

Cr(VI) Ions Removal from Aqueous Solutions Using Natural Adsorbents—FTIR Studies

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ABSTRACT

The ability of eight natural adsorbents were investigated for adsorptive removal of Cr(VI) from aqueous solutions. Various physico-chemical parameters such as pH, initial metal ion concentration, adsorbent dose level and equilibrium contact time were optimized in batch adsorption technique. A detailed Fourier Transform Infrared spectra (FTIR) study of adsorbents and Cr(VI) loaded adsorbents at the optimized condition was carried out to identify the different functional groups that were responsible for the adsorption. The important functional groups like hydroxyl, alkene, aromatic nitro, carboxylate anion, silicon oxide, sulphonic acid etc. were present in the natural adsorbent and were responsible for the chemical adsorption of Cr(VI) from aqueous solutions. The sorption energy calculated from Dubinin-Radushkevich isotherm indicated that the adsorption process were chemical in nature.

Keywords: FTIR, Chromium(VI), Rice Straw, Hyacinth Roots, Saw Dust

1. Introduction

Cr(VI) containing waste water discharged from various industries, including mining, tanning, cement, production of steel and other metal alloys, electroplating operations, photographic material and corrosive painting industries [1,2]. It is carcinogenic, mutagenic and toxic; thus, its presence in the environment poses a significant threat to aquatic life and as well as public health [3].

The maximum permissible limit of Cr(VI) for the discharge to inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L [4,5]. The Ministry of Environment and Forest (MOEF), Government of India has set minimal national standards (MINAS) of 0.1 mg/L for safe discharge of effluent containing Cr(VI) in surface water [6]. To comply with this limit, industries have to treat their effluents to reduce the Cr(VI) concentration in wastewater to acceptable levels. In waste water treatment various technologies are available such as chemical precipitation, ion exchange, electrochemical precipitation, solvent extraction, membrane separation, concentration, evaporation, reverse osmosis, emulsion per traction, adsorption etc. [7]. Among these technologies, adsorption is an user-friendly technique for the removal of heavy metal. This process includes the selective transfer of solute components in the fluid phase onto the surface or onto the bulk of solid adsorbent materials.

In recent years, several natural or agricultural wastes [8-11] have been used for the removal of heavy metal from industrial waste water. In general natural or agricultural waste contains different functional groups like hydroxyl, aldehyde, aliphatic acid, alkene, amide, aromatic nitro, silicate, sulphonate etc. The present paper deals with the identification of functional groups which are responsible for Cr(VI) ion adsorption in the eight bio-adsorbents.

2. Experimental Methods

2.1. Preparation of Adsorbents

Rice straw, rice bran, rice husk, hyacinth roots, neem bark, saw dust of teakwood origin, neem leaves and coconut shell were used as low cost natural or agricultural wastes for Cr(VI) removal from aqueous solutions. All the adsorbents were collected from local area near Kolkota, West Bengal, India.

Rice straw, rice bran, rice husk and hyacinth roots were boiled for 6 hr. to remove color materials. Coconut shell was crashed in roll crusher and then grinded. Sawdust, neem bark, neem leaves and coconut shell were treated with 0.1 N NaOH to remove lignin based color materials followed by 0.1 N H₂SO₄. Finally all the adsorbents were washed with distilled water several time and dried at 105°C for 6 hr to remove the adherent mois-

ture. After drying, all the adsorbents were sieved to obtain particle size of 250 - 350 μm prior to being used for adsorption studies.

2.2. Reagents and Equipments

All the necessary chemicals used in the study were of analytical grade and obtained from E. Merck Limited, Mumbai, India. The pH of the solution was measured with a EUTECH make digital microprocessor based pH meter previously calibrated with standard buffer solutions. UV-Spectrophotometer (U-4100 spectrophotometer, Hitachi, Japan) was used to determine the Cr(VI) content in standard and treated solutions after adsorption experiments. FT-IR (Jasco FT/IR-670 Plus) studies were carried out to determine the type of functional group responsible for Cr(VI) adsorption. The surface area was measured on Micromeritics Surface Area Analyzer (ASAP 2020). The moisture content determination was carried out with a digital microprocessor based moisture analyzer (Mettler LP16). The point of zero charge was determined by solid addition method [12] and reported in **Table 1**.

2.3. Preparation of Standard Cr(VI) Solution

The stock solution containing 1000 mg/L of Cr(VI) was prepared by dissolving 3.73 g of A. R. grade $\text{K}_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$ in 1000 ml double distilled water. Required initial concentration of Cr(VI) standards were prepared by appropriate dilution of the above stock Cr(VI) solution.

2.4. Batch Adsorption Studies

Using the necessary adsorbents in a series of 250 ml stopper conical flask containing 100 ml of Cr(VI) solution batch adsorption were carried out. pH of the solution adjusted by adding 0.1 N HCl or 0.1 N NaOH solution as required. Then the flasks were shaken for the desired contact time in an electrically thermostated reciprocating

shaker with 120 - 125 strokes/minute at 30°C. The time required to reach the equilibrium was estimated by withdrawing conical flask containing treated solution at regular intervals of time (simultaneously 8 conical flasks with same concentrations of all items). The content of these flasks were filtered through filter paper (Whatman no.1). UV-visible spectrophotometer was employed to determine the remaining Cr(VI) concentration in the sample solution using 1,5-diphenylcarbazide method as laid down in standard methods for examination of water and wastewater, APHA, AWWA, WEF, 1998 edition [13]. All the investigations were carried out in triplicate to avoid any discrepancy in experimental results with the reproducibility and the relative deviation of the order of $\pm 0.5\%$ and $\pm 2.5\%$ respectively. The solution pH adjusted to 1.0 ± 0.1 to 9.0 ± 0.1 under thermostated conditions of $30^\circ\text{C} \pm 0.5^\circ\text{C}$.

3. Results and Discussion

3.1. Optimum Operating Condition and Cr(VI) Adsorption Mechanism

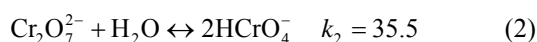
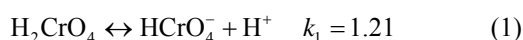
Metal sorption is depends on the solution pH. The range of variables investigated to obtain the optimum condition is shown in **Table 2**. In general adsorption of anion is favored at $\text{pH} < \text{pH}_{\text{pzc}}$. At very low pH, chromium ions exist in the form of HCrO_4^- , at higher pH up to 6 different forms such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , and $\text{Cr}_3\text{O}_{10}^{2-}$, coexists, of which HCrO_4^- predominates. As the pH increases equilibrium shifted form HCrO_4^- to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ [14]. At very low pH values, the surface of adsorbent would be surrounded by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the biosorbent by greater attractive forces. As the pH increased, the overall surface charge on the biosorbents-became negative and adsorption decreased [2]. The following equilibrium may be written for the Cr(VI) anions present in aqueous solutions [9].

Table 1. Different physical characteristics of natural adsorbents.

| Adsorbents | Surface area (m^2/g) | Moisture content (%) | Point of zero charge | Ash content (%) |
|----------------|--|----------------------|----------------------|-----------------|
| Rice straw | 1.21 | 7.26 | 6.85 | 9.40 |
| Rice bran | 0.12 | 10.68 | 6.10 | 11.72 |
| Rice husk | 0.54 | 9.02 | 6.05 | 11.80 |
| Saw dust | 3.85 | 8.63 | 3.90 | 12.35 |
| Neem bark | 3.47 | 9.23 | 4.50 | 10.62 |
| Hyacinth roots | 5.78 | 11.25 | 6.59 | 10.74 |
| Neem leaves | 0.57 | 8.33 | 6.94 | 13.58 |
| Coconut shell | 0.52 | 6.16 | 6.62 | 9.23 |

Table 2. Range of variables for batch experiment.

| Adsorbent | Initial pH | Initial Cr(VI) concentration (mg/L) | Contact time (min) | Adsorbent dosage (g/L) |
|----------------|------------|-------------------------------------|--------------------|------------------------|
| Rice straw | 1 - 9 | 5 - 300 | 0 - 420 | 2.5 - 12.5 |
| Rice bran | 1 - 9 | 5 - 300 | 0 - 420 | 2.5 - 12.5 |
| Rice husk | 1 - 9 | 5 - 300 | 0 - 420 | 2.5 - 12.5 |
| Saw dust | 2 - 8 | 3 - 300 | 0 - 300 | 2.5 - 30.0 |
| Neem bark | 2 - 8 | 3 - 300 | 0 - 300 | 2.5 - 30.0 |
| Hyacinth roots | 1 - 9 | 5 - 300 | 0 - 420 | 2.5 - 12.5 |
| Neem leaves | 1 - 9 | 5 - 300 | 0 - 300 | 2.5 - 12.5 |
| Coconut shell | 1 - 9 | 5 - 300 | 0 - 360 | 2.5 - 12.5 |



Adsorption of Cr(VI) was not significant at pH values more than 6 due to dual complexation of the anions (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and OH^-) to be adsorbed on the surface of the adsorbents, of which OH^- predominates [15]. The optimum adsorbent dosage, equilibrium contact time, optimum initial Cr(VI) ion concentration and maximum adsorption capacities of different natural or agricultural waste adsorbent using Langmuir adsorption isotherm model [16] were experimentally determined in batch process and the results are shown in **Table 3**.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (4)$$

Equation (4) represents the Langmuir adsorption model where C_e is the concentration of Cr(VI) in solution at equilibrium (mg/L), q_e is the amount adsorb per gram of the adsorbent at equilibrium, q_{\max} is the maximum adsorption capacity (mg/g) and b is the Langmuir constant (L/mg). Linear plots of C_e/q_e vs. C_e were employed to determine the value of q_{\max} (mg/g). The maximum adsorption capacity along with correlation coefficient (r^2) obtained were listed in **Table 3**.

3.2. Calculation of Sorption Energy

The Dubinin-Radushkevich [17] isotherm model was used to predict the nature of adsorption processes as physical or chemical by calculating sorption energy. The linear form of the model is described as,

$$\ln C_{\text{abs}} = \ln X_m - \lambda \varepsilon^2 \quad (5)$$

where C_{abs} is the amount of Cr(VI) adsorbed onto adsorbent surface (mol/g) and X_m represents the maximum

adsorption capacity of adsorbent (mmol/g), λ is constant related to sorption energy. The Polanyi potential [18] which is equal to,

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

R is the ideal gas constant in kJ/mol/K and T is the temperature in Kelvin. From the plot of $\ln C_{\text{abs}}$ vs. ε^2 gave a straight line from which the values of λ and X_m for all the adsorbents were calculated. Using the value of λ , the mean sorption energy, E , is evaluated as

$$E = \frac{1}{\sqrt{-2\lambda}} \quad (7)$$

The mean sorption energy, E , which indicated the information about adsorption mechanism. If $E < 8$ kJ/mol, the adsorption process was physical in nature and in the ranges from 8 to 16 kJ/mol, it was chemical in nature [19-21]. The estimated values of E were 14.142 kJ/mol, 13.921 kJ/mol, 13.558 kJ/mol, 9.341 kJ/mol, 9.205 kJ/mol, 12.845 kJ/mol, 14.712 kJ/mol and 15.394 kJ/mol for rice straw, rice bran, rice husk, saw dust, neem bark, hyacinth roots, neem leaves and coconut shell respectively which suggested the adsorption process was chemical in nature *i.e.* the indication of chemical bond formation between metal ion species and the functional group of the adsorbents.

3.3. FTIR Analysis for Cr(VI) Adsorption

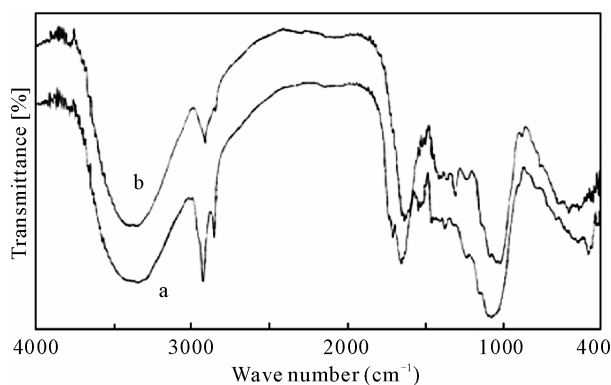
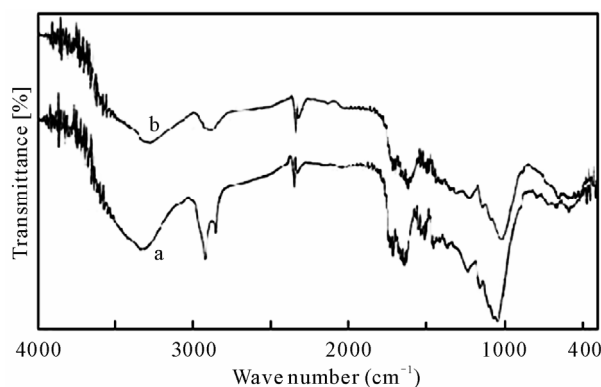
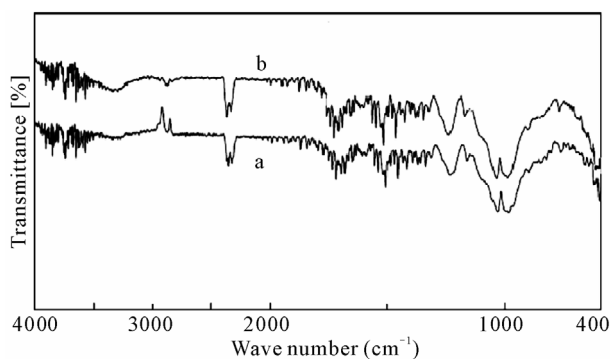
Fouier transform infrared spectra (FTIR) was used to investigate the changes in vibration frequency in the functional groups of the adsorbents due to Cr(VI) adsorption. Each fresh and Cr(VI) loaded adsorbents were mixed separately with KBr of spectroscopic grade and made in the form of pellets at a pressure of about 1 MPa. The pellets were about 10 mm in diameter and 1 mm thickness. Then the adsorbents were scanned in the spectral range of 4000 -

Table 3. Optimum operating condition obtaining in the batch process.

| Adsorbent | Initial pH | Initial Cr(VI) concentration (mg/L) | Contact time (min) | Adsorbent dosage (g/L) | Langmuir isotherm model | |
|----------------|------------|-------------------------------------|--------------------|------------------------|-------------------------|--------|
| | | | | | q_{\max} (mg/g) | r^2 |
| Rice straw | 2 | 25 | 180 | 10 | 12.17 | 0.9801 |
| Rice bran | 2 | 25 | 300 | 10 | 12.34 | 0.9476 |
| Rice husk | 1.5 | 25 | 360 | 10 | 11.39 | 0.9869 |
| Saw dust | 3 | 50 | 240 | 10 | 20.70 | 0.9963 |
| Neem bark | 3 | 50 | 240 | 10 | 19.60 | 0.9959 |
| Hyacinth roots | 2 | 25 | 240 | 10 | 15.28 | 0.9790 |
| Neem leaves | 2 | 25 | 240 | 10 | 15.95 | 0.9652 |
| Coconut shell | 2 | 25 | 240 | 10 | 18.69 | 0.9530 |

400 cm^{-1} . **Figures 1-3** show the FTIR spectra of rice straw, hyacinth roots and coconut shell respectively. Similar type of spectra also occurred for other adsorbents. These spectra indicated a number of absorption peaks showing the complex nature of the adsorbent. The functional group is one of the key factors to understand the mechanism of metal binding process on natural adsorbents.

Tables 4 and 5 represented the shift in the wave number of dominant peak associated with the fresh and Cr(VI) loaded adsorbents in the FT-IR plots. These shifts in the wave length showed that there was metal binding process taking place at the surface of the adsorbents [12,22]. The spectra display a number of absorption peaks, indicating the complex nature of the natural adsorbents. There was a clear shift from wave number of 3348.78 cm^{-1} (rice straw) to 3417.24 cm^{-1} (metal loaded rice straw), 3342.03 cm^{-1} (rice bran) to 3328.53 cm^{-1} (metal loaded rice bran) and 3385.42 cm^{-1} (rice husk) to 3421.10 cm^{-1} (metal loaded rice husk), 3297.75 cm^{-1} (neem bark) to 3266.82 cm^{-1} (metal loaded neem bark), 3328.53 cm^{-1} (hyacinth

**Figure 1. FTIR spectra of (a) rice straw and (b) Cr(VI) loaded rice straw.****Figure 2. FTIR spectra of (a) hyacinth roots and (b) Cr(VI) loaded hyacinth roots.****Figure 3. FTIR spectra of (a) coconut shell and (b) Cr(VI) loaded coconut shell.**

root) to 3305.39 cm^{-1} (metal loaded hyacinth roots) which indicate surface -OH group is one of the functional group responsible for adsorption Cr(VI) on rice straw, rice bran, rice husk, neem bark and hyacinth root. Though surface -OH present as functional group in saw dust but it is not responsible for metal binding in case of adsorption of Cr(VI) on saw dust. This can be inferred

Table 4. Wave number (cm⁻¹) for the dominant peak from FT-IR for Cr(VI) adsorption.

| Functional Groups | Rice straw | Cr(VI) loaded rice straw | Rice bran | Cr(VI) loaded rice bran | Rice husk | Cr(VI) loaded rice husk | Saw dust | Cr(VI) loaded saw dust |
|---------------------------------------|------------|--------------------------|-----------|-------------------------|-----------|-------------------------|----------|------------------------|
| Surface O-H stretching | 3348.78 | 3417.24 | 3342.03 | 3328.53 | 3385.42 | 3421.10 | 3335.10 | 3328.53 |
| Aliphatic C-H stretching | 2918.73 | 2916.81 | 2924.52 | 2924.52 | 2925.48 | 2925.48 | 2917.70 | 2920.66 |
| Aldehyde C-H stretching | x | x | 2854.13 | 2854.13 | 2854.13 | 2854.13 | x | x |
| Aliphatic acid C=O Stretching | x | x | 1709.59 | 1713.44 | x | x | x | x |
| Unsaturated group like alkene | 1644.09 | 1633.41 | 1655.59 | 1644.02 | 1654.62 | 1638.23 | x | x |
| Amide C-O stretching | x | x | x | x | x | x | 1594.04 | 1593.88 |
| Aromatic C-NO ₂ stretching | 1512.88 | 1505.17 | 1546.63 | 1514.81 | 1515.77 | 1509.99 | x | x |
| Carboxylate anion C=O stretching | 1321.00 | 1371.14 | x | x | x | x | x | x |
| Si-O stretching | 1072.66 | 1058.73 | 1079.94 | 1055.84 | 1098.26 | 1075.12 | x | x |
| Sulphonic acid S=O stretching | x | x | x | x | x | x | 1033.60 | 1031.73 |
| Sulphonate S-O stretching | x | x | x | x | x | x | 693.28 | 651.82 |

Table 5. Wave number (cm⁻¹) for the dominant peak from FT-IR for Cr(VI) adsorption.

| Functional Groups | Neem bark | Cr(VI) loaded neem bark | Hyacinth roots | Cr(VI) loaded hyacinth roots | Neem leaves | Cr(VI) loaded neem leaves | Coconut shell | Cr(VI) loaded coconut shell |
|---------------------------------------|-----------|-------------------------|----------------|------------------------------|-------------|---------------------------|---------------|-----------------------------|
| Surface O-H stretching | 3297.75 | 3266.82 | 3328.53 | 3305.39 | x | x | x | x |
| Aliphatic C-H stretching | x | x | 2924.52 | 2923.88 | 2920.28 | 2910.16 | x | x |
| Phosphite ester group | x | x | x | x | x | x | 2353.97 | 2358.78 |
| Aliphatic acid C=O Stretching | x | x | 1713.44 | 1713.44 | 1715.83 | 1715.67 | 1717.73 | 1715.75 |
| Unsaturated group like alkene | x | x | 1644.02 | 1633.41 | x | x | x | x |
| Amide C-O stretching | 1606.40 | 1603.52 | x | x | x | x | x | x |
| Aromatic C-NO ₂ stretching | x | x | 1514.81 | 1505.17 | 1515.46 | 1515.80 | 1507.22 | 1507.19 |
| Alkane group stretching | x | x | x | x | 1455.88 | 1455.98 | 1472.91 | 1456.25 |
| -SO ₃ stretching | x | x | x | x | x | x | 1236.10 | 1226.83 |
| Sulphonyl chlorides stretching | x | x | x | x | 1163.39 | 1162.00 | x | x |
| Sulphonic acid S=O stretching | 1032.91 | 1034.84 | 1055.84 | 1035.59 | x | x | 1031.37 | 1032.23 |
| Sulphonate S-O stretching | 756.92 | 658.57 | x | x | x | x | x | x |

from the peak shift (Tables 4 and 5). Aliphatic C-H stretching may be responsible for Cr(VI) adsorption onto neem leaves as wave number shift from 2920.28 cm^{-1} to 2910.16 cm^{-1} . Unsaturated group like alkenes present may also responsible for adsorption of Cr(VI) on rice straw, rice bran, rice husk and hyacinth root which is inferred from the shift of the peak more than 10 cm^{-1} .

Aromatic nitro, C-NO₂ stretching was found to have major shift of wave number from 1546.63 cm^{-1} to 1514.81 cm^{-1} for the adsorption of Cr(VI) on rice bran. There were also minor shift of peak for the adsorption of Cr(VI) on rice straw, rice husk, hyacinth roots, neem leaves and coconut shell. So the aromatic nitro groups are responsible for adsorption of Cr(VI) on rice bran not for the adsorption on other adsorbents. Alkane group was only responsible for Cr(VI) adsorption onto coconut shell as indicated in Table 5.

FT-IR spectrum of rice straw also showed intense bands around 1321.00 cm^{-1} which shifted to 1371.14 cm^{-1} for Cr(VI) loaded rice straw. This is to be attributed that the carboxylate anion are responsible for the adsorption on rice straw. At 1072.66 cm^{-1} (rice straw), 1079.94 cm^{-1} (rice bran) and 1098.26 cm^{-1} (rice husk) bands can be assigned Si-O stretching. Major shift of these band indicated that Si-OH group is responsible for adsorption.

Tables 4 and 5 also indicated that the minor shift for the other band (aldehyde C-H stretching, phosphate ester group, aliphatic carboxylic acids) which showed that these groups were not involved in the adsorption process. SO₃ stretching were found to be responsible for Cr(VI) adsorption onto coconut shell.

The peak at 1033.60 , 1032.91 , 1055.84 and 1031.37 cm^{-1} for saw dust, neem bark, hyacinth roots and coconut shell can be assigned to the S=O stretching mode of sulphonic acid group. S=O stretching was slightly shifted by Cr(VI) adsorption on saw dust, neem bark and coconut shell while the adsorption on hyacinth root resulted in a large shift of functional group from 1055.84 cm^{-1} to 1035.59 cm^{-1} . This would be imply that S=O stretching of sulphonic acid group is available for the adsorption of Cr(VI) on hyacinth root, however not involved on other adsorbents used in our study.

The observation for the sulphonate group revealed that S-O stretching was highly occurred by Cr(VI) adsorption on saw dust and neem bark. The S-O stretching group was observed to shift clearly from wave number 756.92 cm^{-1} to 658.57 cm^{-1} and 693.28 cm^{-1} to 651.82 cm^{-1} neem bark and saw dust respectively. This indicated that there is a high potential of S-O stretching group from sulphonate involved with Cr(VI) binding on neem bark and saw dust. So S-O stretching was only associated with the adsorption of Cr(VI) on neem bark and saw dust but

not for other adsorbents.

Crystal radius of Cr(VI) is 0.52 \AA . It is moderately large ion, fit into the binding site of the natural adsorbents and bind to several group present in the adsorbents simultaneously.

4. Conclusions

In this study batch adsorption experiments for the removal of Cr(VI) from aqueous solutions has been carried out using eight different natural adsorbents. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and different adsorbent dosages. FTIR analysis confirmed the existence of different functional groups responsible for the adsorption. The obtained results are summarized as follows

- 1) The optimum pH for the removal of Cr(VI) was found to be 1.5 for husk and 2 for other adsorbents.
- 2) Maximum uptake was obtained at adsorbent dosage of 10 g/L for all the adsorbents.
- 3) The equilibrium time for the adsorption of Cr(VI) from aqueous solutions were varied from 3 hr to 6 hr for adsorbents used.
- 4) The maximum monolayer adsorption capacities by the adsorbents were measured using Langmuir adsorption isotherm.
- 5) Sorption energy calculated from Dubinin-Raduskevich (D-R) shows the chemisorptions process for all the adsorbents.
- 6) FTIR studies indicated the following functional groups were responsible for adsorption,
 - a) Rice straw—Surface hydroxyl, unsaturated group like alkene, Carboxilate anion, Silicate groups;
 - b) Rice bran—Surface hydroxyl, unsaturated group like alkene, Aromatic nitro, Silicate groups;
 - c) Rice husk—Surface hydroxyl, unsaturated group like alkene, Silicate groups;
 - d) Saw dust—Sulphonate groups;
 - e) Neem bark—Surface hydroxyl, Sulphonate groups;
 - f) Hyacinth roots—Surface hydroxyl, Unsaturated group like alkene, Sulphonic acid groups;
 - g) Neem leaves—Aliphatic group;
 - h) Coconut shell—Alkane, -SO₃ groups.

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