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Adsorption Studies on Removal of Chromium (VI) Using Activated Carbon Prepared From Eucalyptus Leaves

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Abstract: Hexavalent chromium is considered as a severe environmental pollutant through industries. Studies using adsorbents for controlling Cr (VI) is the mainstream of research on pollution control methods. The activated carbon produced from eucalyptus leaves was physically and chemically activated (ZnCl2) and utilized as an adsorbent for the removal of Cr (VI) from aqueous solution. Adsorption experiments were carried out in a batch process and various experimental parameters such as the effect of contact time, carbon dosage, and pH on percentage removal have been studied. The removal of Cr (VI) was found to be dependent on pH.Equilibrium data were fitted with Langmuir and Freundlich isotherms.

Keywords: Hexavalent chromium, Activated carbon, Adsorption, Eucalyptus leaves.

I. INTRODUCTION

Water is one of the most important resources of nature which covers almost three-quarters of the planet. About 97 % of the world's water resources are locked-up in the oceans and seas which are too saline to be used directly. Almost 2.4 % is trapped in giant glaciers and polar ice-caps. Thus not even 1 % of the total world's water resources are available for exploitation by man for domestic, agricultural and industrial purposes. The water is called the elixir of life because of its multiple uses. Indiscriminate use and misuse of water are making it unfit for human consumption.

Chromium is a priority metal pollutant introduced into water bodies from many industrial processes such as tanning, metal processing, paint manufacturing, steel fabrication, and agricultural run-off. Chromium is also used in explosive ceramic and photography. The toxicity of Cr(VI) is well documented and it is considered a hazard to the health of man and animals. The various compounds of chromium are found to be both corrosive to flesh and carcinogenic. The presence of Cr(VI) in the aquatic environment at high concentration is lethal to marine species[8].

Chromium (VI) is removed from wastewater by various methods such as chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electrodialysis, solvent extraction, and evaporation, etc. These methods have been found to be limited since they often involve high capital and operational costs. Among these methods, adsorption is the most efficient technique because of its convenience, easy operation and simplicity of design. Adsorption which has proven to be effective for the removal of Cr(VI) from aqueous solutions and industrial effluents [13]. Adsorption using low-cost adsorbents is one of the effective and economical methods.

II. MATERIALS AND METHODOLOGY

2.1 Adsorbent

The material used in this research study is Eucalyptus leaves as an adsorbent. For the removal of hexavalent chromium from aqueous solution, the adsorption technique was employed using activated carbon prepared from Eucalyptus leaves. There are two ways to prepare activated carbon, namely

i. Physically activation
ii. Chemical activation, using zinc chloride ($ZnCl_2$) as an activating agent (taking sieve size 150 microns).

2.1.1 Impregnation Ratio

In chemical activation, the degree of I.R. plays an important role. It is the ratio of the weight of anhydrous activating salt to the dry carbonizing material. The effect of the degree of impregnation ratio on the porosity of the resulting product is apparent from the fact that the volume of pores increases with I.R. When the degree of impregnation is further raised the number of pores with large diameter increases and the volume of the smallest decreases. In this study 0.25, 0.50 and 0.75 I.R'S. are used.

2.2 BATCH SORPTION EXPERIMENT:

In batch sorption, a predetermined amount of adsorbent is mixed with the sample, stirred for given contact time and subsequently separated by filtration. Powder adsorbent is more suitable for batch type contact process.

2.2.1Selection of optimum contact time:

The adsorption is strongly influenced by the contact time. To study the effect of contact time 100mL of 10mg/L Chromium(VI) solutions are mixed with 1gm(10g/L) of adsorbents and stirred on Gyro shaker for various time interval such as 5mins, 10mins, 15mins up to 60mins.Then the samples are filtered and analyzed for Cr(VI) concentration using UV visible spectrophotometric method.

2.2.2 Determination of Optimum Dosage

To determine the optimum dosage of adsorbent, various dosages of adsorbents are added to the conical flask containing a known concentration of Cr (VI) (10mg/L). The solution in the conical flask was subjected to stirring for optimum contact time and the dosage varies from 25mg, 50mg, and 75mg up to 250mg. Filtered and analyzed for residual and removal of Cr (VI) concentration.

2.2.3Determination of Optimum pH:

The extent of adsorption is strongly by the pH at which adsorption is carried out. The effect of pH on Cr(VI) adsorption was studied by determining the optimum pH series of conical flasks were taken with 100 mL of 10 mg/L Cr(VI) . The optimum dosage of adsorbents is added to the respective flasks. The pH of the flasks is adjusted ranging from 1.25 to 3.0. The pH of the solution was adjusted by using 0.1N H_2SO_4 or 0.1N NaOH. The flasks were shaken for optimum contact time. After stirring, the samples are filtered and analyzed for the residual Cr (VI) concentration. The two flasks i.e. Containing Cr (VI) which gives minimum residual concentration is selected as the optimum pH.

III. RESULTS AND DISCUSSIONS

3.1 Effect of Contact Time:

Contact time has a greater role in the adsorption process. The effect of contact time on the removal of Chromium (VI) from their synthetic sample at pH 2.0±0.02 using physically and chemically activated ($ZnCl_2$) carbons prepared from eucalyptus leaves with I.R ratio 0.25,0.5 and 0.75.It is observed that contact time differs for different carbons. Effect of contact time is studied and the graph of the percentage of chromium removal versus time is plotted as shown in figure 1 and 2.

From the graph, it is evident that the extent of Cr (VI) adsorption increase in time. The adsorption curves are characterized by a sharp rise in the initial stage and decreases near equilibrium. This is mainly due to the large available surface area and the adsorption sites on the surface area that are open and active in the initial stage and later the adsorbent gets saturated and the removal efficiency decreases near equilibrium.

After equilibrium further increases in time, adsorption is not changing. Hence, the removal efficiency of chromium (VI) by using physically activated carbon was found to be 83.01% with optimum contact time of 30min, the removal efficiency of Cr (VI) by using chemically activated carbon ($ZnCl_2$) with different I.R 0.25, 0.5 and 0.75 was found to be 88.72%, 94% and 99.2% with an optimum contact time of 30min,25min and 20 min respectively.

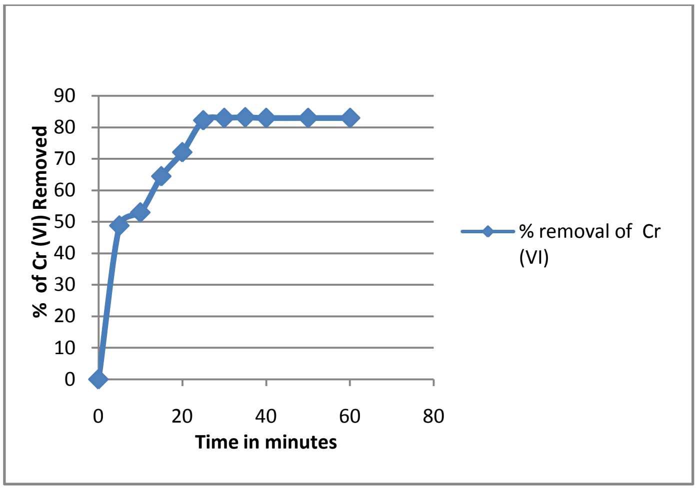

Fig.1: Effect of Contact Time on Cr (VI) Removal by Physically Activated Carbon

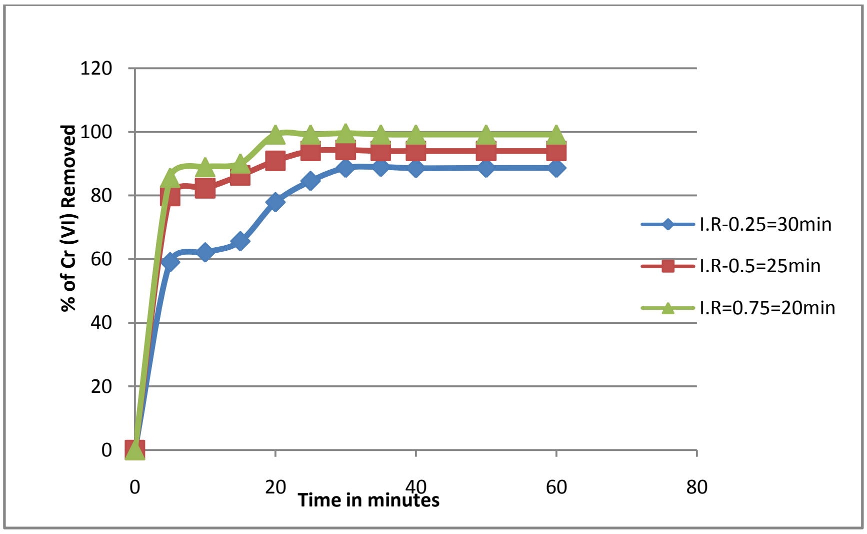

Fig.2: Effect of Contact Time on Cr (VI) Removal by Chemically ($ZnCl_2$) Activated Carbon

3.2 Effect of Adsorbent Dosage:

Adsorption is a process in which continues the transfer of a solute from solution to adsorption occurs until the residual concentration of solution maintains equilibrium with what adsorbed by the surface of adsorbent at constant contact time. Effect of adsorbent dosage is studied and a graph of the percentage of chromium removal versus dosage is plotted as shown in figure 3 and 4.

From the graph, it is observed that, as the dosage of carbon increases, the amount of Chromium (VI)present in the samples decreases sharply in the beginning and attains maximum later. The chemically activated $ZnCl_2$ carbon with I.R 0.75 adsorbs more compared to other physical and chemical activated carbons having I.R 0.25 and I.R 0.5.

Hence the removal efficiency of Cr (VI) by using physically activated carbon was found to be 84.82% with an optimum dosage of 150mg,the removal efficiency of Cr(VI) by using chemically activated carbon ($ZnCl_2$) with different I.R 0.25,0.5,0.75 was found to be 92.30%,99%,99.3% with an optimum dosage of 175mg,150mg,100mg respectively.

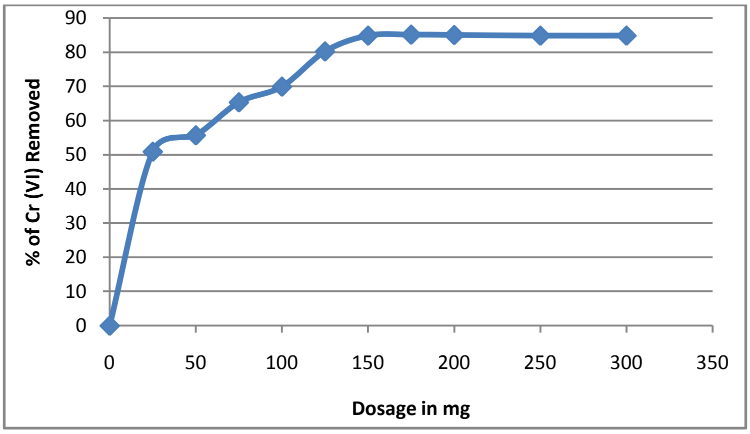

Fig.3:Effect of Adsorbent Dosage on Cr (VI) Removal by Physically Activated Carbon

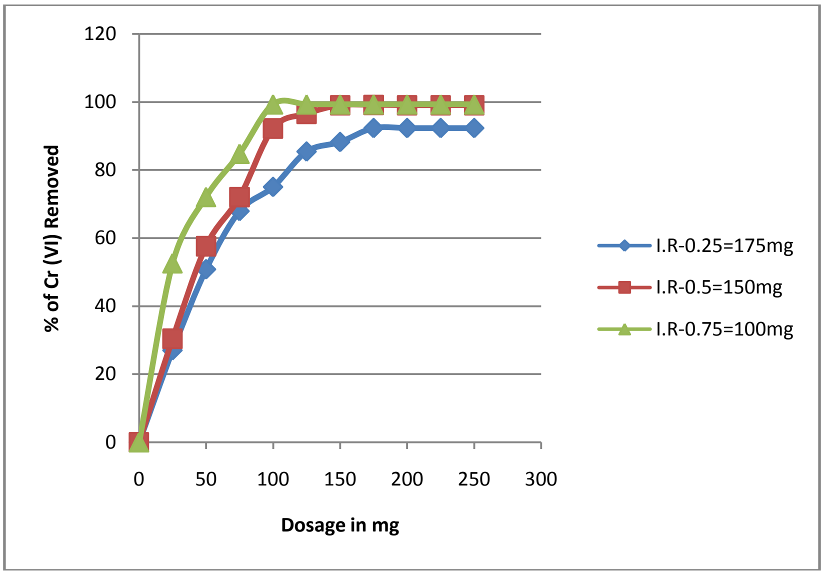

Fig4: Effect of Adsorbent Dosage on Cr (VI) Removal by chemically ($ZnCl_2$)

3.3 Effect of pH on Hexavalent Chromium Removal:

The pH of the solution has an influence on the extent of adsorption removal efficiencies of chromium (VI) by prepared activated carbon at different pH values are shown inFigures 5 and 6. The amount of Cr (VI) not only depends on the surface area, optimum dosage and optimum time but also depends on pH.

From the above-mentioned figures, it is observed that Chromium is removed more effectively in the acidic range. As pH increases, the removable efficiency decreases appreciably. This might be due to the weakening of the electrostatic force of attraction between the oppositely charged adsorbate and adsorbent that ultimately lead to the reduction of adsorption capacity. Hence, the removal efficiency of Cr (VI) by using physically activated carbon is 98% and for $ZnCl_2$ activated carbon at different I.R 0.25, 0.5 and 0.75 are found to be 99.1%,99.2%, and99.8% respectively.

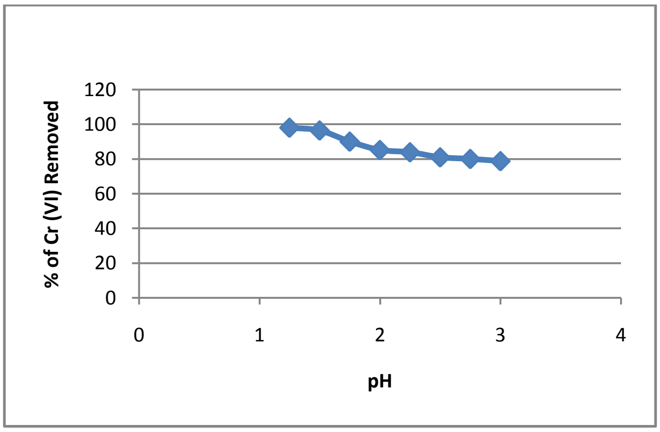

Fig.5: Effect of pH onCr (VI) Removal by Physically Activated Carbon

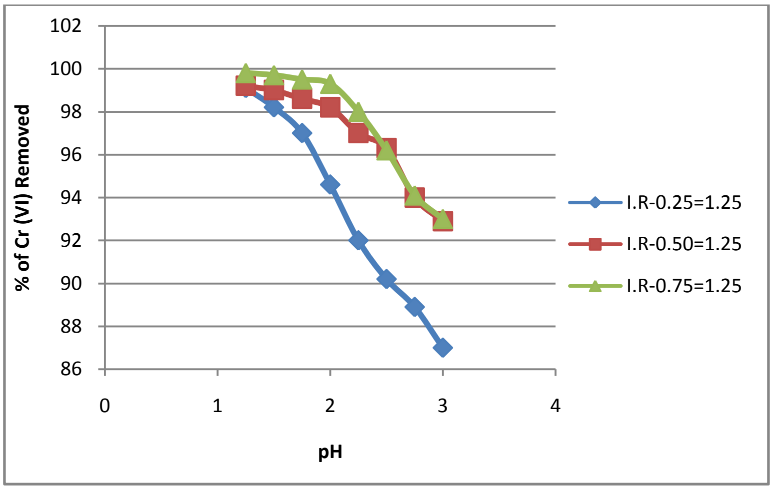

Fig.6: Effect of pH onCr (VI) Removal by Chemically ($ZnCl_2$) Activated Carbon

Table 1:Optimum Contact Time, Optimum Dosage and Optimum pH for Prepared Carbon

Type of carbon	I.R	Optimum time(min)	Optimum dosage (mg)	Optimum pH
1.physically activated carbon	-----	30	150	1.25
2.chemically activated carbon $ZnCl_2$	0.25	30	175	1.25
	0.50	25	150	1.25
	0.75	20	100	1.25

3.4 adsorption isotherms

An adsorption isotherm describes the relationship between the amounts of adsorbate which is adsorbed on the adsorbate and the concentration of dissolved adsorbate in the liquid at equilibrium.[20]. The adsorption isotherm ofchromium (VI) onto the prepared physically activated carbon was fitted by several well-known isotherms models, namely Langmuir and Freundlichmodels.The sorption equilibrium data are filled for both isotherms.

a) Freundlich Isotherm

The linear form of the Freundlich isotherm is$X/M= KC^{1/n}$

Taking log on both sides

Log_{10} X/M = log_{10} K+ 1/n log_{10} …..Eqn(1)

Where, X/M = Amount of sorbate adsorbed per unit weight of adsorbent atEquilibrium, X = Amount of adsorbate removed (mg / L), M = Mass or weight of the adsorbent, C = Equilibrium concentration of adsorbate in solution, K = An empirical constant related or sorption capacity, n = An empirical constant related to sorption intensity

The equation (1) is of the type y = c + m x.

Where, c = log_{10} K; Y = log_{10} X/M; X=log_{10} C and m=l/n

The plot of log_{10} X/M versus log_{10} C gives a straight line with slope 1/n and intercept = log_{10}K, knowing the slope and intercept ―1/n and ―K values are calculated.

The plots of linearisedFreundlich isotherms of physically activated carbon are shown in fig 7 and obtained values of K and 1/n are represented in table2.

The constants K and 1/n are evaluated by least square analysis. k=0.051 and 1/n= 0.372 for Cr (VI) for physically activated carbon.

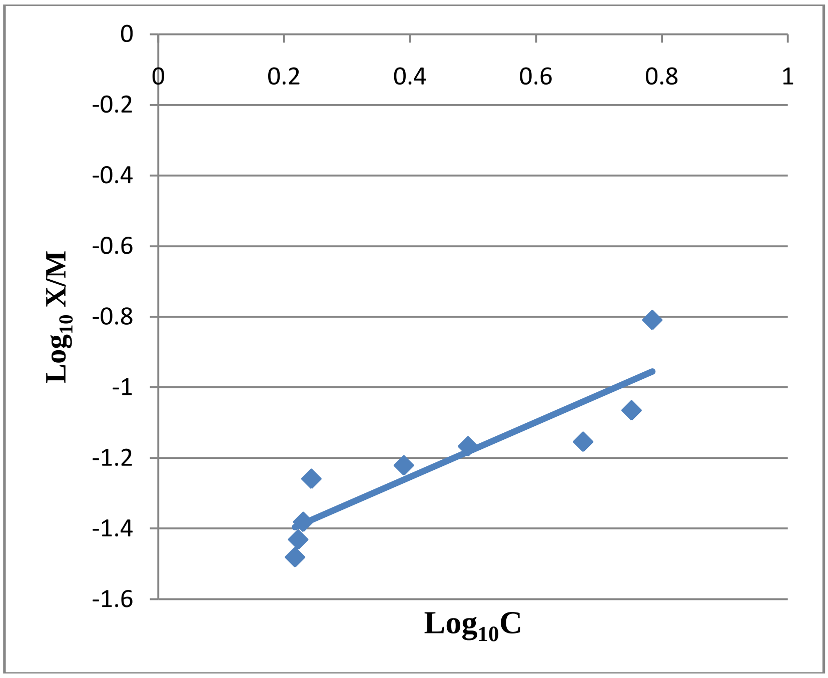

Fig 7.Plots for Freundlich isotherm for physically activated carbon

b) Langmuir's Isotherm

The Langmuir isotherm is used to describe the single layer adsorption and the linear form of the Langmuir's isotherm is, X/M = abc / (a + bc)
C/(X/M) 1/ab+c/a………. Eqn(2)
Where X/M = Amount of adsorbate adsorbed per unit weight of adsorbent.
C= Equilibrium concentration of adsorbent in solution after adsorption or saturated concentration.
'a' and 'b' are empirical constants
The equation (2) is of the type y = c+mx, where c = 1/ab and m = 1/a,the plot of C/(X/M) versus C produces a straight-line graph. The value of constants1/b and 1/ab are calculated by intercept and slope.
1 / ab = intercept; slope = 1/a
Intercept 1/b x slope; b = slope / intercept.
linearised Langmuir isotherm (C / X/M versus C) for adsorbate are shown in fig 8 and obtained values of a and b are represented in table2.

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constants separation or equilibrium parameter which is defined by Webber.
R = 1 / [(1+a) Co]
Where, a = Langmuir constant and, Co = Initial solute concentration (mg/L)
From the above equation Webber has been given parameter indicating the shape of the isotherm are as follows:

VALUES OF R	TYPE OF ISOTHERM
R > 1	Unfavorable
R = 1	Linear
0 < R < 1	Favorable
R = 0	Irreversible

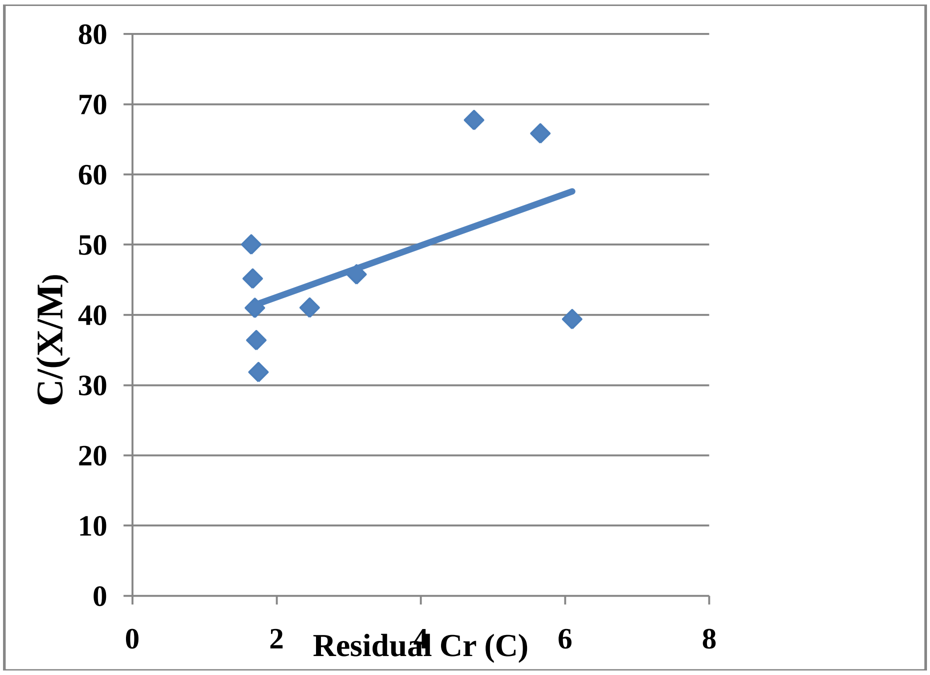

Fig 8.Plots for Langmuir's isotherm for physically activated carbon

Table.1 Freundlich and Langumir Data

S.No	Adsorption Isoterm	Components	Value
1	Freundlich	K	0.051
		1/n	0.372
2	langmuir	a	0.271
		b	0.104

VI. CONCLUSIONS

Based on the experimental study following conclusions are drawn

The Experimental result shows good removal efficiency of chromium (VI) from their synthetic solutions by using activated carbon derived from eucalyptus leaves.

1. The chemical activation of carbons increases the surface area of the adsorbent and also the Cr (VI) removal efficiency.
2. Optimum contact time for physically activated carbon is 30min with removal efficiency of 83.01% for $ZnCl_2$ activated carbon at different I.R 0.25, 0.50 and 0.75 are 30min, 25min, and 20min with removal efficiency of 88.72%, 94%, and 99.2% respectively.
3. The result of the experiment on the optimization of the dosage of adsorbent reveals that an increase in the amount of dosage added increases the removal of Cr (VI) from the solution. Hence optimum dosage for physically activated carbon is150mg with removal efficiency of 84.82% for $ZnCl_2$ activated carbon at different I.R 0.25, 0.50 and 0.75 are 175mg, 150mg and 100mg with removal efficiency of 92.30%, 99% and 99.3% respectively.
4. The removal efficiency of adsorbent increases with a decrease in pH value. It has been observed that maximum adsorption takes place in the acidic medium around pH 1.5 with a removal efficiency of Cr(VI) by physically activated carbon is 98% and for $ZnCl_2$ activated carbon at different I.R 0.25, 0.50 and 0.75 are found to be 99.1%, 99.2%, and 99.8% respectively.
5. The results of the batch experiments follow Freundlich (1/n<1) proves to be favorable adsorption. It also obeys the Langmuir isotherm as separation factor 'R' is lesser than 1 and greater than 0 (0<R<1).

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