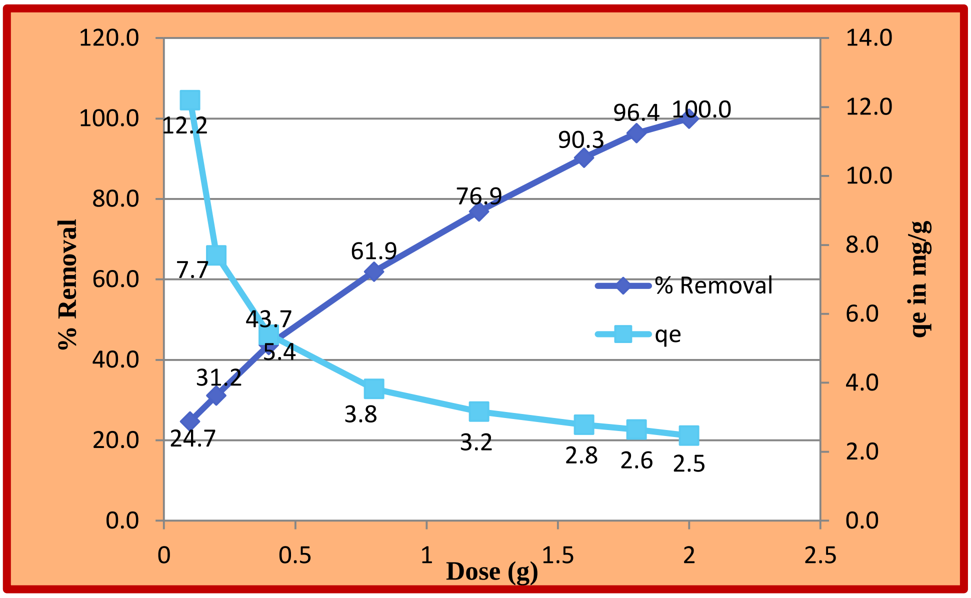

Fig. 4: Optimization of Adsorbent Dose for Lead Adsorption by Cajanus Cajan Hush Adsorbent

Figure 4represents the adsorbent doseimpact on Pb^{++} ions adsorption by Cajanus cajan husk adsorbent. It can be observed that the Pb^{++} ionsremoval was increasing as the dose of adsorbent increased, but adsorption capacity (q_e) was decreasing as the dose of adsorbent increased. The reason for rising adsorption of lead ions due to increasing dose was,the availability of large surface area and adsorption sites, because of availability of high amount of adsorbent mass. Formation of agglomerates of adsorbent with increasing dose of adsorbent was blocking some adsorption sites and masking of some surface area of adsorbent that resulted reduction in adsorption capacity with growing dose of adsorbent[16]. In above study the adsorbent dose 2 g was observed as minimum dose for complete adsorption of lead and hence 2 g adsorbent dose was selected as optimum dose.

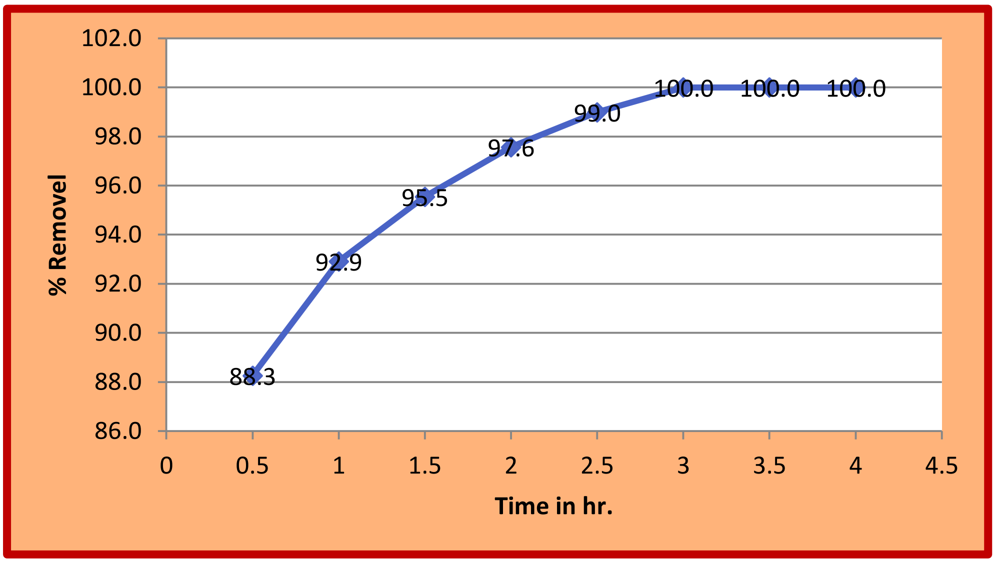

Fig. 5: Optimization of Contact Time for Lead Adsorption by Cajanus Cajan Hush Adsorbent

Figure 5is showing the effect of contact time on Pb^{++} ions adsorption by Cajanus cajan husk adsorbent. It is clear in above graph that as the contact time increased the adsorption also increased and attended complete adsorption at contact time 3 hr. The contact time for said adsorption was therefore optimized as 3 hr. During low contact time, the adsorption was less but effective due to the availability of large surface area. During high contact time the adsorption observed was high but less effective due to exhaustion of adsorption sites of adsorbent[17].

3.2Results of Thermodynamic Study

Table 1: Standard Gibb's Free Energy forAdsorption of LeadIons (Pb^{++}) by Cajanus Cajan Hush Adsorbentat Different Temperature

Temperature T		1/T	Ad_1					
			Pb Ions solution Initial Concentration (C_i)	Pb Ions solution Equilibrium Concentration (C_e)	$C_\partial = C_i - C_e$ (mg/L)	$K_C = C_\partial / C_e$	$\ln K_C$	$\triangle G^0 = -RT \ln K_C$ (J/mol)
^0C	^0K		ppm (mg/L)	ppm (mg/L)				
10	283	0.0035	49.40	33	16.4	0.4970	-0.70	1645.18
20	293	0.0034	49.40	32.2	17.2	0.5342	-0.63	1527.51
30	303	0.0033	49.40	31.2	18.2	0.5833	-0.54	1357.81
40	313	0.0032	49.40	30.1	19.3	0.6412	-0.44	1156.51
50	323	0.0031	49.40	29	20.4	0.7034	-0.35	944.63
60	333	0.0030	49.40	27.9	21.5	0.7706	-0.26	721.41

Table 1 is showing the Standard Gibb's free energy for Lead ions (Pb^{++}) adsorption by Cajanus cajanhush adsorbent at various temperature. The value of standard Gibb's free energy, observed to be high a thigh temperature and low at low temperature. The standard Gibb's free energy was positive for all the temperature and confirmed on-spontaneity of the described adsorption process [18].

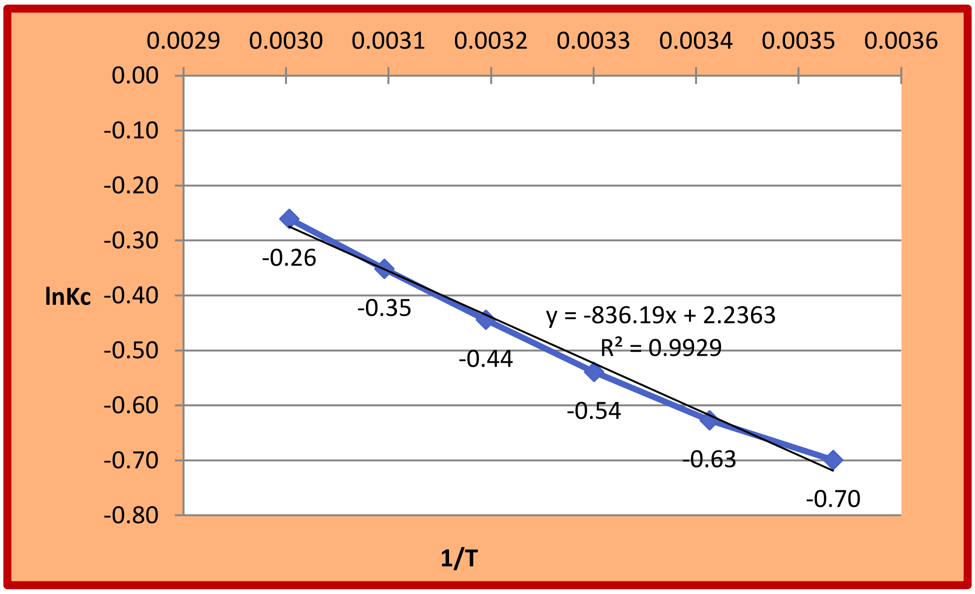

Fig. 6: Plot of $\ln K_C$ vs 1/T for Lead Adsorption by Cajanus Cajan Hush Adsorbent

Figure 6 is nothing but the plot of $\ln K_C$against 1/T forPb^{++} ions removal (adsorption) by Cajanus cajan husk adsorbent to determine ΔH^0 and ΔS^0 values. The line of plot showing to fit the data well as the coefficient of determination R^2 = 0.9929 was high. Plot line had slope -836.19 and y-intercept 2.2363 which was requiredto calculate ΔH^0 and ΔS^0 byVan't Hoff equation.

Table 2: Determination of ΔH^0 and ΔS^0 ValuesforAdsorption of LeadIons (Pb^{++}) by Cajanus Cajan Hush Adsorbentby Van't Hoff Equation

Van't Hoff Equation	Line Equation with Correlation coefficient	Slope	Y Intercept	ΔH^0 (J/mol)	ΔS^0 (J/mol K)
$\ln K_C = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	y = -836.1x + 2.236 R^2 = 0.992	-836.19	2.2363	6951.33	18.59

Table 2 is showing the Van't Hoff equation and the calculated value of ΔH^0 andΔS^0. It can be seen that ΔH^0 and ΔS^0 were positive for the Pb^{++} ions adsorption by the prepared Cajanus cajan husk adsorbent and predictedthatthe said adsorption reaction was endothermic and was unfavourable for enthalpy but favourable for entropy[19, 20].

4. CONCLUSION :

The research work conducted on the adsorbent prepared from *Cajanus cajan*husks by their carbonization concluded that the prepared adsorbent was capable to adsorb lead ions. The optimum conditions at which the prepared adsorbent adsorbed all the Lead (Pb^{++} ions) from its100 ml, 50 ppm solution were,agitation speed 150 rpm,pH 6.0, temperature 60 ^{0}C, dose of adsorbent 2 gm and contact time 3 hr. The thermodynamic study concluded that the Lead ions (Pb^{++}) removal from its aqueous solution by prepared adsorbent was nonspontaneous, endothermic, and favourable for entropy.

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