Batch Adsorption Assessment of Neem Nut Carbon for Abating Chromium(VI) in Wastewater

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Authors’ contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Discharge of Cr(VI) laden effluents is highly toxic and decontaminating the wastewater from Cr(VI) is necessary for Environmental Protection. An investigation on the adsorption characteristics of activated carbon prepared from neem nut (NNC) for the removal of Cr(VI) from wastewater by varying the parameters such as carbon dose, pH, equilibration time by batch studies was found to be effective for the removal of Cr(VI) from wastewater. Carbon characteristics of activated neem nut carbon were ascertained. Evaluation were done by varying the pH from 1 to 6, carbon dose from 0.1 g to 0.5 g and equilibration time from 1 to 6 hours. Maximum Cr(VI) removal of 95% took place when batch studies were done at an optimal pH of 2, carbon dose of 0.2 g/100mL, and equilibration time of 4 hours. Freundlich and Langmuir adsorption isotherm models were considered for analysis.

Keywords: Neem nut carbon; Adsorption, Chromium(VI) removal; Carbon characteristics; Batch studies; Isotherm studies.

1. INTRODUCTION

Environmental toxicity due to heavy metal ions pollution in water bodies has become a major thrust upon mankind. Chromium was discovered in 1797 by the French chemist Louis Vauquelin. It was named chromium (Greek Chroma, ‘color’)

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because of many different colors found in its compounds. Chromium is the Earth’s 21st most abundant element and the sixth most abundant transition metal. The principal chromium is ferric chromite, FeCr₂O₄, found mainly in South Africa (with 96% of the world’s reserves), Russia, and Philippines. Less common sources include crocoite, PbCrO₄ and chrome ochre, Cr₂O₃. The gem stones Emerald and Ruby owe their colors to traces of chromium [1]. Chromium and its alloys have wider application in industries such as metal finishing, dyes, pigments, inks, glass, ceramics, tanning, textile, wood preserving and glue. The effluents released from these industries are majorly contaminated with hexavalent chromium ions Cr(VI) with concentrations ranging from 10 to 3000 mg/L [2]. United States Environmental Protection Agency[USEPA] and Indian Standards[IS] have fixed the maximum permissible limit of Cr(VI) in drinking water as 0.05 ppm [3,4]. Similar limits have been set by other nations taking into consideration of the local geographic, socio-economic, dietary and industrial conditions. Exposure to Cr(VI) causes cancer in digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [5].

Adsorption by activated carbon is one of the cost effective successful techniques for Cr(VI) ion removal from wastewater due to the high surface area and porous nature of activated carbon. Decontaminating chromium(VI) in water by activated carbon prepared from agricultural wastes such as rice straw [6],coconut shell [7], Russian knapweed flower powde r[8], neem leaves [9], moringa Leaves [10], peanut shell [11], moringa stenopetala seed powder and banana peel powder [12] etc have been reported.

Neem, *Azadirachta indica* grows in tropical regions such as India. Neem can grow in different types of soil. It can tolerate high to very high temperatures. The trees are not at all delicate about water quality and thrive on the merest trickle of water. In India and tropical countries it is very common to see neem trees used for shade lining streets. The bark, leaves, and seeds are used for making medicines. Neem nuts are available abundantly as agricultural wastes. This study aims the evaluation of neem nut carbon as a new sorbent for the removal of Cr(VI) from wastewater.

## 2. MATERIALS AND METHODS

All chemicals used in this study were of analytical reagent grade. Synthetic stock solution was prepared by dissolving potassium dichromate in distilled water. Stock solution was diluted with distilled water for preparing chromium solution for batch adsorption experiments. The pH of the solution was adjusted accordingly with a pH meter. Batch experiments were conducted in polythene bottles of 300 mL capacity provided with screw caps in mechanical shaker. Neem nuts were collected locally and dried.

### 2.1 Preparation of High Temperature Neem Nut Carbon

High temperature neem nut carbon was prepared by modified dolomite process [13]. Fifty grams of Neem nut were placed between a bed of CaCO₃ of 1 cm thickness and subjected to pyrolysis at 600 °C for 1h. The char was maintained at 900 °C for 30 min. for activation by CO₂ liberated by the decomposition of CaCO₃. The activated material was left soaked in 10 % HCl, washed with distilled water, dried at 105 ± 5 °C. The carbon was designated as NNC.

### 2.2 Evaluation of Carbon Characteristics

The important Carbon characteristics of NNC such as bulk density, moisture content, ash, matter soluble in water, matter soluble in acid, pH, decolourisation property, phenol number, ion exchange capacity, surface area and iron content were analyzed( ISI 1977) [14].

### 2.3 Batch Studies

The Cr(VI) content was established by diphenyl carbazide method spectrophotometrically at 540nm [15]. One of the important parameters while assessing the adsorption capacity of an adsorbent for metal ion sequestration from aqueous solution is the pH. Adsorption experiments were carried out in the pH range of 1.0-6.0 ( contact time = 24 hrs, adsorbent dose = 0.5g, and room temperature) with 100 mL of 10 mg of Cr(VI)/L solutions. Effect of carbon dose at optimum pH and effect of equilibration time at optimum pH and carbon dose were also investigated.

## 3. RESULTS AND DISCUSSION

The results of carbon characteristics [As per IS] are shown in Table 1. NNC has high bulk density
and it is a measure of activity of the carbon. The carbon have low moisture and ash content. Matter soluble in water and acid is less so that when the carbon is in contact with water the desired quality of effluent will not be altered. High surface area shows that NNC has high capacity for the removal of contaminants by adsorption process.

3.1 Effect of pH

As depicted in Fig. 1 the maximum removal of chromium(VI) was at pH 2. The dominant form of Cr(VI) at pH 2.0 is HCrO$_4^-$ . In highly acidic media, the adsorbent surface might be highly protonated and favour the uptake of Cr(VI) in the anionic form HCrO$_4^-$ [16].

3.2 Effect of Carbon Dose

From Fig. 2, for 95 % removal of Cr(VI) a minimum dose of 0.2 g of NNC was required(pH=2, equilibration time=24h) Increase in adsorption with dose can also be attributed to increase in surface area and the availability of more adsorption sites [17]. Since the quantity of metal ion is constant, an increase in the amount of adsorbent above a quantity that can completely adsorb the available Cr(VI) had no apparent effect on further increase of percent adsorption [18].

3.3 Effect of Equilibration Time

Fig. 3 represents the effect of equilibration time on removal of Cr(VI) by 0.2 g NNC at pH of 2. For NNC, an optimum time of 4 hours was enough for 95 % removal of Cr(VI). After that the percentage adsorption remains uniform. Further increase in contact time has a negligible effect on the percentage removal of Cr(VI). At the beginning of the process, adsorption is fast due to the availability of large active binding sites but as time has gone, the process slow down as active binding sites are filled by the metal ion [12].

Table 1. Carbon Characteristics of NNC

| S.No. | Parameter                              | Value     |
|-------|----------------------------------------|-----------|
| 1.    | Bulk density (g/cc)                    | 0.52      |
| 2.    | Moisture (%)                           | 2.84      |
| 3.    | Ash (%)                                | 3.01      |
| 4.    | Matter soluble in water (%)            | 1.36      |
| 5.    | Matter soluble in 0.25 M HCl (%)       | 1.43      |
| 6.    | Decolourising Power (mg/g)             | 83        |
| 7.    | Phenol Number (mg)[Iodine Method]      | 51        |
| 8.    | Ion Exchange capacity (meq./g)         | Nil       |
| 9.    | Surface area (m$^2$/g)[N$_2$-BET]      | 653       |
| 10.   | pH                                     | 6.2       |
| 11.   | Iron content (%)                       | 0.34      |

![Fig. 1. Effect of pH on Cr(VI) removal](image-url)
4. ADSORPTION ISOTHERMS

Isotherm studies are essential to interpret the adsorption process. The Freundlich and Langmuir isotherms have been considered for these studies.

The linear form of Freundlich equation is

\[ \log \frac{x}{m} = \log k + \frac{1}{n} \log C_e \]  

where

- \(x\) = amount of solute adsorbed in mg/L
- \(m\) = the weight of the adsorbent in g/L
- \(k, 1/n\) = constants characteristics of the system and are the measures of adsorption capacity in mg/g and intensity of adsorption in L/mg.

The Langmuir adsorption isotherm equation is expressed as

\[ \frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \]  

where

- \(C_e\) = equilibrium concentration of the solute in mg/L
- \(Q_o\) = equilibrium concentration in mg/L
- \(q_e\) = the amount adsorbed at equilibrium in mg/g
Q₀ and b= Langmuir constants related to adsorption capacity in mg/g and energy of adsorption in L/mg

Plots of log x/m Vs log Cₑ were linear for NNC. The straight line indicated that the process followed was of Freundlich adsorption type the values of 1 < n < 10 indicated favourable adsorption of adsorbate on the carbons. From Freundlich isotherm high value of k (greater than 1) suggested that the adsorption capacity of carbon was significant. The monolayer coverage of adsorbed species on the carbon surface is shown by Regression co-efficient (R²) values close to unity [19].

The linear plots of Cₑ/ qₑ Vs Cₑ showed that the adsorption obeys Langmuir model for NNC. The monolayer adsorption capacity Q₀ value and energy of adsorption or surface energy (b) of NNC is significant. The regression co-efficient (R²) values close to unity indicated the applicability of the Langmuir isotherm and the monolayer coverage of adsorbate on the carbon surface. Constant separation factor or equilibrium parameter R_L = 1 / 1 +bC₀ where b is Langmuir constant and C₀ is the initial concentration of Cr(VI). Its value indicates that the sorption process could be favourable, linear, unfavourable, irreversible when 0<R_L<1, R_L = 1, R_L>1, R_L = 0 respectively [20]. In the present study, the values of the dimensionless factor, R_L, were between 0 and 1 which suggested a favorable adsorption between NNC and Cr(VI).

Fig. 4. Freundlich adsorption isotherm on Cr(VI) removal

Fig. 5. Langmuir adsorption isotherm on Chromium(VI) removal
**Table 2. Results of isotherm models for the adsorption of Cr(VI) on NNC**

| Adsorption isotherm constants | Values          |
|------------------------------|----------------|
| Freundlich isotherm          |                |
| n (mg/L)                     | 2.3585         |
| k (mg/g)                     | 6.5313         |
| $R^2$                        | 0.9990         |
| Langmuir isotherm            |                |
| $Q_o$ (mg/g)                 | 34.5           |
| b (L/mg)                     | 0.1584         |
| $R^2$                        | 0.9880         |
| $R_L$                        | 0.2399         |

On comparing the regression co-efficient ($R^2$) values of Freundlich and Langmuir adsorption isotherms, it was found that the $R^2$ values of Freundlich adsorption isotherm were closer to one than that of Langmuir adsorption isotherms. So adsorption fitted the Freundlich adsorption isotherm better when compared to Langmuir adsorption isotherm.

**5. CONCLUSION**

The investigation shows that high temperature neem nut carbon is a productive sorbent for the removal of Cr(VI) from aqueous solution. Carbon characteristics showed that Neem nut carbon can be used as a successful adsorbent. Batch assessment revealed that removal was effective at pH 2. An optimum dose of 0.2 g of NNC was enough for the removal of 95 % removal of Cr(VI) for 4 hrs of equilibration time. The process followed Freundlich and Langmuir adsorption isotherms and fitted the Freundlich adsorption isotherm better.

**COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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