Removal of Chromium (VI) from aqueous solutions using natural adsorbents – FTIR studies

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ABSTRACT

The ability of eight natural adsorbents for adsorptive removal of Chromium (VI) from aqueous solutions was investigated. 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 Chromium (VI) loaded adsorbents at the optimized condition was carried out to identify the different functional groups that were responsible for adsorption. It was estimated that important functional groups like hydroxyl, alkene, aromatic nitro, carboxilate anion, silicon oxide, sulphonic acid etc. were present in the natural adsorbents which were responsible for the chemical adsorption of Chromium (VI) from aqueous solutions.

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INTRODUCTION

Chromium is a heavy metal of great significance whose chemical and toxicological effect on living organisms have been studied in detail and serious implications have been withdrawn. Chromium exists in two oxidation states viz. III and VI out of which Chromium (VI) has been found to be a more serious biological and environmental contaminant. Chromium (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 has been found to be carcinogenic, mutagenic and toxic [1,2]; 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 permissible limits and lower. Waste water treatment has therefore become extremely significant and now a days 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. that help in eradication of minimization of toxic substances and heavy metals from the waste water being released in the open environment [7] and among these technologies, adsorption is a user-friendly technique. This process includes the selective transfer of solute components in the fluid phase onto the surface or onto the bulk of solid adsorbent materials.

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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 used.

EXPERIMENTAL SECTION

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 areas near Allahabad, Uttar Pradesh, India.

Rice straw, rice bran, rice husk and hyacinth roots were boiled for 6 hours to remove colored materials. Coconut shell was crashed in roll crusher and then ground. Saw-dust, neem bark, neem leaves and coconut shell were treated with 0.1 N NaOH to remove lignin based colored materials followed by 0.1 N H_2SO_4. Finally all the adsorbents were washed with distilled water several time and dried at 105°C for 6 hours to remove the adherent moisture. After drying, all the adsorbents were sieved to obtain particle size of 250 - 350 μm prior to being used for adsorption studies.

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. FTIR (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 (Metteler LP16). The point of zero charge was determined by solid addition method [12] and reported in **Table 1**.

Table 1 - Different physical characteristics of natural adsorbents

Adsorbents	Surface area (m2/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

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 K_2CrO_4, $2H_2O$ 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.

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 ±0.5% and

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±2.5% respectively. The solution pH adjusted to 1.0 ± 0.1 to 9.0 ± 0.1 under thermostated conditions of 30°C ± 0.5°C.

RESULTS AND DISCUSSION

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 pH < pHpzc. At very low pH, chromium ions exist in the form of $HCrO_4^-$, at higher pH up to 6 different forms such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$ coexists, of which $HCrO_4^-$ predominates. As the pH increases, equilibrium shifted from $HCrO_4^-$ to CrO_4^{2-} and $Cr_2O_7^{2-}$ [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 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

$$H2CrO4 \longleftrightarrow HCrO_4^- + H^+ \qquad k_1 = 1.21 \qquad (1)$$

$$Cr_2O_7^{2-} + H_2O \longleftrightarrow 2HCrO_4^- \qquad k_2 = 35.5 \qquad (2)$$

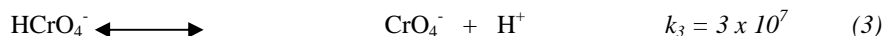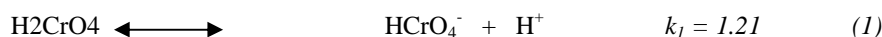$$HCrO_4^- \longleftrightarrow CrO_4^- + H^+ \qquad k_3 = 3 \times 10^7 \qquad (3)$$

Table 3. Optimum operating condition obtaining in the batch process

Adsorbent	Initial pH	Initial Cr(VI) conc. (mg/L)	Contact time (min)	Adsorbent dosage (g/L)	Langmuir isotherm model	
					$q$max (mg/g)	r2
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

Adsorption of Cr(VI) was not significant at pH values more than 6 due to dual complexation of the anions [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**.

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

Equation (4) represents the Langmuir adsorption model where *Ce* is the concentration of Cr(VI) in solution at equilibrium (mg/L), *qe* is the amount adsorb per gram of the adsorbent at equilibrium, *qmax* is the maximum adsorption capacity (mg/g) and *b* is the Langmuir constant (L/mg). Linear plots of *Ce/qe* vs. *Ce* were employed to

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determine the value of *qmax* (mg/g). The maximum adsorption capacity along with correlation coefficient (*r*2) obtained were listed in table 3.

FTIR Analysis for Cr(VI) Adsorption

Fourier 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 - 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.
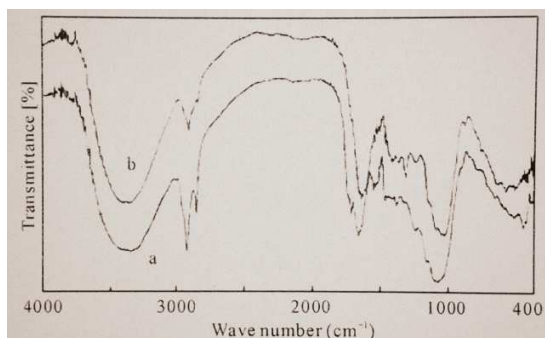

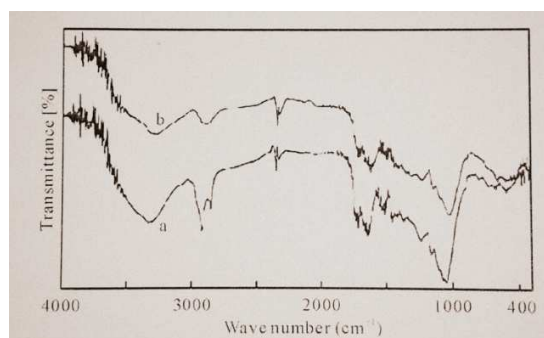Figure 1. FTIR spectra of (a) rice straw and (b) Cr(VI) loaded rice straw.

Figure 2. FTIR spectra of (a) hyacinth roots and (b) Cr(VI) loaded hyacinth roots.
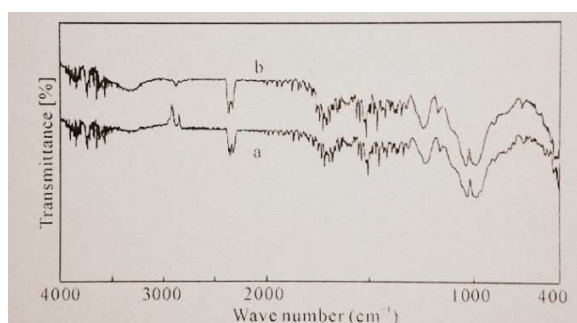

Figure 3. FTIR spectra of (a) coconut shell and (b) Cr(VI) loaded coconut shell.

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 FTIR 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 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 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.

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Table 4. Wave number (cm−1) for the dominant peak from FTIR 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-NO2 stretching	1512.88	1505.17	1546.63	1514.81	1515.77	1509.99	x	x
Carboxilate 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

Aromatic nitro, C-NO$_2$ 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 shifts 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**.

Table 5. Wave number (cm−1) for the dominant peak from FTIR 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-NO2 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
-SO3 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

FTIR 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

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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. SO_3 stretching were found be to 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 Å. It is moderately large ion, fit into the binding site of the natural adsorbents and bind to several group present in the adsorbents simultaneously.

CONCLUSION

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) 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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