



Investigation of the activity of sawdust as biosorbent towards Cr (VI) removal from waste water: Kinetic and thermodynamic studies

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Abstract

Cr (VI) removal from aqueous solutions by *Ziziphus mauritiana* (Indian jujube) sawdust biosorbent (ZMSDB) was studied in a batch mode technique. The effect of pH (2-7), contact time (10-360 minutes), temperature (293-313 K) and biosorbent dosage (0.2-1.0 g) was investigated for Cr (VI) uptake. Maximum removal of Cr (VI) was found at pH 2.0 and 3.0. Equilibrium was established in 360 minutes. The adsorption rate was best described by pseudo-second order equation. Langmuir adsorption isotherm determines the adsorption equilibrium and the monolayer adsorption capacity of Cr (VI) was found to be 3.66 mg g⁻¹ at 313 K. The values of separation factor, R_L , was in flanked by 0.019 -0.0557 which pointed out constructive exclusion of Chromium (VI) over ZMSDB. Thermodynamic parameters (ΔH , ΔG and ΔS) values exposed the endothermic biosorption of Cr (VI) on ZMSDB, no-spontaneity and low entropy in nature.

Keywords: pH, separation factor, Langmuir, pseudo-second order, kinetic, adsorption.

Introduction

Water is the basis of life but if contaminated with chemical and organic substances, then it can cause death. Water contaminated with heavy metals has drawn much attention in the last few decades. The amassing of heavy metals in living tissues of the public has a serious health damaging characteristics. Waste effluents come out from various industries mainly electroplating, steel and tanning industries contains heavy metals¹. Among them, chromium (Cr) has been considered as one of the toxic pollutant and is found in its two most stable oxidation states i.e., Cr (III) and Cr (VI). Cr (III) is the essential nutrient required for fat and sugar metabolism. However, its maximum exposure causes cancer and allergic skin reactions². Cr (VI) due to its toxic nature causes teratogenic, mutagenic and carcinogenic symptoms in biological systems. That's why removal of Cr (VI) from aqueous solutions and industrial waste waters has pulled much attention. According to US EPA, 0.05 mg/L–0.1 mg L⁻¹ Cr (VI) is permissible in common use water^{3,4}. Therefore it is necessary to treat the waste water for further better use. So far, a range of techniques such as solvent extraction, chemical precipitation, electrochemical precipitation, ion exchange, membrane separation, reduction and adsorptions have been applied for waste water treatment. However, these methods have considerable drawbacks for example incomplete removal, high cost, regular monitoring, energy consumption and further production of the toxic sludge or disposable wastes.

Adsorption on the activated carbon (powdered and granular) is much effective for the treatment of waste water due to its tremendous porous surface structure but its applicability has been restricted as per high cost of fabrication and regeneration⁵. So there is a need to use such materials as adsorbents with low-

cost and good removal capacity of heavy metals. From the environmental and economical point of view, particular consideration has been focused on the natural bio wastes to use as adsorbent in waste water treatment. A number of biomasses have been reported for their use in purification of waste waters. Some of them are potato peel⁶, distillery sludge⁷, coconut tree sawdust⁸ and tamarind seeds⁹ etc. Moreover, to reduce the problem of heavy metals pollution further investigations are still needed for the addition of available low-cost biosorbents.

Herein we focused on the biosorption capacity of *Ziziphus mauritiana* (Indian jujube/Berry) sawdust for Chromium (VI) from water. The effect of pH, biosorbent quantity, time of contact and hotness (T) was also considered in a batch mode technique.

Material and Methods

Study area and collection of adsorbent samples: In Khyber Pakhtoonkhwa (Pakistan), District Bannu is famous for the congested trees of *Ziziphus Mauritania*. A number of carpenters are engaged to design various furniture from the timbers of this tree. *Ziziphus Mauritania* sawdust samples were collected from the saw machines of the carpenters. The samples were washed with water and were dried at 120 °C. The dried samples were then passed through micro sized mesh and were used as adsorbent.

Material Used: 1, 5 Diphenylcarbazide 98 % (Scharlau Cat No. D10650), sodium hydroxide 100 % (Scharlau Cat No. SO0420), acetone 99 % (Scharlau Cat No. AC03121000), hydrochloric acid 38% (Merck Cat No. K27932914), sulfuric acid 98 % (BDH Cat No. 30325) and potassium dichromate 99 % (Across Cat No. 196595000) were utilized as obtained.

Testing Solutions: Chromium (VI) solution was prepared by dissolving 2.83g potassium dichromate in de-ionized water. Then it was further attenuated with deionized H₂O and the solution of desired concentrations were formed. Acidity of the prepared solutions was accustomed with 0.1 M sodium hydroxide and HCl respectively.

Adsorption Experiments: Adsorption experiments of Cr (VI) were performed via batch mode technique. pH (2-7) effect, adsorbent concentration (0.2-1.0g), temperature (293-313 K) and contact time (360 minutes) was investigated for Cr (VI) adsorption. For each batch experiment, 40 mL chromium (VI) solution of with different conc. was applied. When Cr (VI) solution and adsorbent dosage were added to the conical flasks the pH of solutions were adjusted and then shaken up to the equilibrium. After adsorption, mixture of Cr (VI) and adsorbent was filtered. A standard colorimetric method was used to determine residual Cr (VI) concentrations in solution. A red-violet colored complex was formed between the reaction of Cr (VI) and 1, 5- Diphenylcarbazide in acidic medium. The removal percentage (*R%*) and unit adsorption (*Q_{ad}*) of Cr (VI) for each experiment was investigated by using equations 1 and 2.

$$R\% = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (1)$$

$$Q_{ad} = \left(\frac{C_i - C_e}{W} \right) \times V \quad (2)$$

Where *C_i* (primary conc.), *C_e* (stable con.), *W* (weight), *V* (capacity) are the relevant properties of the biosorbent and that of adsorbate with their respective units shown in tables.

Physico-chemical Study: FTIR confirmed various bond strength variations of biosorbent. Scanning Electron Microscopy (SEM) was used to study the surface morphology of the adsorbent and the surface area of the adsorbent was calculated by using surface area analyzer.

Results and Discussion

Effect of Initial Solution pH: pH reflects the internal contamination and thus its effects in water¹⁰. The adsorption of Chromium (VI) adsorption was done on pH (2-7) keeping all the other parameters invariable. The exclusion competence enhanced from 15 to 99.9 % and from 16.99 to 99.9 % correspondingly as the preliminary pH of the solution varies downward. Solution pH between 2 and 3 was found to show maximum adsorption. The trend is shown in figure 1. It was found that at low pH the face moves to positive version which strengthens the contact between adsorbate ions and biosorbent faces having opposite charges. Low pH shows that the prevailing group is HCrO₄⁻ that produces from (Cr₂O₇²⁻)²⁻ hydrolysis. With increase in pH (> 6.5) HCrO₄⁻ converted into

CrO₄²⁻ and Cr₂O₇²⁻. As a result repulsion between the biosorbent surface and doubly adsorbate anions increases which leads to decrease in Cr (VI) ions removal.

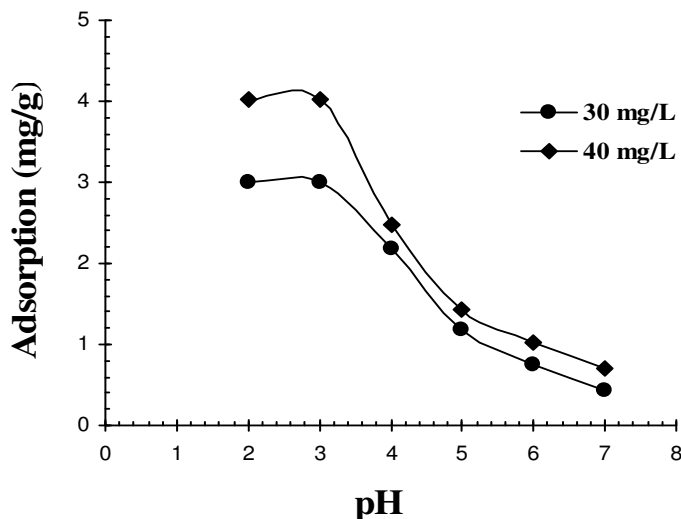


Figure-1
Effect of pH on the removal of Cr (VI)

Contact Time Effect: It has been found that contact time has also great impact on the adsorption of heavy metals from aqueous solution as reported in literature for Cd on chitosan¹¹. Figure 2 explores the consequence of this result.. It was found that time has a major influence on the removal of Chromium (VI). Initially the uptake of Cr (VI) was in lowest amount, however, within 30 minutes a regular increase was noted. The stability reached in 6 hours and no significant change was observed further. Maximum removal was noted in the first 30 minutes. This may be attributed to high Conc. of the adsorbate and large surface of the biosorbent. It has been observed that with the passage of time the biosorbent surface is covered by the adsorbate molecules and the removal efficiency decreases¹².

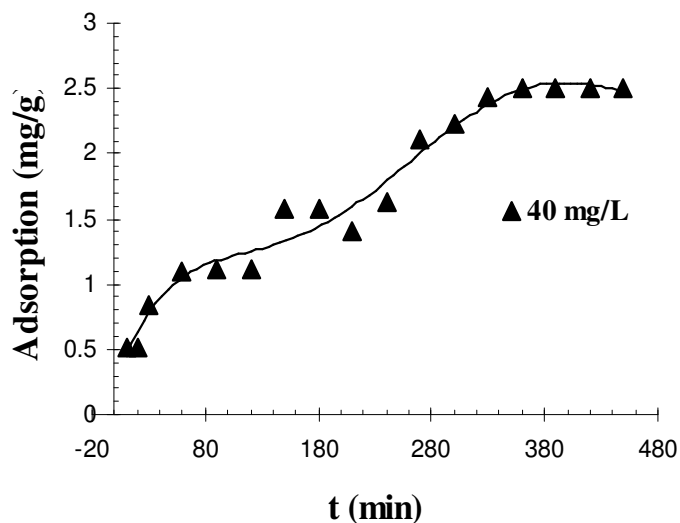


Figure-2
Effect of contact time on Cr (VI) adsorption

Dose Influence: Dose control is revealed in figure 3. The quantity taken was in the range from 0.2 to 1.0 g 40 mL⁻¹. Other respective bounds were reserved invariable. It was investigated that % adsorption effectiveness grew from 45 to 99 % while remained continuous afterwards at 1.0 g. However, the decrease in Cr (VI) uptakes from 2.82 to 1.21 mg g⁻¹ and 3.75 to 1.64 mg g⁻¹ at higher adsorbent dosage (0.2-1.0 g 40 mL⁻¹) is considered to be due to the taking over the sights of the biosorbent by chromium (VI) ions¹³.

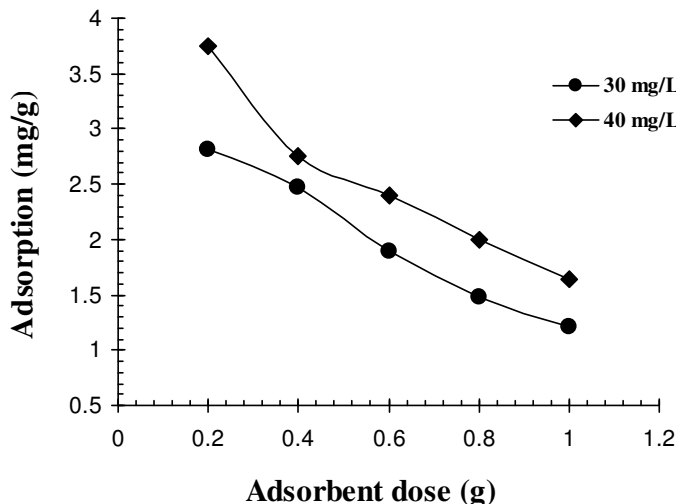


Figure-3
 Effect of biosorbent dosage on removal of Cr (VI)

Temperature Study: Experiments at 293, 303 and 313 K. adsorption of Cr (VI) were increased with temperature i.e., endothermic process (figure 4). The porous surface is very active at high temperature so it shows high adsorption¹⁸. It has been investigated that high temperature increases the kinetic energy that maximize particles (adsorbent) and adsorbate ions collision. Bond splitting has also been noted at elevated temperature that satisfies the formation of new functional sights on the sawdust faces. Such types of temperature variations encourage the exclusion of chromium (VI) from water¹⁴.

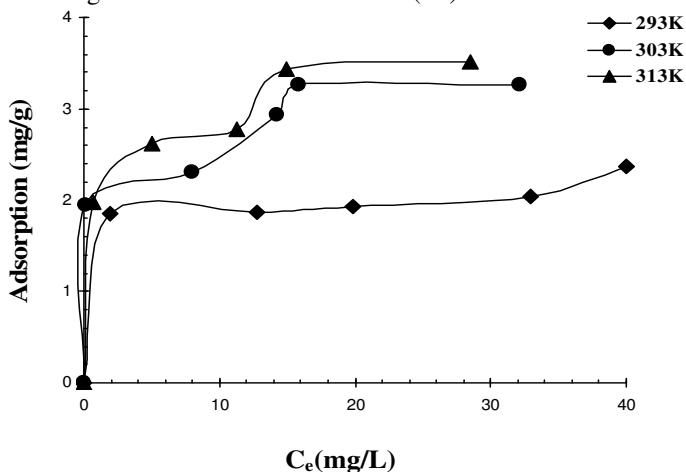


Figure-4
 Effect of temperature on removal of Cr (VI)

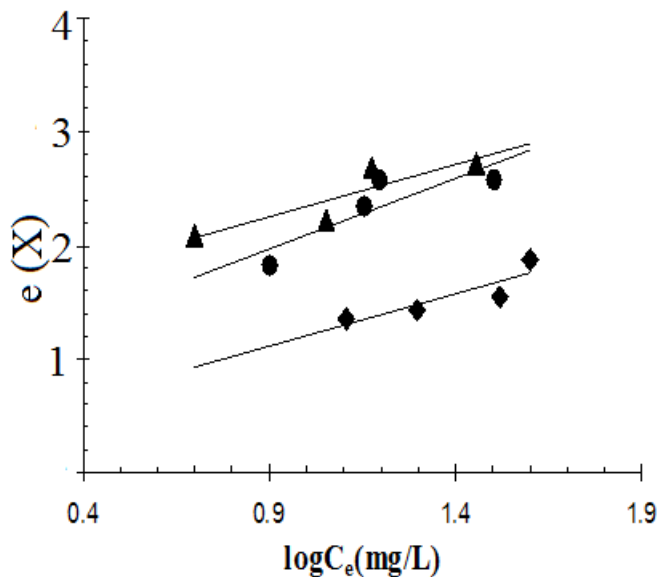


Figure-5
 Freundlich plot for Cr (VI) adsorption on ZMSDB

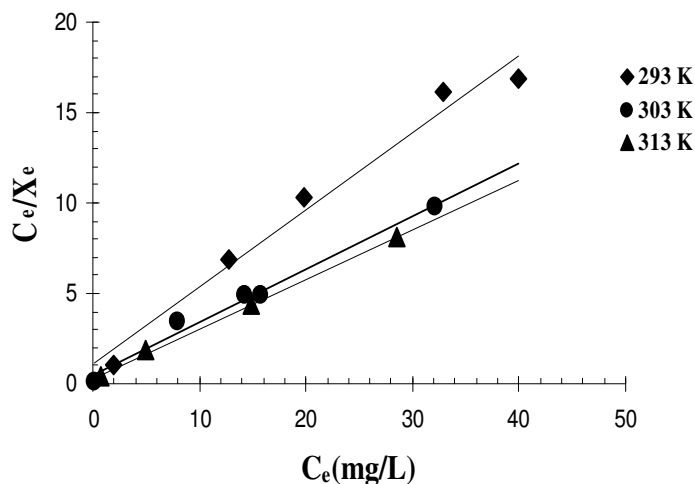


Figure-6
 Langmuir plot for Cr (VI) adsorption on ZMSDB

Measurement of the Surface Area: Surface area of the adsorbate is very important for the removal of contaminants form water. In our case, we determined BET surface area with proper instrumentation. The procedure was that of degassing of the sample in N₂ environment for one hour at raised temperature. The determined surface area was 1.46 m²/g.

Implementation of Adsorption Equations (Isotherms): Adsorption equilibrium can be used to identify the threshold of adsorption. The adsorption isotherms studies were done by varying Cr (VI) amount from 20 to 60 (mg L⁻¹) at invariable sawdust dosage (10 g L⁻¹). Freundlich (FAI) and Langmuir (LAI) equations (isotherms) were applied in our case¹⁵. (FAI)

illustrates multilayer deposition on surfaces with variable morphology. General and logarithmic form of the Freundlich adsorption isotherm is shown in equation 3 and 4 below:

$$X_a = K_f C_e^{1/n} \quad (3)$$

$$\log X_a = \log K'_f + \frac{1}{n} \log C_e \quad (4)$$

In these equations, K_f is FAI constant, C_e , equilibrium con., n , strength and X_a is the amount of adsorbate per unit mass of the adsorbent. The potential data was measured from the plot.

LAI explains unilayer deposition on the homogeneous surface. Adsorbate particles are considered here independent entities. Also the molecules adsorbed have no interaction to change their position on the surface. Langmuir adsorption isotherms are represented in equations 5 and 6 as follow:

$$X_e = \frac{q_m K_l C_e}{1 + K_l C_e} \quad (5)$$

$$\frac{C_e}{X_e} = \frac{1}{K_l q_m} + \frac{1}{q_m} C_e \quad (6)$$

All the parameters are the same as that of FAI except q_m which is used for the total amount of the adsorbate entire unilayer coverage of the surface. q_m and K_l were determined from $\frac{C_e}{X_e}$ versus C_e .

The regression constants (R^2) values signify that the LAI ($R^2 = 0.9978$) is most excellent appropriate to the experimental data than FAI ($R^2 = 0.8037$) as given in table 1. R_L which is known as equilibrium factor verifies important feature of LAI as shown in equation 7 as:

$$R_L = \frac{1}{1 + K_l C_o} \quad (7)$$

Where K_l is the Langmuir constant and C_o is the initial Cr (VI) concentration. R_L values confirm whether the adsorption is positive, adverse, unalterable or proportional directly as explained in literature. R_L data obtained for 20-60 mg L⁻¹ at 313

K was 0.0194 and 0.0557 which is in between zero and one signifying good biosorption of Chromium (VI) ions on ZMSDB.

Kinetics Study: Kinetic studies were carried out to demonstrate the mechanism of the removal of chromium (VI). A number of basic kinetic models were implemented in this regard:

Pseudo-1st (ρ-1) Kinetics: ρ-1 Indicates adsorbate system in solution. This is written as:

$$\frac{dq_i}{dt} = k_1 (q_e - q_i) \quad (8)$$

q_e and q_i (Stable adsorption capabilities), k_1 , rate constant of ρ-1. Rearranging equation 8 with adjustable values, equation 9 is obtained.

$$\ln(q_e - q_i) = \ln q_e - k_1 t \quad (9)$$

$\ln(q_e - q_i)$ is directly proportional to time t . Graphical representation of equation 9 (figure 7) provide an immediate line from which the factors are find out.

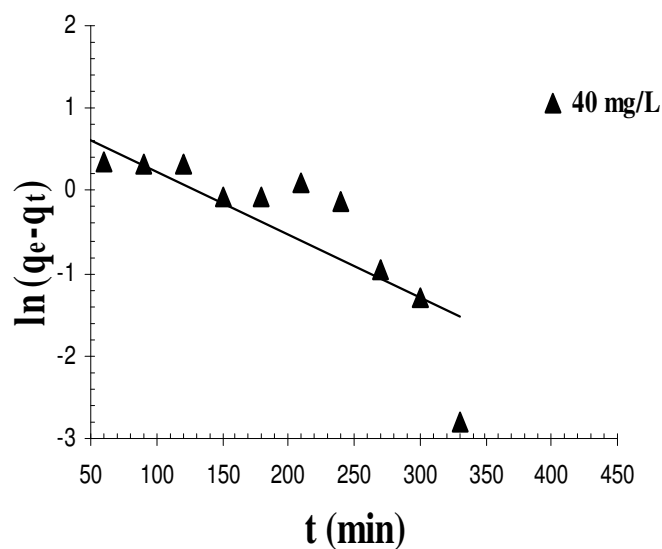


Figure-7
Pseudo-first order plot for the adsorption of Cr (VI)

Table-1
Langmuir and Freundlich isotherms constant for sawdust adsorbent

S. No	Langmuir Adsorption Isotherm			Freundlich Adsorption Isotherm		
	Temperature (K)	q_{max} (mg g ⁻¹)	K_l (L mg ⁻¹)	R^2	n	K'_f (L mg ⁻¹)
293	2.34	0.40	0.9764	1.18	1.13	0.7772
303	3.40	0.61	0.9850	4.02	1.47	0.7369
313	3.66	0.82	0.9978	3.52	1.92	0.8037

Pseudo-2nd (ρ-2) Kinetics: The ρ-2 kinetic rate equation is given below:

$$\frac{dq_i}{dt} = k_2(q_e - q_i)^2 \quad (10)$$

Here: k_2 is the rate constant of ρ-2, By integrating 10, 11 is obtained.

$$\frac{1}{q_e - q_i} = \frac{1}{q_e} + kt \quad (11)$$

By rearranging 11, equation 12 is come out to be:

$$\left(\frac{t}{q_i}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (12)$$

t/q_i versus t offer the direct line having $\left(\frac{1}{q_e}\right)$ slope and

$\left(\frac{1}{k_2 q_e^2}\right)$ intercept as shown in figure 8.

By comparing the $R^2 = 0.9020$ of ρ-2 with that of ρ-1 ($R^2 = 0.6790$), it is evident that the present matches well with ρ-2 regarding kinetics. According to ρ-2, chemical biosorption consisting of chemical interactions via the distribution or transfer of electrons linking the adsorbate and adsorbent¹⁶ that confers the speed preventive step of the process. The constant values determined for pseudo-first and pseudo-second order models are given in table 2.

Thermodynamic Parameters: The thermodynamic parameters (ΔH , ΔG and ΔS) were calculated using the following equations.

Table-2
Assessment of kinetic parameters of Chromium (VI) deposition over sawdust

	Pseudo-1 st (ρ-1) Form			Pseudo-2 nd (ρ-2) Form		
	K_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g min mg^{-1})	q_e (mg g^{-1})	R^2
Cr (VI) Conc.40 mgL^{-1}	7.00×10^{-3}	2.74	0.7410	2.00×10^{-3}	3.17	0.8671

Table-3
Thermodynamic parameters for Cr (VI) adsorption on ZMSDB

Temperature (K)	ΔG (kJ mol^{-1})	ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)	ΔH (kJ mol^{-1})
293	2.16	86.11	27.39
303	1.30		
313	0.44		

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

$$\ln K_l = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (14)$$

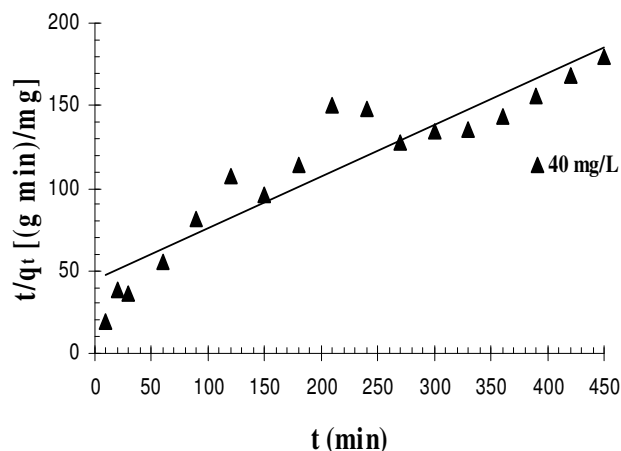


Figure-8
Pseudo-second order plot for Cr (VI) adsorption

Here K_b is equilibrium constant, ΔH is enthalpy change, ΔG free energy change, ΔS entropy change, R is universal gas constant and T is the adsorption temperature respectively.

From Vent Hoff plot using equation 14, the plot of $\ln K_b$ versus $1/T$ is given in figure 9. ΔH and ΔS measured from the plot slope and intercept shows the validity of the adsorption in endothermic and much disordered phase¹⁷. ΔG data suggests non-spontaneity of the system (table 3).

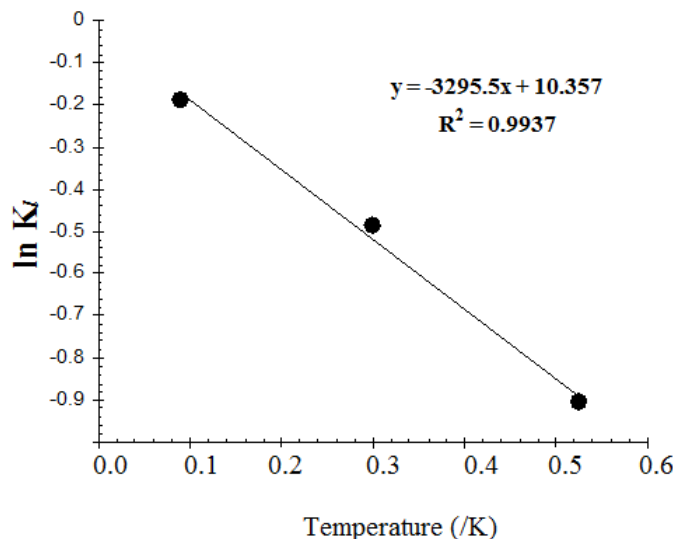


Figure-9

Von't Hoff plot for the determination of thermodynamic parameters

Comparison of ZMSDB with other Adsorbents: Several studies have been reported using various types of adsorbents for Cr (VI) adsorption. A comparison of various adsorbents has shown in table 4 in terms of their monolayer capacity (q_{max}). It can be observed from the table that in some cases adsorption capacity of ZMSDB is comparable. This shows that untreated ZMSDB can be used as suitable adsorbent for the removal of Cr (VI) from aqueous solutions.

Table-4

Comparison of the present data with that reported earlier

Material Used	Capacity (q_{max})	Finest pH	References
Neem leaves	62.97	3.2	[26]
Eucalyptus bark	45.00	2.00	[27]
Distillery sludge	5.70	2.50	[11]
Coconut tree sawdust	3.46	3.00	[12]
Indian jujube sawdust	3.66	4.00	Present study
Clinoptilolite	2.40	4.00-5.00	[28]
Red mud	1.60	5.20	[29]
Sawdust	3.30	6.00	[30]

FTIR Analysis: FTIR performed to recognize the surface active sites accountable for the removal of Cr (VI) out of solution. IR spectra of ZMSDB taken from 650-4000 cm^{-1} (figure 10). Peaks at 3448 to 3430 cm^{-1} govern $-OH^-$ and $-NH_2$ functionalities on the biosorbent surface. An aromatic C-H stretching vibration is shown in the range between 2985 cm^{-1} to 2934 cm^{-1} while C=O and COO^- stretching movements are associated with 1745-1720 cm^{-1} . Bands at 1527 and 1018 cm^{-1} are thought to be due to

the stretching and wagging of 2nd amines and $-C-C-$ groups¹⁹. A wide band 2361 cm^{-1} is associated with the possible presence of primary amine group²⁰. The additional peaks at 786 and 894 cm^{-1} is due to the bending modes of aromatic functionalities. In Cr (VI) ZMSDB spectra, the peaks around 3448, 2985, 786 and 894 cm^{-1} are completely disappeared in the loaded ZMSDB. Furthermore Cr (VI) loaded biosorbent shows a remarkable shift in positions and intensities of primary amines, aromatic C-H stretching vibrations and $-C-C-$ groups. FTIR confirmed the complexations of Cr (VI) with ZMSDB.

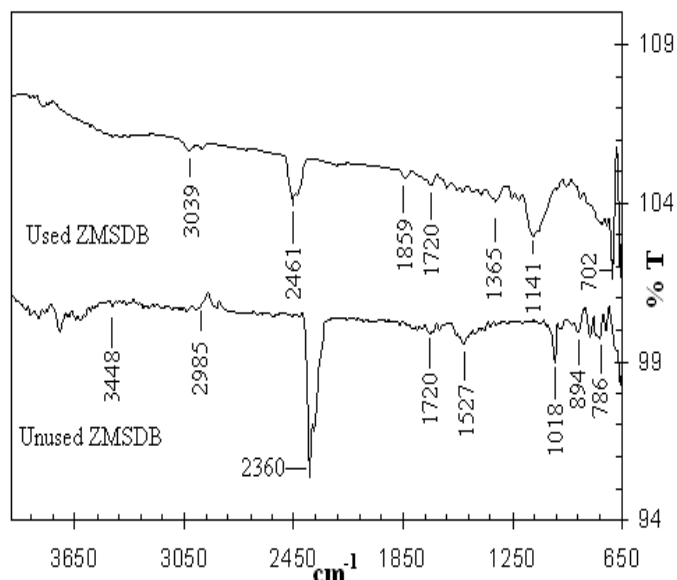


Figure-10

FT-IR Spectra of ZMSDB before and after adsorption

SEM Analysis: SEM micrographs of ZMSDB examined pre and post adsorption are shown in figures 11 and 12. The morphology of unemployed ZMSDB as shown in figure 11 reveals bar like structures of the biosorbent particles accompanied porosity. Morphology of employed biosorbent as shown in figure 12 indicates the sparkly shells exploring the coverage of adsorbent faces i.e., ZMSDB. It also determined that particles associate themselves with the acidic medium and is expected to integrate in solution²¹. This examination facilitated us to reuse the biosorbent for further processing.

Conclusion

Biosorption of Cr (VI) on ZMSDB was found to be strongly dependent on pH, adsorbent dosage, contact time, and temperature. Maximum uptake of Cr (VI) was achieved at low pH. The data was analyzed by the FAI and LAI adsorption isotherms. The LAI was best applicable. Maximum removal of Cr (VI) ions on ZMSDB in term of monolayer capacity was 3.66 $mg\ g^{-1}$ for 20 to 60 $mg\ L^{-1}$. Results showed that pseudo-second order model best described the experimental data. Thermodynamic studies elaborated the endothermic and non spontaneous nature of Cr (VI) adsorption on ZMSDB. It is concluded that ZMSDB may be applied a second to none cheap

and effective adsorption surface to treat waste water containing Chromium (VI) as a major heavy metal.

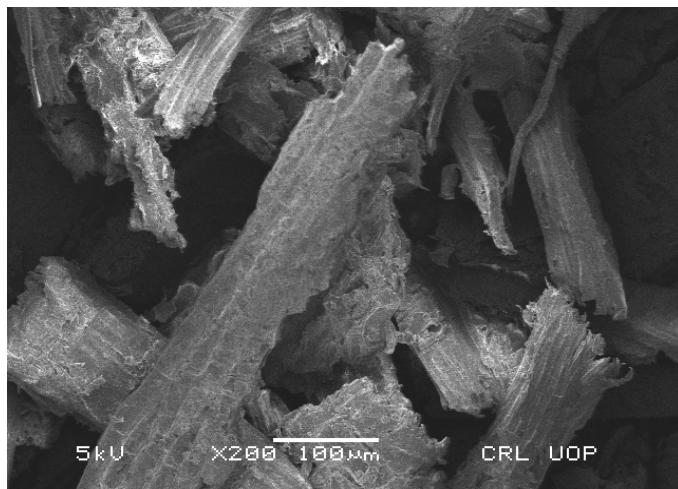


Figure-11
SEM image of unused adsorbent

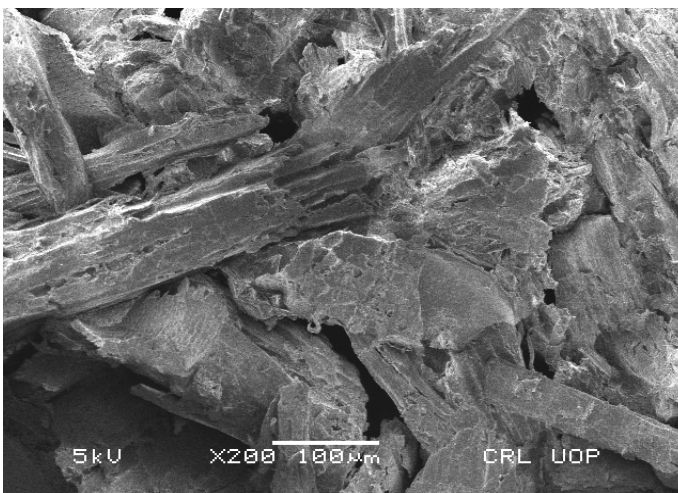


Figure-12
SEM image of used adsorbent

Acknowledgements

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