# Reduction of Hexavalent Chromium from aqueous solution using activated carbon produced from Mangifera Indica fruit seed shell

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**Abstract: Activated carbon produced from Mangifera Indica fruit seed shellsandcommercially available activated carbon were usedto eliminate Cr (VI) from the aqueous solution. In the experimental investigation, it was observed that adsorption /removal of hexavalent chromium enhances with the surface area and contact time and reaches equilibrium at the specific time period. Freundlich and Langmuir isotherms were evaluated for both the adsorbent (activated carbon) and the adsorbate [Cr (IV)], and found that adsorption obeys both of the isotherms and validated thedata obtained from experimentation. Kinetics data was analyzed using the pseudo first order rate equation in order to apprehend the reaction rate constant. In the study it was recorded that the adsorption capacity of Mangifera Indica fruit seed shell activated Carbon is found to be higher than commercial activated carbon.Seeds extracted from Mangifera Indica fruit are the waste product and extensively available with greater functional values, hence it can be effectively treated in lieu of commercial activated carbon.**

**Keywords: Cr(VI), Mangifera Indica fruit seed shell, commercial activated carbon, Freundlich and Langmuir isotherms, Pseudo first order kinetics.**

## Introduction

Hexavalent chromium [Cr (VI)] is one of the most toxic/ hazardous metals found in environment, out of threemost prevalent chromium elements viz,metallic (Cr) and trivalent Cr(III) and hexavalent Cr, due to itscarcinogenicity and a range of many other health intricacies.Metallic chromium does not exist in its purest form, in nature.The trivalent chromium ion, Cr(III), which is essential for the metabolism of insulin, sugar, and fat, is present in human bodies in minute quantities.Extremely dangerous Cr(VI) hexavalent chromium compounds cause cancer, mutagenize DNA, and induce genetic/ birth defects in a range of biological systems[1]. The main sources of contamination include industries like leather tanning, steel manufacture, metal polishing, and other industrial sources connected to wood preservation[2]. Hexavalent chromium exposure in humans can lead to dermatitis, lung cancer, kidney malfunctioning, liver failure, as well as pulmonary inflammation[3], [4]. Therefore, reducing Cr would be crucial to enhance the water quality, thus resulting in longevity of human life.According to W.H.O., which offers standard standards for drinking waters [5], and BIS 10,500[6]specifies that the maximum permissible concentration for Cr(VI) in drinking water shall not exceed 0.05 mg/L[7]. Hence, it must be eliminated from the environment to prevent endangering the ecology and the general public's health. Due to increasing environmental laws, enterprises are looking for a cost-effective alternative technique for the treatment of Cr (VI) contaminated wastewater. As a result, a simple, effective, and low-cost treatment approach for removing Cr (VI) from wastewater is urgently needed. Adsorption process can be a adaptable and economical method for eliminating Cr (VI) when used in conjunction with the proper desorption procedure and skirting the issue of adsorbent disposal.The advantages of the adsorption process urge the use of various materials with structural, compositional, or chemical properties ideal for making this technology with enhancedhexavalent Cr retention values, and thus it has a strong potential for removing Cr (VI) from water/wastewater streams. It indicates that choosing an adsorbent is an important consideration when using adsorption as a Cr (VI) removal strategy. The high cost of current adsorbents makes the adsorption method prohibitively expensive, prompting researchers to look for novel ways to manufacture low-cost adsorbents with high Cr (VI) removal capacity [8].

## Materials and Methods

***Material:***Systematically processed activated carbon from Mangifera Indica fruit seed shell and commercially available activated carbon were chosen as adsorbents for the elimination of Cr (VI) from water. Based on the impregnation ratio, a relativeamount of purified and dried seed shell powder of Mangifera Indica fruit with the approximate size od 300µ was blended with the activating agents (ZnCl2) and (MgCl2) in the appropriate quantity with reference to impregnation ratio (I.R). In this investigation, Cr (VI) was opted as an adsorbate. 282.8 mg of potassium dichromate (A.R) was dissolved in one liter of deionized distilled water to create the synthetic hexavalent stock chromium solution, yielding 100g of chromium per ml of solution. The standard chromium solution was made by diluting 10mL of stock chromium solution into 100mL to achieve a chromium content of 10mg/L.

*Experimentation with Batch Sorption*

In a batch sorption, a specified adsorbent powder is combined with the specimen sample, agitated for a determined by varying contact time, followed by filtration.Particulate/ powdered adsorbent possess high significance and effective in batch contact processes.

Amount of hexavalent chromium at equilibriumremoval is evaluated in (R %):

$$R\% = \frac{Co-Ce}{Co} x100$$

Where $C_o$ and $C_e$ (in mg/L) are initial and equilibrium concentration in aqueous solution respectively.

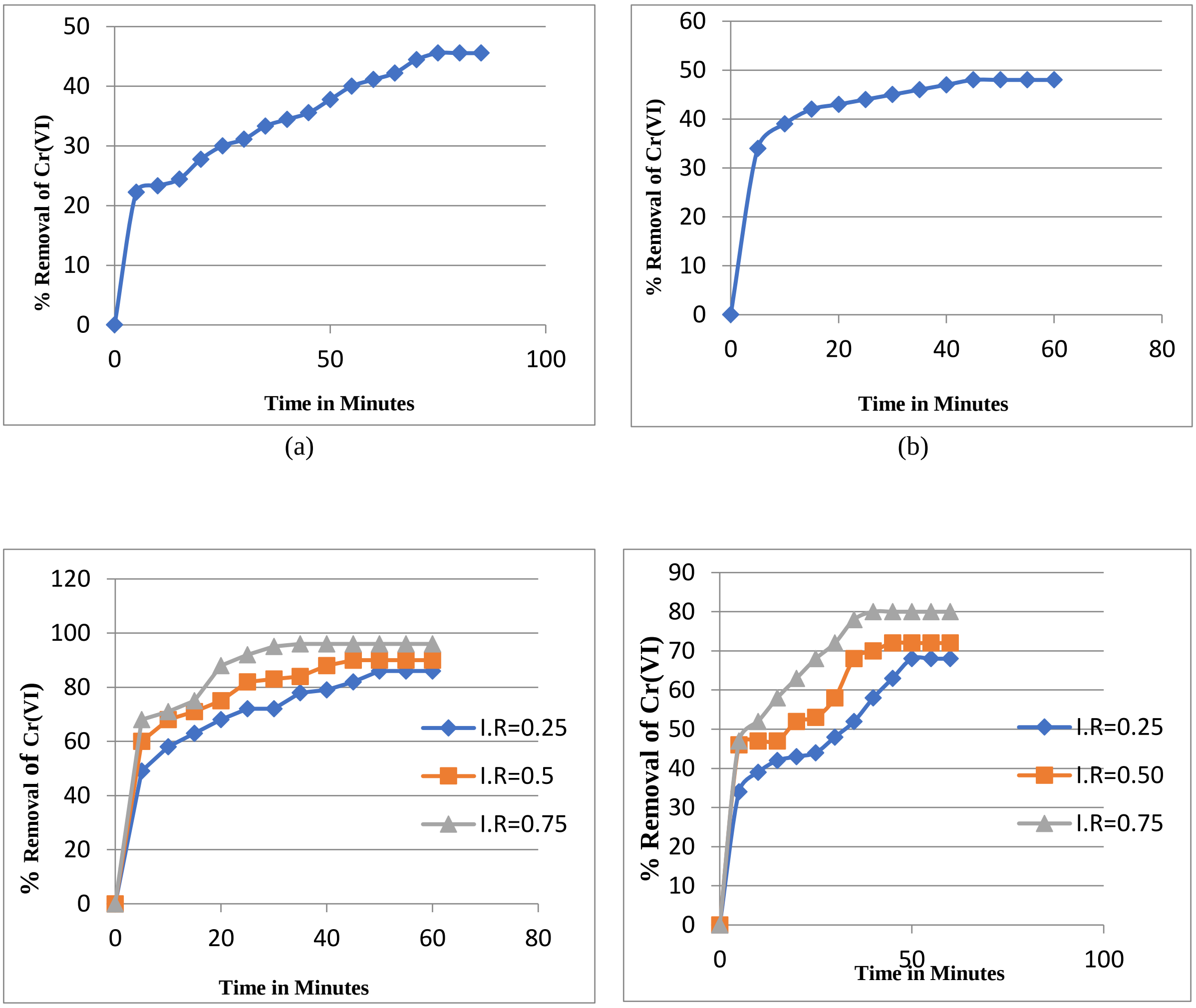
**Results and Discussion**

The effectiveness of Cr(VI) removal has been investigated in terms of the following factors:

a) contact time,
b) dose, and
c) pH.

*Contact Time response on Adsorption:*

At room temperature, the effect of contact time on the adsorption of commercial activated carbon for Cr(VI) and physically and chemically activated (MgCl2 & ZnCl2) carbon produced from Mangifera Indica fruit seed shells is shown in below figures. In the figure it is noted that in the beginning of adsorption, Cr (VI) removal rate is high and the amount adsorbed grew with contact time until it reached equilibrium. The adsorption of Cr(VI) was quick at first due to the presence of active sites on the outer surfaces, but after the saturation of active sites, Cr(VI) entered the micro pores of the adsorbent at a slower rate to reach the equilibrium time [9]. The fruit seed shell of Mangifera Indica was impregnated with I.R. 0.25, 0.50, and 0.75, as demonstrated in figure 1.



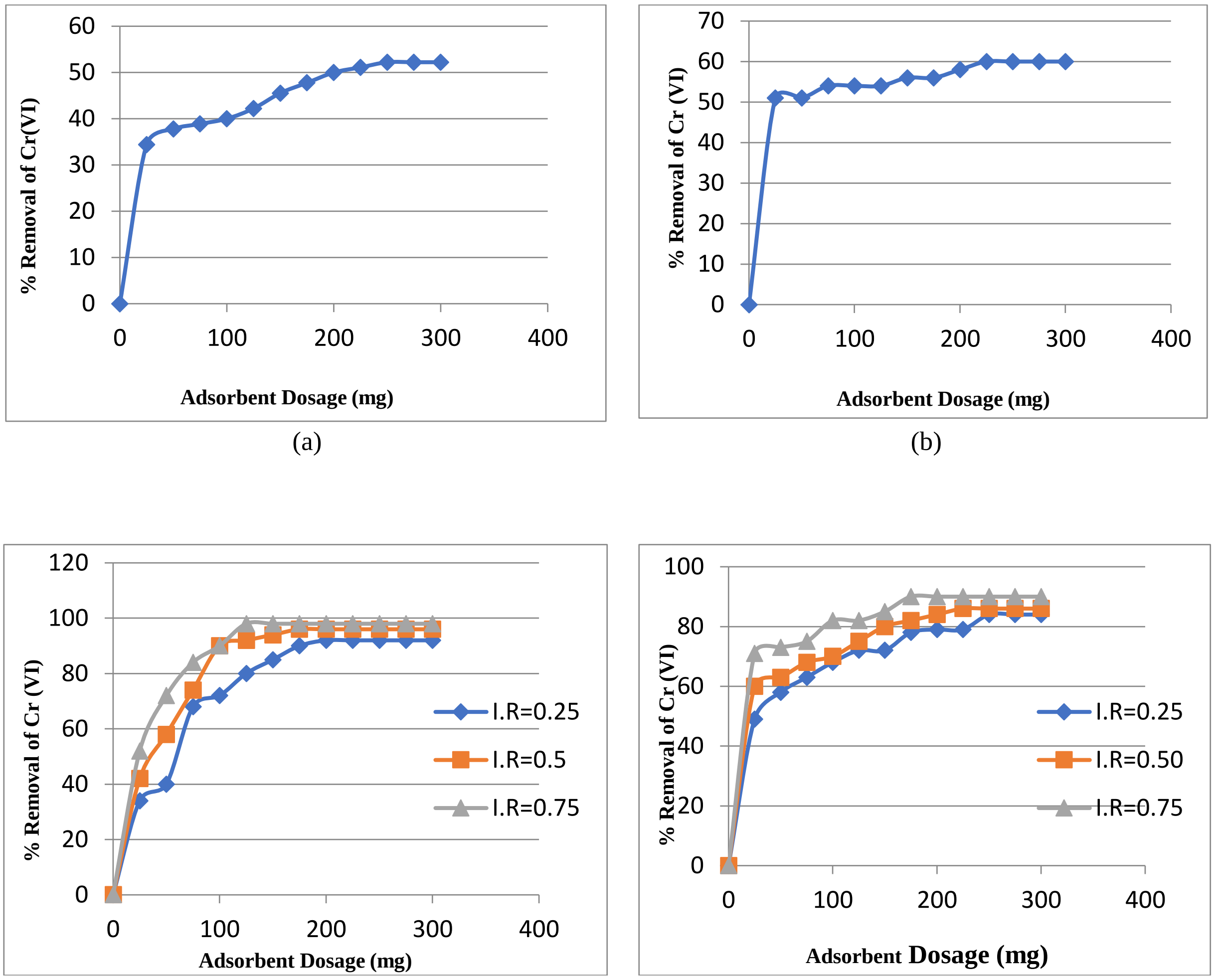
(a) (b)

(c) (d)

Fig.1 Contact time response on Adsorptionby (a) Commercially available Activated Carbon (b) Physically Activated Carbon and (c) Chemically ($MgCl_2$) Activated Carbon, and (d) Chemically ($ZnCl_2$) Activated Carbon by varied Impregnation ratio.

*Impact of adsorbent dosage:*

The effect of adsorbent dosage has been investigated, and a graph showing % of residual Cr (VI) removal versus dosage is presented in figure 2. As the carbon dosage increases, the amount of residual chromium reduces dramatically and reaches equilibrium, as seen in the graph. The dosage that achieves maximal removal is referred to as the optimum dosage. After then, even after increasing the carbon dosage, there isn't much of a difference.



(a) (b)

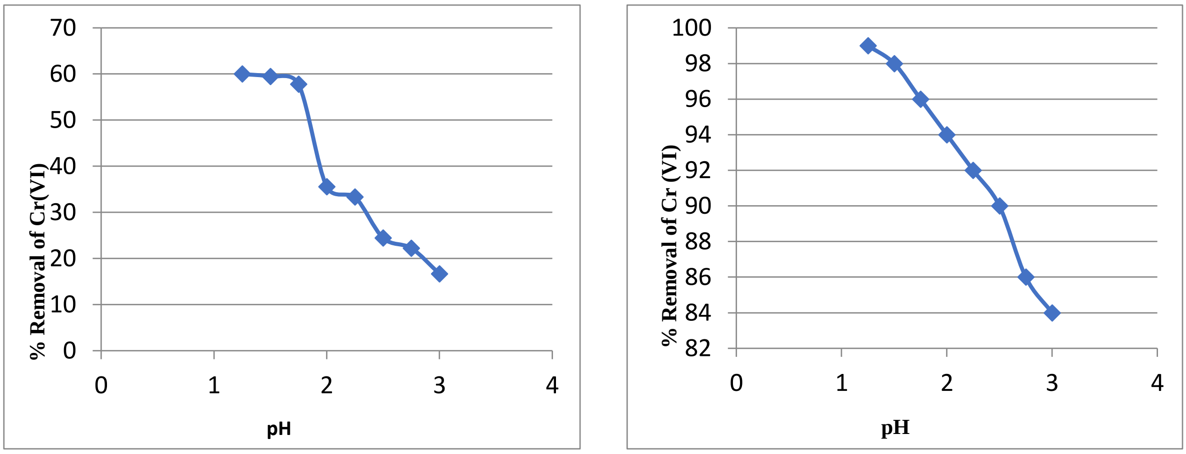
(c) (d)

Fig.2. (a) Impact of Adsorbent Dosage on Adsorption/ Cr (IV) removalby,(a) Commercially available Activated Carbon (b) Physically Activated Carbon and (c) Chemically ($MgCl_2$) Activated Carbon, and (d) Chemically ($ZnCl_2$) Activated Carbon by varied Impregnation ratio.

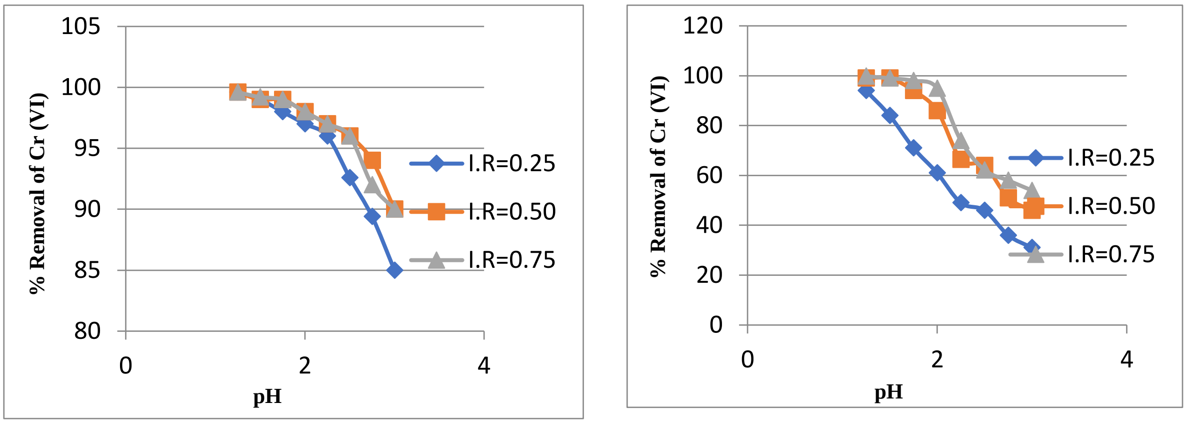
*Influence of pH on Cr (VI) removal:*

pH in the solution plays a significant role and in adsorption process of Cr(VI) using activated carbons. [10]examined the removal of Cr(VI) from coconut shell activated carbons at pH levels ranging from 2.0 to 8.0 and found the significant fall of adsorption rate with the elevation of pH level, recording peak of adsorption at pH 2.0 similar case study is investigated and evident by [11], [12]

Efficacy of adsorption in the process of eliminating hexavalent chromium by domestically developed activated carbon and commercially available activated carbon at different pH levels has shown its direct influenceby the pH of the solution, as illustrated in figure 3. In the acidic range, Cr (VI) is eliminated more effectively, as seen in the figure. Adsorption of Cr(VI) by activated carbons made from coconut coir[13], burnt rubber of tyres, tea waste, coconut husk[14], [15], treated oil palm fibers[16], and hazelnut shells has been observed[17]. Due to the precipitation of carbon surface by nucleation, the removal efficiency falls significantly with the raise of pH[18], [19].



(a) (b)



(c) (d)

Fig.3 (a) Influence of pH on Removal of Cr (IV) by(a) Commercially available Activated Carbon (b) Physically Activated Carbon and (c) Chemically ($MgCl_2$) Activated Carbon, and (d) Chemically ($ZnCl_2$) Activated Carbon by varied Impregnation ratio.

*Sorption Kinetics*

Sorption kinetics of Cr(VI) removal was studied at room temperature by specifically varied time intervals of adsorption. Figures 4, 5, 6, and 7 show the plots that resulted. Table 1 shows the calculated and graphical values of K for prepared carbon. Rate constant for the first order reaction can be evaluated by:

$$K = (2.303 / t) \times (\log_{10} a / (a-x))$$

Where a = initial concentration of the Cr(VI)
x = amount of Cr(VI) adsorbed at any time ‘t’
(a-x) = Hexavalent Cr residue
K = rate constant

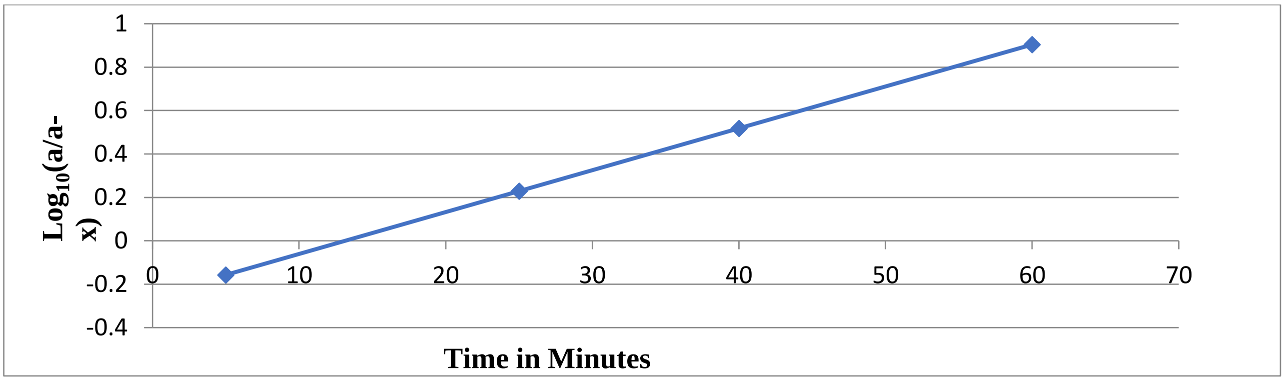


Fig., 4 Reaction Rate Constant for Commercial Activated Carbon

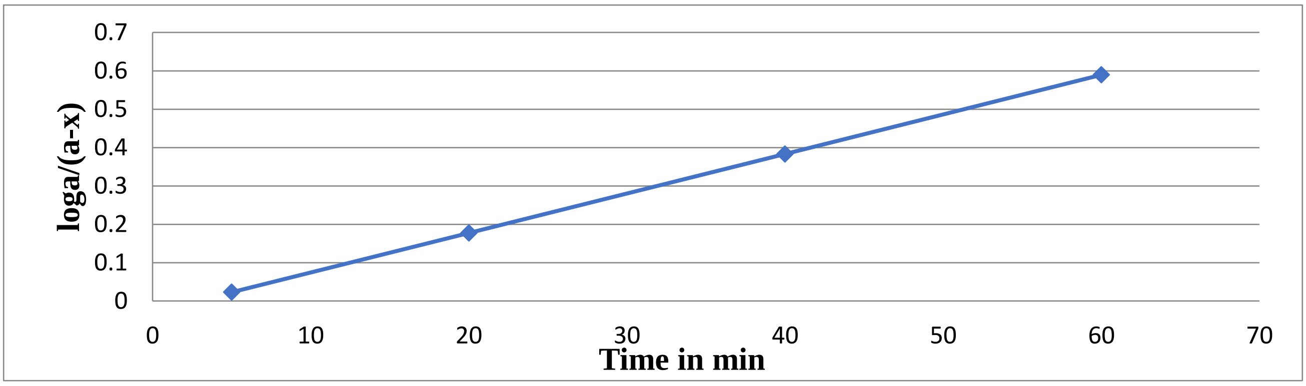


Fig., 5 Reaction Rate Constant for Physically Activated Carbon

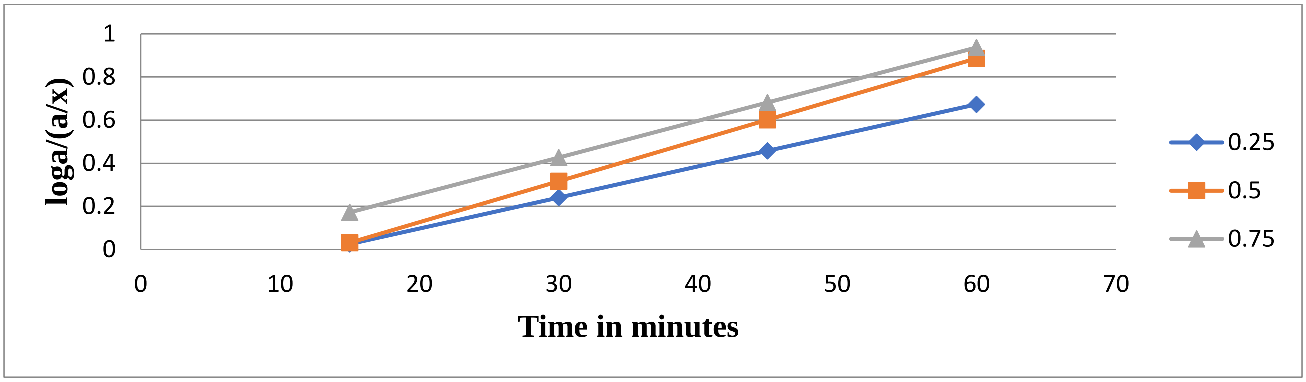


Fig., 6 Reaction Rate Constant for Chemically ($MgCl_2$) Activated Carbon at different IR

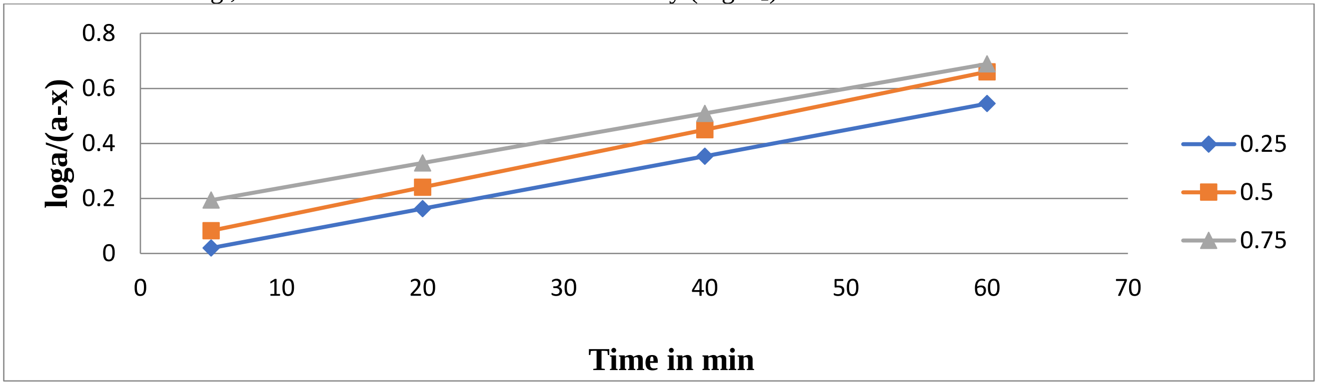


Fig., 7 Reaction Rate Constant for Chemically ($ZnCl_2$) Activated Carbon at different IR

**TABLE- 1** REACTION RATE CONSTANTS FOR VARIOUS ACTIVATED CARBONS AT DIFFERENT IMPREGNATION RATIOS

| Category of Activated carbon | I.R. | 'K' values from calculation | 'K' values from graph |
|---|---|---|---|
| 1. Commercial Activated carbon | - | 0.0444 | 0.021 |
| 2. Mangifera Indica fruit seed shell Physically activated carbon | - | 0.023 | 0.022 |
| 3.Chemically activated carbon<br>a) ($MgCl_2$) | 0.25 | 0.0322 | 0.0151 |
| | 0.50 | 0.043 | 0.020 |
| | 0.75 | 0.0391 | 0.032 |
| b) ($ZnCl_2$) | 0.25 | 0.0313 | 0.0207 |
| | 0.50 | 0.029 | 0.023 |
| | 0.75 | 0.0378 | 0.0207 |

*PORE DIFFUSION:*

Pore diffusion rate can be determined by,

$$C / C_0 = K_p x\ t^{1/2}$$

Where,

C = Concentration of sorbate at any time "t" in (hr)

$C_0$ = Initial concentration of sorbate in mg/L

t = Time taken for sorption

$K_p$ = Rate of pore diffusion

The plot of $C / C_0$ Vs $t^{1/2}$ for Cr(VI) is shown in figure 8, 9, 10 and 11 which is straight line graph. The calculated and graphical values of $K_p$ for prepared carbon are shown in table 2.

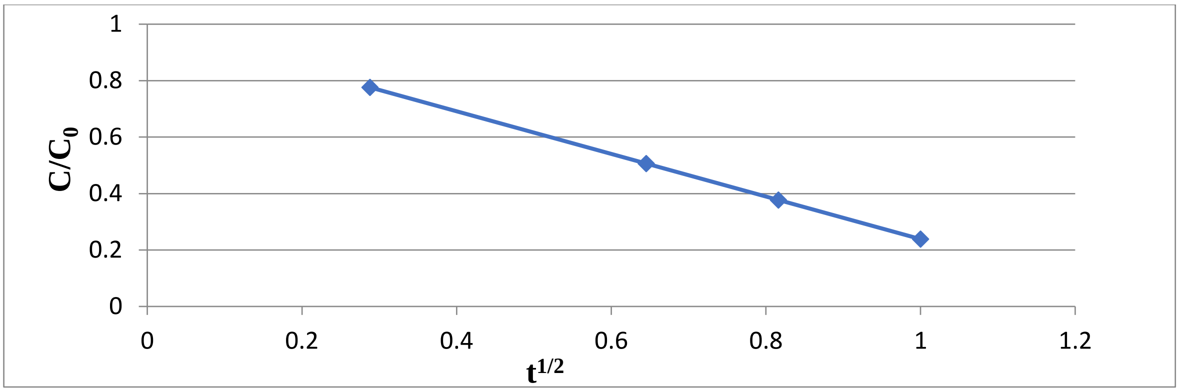


Fig., 8 Webber and Morris Plot of Commercial Activated Carbon

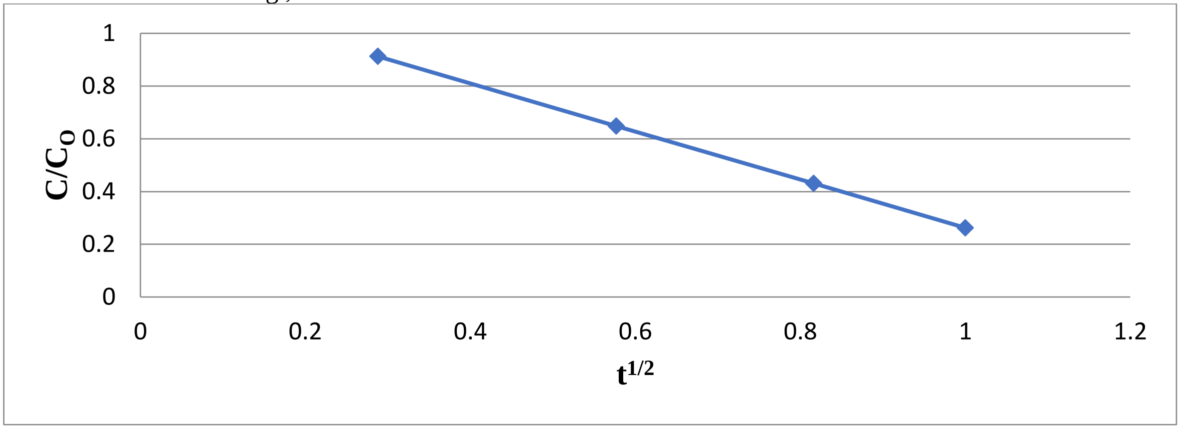


Fig., 9 Webber And Morris Plot of Physically Activated Carbon

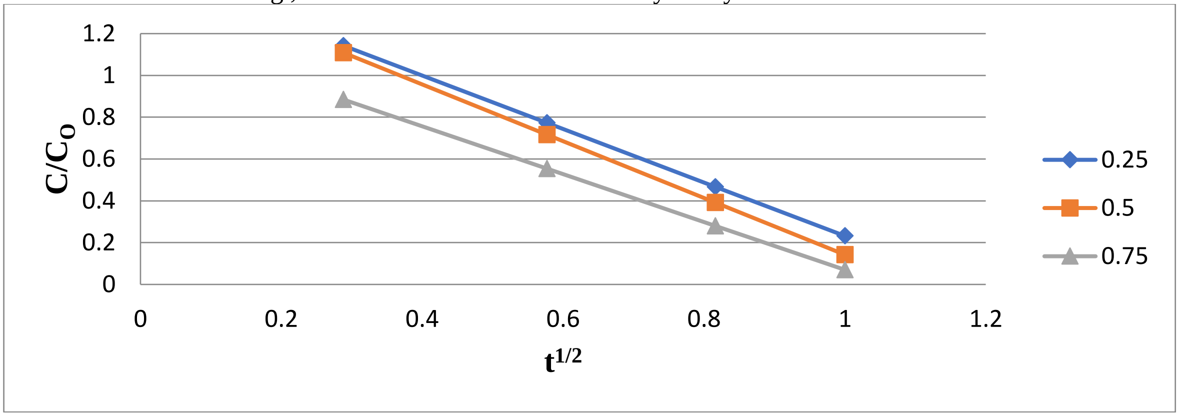


Fig. 10 Webber and Morris Plot of Chemically ($MgCl_2$) Activated Carbon at different IR

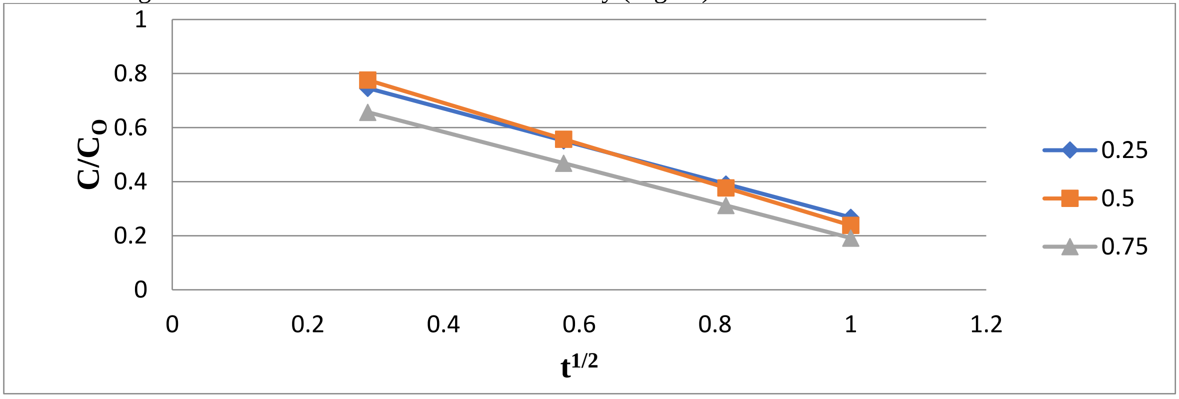


Fig. 11 Webber and Morris Plot of Chemically ($ZnCl_2$) Activated Carbonat different IR

TABLE- 2 “Kp” VALUES FOR PREPARED CARBON

| Type of carbon | I.R. | ‘$K_p$’ values from calculation | ‘$K_p$’ values from graph |
|---|---|---|---|
| 1. Commercial Activated carbon | - | 0.706 | 0.896 |

| | | | |
|---|---|---|---|
| 2. Mangifera Indica fruit seed shell Physically activated carbon | - | 0.985 | 1.190 |
| 3.Chemically activated carbon c) (MgCl$_2$) | 0.25 | 1.151 | 1.256 |
| | 0.50 | 1.054 | 1.173 |
| | 0.75 | 0.825 | 0.968 |
| d) (ZnCl$_2$) | 0.25 | 0.830 | 1.056 |
| | 0.50 | 0.850 | 0.965 |
| | 0.75 | 0.719 | 0.902 |

*Sorption Equilibrium*

Sorption equilibrium isotherms can be used to calculate the quantity of sorbent necessary to remove a specific amount of sorbate from a solution.

Freundlich and Langmuir isotherms are the most commonly used equations for presenting adsorption data.Freundlich Isotherm

The Freundlich equation was used to describe the adsorption analytical results. Over a moderate range of adsorbate concentrations, its empirical result fits quite well with the Langmuir equation and experimental evidence. The equationis used to represent it.

$$\log x/m = \log K + 1/n \log C$$

whereC is the Equilibrium concentration (mg/L), x/m is the quantity absorbed per unit mass of Mangifera Indica fruit seed shell activated Carbon or commercial activated carbon (mg/g), n is the favorability indicator, and K is the adsorbent's capacity. log x/m vs log C plot is linearly proportional, hence resultantslope of 1/n is observed with the interceptlog K [20], [21].

Figures 12, 13, 14, and 15 show the various plots. Table 3 shows the computed K values and n values for commercial activated carbon and Mangifera Indica fruit seed shell activated carbon, indicating favorable adsorption process of Cr(VI) on both Mangifera Indica fruit seed shell activated Carbon and commercial activated carbon. Similar studies and respective outcomes are observed by [22], [23]

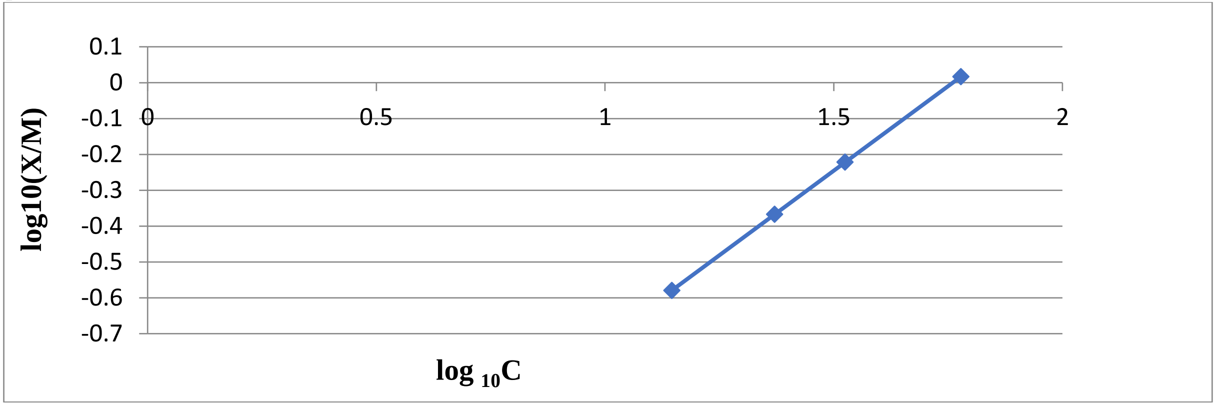


Fig. 12 Freundlich Isotherm for Commercial Activated Carbon

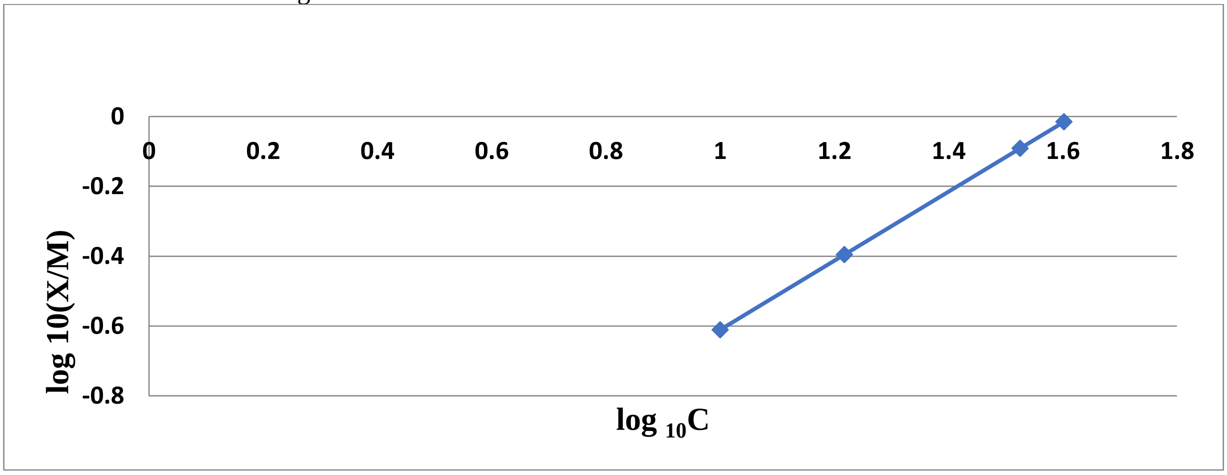


Fig. 13 Freundlich Isotherm for Physically Activated Carbon

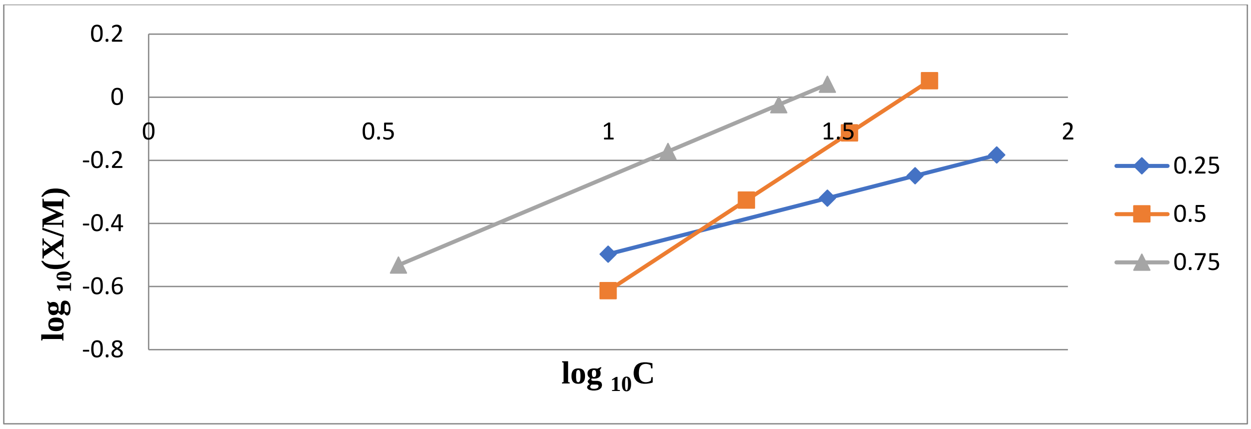


Fig. 14 Freundlich Isotherm for Chemically ($MgCl_2$) Activated Carbon

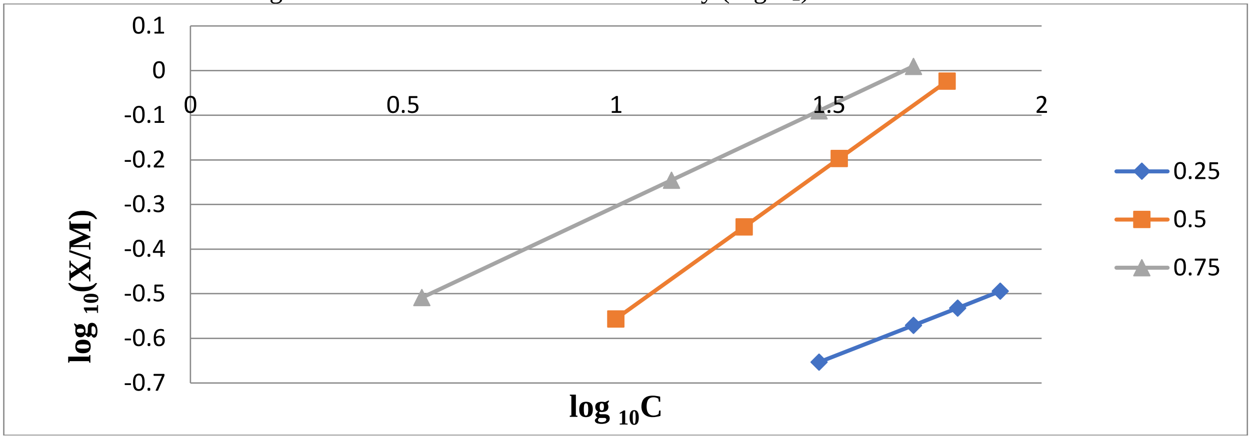


Fig. 15 Freundlich Isotherm for Chemically ($ZnCl_2$) Activated Carbon

*Langmuir Isotherm*

Langmuir proposed a new Adsorption Isotherm, the Langmuir Adsorption Isotherm, in 1916. According to the Langmuir isotherm model, the adsorption sites are equally identical and the adsorbed molecules are not enticed to one another, resulting in a monolayer of molecules being deposited on the adsorbent [24]

This isotherm is rooted on a number of hypotheses, one of which is that adsorbed and free gaseous molecules are in a dynamic equilibrium.

The Langmuir equation is usually written like this:

$$\frac{C}{x/m} = \frac{1}{ab} + \frac{C}{a}$$

Webber and Chakarvarthi defined,.

$$R = \frac{1}{(1+a)C_0}$$

This equation is a dimensionless parameter known as equilibrium parameter or separation factor [25], [26]

The parameters provided by Webber and Chakarvarthi showing the form of the isotherm from the equation above are as follows.

| **R Value** | **Type of isotherm** |
|---|---|
| R>1 | Unfavourable |
| R=1 | linear |
| 0<R>1 | favourable |
| R=0 | irreversible |

Figures 16, 17, 18, and 19 illustrate the linearised Langmuir isotherm [C / (X/M) against C] for various adsorbents.

The slope and intercept of the above graphs are used to evaluate 'a' and 'b.' Least square analysis can be used to verify this, and the graphical results are shown in table 3.

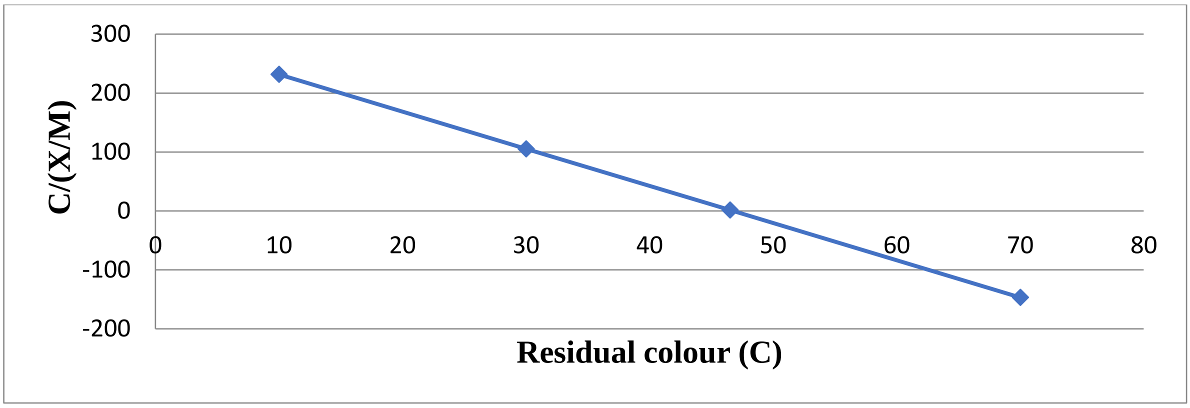


Fig. 16 Langmuir Isotherm for Commercial Activated Carbon

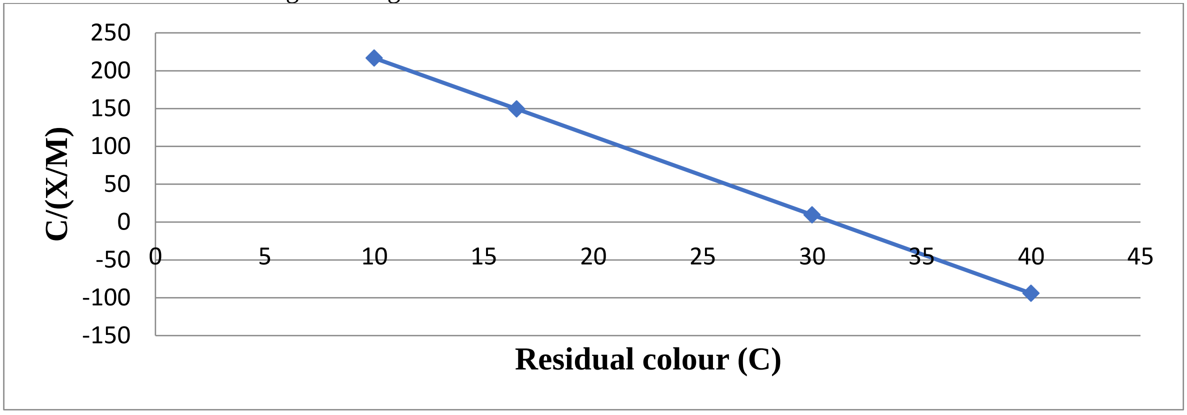


Fig. 17 Langmuir Isotherm for Physically Activated Carbon

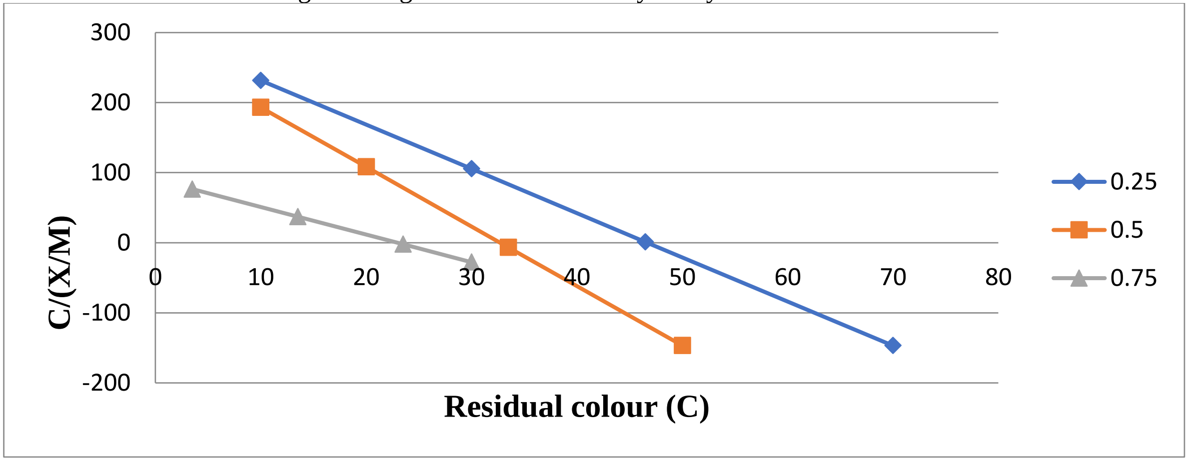


Fig. 18 Langmuir Isotherm for Chemically ($MgCl_2$) Activated Carbonat different IR

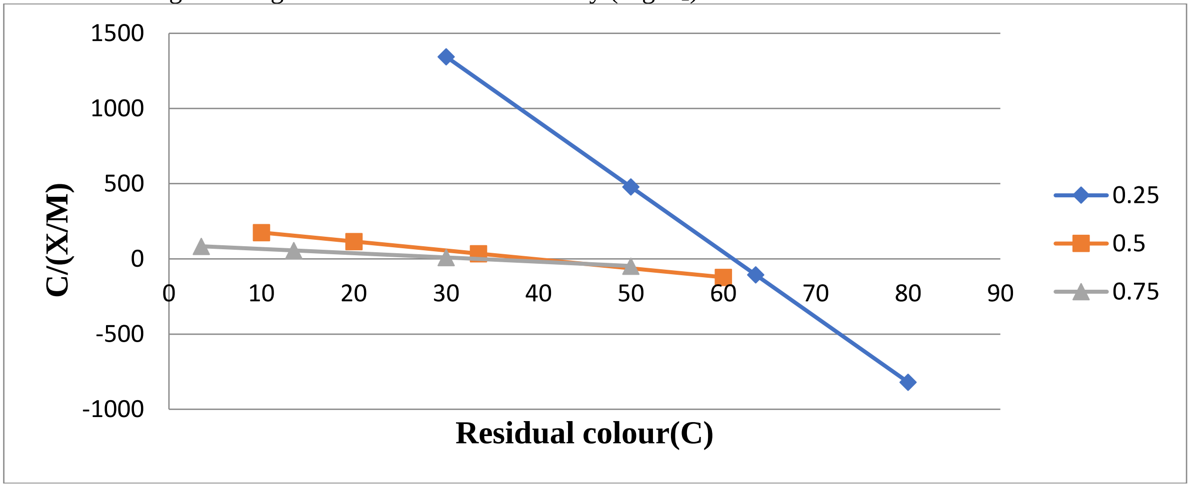


Fig. 19 Langmuir Isotherm for Chemically ($ZnCl_2$) Activated Carbonat different IR

Table 3 Comparison of Freundlich and Langmuir Isotherms constants for the Cr (VI) adsorption on Mangifera Indica fruit seed shell and commercial activated carbon samples

| Isotherm Parameters | Commercial Activated Carbon | Physically Activated Carbon | Chemically Activated Carbon | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Magnesium Chloride ($MgCl_2$) | | | Zinc Chloride ($ZnCl_2$) | | |
| | | | I.R 0.25 | I.R0.5 | I.R0.75 | I.R0.25 | I.R0.5 | I.R0.75 |
| Freundlich Isotherm | | | | | | | | |
| 1/n | 0.9430 | 0.989 | 0.371 | 0.952 | 0.614 | 0.373 | 0.684 | 0.449 |
| K | 0.0218 | 0.025 | 0.135 | 0.027 | 0.136 | 0.062 | 0.057 | 0.176 |
| Langmuir Isotherm | | | | | | | | |
| Constant a | -0.146 | -0.096 | -0.158 | -0.117 | -0.253 | -0.023 | -0.168 | -0.354 |
| b | -0.018 | -0.032 | -0.021 | -0.030 | -0.043 | -0.016 | -0.025 | -0.030 |
| R | 0.0130 | 0.0122 | 0.0131 | 0.0125 | 0.0148 | 0.0113 | 0.0133 | 0.0170 |

## Conclusion

Activated Carbon derived from Seed shell of Mangifera Indica fruit exhibit the excellent adsorption properties for the removal of hexavalent Chromium from aqueous solution.Mangifera Indica fruit seed shell activated carbon has a better removal effectiveness than commercial activated carbon. It's also widely available as a waste product that can be treated to substitute for commercial activated carbon. Data kinetics analysis revealed that the adsorption follows pseudo first order kinetics. The appropriateness of the Freundlich and Langmuir isotherms for each carbon was also studied, indicating that Cr(VI)adsorption is favorable.

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