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Mechanism of Cr (VI) Biosorption by Neem Sawdust

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Abstract: The mechanism of Cr (VI) uptake by neem sawdust was investigated using different chemical and instrumental techniques. Batch biosorption studies after the removal of the components viz. lignin and cellulose of the biosorbent revealed that lignocellulosic moieties play a predominant role in the biosorption of Cr (VI). FTIR analysis showed that the bonded-OH groups, C=O groups, SO_3 stretching, C-O stretching and-CN stretching were involved in Cr (VI) biosorption. The biosorbent was analyzed for its elemental composition using EDAX. The oxidation state of chromium in neem sawdust after Cr (VI) adsorption from aqueous solution was investigated using electron spin resonance (ESR). ESR experiments confirmed that Cr (VI) was reduced to Cr (III) on lignin component of neem sawdust. The mechanism involved in biosorption of Cr (VI) was found to be adsorption coupled reduction.

Key words: Biosorbent · Chromium (VI) · Chromium (III) · Mechanism

INTRODUCTION

Chromium, a priority metal pollutant is widely used by various modern industries like electroplating, tanning, textile, etc. resulting in discharge and accumulation in large quantities into the environment (Sharma, 2003). Chromium exists in environment both as trivalent (Cr (III)) and hexavalent (Cr (VI)) forms of which, hexavalent form is 500 times more toxic than the trivalent one [1]. Human toxicity of Cr (VI) includes skin irritation, lung cancer, as well as kidney, liver, and gastric damage [2]. The usual methods to remove Cr (VI) from aqueous effluents include chemical reduction [3], nanofiltration [4], bioaccumulation [5], ion exchange [6], adsorption on silica composites [7, 8] and on activated carbon [9]. However, these approaches are not cost-effective and difficult to implement in developing countries. Biosorption, a technically feasible and economical process, has gained increased creditability during recent years [10]. A number of agricultural wastes have been reported as biosorbents for chromium removal [11-14]. Though some workers [15-17] have reported the potential use of sawdust for removal of chromium from aqueous solution, a detail study on mechanism of chromium removal has not been reported so far. Therefore, the objective of the present study is to investigate the mechanism of Cr (VI) sorption by neem sawdust using different experimental approaches involving biochemical and instrumental analysis.

METHODS

Biosorbent Preparation: Neem sawdust was collected from the local Sawmill and washed with deionised water, oven dried at 60°C for 24 hrs and then pulverized. The materials were kept in air tight plastic bottles. The particle size was maintained in the range of 425-600 µm.

Metal Solution: Cr (VI) solutions were prepared using $K_2Cr_2O_7$. Stock solution (1000 mg/L) of Cr (VI) was prepared by dissolving required quantity of $K_2Cr_2O_7$ in deionised water. For biosorption experiments, Cr (VI) solutions having 100 mg/ L were prepared and used. The pH of the solution was adjusted with 0.1 N HNO_3 and NaOH solutions.

Removal of Major Neem Sawdust Constituents: In order to assist in the elucidation of the role of major constituents of neem sawdust (cellulose and lignin) in the chromium sequestering process, chemical treatments were employed.

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Removal of Lignin: Delignification of the biosorbent to obtain the cellulose was carried out following the method suggested by Sengupta *et al.* [18]. Finely powdered neem sawdust was thoroughly cleaned of wax and oils in a soxhlet apparatus using a mixture of benzene and ethanol (2: 1 v/v) and dried under vacuum. Five grams of the sample was treated with 0.7 % sodium chlorite solution at pH 4.0, maintained by acetic acid (0.2 M) for 2 hrs in a boiling water bath. The process was repeated three times and the samples were brought to neutral pH by washing with 2 % sodium metabisulphite and water at 60°C, cooled and dried in P_2O_5 desiccators. The product was denoted as S_c.

Removal of Cellulose: Removal of cellulose from the metal loaded biosorbent was carried out following the method suggested by Giger (1985) [19]. Five grams of neem sawdust was heated to 30°C for 1 hr in 72% H_2SO_4 followed by dilution (1:25) with water and autoclaving at 120°C for 1 hr. The H_2SO_4 concentration of 72% was chosen because cellulose is not completely hydrolysed at concentration below 65%. The product was denoted S_L.

Batch Equilibrium Studies: Batch equilibrium studies were conducted with different biosorbents (S_R, S_L and S_C) contacted with various concentration of Cr (VI) solution (10-150 mg/L) at pH 2 with contact time (2 hrs). The reaction mixtures were agitated on a rotary shaker at 120 rpm, filtered through whatman no.1 filter paper and the filtrates were analyzed for Cr (VI) concentration using UV spectrophotometer at a wavelength of 540 nm following 1, 5-diphenyl carbazide method [20]. From the experimental data, the applicability of Langmuir model was judged. Linear regression coefficient (R^2) and isotherm constants values were determined from the model.

Fourier Transform Infrared Spectroscopy (FT-IR): Infrared spectra of raw and chromium loaded biosorbent (neem sawdust) were obtained using a Fourier transform infrared Spectrophotometer (Thermo Nicolet, model 330 FTIR). Adsorbents were dried in an oven at 60°C for 24 hrs. Approximately 5 mg of finely ground sorbent was encapsulated in 1000 mg of KBr pellet (Sigma, USA) in order to prepare translucent sample disks. The tablet recovered with a clip was immediately analyzed with the spectrophotometer in the range of 4000-400 cm^{-1}. Spectra of the sorbent before and after Cr (VI) sorption were recorded.

Energy Dispersion Analysis by X-ray (EDAX) Analysis: EDAX analysis was conducted using the Noran System Six model Energy Dispersive X Ray Microanalysis System (Thermo Electron Corporation) attached to the SEM with the voltage of 15 KV to facilitate the emission of secondary X-rays. The raw and the chromium treated biosorbents were analyzed for their elemental compositions.

Electron Spin Resonance (ESR) Measurements: Electron spin resonance (ESR) studies were carried out to identify the major constituent of neem sawdust involved in the reduction of Cr (VI) to Cr (III).

Ten milligram samples were loaded into a quartz sample tube with 5 mm diameter, and then analyzed by electron spin resonance using X-band ESR spectrometer (JEOL, JES TE-100) under the operation conditions of microwave power 5 mW, a microwave frequency 9.44 GHz, an external magnetic field of 340 mT, a field amplitude 10 mT, a field modulation 100 kHz, a modulation width 0.1 mT, a time constant 0.3 s, and sweep time of 3 min.

RESULTS AND DISCUSSION

The biosorbent employed in the present investigation is neem sawdust which is a waste product of the timber industry used either as cooking fuel or packing material. The constituents of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds. Lignin, the major component of the wood cell wall, is a polymer material [21]. The composition of typical neem sawdust reported by Khattri and Singh [22] is presented in Table 1.

In the present study, lignin from raw neem sawdust (S_R) was removed and the derivative obtained was denoted as S_C. In another set, cellulose was removed from raw neem sawdust and the derivative designated as S_L.

Equilibrium Cr (VI) uptake studies were conducted with the two derivatives (S_C and S_L) obtained from raw neem sawdust after chemical treatment. The chromium (VI) uptake potential (q_{max} values) for raw neem sawdust, sawdust without cellulose (S_L) and sawdust without lignin (S_C) shown in the Table 2 indicated that Cr (VI) uptake was drastically reduced after the removal of lignin. The removal of cellulose (S_L) resulted in reduction of metal uptake capacity to 56.4% whereas the removal of lignin (S_C) showed a maximum decrease in metal uptake capacity i.e. 81.9 %. Therefore, the present data confirmed the role of lignin as major component for Cr (VI) adsorption on neem sawdust.

Table 1: Composition of typical neem sawdust (Khattri and Singh, 2009)

Component of neem sawdust cell wall	% of Total
Cellulose	36.65
Lignin	49.35

Table 2: Cr (VI) uptake capacity of selective components of neem sawdust

Biosorbent (neem sawdust)	Cr (VI) uptake capacity (q_{max}) mg/g
S_R (raw)	58.82
S_L (without cellulose)	25.64
S_C (without lignin)	10.63

(Cr (VI) concentration = 100 mg/L, contact time 2 h and dosage = 2 g/L)

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Fig. 1 displays a number of absorption peaks, indicating the complex nature of neem sawdust. The FTIR spectroscopic analysis indicated broad bands at 3418 cm^{-1}, representing-OH and-NH stretching (the surface hydroxyl & amine groups). The bands observed at about 2930 cm^{-1} could be assigned to the aliphatic C-H group. The band present at 1745 cm^{-1} could be assigned to-C=O (band from carboxylic groups or ester groups). The peak around 1642 cm^{-1} corresponds to-C=O (amide band primarily a stretching band). The band at 1540 cm^{-1} corresponds to-C=O (carbonyl stretching bands).

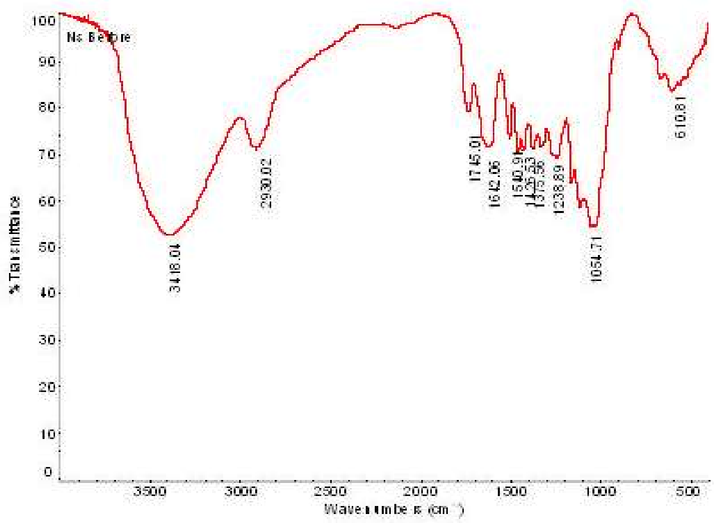

Fig. 1: FT-IR spectrum of neem sawdust before Cr (VI) adsorption

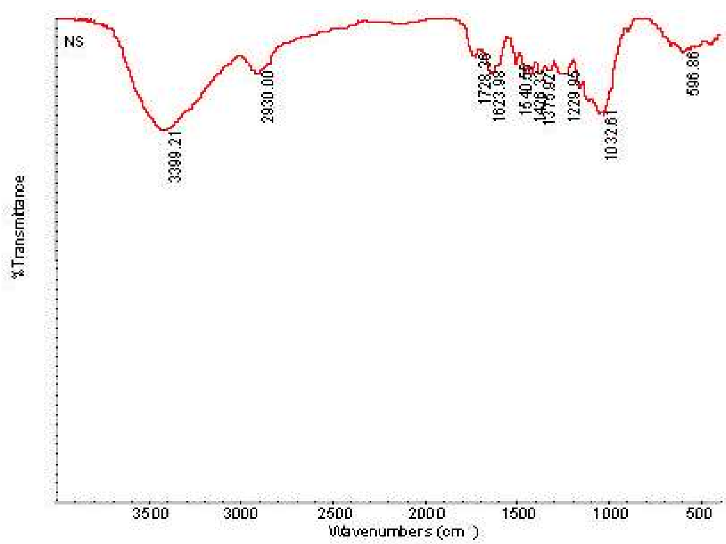

Fig. 2: FT-IR spectrum of neem sawdust after Cr (VI) adsorption

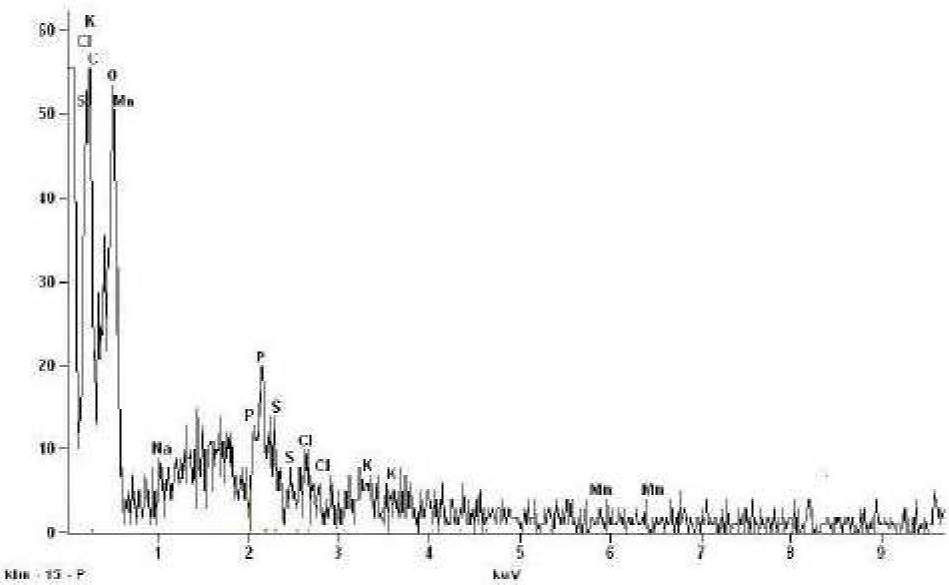

Fig. 3: EDAX Spectrum of biosorbent before Cr (VI) uptake

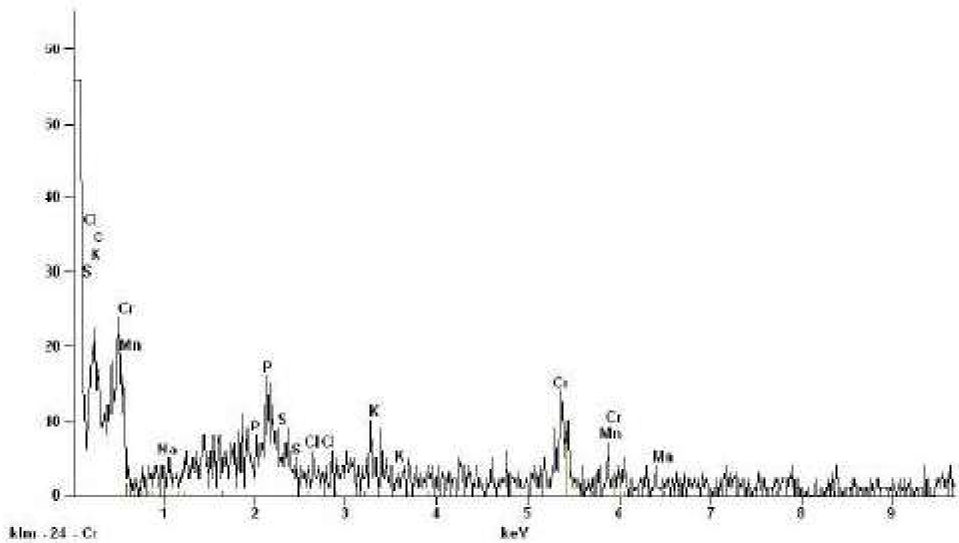

Fig. 4: EDAX Spectrum of biosorbent after Cr (VI) uptake

Symmetric bending of CH_3 is observed to shift at 1426 cm^{-1}. The peak 1375 cm^{-1} indicates the stretching vibrations of the NO_2. The peaks observed at 1238, 1054 and 610 cm^{-1} could be assigned to-SO_3 stretching, C-O stretching of polysaccharides and-CN stretching, respectively. Fig. 2 shows the spectral analysis after metal adsorption. There were clear band shifts and intensity decrease of the band at 3418, 1745,1642, 1238, 1054 and 610 cm^{-1} indicating that bonded-OH groups, C=O groups, SO_3 stretching, C-O stretching and-CN stretching were especially involved in Cr (VI) biosorption.

Energy dispersive X-ray analysis (EDAX) provides elemental information through analysis of X-ray emissions caused by a high energy electron beam. EDAX technique can be beneficially employed to understand the elemental composition of the biosorbent. In the present study, X-ray dispersion analyses of the raw as well as chromium adsorbed neem sawdust were evaluated. The EDAX spectrum of biosorbent before chromium (VI) uptake indicated the presence of S, Cl, C, O, K, Mn, Na, and P as natural species on the biosorbent (Fig. 3). In case of treated biosorbent (Fig. 4) chromium was present along

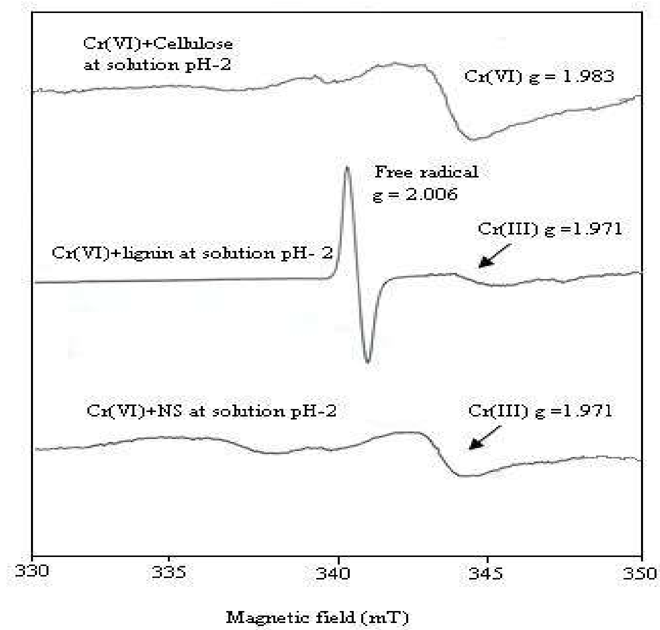

Fig. 5: ESR Spectra of various adsorbents adsorbed Cr (VI) at solution pH 2
(Cr (VI) concentration = 100 mg/L, contact time 2 h and dosage = 2 g/L)

with all other natural elements indicating that ion exchange is not the mechanism involved in adsorption of Cr (VI).

The ESR analysis of neem sawdust (devoid of lignin) and neem sawdust (devoid of cellulose) after Cr (VI) adsorption at solution pH 2 were investigated to clarify the mechanism of Cr (VI) reduction on neem sawdust. (Fig. 5).

The Cr (VI) signal (g = 1.984) in the ESR spectra of neem sawdust (Cr (VI) + cellulose) revealed that there was no reduction of Cr (VI) on the cellulose part. Whereas the Cr (III) signal (g = 1.971) noted in the ESR spectra of neem saw dust (Cr (VI) + lignin) confirmed the reduction of Cr (VI) to Cr (III) on lignin itself. The results of the present study are in agreement with the work of Suksabye *et al.* [23]. Generally, the reduction of Cr (VI) to Cr (III) requires a large amount of protons and electrons [24]. The reduction from Cr (VI) to Cr (III) could occur due to the fact that the hydroxyl groups [25] and carbonyl groups [26] contained in lignin played a role as electron donor for the reduction reaction.

Therefore, the experimental results confirmed that Cr (VI) was reduced to Cr (III) on neem sawdust proving the mechanism involved in Cr (VI) biosorption was adsorption coupled reduction.

CONCLUSIONS

The Cr (VI) uptake capacity of neem sawdust was significantly reduced after the removal of lignin and cellulose which indicated the involvement of lignocellulosic components for Cr (VI) adsorption. FTIR analysis revealed that OH groups, C=O groups, SO_3 stretching, C-O stretching and-CN stretching were especially involved in Cr (VI) biosorption. EDAX analysis presented the elemental composition of neem sawdust before and after biosorption. The presence of Cr (III) signal in the ESR spectra of lignin of indicates that the reduction from Cr (VI) to Cr (III) occurred in the lignin part of neem sawdust after Cr (VI) adsorption which proves the mechanism of Cr (VI) removal by neem sawdust is adsorption-coupled reduction.

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