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Chromium Adsorption onto Activated Carbon Derived from Tendu (*Diospyros melanoxylon*) Leaf Refuse: Influence of Metal/Carbon ratio, time and p^H

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ABSTRACT

*The activated carbon produced from tendu (*Diospyros melanoxylon*) leaf refuse (TLR) was chemically activated using sulfuric acid and utilized as an adsorbent for the removal of chromium ion (VI) from aqueous solution in the concentration range 50 – 250 mg/L. Adsorption experiments were carried out in a batch process and various experimental parameters such as effect of contact time, initial chromium ion concentration, carbon dosage and p^H on percentage removal have been studied. Adsorption results obtained for activated carbon (CA-TLR) were compared with the commercial activated carbon (CA-CAC). Adsorption results obtained, shows that the Cr (VI) uptake being attained at p^H 2. The equilibrium adsorption data was better fitted to the Langmuir's and Freundlich adsorption models. It was concluded that activated carbon produced from tendu leaf refuse (CA-TLR) has an efficient adsorption capacity compared to (CA-CAC) sample.*

Key words : Activated carbon, Tendu leaf refuse, Chromium, Adsorption.

INTRODUCTION

Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms [1]. Chromium and its compounds are toxic metals introduced into natural water from a variety of industrial wastes. The major sources are from leather tanning, textile dyeing, electroplating and metal finishing industries which cause severe environmental and public health problems. The hexavalent form of chromium is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties[2]. It leads to liver damage, pulmonary congestion, edema and causes

skin irritation, resulting in ulcer formation [3]. Its concentration in industrial waste water ranges from 0.5 mg/L to 270,000 mg/L [4]. The tolerance limit for the discharge of Cr(VI) into inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L [5]. A wide range of physical and chemical processes are available for the removal of Cr(VI) from waste water as electro-chemical precipitation, ultra-filtration, ion exchange, electro-dialysis, reverse osmosis, chemical precipitation and adsorption [6,7,8,9]. The major drawbacks with these processes are high cost, toxic sludge generation or incomplete metal removal.

Activated carbon is a microcrystalline, non-graphitic form of carbon with porous structure that has been processed to develop its internal porosity[10]. The use of commercial activated carbon is well-known adsorbent for the removal of heavy metals from water and wastewater, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence it is a growing need to derive the activated carbon from cheaper and locally available waste materials. Several research workers used different low-cost adsorbents from agricultural wastes such as coconut coirpith, saw dust, rice husk, banana pith, cottonseed hulls, apple wastes, sugarcane bagasse pith, peanut hull carbon, activated carbons obtained from agricultural by-products and Mn-oxide coated granular activated carbon for the removal heavy metals from water and wastewater [11-20]. Studies were carried out in the removal of chromium from aqueous solutions using activated carbon derived from tendu leaf.

Tendu (*Diospyros melanoxylon*) leaf refuse, which itself is an environmental pollutant, generated during the manufacture of Indian crude cigarette bears this investigation. A bidi is smaller and less expensive than a cigarette and is considered a poor man's cigarette in India. Bidi is an indigenous crude cigarette in which tobacco is rolled in a small cut portion of tendu leaf and tied with a cotton thread. Tendu leaf is used as bidi wrapper on account of the ease with which it can be rolled and its wide availability. It also has agreeable flavor, resistance to decay and capacity to retain fires. Bidi rolling is a home industry covering thousands of homes in the industrial towns of Jabalpur and Solapur in India.

This home industry of bidi making produces cuttings of tendu leaf as refuse which pollutes the dumping sites creating solid waste disposal problem of alarming scale. About 7200 tones of tendu leaf waste is generated per annum in the industrial town of Solapur, Maharashtra. The goal of this research was to demonstrate the efficiency of using carbonized tendu leaf for removal of Cr (VI) from aqueous solutions.

MATERIALS AND METHODS

Experimental

Instrumentation

Elico- SL 164 UV- Double beam spectrophotometer was used for determining chromium concentrations. An Elico (LI - 120) P^H meter was used for p^H measurements. Remi mechanical shaker was used for agitating the samples.

Chemicals

All the chemicals used were of analytical reagent grade. Deionised doubly distilled (DDD) water was used throughout the experimental studies. Stock chromium solutions (1 mg/ml) were

prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in 1000 ml of DDD water. Working standards were prepared by progressive dilution of stock chromium solutions using DDD water. ACS reagent grade HCl and NaOH were used to adjust the solution p^{H} .

Procedure for adsorbent preparation and activation

The tendu leaf refuse was obtained from the dumping sites near bidi industries in the town of Solapur, India. The leaf refuse was cut into small pieces, dried in sunlight and further dried in a hot air oven at 60°C for 24 hour. The completely dried material was chipped, powdered well and stored in desiccators for further experiment.

Activated carbon of the material was prepared by treating with the concentrated Sulphuric acid (Sp. gr.1.84) in a weight ratio of 1:1.8 (material: acid). The resulting black product was kept in an air-free oven maintained at $160 \pm 5^\circ\text{C}$ for 8 hours followed by washing with distilled water until it becomes free of excess acid and dried at $105 \pm 5^\circ\text{C}$. The activated carbon obtained from biomaterial was ground and sieved with 80-mesh siever and was used for metal adsorption experiments.

Adsorption studies

Batch adsorption experiments were carried out in a series of stoppered reagent bottles (250 ml). A weighed amount (0.5 g) of adsorbent was introduced into reagent bottles containing various concentrations of chromium. The solution p^{H} was adjusted to the desired value by adding HCl or NaOH. Then, the bottles were shaken at room temperature ($30 \pm 1^\circ\text{C}$) using a mechanical shaker for a prescribed time to attain the equilibrium. The solutions were filtered and the concentrations of metal ions were determined by s- Diphenylcarbazide method. The effects of concentration (50 – 250 mg/l), contact time (15 – 180 min), solution p^{H} (2 - 10) and adsorption dose (0.5 – 2.0 g) were studied. Blank solutions were treated similarly (without adsorbent) and the recorded concentration by the end of each operation was taken as the initial one.

The adsorption capacity, q_e were calculated from the difference between the initial concentration and equilibrium concentration, which can be calculated from:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

Where q_e is adsorption capacity (mg/g), C_0 and C_e are initial and equilibrium concentration (mg/l) respectively, M is the adsorbent dosage (g) and V is the volume of solution (L).

Percentage removal of heavy metal from initial solution concentration calculated from the following equation. Adsorption capacity and percent removal were used to optimize the activation conditions:

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Sorption isotherm models

The sorption equilibrium data of chromium on activated carbon were analyzed in terms of Freundlich and Langmuir model (Glasstone, 1981). Freundlich isotherm equation $X/m = k_F C_e^{1/n}$ can be written in the linear form as given below.

$$\log \frac{X}{m} = \log K_F + \log C_e \quad (3)$$

where X/m and C_e are the equilibrium concentrations of chromium in the adsorbed and liquid phases in mg/g and mg/l respectively. k_F and n are Freundlich constants that are related to the sorption capacity and intensity, respectively. Freundlich constants k_F and n can be calculated from the slope and intercept of the linear plot, with $\log (X/m)$ versus $\log C_e$.

The Langmuir sorption isotherm equation $X/m = Q_m k_L C_e / (1 + k_L C_e)$ on linearization becomes

$$\frac{C_e}{(x/m)} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (4)$$

Where Q_m and k_L are Langmuir constants which are related to sorption capacity and energy of sorption, respectively and can be calculated from the intercept and slope of the linear plot, with $C_e / (X/m)$ versus C_e .

RESULTS AND DISCUSSION

Characteristics of the adsorbent:

The adsorption of Cr(VI) in aqueous solution on commercially activated carbon and chemically activated tendu leaf refuse (CA-TLR) were examined by optimizing various physicochemical parameters such as; pH, contact time, and the amount of adsorbent and adsorbate. The results of the adsorbents characteristics used in this study are given in Table 1.

Table 1. Physical parameters of chemically activated tendu leaf refuse

Parameters	Characteristic value
pH	6.45
Moisture (%)	9.15
Ash content (%)	4.04
Bulk density (g/ml)	0.48

Effect of Initial Chromium Concentration

The present uptake of Cr(VI) with the two adsorbent was studied by varying chromium concentration (50, 100, 150 200 and 250 mg/L), keeping constant the adsorbent dose (0.5 g), stirring speed (250 rpm), and contact time (180 min). The percent sorption is given in Fig.1, which showed that the percentage of Cr(VI) sorption increases with decreasing sorbate concentration in both CA-TLR and CA-CAC [21]. This is because at lower concentration there are sufficient active sites that the sorbate can easily occupy. However, at higher concentrations, active sorption sites are not sufficiently available for the sorbate to occupy. Hence, Cr(VI) ions not completely adsorbed in solution due to the saturation of binding sites. In addition, the electrostatic repulsion between negative charges of adsorbate ions results in the decrease of the adsorption percentage [22].

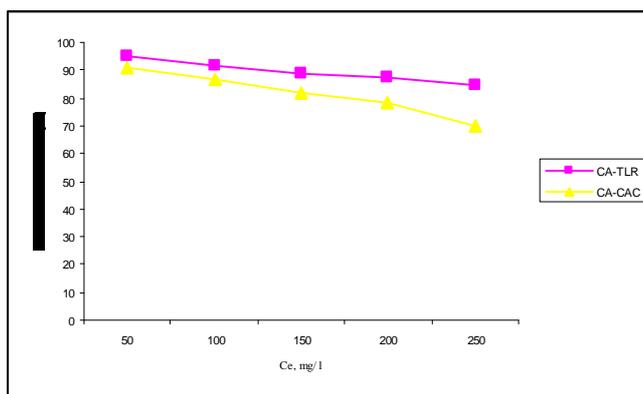


Figure 1: Effect of initial concentration on percent removal of Chromium (VI) ions by CA-TLR and CA-CAC (adsorbent dose, 0.5gm/100ml ; contact time, 180 minutes.)

Kinetic Studies

The time-dependent behavior of Cr(VI) uptake adsorption was measured by varying the equilibrium contact time in the range of 15-180 min. The Cr(VI) concentration was kept at 50 mg/L, while the amount of added carbon dose was 0.5 gm/L. The adsorption efficiency of Cr(VI) removal by CA-CAC at p^H 2 increased from 16 - 63.12% with an increase in contact time. Equilibrium was attained within 120 minutes and, thereafter, it become constant. From fig. 2, it was also observed that the equilibrium time for CA-TLR to attain equilibrium to sequester the anion from the solution was 30 minutes. The adsorption efficiency of Cr(VI) removal by CA-TLR at p^H 2 increased from 85.3-95.2% with an increase in contact time. This indicates that the process was uniform with time [23].

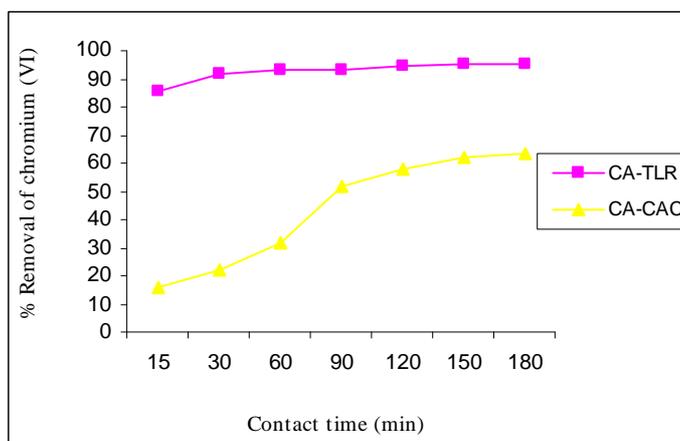


Figure 2: Effect of contact time on percent removal of Chromium (VI) ions by CA-TLR and CA-CAC (adsorbent dose, 0.5gm/100ml; p^H , 2; initial concentration, 50 mg/l.)

Sorption as a Function of Dosage

The carbon dosage is another important variable during metal uptake. At a given equilibrium concentration, the carbon takes up more metal ions at lower than at higher carbon densities [24]. It has been suggested that electrostatic interactions between the carbon can be a significant factor in the relationship between carbon and metal sorption. In this connection, at a given metal concentration, the lower the carbon concentration in suspension, the higher will be the

metal/biosorbent ratio and the metal retained by sorbent unit, unless the carbon reaches saturation. High carbon concentrations can exert a shell effect, protecting the active sites from being occupied by metal. The result of this is a lower specific metal uptake, that is, a smaller amount of metal uptake per carbon unit. Fig. 3, shows this influence using CA-CAC and CA-TLR as sorbent. In the tests, the initial metal concentration (50 mg/L) and the p^H value were kept constant. The carbon dose was tested at 0.5, 1.0, 1.5 and 2.0 g/L. The fig. 3, shows that for both CA-CAC and CA-TLR the maximum sorption capacity corresponded to the lowest carbon concentration of the four used (0.5 g/L), which confirms the loss of biosorbent effectiveness at high concentrations.

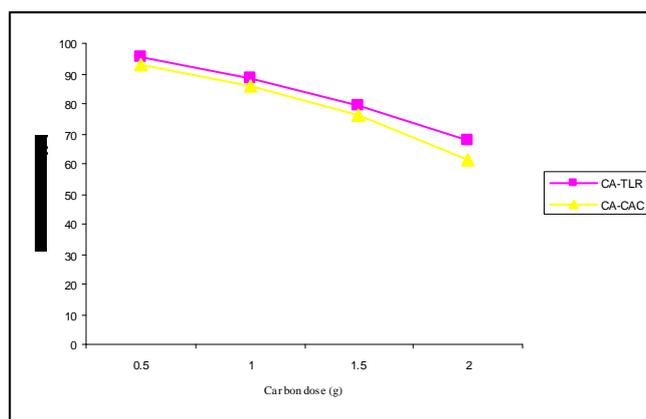


Figure 3: Effect of adsorbent dosage on percent removal of Chromium (VI) ions by CA-TLR and CA-CAC (contact time, 180 minutes; initial concentration, 50 mg/l, p^H .)

Effect of Initial p^H

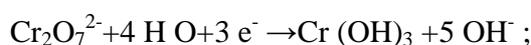
Solution p^H is one of the most important parameters while assessing the adsorption capacity of an adsorbent for metal ion sequestration from aqueous solution [25]. The p^H of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent and ionic forms of the chromium solutions. Adsorption experiments were carried out in the p^H range of 2.0-10.0, keeping all other parameters constants, (stirring speed = 250 rpm, contact time = 180 min, adsorbent dose = 0.5 g, initial chromium concentrations = 50 mg/L and room temperature). The p^H of the solution was adjusted after adding the adsorbent. As depicted in Fig. 4, the maximum removal of chromium was 95.2 % for CA-TLR and for CA-CAC was 63.12 % from a solution 50 mg/L at p^H 2. there was a sharp decline in percent adsorption with an increase in p^H of the aqueous solution due to the fact that the covalent coordination bonds between Cr(III) ions and the surface functional groups of both activated carbons, such as carboxylic and hydroxyl are very weak in basic conditions [26]. Maximum adsorption was observed at p^H 2. our results are consistent with other workers, that the removal of Cr(VI) decreases with the increase of p^H . The p^H dependence of metal adsorption can largely be related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry in solution [8]. In the p^H range of 2.0 – 6.0, chromium co-exists in different forms such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ of which $HCrO_4^-$ predominates. As the p^H of the solution increases, the predominant species are then CrO_4^{2-} and $Cr_2O_7^{2-}$. More adsorption at acidic pH indicates that the lower pH results in an increase in H^+ ions on the adsorbent surface that results in significantly strong electrostatic attraction between positively charged adsorbent surface and chromate ions. Lesser

adsorption of Cr(VI) at pH values greater than 6.0 may be due to the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent, of which OH^- predominates. This is in accordance with earlier studies that reported the removal of Cr(VI) by different adsorbents [27]. It has also been postulated that, under acidic conditions, Cr(VI) could be reduced to Cr(III) in the presence of an adsorbent. Dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) under acidic conditions get reduced to Cr^{3+} :



$$E^0 = 1.33 \text{ V [28]}$$

However, in basic solutions it is much less oxidizing and exists as $\text{Cr}(\text{OH})_3$:



$$E^0 = -0.13 \text{ V}$$

The favorable effect at low pH can be attributed to the neutralization of negative charges on the surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion of the hydrogen chromate ion (HCrO_4^-) and its subsequent adsorption, because HCrO_4^- is the dominant anionic form of Cr(VI) between pH 1.0 and 4.0. This ionic form was found to be preferentially adsorbed on the surface of carbon. The negative charges could result from oxygenated functional groups of basic character such as lactone or hydroxyl groups, chemisorbed at the surface of the pores. The possible explanation for higher adsorption in the acidic region is that the $\text{Cr}_2\text{O}_7^{2-}$ ion is oxidized to Cr^{3+} . Being small in size, it can be easily replaced by the positively charged species [28].

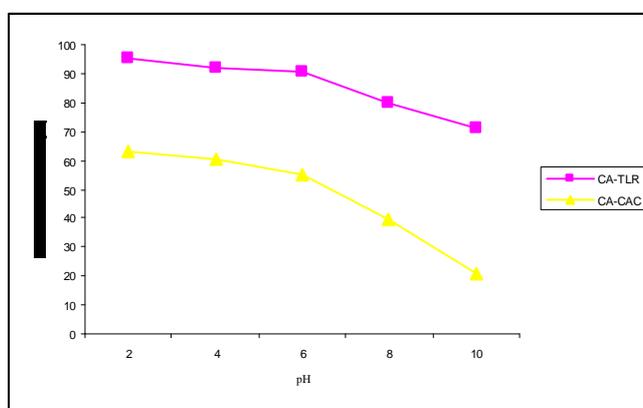


Figure 4: Effect of pH on percent removal of Chromium (VI) ions by CA-TLR and CA-CAC (initial concentration, 50 mg/l; adsorbent dose, 0.5gm/100ml; contact time, 180 minutes.)

Adsorption Isotherms

The isotherm of adsorption indicates how the quantities of target species are distributed between the liquid and solid phases when the adsorption process reaches balance. It is employed to establish the maximum capacity of adsorption of metals on adsorbents, which is expressed in terms of quantity of metal adsorbed per unit of mass of adsorbent used (mg/g). In the present investigation, the data have been correlated with a suitable isotherm. The Langmuir and

Freundlich equations are commonly used for describing the adsorption equilibrium for Cr(VI) removal[29].

The isotherm constants of Freundlich and Langmuir were calculated from the plots of C_e / q_e vs. C_e and $\log q_e$ vs. $\log C_e$, as depicted from Fig. 5 and 6, respectively, and the results are listed in Table 2. The values of the coefficient of determination (R^2) are (0.977 and 0.994) for CA-CAC and (0.974 and 0.999) for CA-TLR.

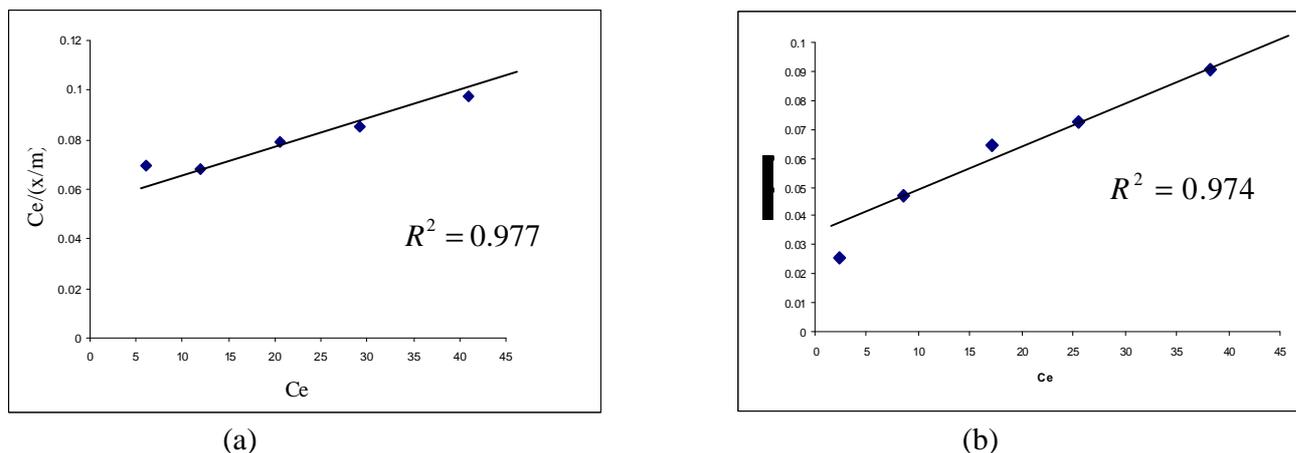


Figure 5: Langmuir plot of Chromium (VI) loaded onto (a) CA-CAC and (b) CA-TLR sample.

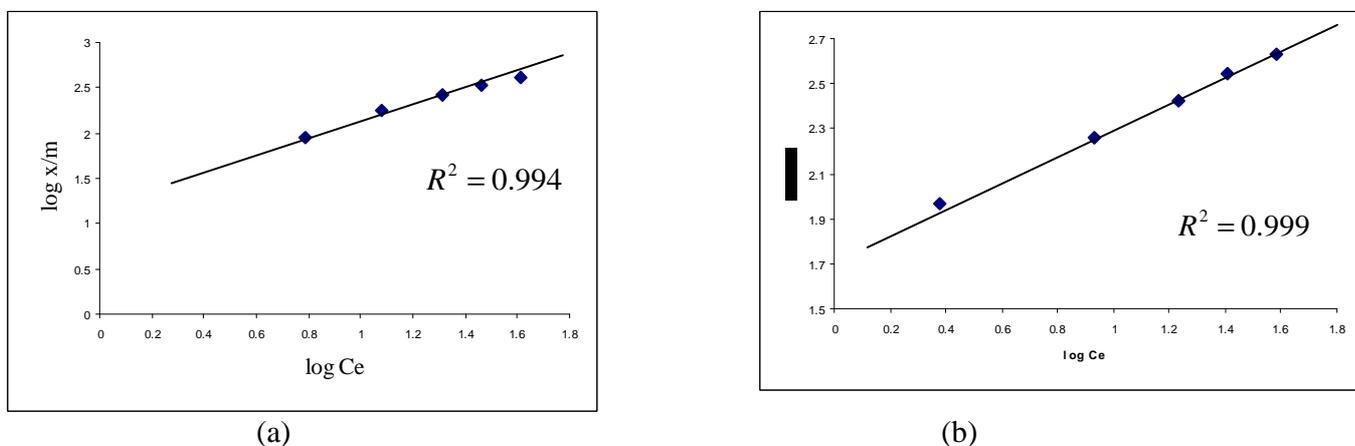


Figure 6: Freundlich plot of Chromium (VI) loaded onto (a) CA-CAC and (b) CA-TLR sample.

Table 2: Adsorption constants of Langmuir and Freundlich isotherms for Cr(VI) adsorption onto (CA-TLR) and (CA-CAC) at pH 2.0.

Adsorbent	Initial pH	Langmuir Constants			Freundlich constants		
		Q_0	Q_m	R^2	K_F	n	R^2
CA-TLR	2.0	95.20	0.00136	0.974	0.1504	1.74	0.999
CA-CAC	2.0	63.12	0.00100	0.977	0.1324	1.12	0.994

Comparison with Other Adsorbents

The adsorptive capacities of (CA-CAC) and (CA-TLR) have been compared with other adsorbents reported in the literature as having been examined for the removal of Cr(VI) under similar conditions to those employed in the present work. These have been tabulated in Table (3). It is clearly seen that both (CA-TLR) and (CA-CAC) exhibited considerably higher adsorption capacity when the removal of Cr(VI) was undertaken at very low p^H values.

Table 3: Summary of chromium adsorption capacities of various adsorbents

Type of adsorbent	Q ₀ (mg/g)	Optimum p ^H	Reference No.
Hazelnut-AC	170	1.0	30
Neem leaves	63	2.0	26
Black tea leaves	45.5	2.0	31
AS-received CA-CAC	4.72	6.0	32
Nitric-oxidized CA-CAC	15.5	4.0	32
Waste tyre	58.5	2.0	33
Leaf mould	43	2.0	28
Alligator weed	82.6	1.0	34
Alfa grass	75.8	2.0	23
TLR- Sulphuric acid AC	95.2	2.0	This work

CONCLUSION

New alternative adsorbents for Cr(VI) removal have been explored by making simple chemical modifications of tendu leaf refuse by sulfuric acid and commercial active carbon. The results indicate that the biomass (CA-TLR) activated carbon is a good sorbent as compared to the treated commercial active carbon (CA-CAC). The adsorption of Cr(VI) was found to be highly dependent on the pH value of the system, with the best results being obtained at pH 2.0. A high percentage of Cr(VI) may be reduced to the Cr(III) form at low pH values. Chromium (VI) was rapidly adsorbed when lower concentrations were used. The Langmuir isotherm provided the best correlation for adsorption of Cr(VI) onto the activated carbons. The adsorption capacity as calculated from the Langmuir isotherm was 95.2 mg/g at initial pH 2.0 for a 50 mg/L Cr(VI) solution.

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