

## Removal of Chromium (VI) from aqueous solutions using chemically activated Syzygium cumini leaves carbon Powder as an adsorbent

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**Abstract:-** With the inception of industrialization mankind has witnessed various environmental issues in the society. This industrialization has not only brought development and prosperity but eventually troubled the ecology. One of the impacts is visible, in form of water pollution. Hexavalent chromium is considered as a severe environmental pollutant through industries. Studies using adsorbents for controlling Chromium (VI) is the main stream of research on pollution control methods. This study is aimed at utilizing Chemically activated syzygium cumini Leave carbon(CASLC) as low cost adsorbent material for removal of Cr-(VI) from aqueous solution. Investigations have been made to optimize various physico chemical parameters such as pH, adsorbent dosage, initial chromium concentration and contact time with a particle size of the adsorbent is 90 for the maximum removal of chromium (VI) from the aqueous solution on batch technique. Maximum adsorption (96%) was observed at room temperature under acidic condition of pH 3-4 with a contact time of 90 minutes and maximum amount of adsorbent dosage is 1gm per 50 ml of 100ppm chromium (VI) solution. Freundlich and Langmuir adsorption models are performed and adsorption isotherm model reveals that langumuir model is fit and indicates the adsorption on the surface of the adsorbent is unilayered. Based on these investigations activated Syzygium Cumini leaves carbon powder can be used as a low cost alternative and remarkably successful in removing the Chromium (VI) from industrial effluents and aqueous solutions.

**Keywords:** Hexa-valent Chromium , Removal, adsorption, Syzyium cumini leaves.

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### I. Introduction

Water is universally most abundant, important and widespread compound in nature and is required for sustaining of all forms of living organisms, production of food, economical development of industry. The presence of heavy metals like Chromium, lead, Mercury, Arsenic surface water and ground water is becoming a harsh environmental problem and people's health problem. Heavy metals contamination of surface water occurs due to a more industries like tanneries, Cement industry, metal plating, Nuclear Power-plants, alloy industries, storage battery industries, etc[1]. Chromium is released into the environment from natural processes like weathering of rocks and by volcanic activity [2]. Chromium VI compounds are most harmful water pollutant getting from industries like Mining industry, Leather Tanning industry, Production of steel and other metal alloys industry, Photographic material and corrosive paints[3]. Chromium ion in industrial wastewater occurs in two forms; trivalent Cr(III) ion and hexa-valent Cr(VI) ion. Trivalent chromium is not toxic but when disposed from the sources of industries as in the form of liquid effluents Cr(III) can be oxidised to ChromiumVI. The ChromiumVI is 500 times high toxic nature than Cr(III) . It is more toxic to Human beings, animals and plants. Human toxicity includes lung cancer as well as kidney, liver, and gastric damage[4]. Cr(VI) concentrations in industrial waste waters range from 0.5 to 270.000 mg/l. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/l and in potable water is 0.05 mg/l[5]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) to acceptable levels. So assurance of safe water for drinking is a key point for the prevention of waterborne diseases [6,7]. Various technical methods are well known for removal of chromium(VI) like ion exchange, precipitation, reverse osmosis etc. but these methods have a lot of drawbacks like a more amount of toxic sludge are formed, incomplete Cr(VI) removal and more energy requirements. An adsorption technique [8] by using an adsorbent is a low cost method for

removal of Cr(VI) in water [9]. Adsorption using cheaper cost adsorbent materials are highly more effective. Studies have been carried out using different naturally available materials for chromium removal. Low cost adsorbents have been developed using coconut fiber.[10] Hevea brasiliensis saw dust activated carbon [11]. Neem Saw dust[12], Rice husk carbon [13]. Chemically Activated Carbon of Hibiscus rosa-sinensis Flowers[14]. Leaves Powders of Justicia adhatoda, Cissus quadrangularis, Soapnut Acacia[15].

Adsorption using activated carbon is found to be highly effective due to the higher surface area of the carbon which enhances the adsorption capacity [16]. Removal efficiency depends on surface area and will be higher for higher surface area [17]. By using Syzygium cumini seed carbon is most effective material for removal of Cr(VI) from waste water[18]. Literature survey reveals that in most of the peer reviewed journals, the adsorption study of Cr (VI) with Syzygium cumini Leaves powdered carbon as an adsorbent has not been investigated and present work is a brief study of adsorption characteristics of Syzygium cumini Leaves powdered carbon towards Chromium(VI) in developing a simple and versatile procedures for its removal.

## **ii. Materials And Methods**

### **2.1. Objective of the Study**

The main objective of present studies is to investigate the adsorption behaviour of Cr<sup>6+</sup> ions on to chemically activated syzygium cumini Leaves carbon powder (CASLC). Main parameters considered are variation of pH, contact time, Initial chromium(VI) ion concentration and adsorbent dose during removal of Cr<sup>6+</sup> using natural adsorbent by adsorption technique with Batch mode experiments.

### **2.2. Plant Description**

*Syzygium cumini*, known as jambul, or jamun, is a tropical tree in the flowering plant family Myrtaceae. It is native to the Indian Subcontinent [19] It is a slow growing species, it can reach heights of up to 30 m and can live more than 100 years. The leaves (Fig.1) which have an aroma similar to turpentine. The leaves are used as food for livestock, as they have good nutritional value.

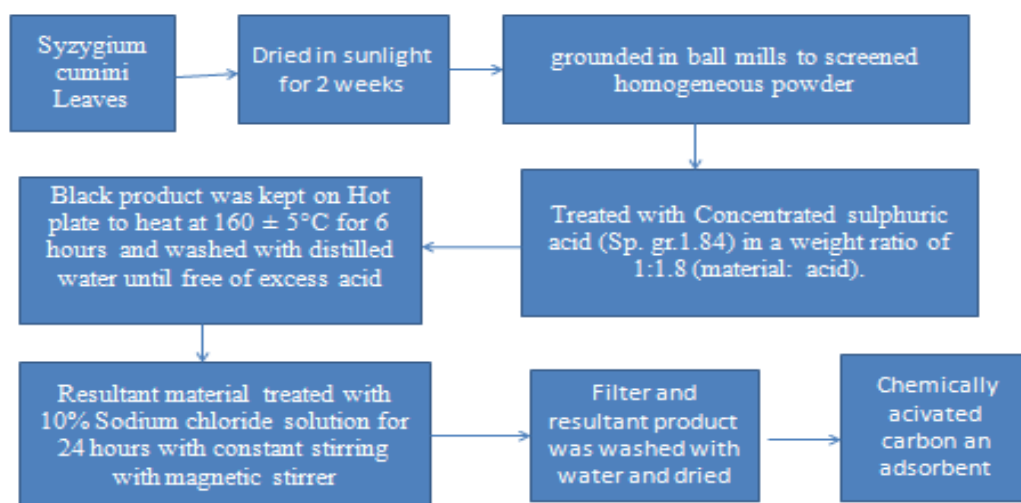


**Fig.1** Syzygium cumini leaves

### **2.3. Preparation of Chemically activated Syzygium cumini leaves carbon (CASLC)**

Syzygium Cumini leaves were collected from the local area and washed repeatedly with triple distilled water to remove dust and soluble impurities. It was dried in natural sunlight for about two weeks after that the syzygium cumini leaves were grounded in to powder. Then the powder is treated with concentrated sulphuric acid (Sp. gr.1.84) in weight ratio of 1:1.8 ( syzygium cumini leave powder: sulphuric acid). Now the resultant product is heated at  $160 \pm 5$  °C on hot plate for 6 hours and followed by washing with triple distilled water continuously until h free from acid. After that the sample is dried at  $105 \pm 5$  °C. The dried black coloured sample was treated with 10% sodium chloride solution and stirring with magnetic stirrer for 24 hours. Filter the whatmann filter paper and the resultant material was wash seeral times with triple distilled water and dried at  $105 \pm 5$  °C. Finally grind it in to required particle size of 90µm.

## Adsorbent Preparation:



### 2.4. Preparation of Cr(VI) Solution

All the chemicals used were of analytical reagent grade. The standard stock Cr (VI) was prepared by dissolving 2.83 g of  $K_2Cr_2O_7$  in 1000 ml of distilled water. For working solutions it was further diluted to desired concentrations ranging as 20,40,60,80 and 100 mg/L by diluting desired quantity of the above stock solution. The pH was adjusted using Hydro chloric acid and sodium hydroxide.

### 2.5. Batch experiments

The experiments were carried out in conical flasks by agitating a different weighed amount of Chemically activated powdered adsorbent of *Syzygium Cumini* leaves carbon(CASLC) with the aqueous chromium (VI) ion solutions for a predetermined period. The CASLC doses were maintained 0.25 to 1.5 gm per 50ml of 100ppm Cr(VI) and all the samples were mechanically agitated at 250 rpm for different experiments carried out under room temperature. The adsorbent was filtered using whatman filter paper ( no 41) and to the filtrate the concentration of Cr(VI) ion was measured by UV-Visible double beam spectrophotometer. The effect of pH, the effect of adsorbent dosage, effect of the time duration were also studied in the same manner. The removal percentage (R %) of chromium was measured:

$$R (\%) = [(C_i - C_e) / C_i] \times 100$$

Where  $C_i$ - initial concentration of chromium(VI) ion in the solution.  $C_e$ - final concentration of chromium(VI) ion in the solution

The amount of Cr(VI) metal ions adsorbed per unit mass of the adsorbent was evaluated by using the following equation

$$(Q_e) = \frac{C_0 - C_e}{m} \times V, C_0 \text{ and } C_e \text{ are initial and remaining concentration of Cr(VI) ion solution (mg /L), } m \text{ (g) is the dry weight of adsorbent and } V \text{ is the volume of Chromium(VI) ion solution(L).}$$

## iii. Results And Discussion

### 3.1)Effect of Adsorbent Dose:

The experiments carried out with 50 mL of 100 mg/L Cr(VI) solutions for predetermined time period of 90 minutes and pH of 3.5 were taken and experiments were carried out at different dosages from 0.25gm to 1.5 gm .All the samples were mechanically agitated at 250 rpm under room temperature. The adsorbents of each sample was filtered using whatman filter paper ( no 41) and to the filtrate the concentration of Cr(VI) ion was measured by UV-Visible double beam spectrophotometer at 540 nm wavelength . The optimum removal of Cr(VI) ions was at 1gm that can shown in the Fig.2. and amount of Cr(VI) ion uptake as shown in Fig.3.

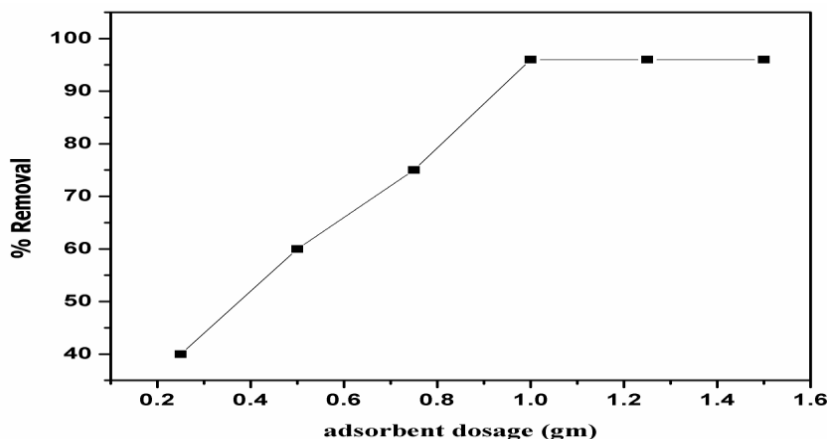


Fig.2. The effect of adsorbent dosage Vs % removal of Cr(VI) ion

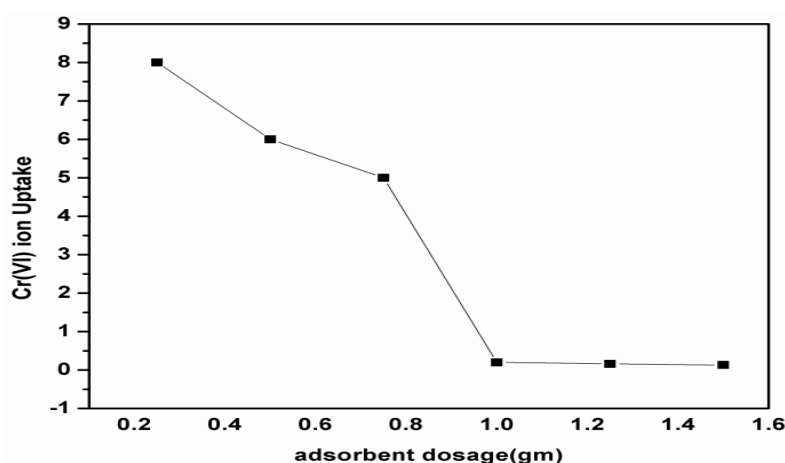


Fig.3. The effect of the adsorbent dosage Vs Cr(VI) ion Uptake on the surface of the adsorbent

### 3.2) Effect of Contact Time:

The experiments carried out with 50 mL of 100 mg/L Cr(VI) solutions for predetermined adsorbent dose of 1.0 g and pH of 3.5 were taken and experiments were carried out at different time intervals from 30 minutes to 120 minutes. All the samples were mechanically agitated at 250 rpm under room temperature. The adsorbents of each sample was filtered using whatman filter paper (no 41) and to the filtrate the concentration of Cr(VI) ion was measured by UV-Visible double beam spectrophotometer at 540 nm wavelength. The optimum removal was at time period of 90 minutes that can show in the Fig.4. and amount of Cr(VI) ion uptake as shown in Fig.5.

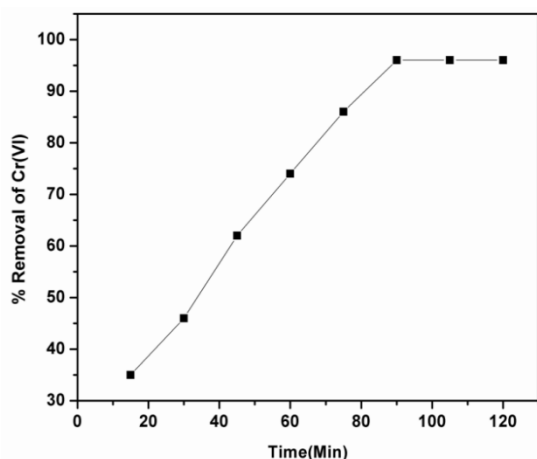


Fig.4. The Effect of Time (min) Vs % removal of Cr(VI) ion

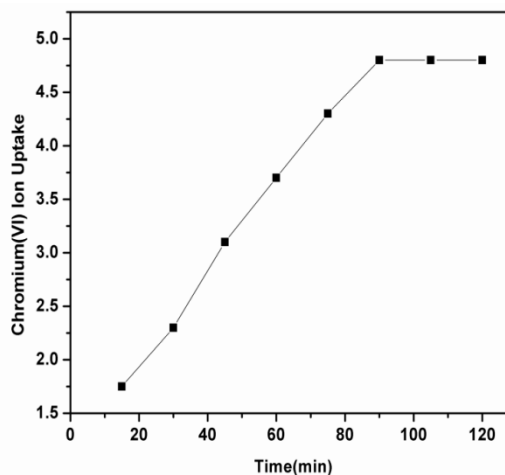
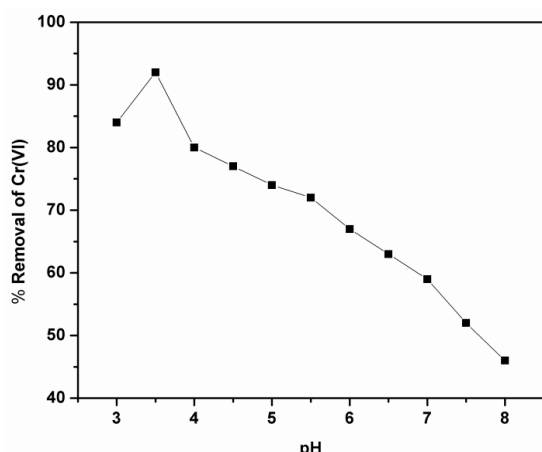


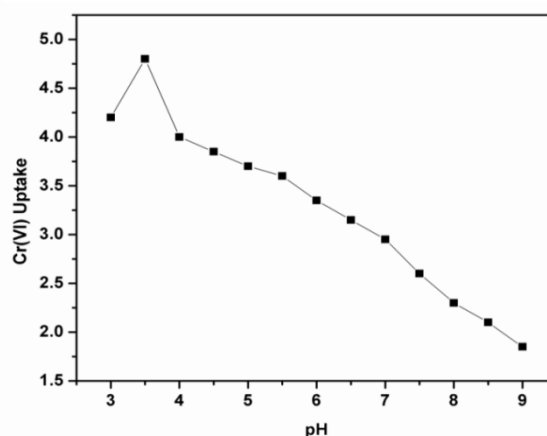
Fig.5. The Effect of time (min) Vs amount of Cr(VI) ion Uptake

### 3.3) Effect of pH:

The pH is the most important factors that influence the removal of Metal ions[20] like Cr(VI) ions from aqueous solutions by the adsorption process. The experiments carried out with 50 mL of 100 mg/L Cr(VI) solutions for predetermined time of 90 minutes and adsorbent dose of 1.0 g were taken and experiments were carried out at pH 3 to 7 and all the samples were mechanically agitated at 250 rpm under room temperature. The adsorbents of each sample was filtered using whatman filter paper ( no 41) and to the filtrate the concentration of Cr(VI) ion was measured by UV-Visible double beam spectrophotometer at 540 nm wavelength. The optimum pH for the maximum removal of Cr(VI) ion was at 3.5. The influence of pH on the adsorption capacity for the Cr(VI) ions is shown in Fig.6 and amount of Cr(VI) ion uptake as shown in Fig.7. It clearly shows that the prepared CASLC material was active enough in the acidic range, i.e., pH 3.5. There is a slight decrement in the adsorption capacity when pH is raises from 3.5 to 9.0. Similar adsorption studies were reported earlier by several workers [21]. The decrease in the adsorption of Cr(VI) ions with increase of pH was due to the decrease in the electrostatic force of attraction between the adsorbent and the Cr(VI) ions. In lower pH ranges, due to the high electrostatic force of attraction, the percentage of Cr(VI) removal is higher. A decrease in adsorption above pH 3.5 may be due to occupation of the adsorption sites by anionic species like  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$  etc., which retards the approach of such ions further toward the sorbent surface. Some amount of the Cr(VI) removal was also may due to ion exchange process, since the carbon material was treated with 10% Sodium chloride and hence there are some sodium ion which can entrapped on the adsorbent which can exchange the Cr(VI) ion in the solution.



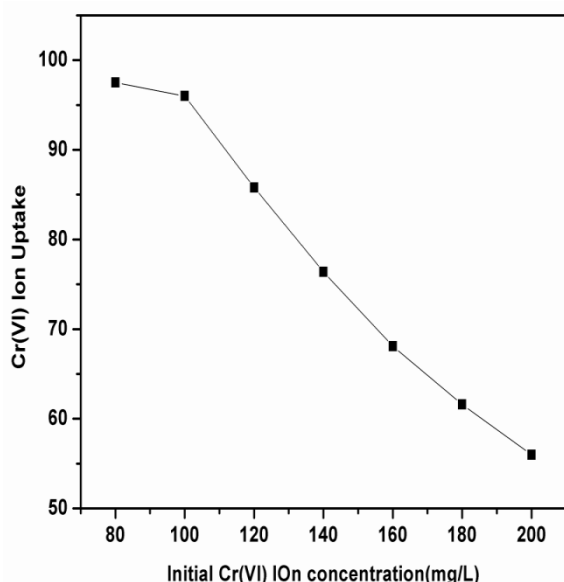
**Fig.6.** The Effect of Time (min) Vs % removal of Cr(VI) ion



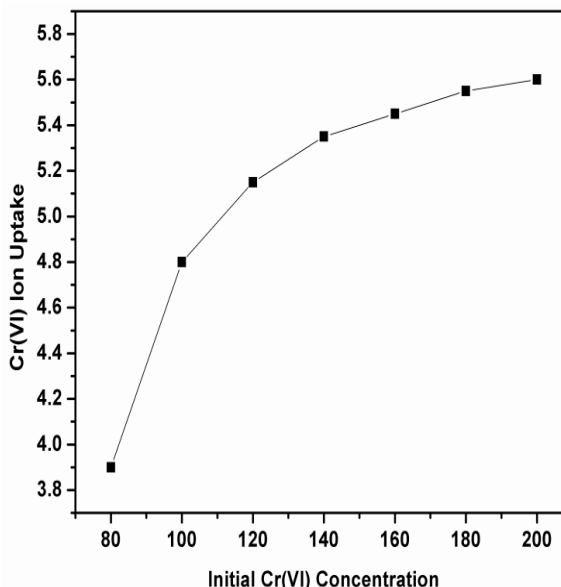
**Fig.7.** The Effect of Time (min) Vs % removal of Cr(VI) ion

### 3.4) Effect of Initial Chromium(VI) ion concentration:

By maintaining the optimum pH(3.50), time period of 90 minutes and adsorbent dosage (1gm), the adsorption capability of CASLC were investigated with varying of Cr(VI) ion concentration from 80 mg/L to 200 mg/L and all the samples were mechanically agitated at 250 rpm under room temperature. The adsorbents of each sample was filtered using whatman filter paper ( no 41) and to the filtrate the concentration of Cr(VI) ion was measured by UV-Visible double beam spectrophotometer at 540 nm wavelength. The experimental results (% removal of Cr(VI) ion Fig.8 and amount of Cr(VI) ion uptake as shown in Fig.9) clearly indicates that at 100mg/L Cr(VI) ion concentration, the maximum removal(96%) of Cr(VI) was observed. The removal of Cr(VI) ion was dependent on the initial concentration of Cr(VI) ions in solution. At lower concentrations, the Cr(VI) ions in the solution would interact with the binding sites and thus facilitated high adsorption, while with increasing Cr(VI) ion concentrations the specific sites are saturated and the exchange sites are filled[22]. This indicates that less sites are present to involved with increasing Cr(VI) ion concentrations in the aqueous solution.



**Fig.8.** The Effect of initial concentration of Cr(VI) Vs Cr(VI) % removal of Cr(VI) ion



**Fig.9.** The Effect of initial concentration of Vs amount of Cr(VI) ion uptake

### 3.5 Adsorption isotherms:

The adsorption isotherms gives the relation between the equilibrium amount of solute material on the applied adsorbent material and plays a vital role for predicting the adsorption capacity of the adsorbent[23]. The adsorption mechanism of Cr(VI) ions on the adsorbent was studied using Freundlich[24] and Langumier[25]. The Linear form of Freundlich isotherm rpresented as  $\log q_{eq} = \log K_f + 1/n_f \log C_{eq}$ , where  $Q_e$  is the amount of Cr(VI) ion adsorbed per unit weight of the adsorbent(mg/g) ,  $C_{eq}$  is the equilibrium concentration of adsorbate ( mg/L) and  $K_f$  ,  $1/n_f$  were the Freundlich constants .In the present study , plots of  $\log q_{eq}$  vs  $\log C_{eq}$  at different Cr(VI) ion concentration are found to be linear as shown in Fig.10 and obtained values of  $K_f$  and  $1/n_f$  are presented in Table.1 and its confirm the acceptance of freundlich isotherm model for the removal of Cr(VI) ion by the CASLC as an adsorbent.

The linear form of Langmuir equation is represented as  $\frac{1}{q_{eq}} = \frac{1}{q_{max}K_L C_{eq}} + \frac{1}{q_{max}}$

where  $Q_e$  is the amount of Cr(VI) ion adsorbed per unit weight of the adsorbent material(mg/g) ,  $C_{eq}$  is the equilibrium concentration of adsorbate ( mg/L) and the Langmuir isotherm constants are  $q_{max}$  and  $K_L$  respectively. In the present work, graphs of  $1/q_{eq}$  vs  $1/C_{eq}$  at different Cr(VI) ion concentration are found to be linear as shown in Fig.11 and Langmuir constants ( $q_{max}$  and  $K_L$ ) were determined from the slope and intercept of the linear plot of  $1/q_{eq}$  vs  $1/C_{eq}$ . and was presented in Table.1 The essentially and more important feature of

Langmuir isotherm form was defined by a separation factor  $R_L$  which was represented as  $R_L = \frac{1}{1 + K_L C_i}$ ,

where  $C_i$  is the initial Cr(VI) ion concentration(mg/L) and  $K_L$  is the Langmuir constant. The adsorption is unfavorable if  $R_L > 1$ , linear if  $R_L = 1$ , and favorable if  $R_L = 0 < R_L < 1$  or irreversible if  $R_L = 0$ . [26]. In the present work, the  $R_L$  value is 0.0078 which is less than unity represents the favorability of adsorption for removal of Cr(VI) ion. Moreover,  $R^2$  value of Langmuir model is 0.9717 which is greater than freundlich model  $R^2$  Value is 0.8677 and hence adsorption is well defined and fitted by Langmuir isotherm model. In summary the adsorption process is unilayered [27].

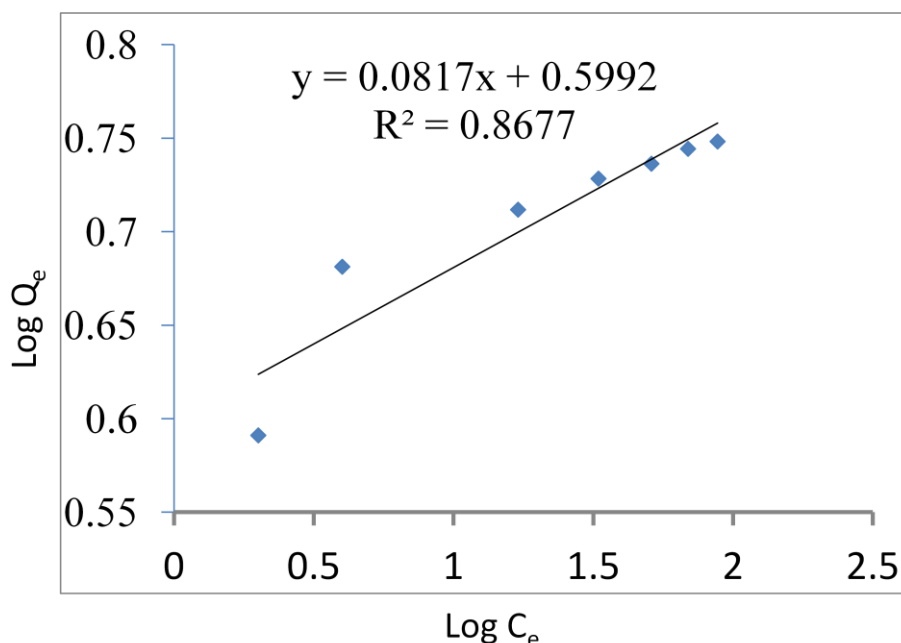


Fig.10. Freundlich curve(log Ce Vs Log Qe)

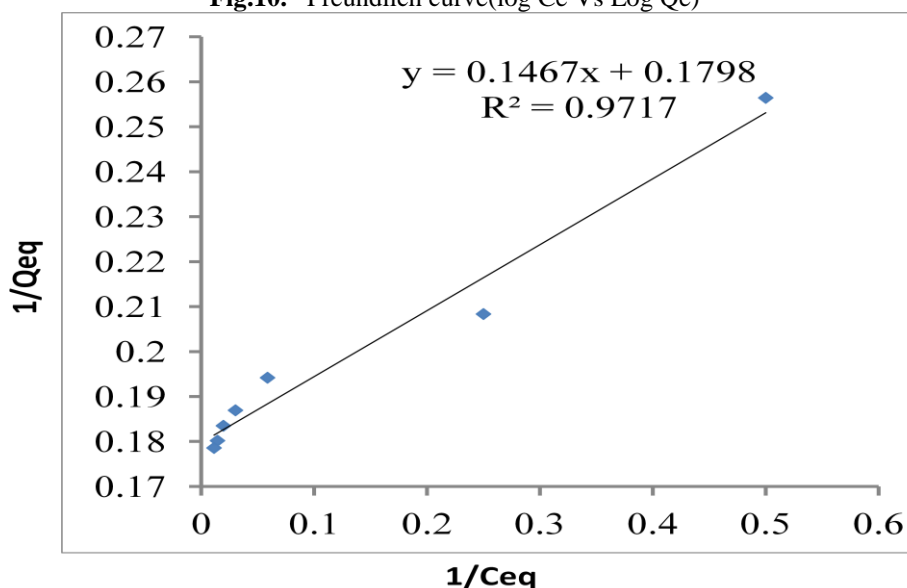


Fig.11 Langmuir curve( 1/Ce Vs 1/Qe)

Table.1 Freundlich and Langmuir Data

S.No	Adsorption Isotherm	Components	Value
1	Freundlich	$K_f$	3.9737
		$R^2$	0.8677
		$1/n_f$	0.0817
2	Langmuir	$K_L$	1.2256
		$R_L$	0.0078
		$R^2$	0.9717

#### IV. Conclusions

This study clearly indicated the advantage and applicability of CASLC as an adsorbent for the removal of Cr (VI) ion from aqueous solution. CASLC is to be the most effective material, for which the removal efficiency reached to 96% of Cr(VI) ion at room temperature and an adsorbent dose of 1gm/50ml of the Cr(VI) ion solution. The optimum value pH for the removal was found to be at 3.5. The optimum adsorbent dosage was found to be 1gm and optimum contact time was found to be 90 minutes for the 96 % removal of Cr(VI) ion.

Increasing in the initial Cr(VI) concentration, the Cr(VI) removal percentage decreases by keeping the other parameters like pH, amount of the adsorbent and period. The results obtained using two isotherm models: Freundlich & Langmuir were well described and the Langmuir model was well fit. So the adsorption process is homogenous and unilayered. Some amount of the Cr(VI) removal from solution was also may due to ion exchange process, since the carbon material was treated with 10% Sodium chloride and hence there are some sodium ions which can entrapped on the adsorbent and which can exchange the Cr(VI) ion in the solution. Hence there is a scope for further investigation by characterization techniques.

### References

- [1]. Vivek, N.N., Mahesh, G. Use of adsorption using granular activated carbon (GAC) for the enhancement of removal of chromium from synthetic wastewater by electro coagulation. *Journal of Hazardous Materials*. 161(2009) 575-580.
- [2]. Natale, F.D., Lancia, A., Molino, A., Musmarra, A. Removal of chromium ions from aqueous solutions by adsorption on activated carbon and char. *Journal of Hazardous Materials*. 145(3) (2007) 381-390.
- [3]. Umesh, K.G., Kaur, M.P., Dhiraj, S. and Garg, V.K. Removal of hexavalent chromium from aqueous solution by adsorption on treated sugarcane bagasse using response surface methodological approach. *Desalination*, 249(2) (2009) 475-479.
- [4]. US Department of Health and Human Services, 1991; Cieslak-Golonka, 1995.
- [5]. WHO, *Guidelines for Drinking-water Quality, Recommendations*, 3rd ed., WHO, Geneva, (2004) p. 334.
- [6]. *Guidelines for drinking-water quality, fourth edition, 2011*, ISBN: 978 92 4 154815 1, World Health Organization (WHO), Geneva (2011).
- [7]. *Guidelines for Drinking – Water Quality [electronic resource]: incorporating 1st and 2<sup>nd</sup> addenda, Vol.1, Recommendations. – 3rd ed*, World Health Organization, Geneva (2008).
- [8]. *Novel Carbon Adsorbents*, Edited by Juan Tascón, 1st Edition, Elsevier, 13th August 2012. **eBook ISBN: 9780080977454. Hardcover ISBN: 9780080977447.**
- [9]. Albino, K.P., Manabendra, R., Saswati, C. Hexavalent chromium removal from wastewater using aniline formaldehyde condensate coated silica gel. *Journal of Hazardous Materials*, 143(2006) 24-32.
- [10]. Manju, G.N., Anirudhan, T.S. *Indian Journal of Environment Health*. 39 (1997) 289-98.
- [11]. Karthikeyan, T., Rajgopal, S., Miranda, L.R. *Journal of Hazardous Materials*, **2005**, B124, 192,199.
- [12]. V.Vinodhini, Nilanjana Das, *American-Eurasian J of Scientific Research*, **2009**, 4(4)L, 324,329.
- [13]. Srinivasan K, Balasubramanian N and Ramakrishna T.V. Studies on Chromium Removal by Rice husk Carbon. *Indian Journal of Environ. Health*, 30(4) (1988) 376-387.
- [14]. Renny Mariam Mathew, M. Arthy, M. P. Saravanakumar and C. Balamurali Krishna. Removal of Hexavalent Chromium from Aqueous Solution by Adsorption on Raw Powder and Chemically Activated Carbon of Hibiscus rosa-sinensis Flowers. *Nature Environment and Pollution Technology*. 12(3) (2013) 475-478.
- [15]. K. P.C. Sekhar, R. V. Vishnu Babu, D. Srividhya, K. Ravindhranath. Removal of Chromium (VI) from Waste Waters Using Leaves Powders of *Justicia adhatoda*, *Cissus uadrangularis*, *Soapnut Acacia*. *Der Pharma Chemica*, 4 (2) (2012) 664-673.
- [16]. Mojdeh, O., Mohamed, K.A. and Wan, M.A.W.D. Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine. *Bioresource Technology*, 101(14) (2010) 5098-5103.
- [17]. Nadhemi, K.H., Xiao, D.C., Mohammed, M.F. and Max, G.Q.L. Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust. *Chemical Engineering Journal*, 84(2) (2001) 95-105.
- [18]. Sibichakkaravarthi L.M, Viniitha Judith. Removal of hexavalent chromium from wastewater using syzygium cumini seed as an adsorbent. *International journal for technological research in engineering*. 2(9)2015.
- [19]. *Syzygium cumini: World Checklist of Selected Plant Families (WCSP)*. Royal Botanic Gardens, Kew. Retrieved 16 June 2017.
- [20]. Seco, A., Gobaldon, C., Marzal, P., Aucejo, A., *Journal of Chemical Technology Biotechnology*. **74**(1999) 911.
- [21]. Pradhan, J., Das, J., Das, S. N., Thakur, R. S., *J. Colloid Interface Sci.* 203 (1998) 169.
- [22]. Amuda, O.S., Giwa, A.A. Bello, I.A. Removal of heavy metal from industrial waste water using modified activated coconut shell carbon. *Biochemical Engineering Journal*. 36(2) (2007) 174-181.
- [23]. S.M. Maliekkal, S. Shukla, L. Philip, I.M. Nambi, Enhanced Fluoride removal from drinking water by magnesia-amended activated alumina granules, *Chemical Engineering Journal*. 140(2008) 183-192.
- [24]. H.M.F. Freundlich, over the adsorption in solution, *J. phys. Chem.* 57(1906) 385-471.
- [25]. Langmuir. The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40(1918) 1361-1368.
- [26]. Hall, K.R., Eagleton, L.C., Acrivos, A., Vermevlem, T. Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, *Indian Eng. Chem. Fundam.* 5(1966) 212-219.
- [27]. R. Sujitha, K. Ravindhranath, defluoridation studies using active carbon derived from the barks of *Ficus racemosa* plant, *Journal of Fluorine Chemistry*. 193(2017) 58-66.

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