

# An Approach to access the performance of sawdust as adsorbent for Cr (VI) Ions removal from Contaminated Water

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**Abstract:** This work deals with the use of chemically activated Neem (*Azadirachta indica*) and rice husk (*Oryza Sativa*) Sawdust (RH) as an adsorbent for the retention of chromium (VI) Ions from synthesized contaminated water. A batch wise experiment was performed in order to investigate the various parameters such as contact time, effect of temperature and initial concentration of the metallic ion. The adsorbent showing highest chromium (VI) removal was found to be Neem sawdust with highest loading capacity of 11.86 mg/g at 305 K and 100 mg/L of initial chromium concentration. Isothermal models like Langmuir and Freundlich Isotherm ( $R^2=0.987$ ).

**Key Words-** Chromium, Hexavalent Chromium, Chromium removal, Adsorption, Low cost adsorbent, Kinetics, Wastewater

**Introduction -** The growth of society & industrialization has established many harmful changes in environmental problems, [1] consequently the water containing heavy metals have some harmful problems all over the world. Chromium is listed among top pollutants and is ranked 16<sup>th</sup> harmful pollutant due to its carcinogenic and teratogenic characteristics on the community [2]. In the environment Chromium exists in two stable states, viz. Cr (VI) & Cr (III) [1]. Chromium (VI) discharge into the environment can be due to various large numbers of industrial functions like metal finishing industry, iron & steel industry & inorganic chemical productions [3]. Soils and sediments are polluted with Chromium owing to the dumping of sewage sludge or discarding chromium wastes from industries [4]. Hexavalent Chromium is 100 times more toxic [5] than trivalent chromium and 1000 times more mutagenic as per studies. Non- occupational exposure to the metal occurs via ingestion of chromium containing food & water, whereas occupational exposure occurs via inhalation [6]. Major diseases caused by toxic hexavalent chromium ions are bronchial asthma and lungs cancer. Unlike the organic pollutants, the metals are very harmful because they are not bio-degradable & accumulate in the human body.

They are very harmful for human beings, animals & other living organisms [1]. The maximum levels of chromium allowed in wastewater for trivalent chromium and hexavalent chromium are 5 mg/L and 0.05 mg/L respectively [7]. A number of methods are applied to reduce chromium concentration from industrial wastewater. There are various methods that used to remove heavy metal from waste water like chemical precipitation [8], ion exchange [9], reduction [10], electrochemical precipitation [11], solvent extraction [12], membrane separation [13] and evaporation [14]. Above mentioned conventional methods for Cr (VI) elimination are costly or unproductive at small concentrations. On the other hand some agricultural wastes like sawdust, rice husk, coconut shell etc. are preferred because of their low cost, availability at ease and good adsorption capability towards Cr (VI) metal ions removal [15].

## Materials and methods

**Chemical reagents-** Chemicals used for preparing chromium solution and analyzing chromium metal content in the solution were of analytical grade and purchased from Merck and Rankem, India.

**Preparation of Adsorbent:** Biowaste adsorbents used for chromium metal ion removal were taken as Neem and Rice Husk saw dust, taken from local market. Adsorbents were washed properly with hot distilled water to remove adhering dirt and dried in oven at 80°C. Then adsorbents were chemically activated with sulfuric acid at 150°C and then soaked in Sodium bicarbonate solution overnight to remove extra acid. Activated adsorbent thus obtained for kept in air tight containers for further use.

**Determination of Chromium Content:** Residual chromium in the aqueous solution was determined with the help of UV Visible Spectrophotometer by colorimetric method at 540nm.

**Experimental:** Stock solution of chromium (VI) was prepared by adding 2.826 g of  $K_2Cr_2O_7$  in 1 liter of deionized water and subsequent solution of desired concentrations were prepared by diluting the stock solution. In the present work adsorption experiment was performed batch wise by taking known amount of chromium concentration (mg/L) in 250 ml conical glass mixed with fixed amount of adsorbent (g/L). Solution mixture was stirred in shaking incubator at 150 rpm and 38°C. At definite time intervals, 5 ml of

sample from solution mixture was taken, filtered and tested for residual concentration of chromium by colorimetric method in UV Visible Spectrophotometer.

Adsorption of Chromium Ion (mg) per unit gram of adsorbent and adsorption efficiency in percent can be calculated as per the following equations [16]:

$$q = \frac{(C_0 - C_e) \cdot V}{M}$$

$$E = \frac{(C_0 - C_e)}{C_0} \cdot 100$$

where, unit of adsorbent loading, q is mg of chromium adsorbed per gram of adsorbent.  $C_0$  and  $C_e$  are Initial and Equilibrium chromium concentrations in mg/L. V is the volume of solution in liter. M is mass of adsorbent in gram and E is Sorption Efficiency.

## RESULTS AND DISCUSSIONS

**Performance Evaluation of Adsorbents for Cr (VI) Removal:** To evaluate the comparative performance i.e. Cr (VI) percent removal and loading capacity, two different adsorbents viz., Neem Sawdust and rice husk Sawdust were used. Experiments were performed by keeping constant values of parameters like initial Cr (VI) metal ions of 50 mg/L, adsorbent dose of 5 g/L and shaking speed of 120 rpm. Results shown in Figure 1 and Figure 2 are percent removal of Chromium Ions and uptake capacity for two adsorbents for 50 mg/L initial chromium ions in the solution. At 311K Chromium percent removal for Neem and rice husk sawdust are 66 and 46 % respectively. Analysis of results shows high uptake capacity of Neem sawdust (6.84 mg/g) at 311K temperature as compared to rice husk (4.63 mg/g) when compared at 50 mg/L of initial Cr concentration.

These results indicate that Neem Sawdust has better capability of Chromium removal at 311K compared to rice husk Sawdust adsorbents.

**Effect of Contact Time on Adsorption:** Percent removal of Cr (VI) at Equilibrium versus initial chromium (VI) concentration for 380 min contact time is shown in Figure 3. It was observed from figure that the percentage removal of chromium for 50 mg/L and 100 mg/L first increases up to 175 min and then become almost constant as the time proceeds further. The initial faster rate for chromium ions removal was because of the availability of more number of active sites, which were progressively occupied by the chromium ions as time progressed [17].

### Effect of Initial Chromium metal ion Concentration:

Percent removal of Cr (VI) with respect to Initial concentration of Chromium ions (mg/L) is shown in Figure 4. It is observed from the figure that percent removal of chromium increases as initial chromium concentration increases from 68.42 to 78.53 % as concentration of chromium in the solution increases from 50 mg/L to 100 mg/L respectively. According to Figure 3 Chromium metal uptake  $q_e$  at 50 mg/L and 100 mg/L initial Cr (VI) concentration are found to be 6.84 and 11.86 mg/g respectively. This phenomenon can be explained by considering the fact that higher initial adsorbate concentration provides higher driving force to overcome mass transfer resistance of the metal ions from the aqueous to the solid phase.

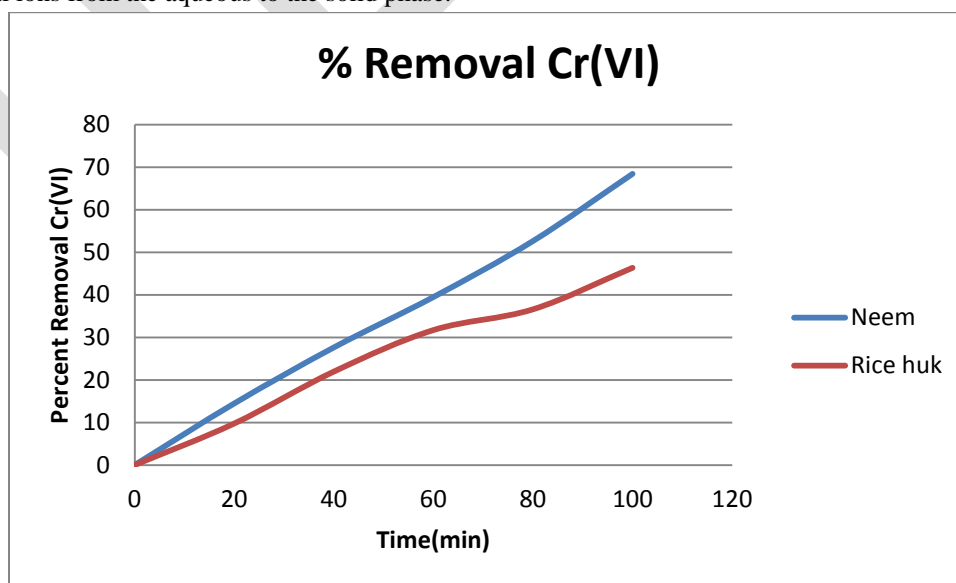


Figure1: Percent Removal of Chromium Ions on Neem and Rice Husk Sawdust at 50mg/L of initial Concentration

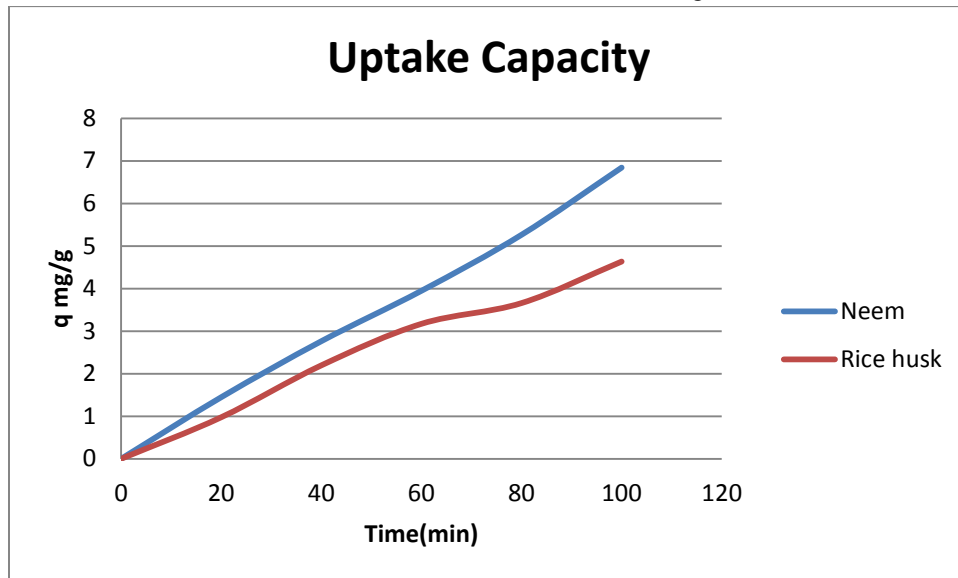


Figure2: Comparison of uptake capacity q (mg/g) between Neem and Rice Husk Sawdust

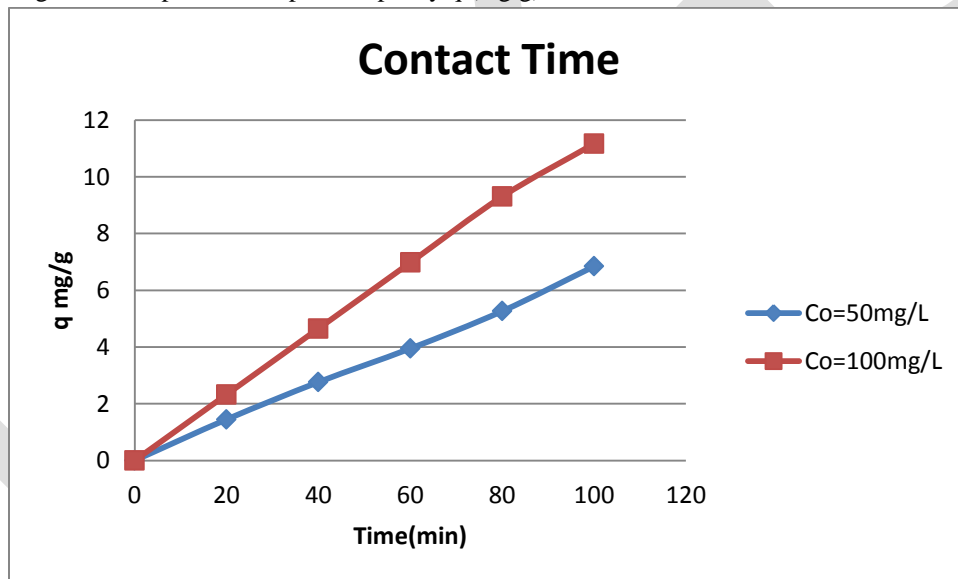


Figure3: Effect of contact time on Chromium (VI) metal ion removal.

**Biosorption Isotherms:-** The equilibrium of adsorption of heavy metal chromium ion Cr(VI) on Neem Sawdust is modelled using two isothermal adsorption models viz. Langmuir and Freundlich isotherms.

The Freundlich adsorption model is the most extensively used mathematical model in aqueous system. Equation written below is a nonlinear sorption model.

$$q_e = K_f C_e^{1/n}$$

where  $K_f$  is adsorption capacity (mg/g),  $n$  is adsorption intensity,  $C_e$  is equilibrium chromium concentration and  $q_e$  chromium uptake on dry adsorbent (mg/g).

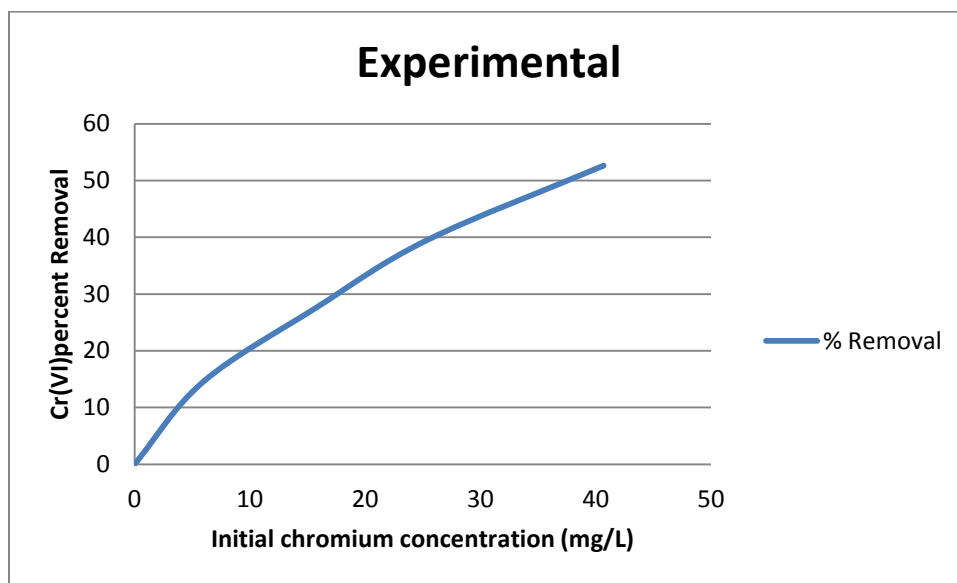


Figure4: Effect of Initial chromium metal ion Concentration

Table1-**Neem**: Linear regression data for Langmuir and Freundlich isotherms for chromium (VI) biosorption.

Parameters	Freundlich			Langmuir		
	$K_f$ (L/mg)	$1/n$	$R^2$	$q_{max}$ (mg/g)	$b$ (L/mg)	$R^2$
Values	1.350789	0.58619	0.983	18.491002	0.0439449	0.987

Freundlich model offers a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules.

The logarithmic form is:

$$\ln q_e = \ln K_f + \frac{1}{n} C_e$$

The Langmuir model predicts the maximum chromium uptake  $q_{max}$  and represents one of the first theoretical treatments of nonlinear sorption and suggests that chromium uptake occurs on a homogeneous surface by monolayer sorption, where no interaction between adsorbed molecules takes place. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir isotherm is written according to following equation:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e}$$

Where  $q_{max}$  (mg/g) and  $b$  are Langmuir constants related to adsorption capacity and the energy of Biosorption, respectively.

The adsorption data obtained for chromium metal ions adsorption onto the Neem sawdust used as Biosorbents in the present analysis were modeled. Values of the Freundlich constants ( $K_f$ ,  $1/n$ ) and Langmuir constants ( $q_{max}$ ,  $b$ ) are listed in Table 1. In the present work Neem sawdust was found to have the maximum metal uptake capacity of 11.86 mg/g at 100 mg/L of initial chromium concentration when compared to Rice Husk sawdust. Model prediction shows that the  $R^2$  value is more in Freundlich isotherm compared to Langmuir isotherm. In the Langmuir model, the linear plot of  $1/q_e$  vs.  $1/c_e$  give a straight line for Neem sawdust ( $R^2 = 0.987$ ) with slope  $1/q_{mb}$  and intercept  $1/q_m$ . For Freundlich model, the linear plot of  $\log q_e$  vs  $\log c_e$  give a straight line ( $R^2 = 0.983$ ) with slope

(1/n) and intercept  $\log K_f$ . The present study of model fitting concludes that Freundlich isotherm model fits best to the sorption data of chromium (VI).

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**Conclusion:-** The aim of this work was to find out the adsorption characteristics of bio-waste materials for the removal of Cr (VI) ions. Effect of contact time on loading capability shows that most of the adsorption takes place in first 175 minutes, chromium uptake capacity increased with increase in initial chromium concentration in the aqueous mixture [18-21]. The Freundlich and Langmuir Biosorption models were used for the mathematical description of the biosorption equilibrium of Cr (VI) ions to biosorbents. The biosorption equilibrium data fitted well to the Langmuir isotherm (0.987). The sorption capacities obtained as 3.18, 6.84, 9.92 and 11.86 mg/L at 25, 50, 75 and 100 mg/L of initial Cr (VI) Concentration respectively. Neem sawdust (NS) presented the low cost and higher adsorption capacities for the chromium ions as compared to rice husk.

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