Removal of Chromium (VI) Ions from Aqueous Solution Using Leaves of *Cordia Africana* and Sawdust of *Acacia Albida*

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Abstract: The use of two biosorbents obtained from plant materials, viz. sawdusts of *Acacia albida* and leaves of *Cordia africana* was tested for their efficiency in removing Cr(VI) ions from aqueous solution through batch mode experiments. Effects of different parameters (such as pH, contact time, amount of biosorbents, and initial metal ion concentration) were investigated for the removal of Cr(VI) ions using the aforementioned biosorbents. Known amounts of the biosorbents were added to the solution. The mixture was stirred gently using plate magnetic stirrer at room temperature for predetermined time. The suspensions were analyzed using UV–visible double-beam spectrophotometer. Among the four parameters, pH was found the most important parameter that influences the adsorption process. The investigation revealed that almost a complete removal of Cr(VI) (> 99 %) was with 5 g/L of leaves of *C. africana* and greater than 98 percentage removal using 10 g/L sawdusts of *A. albida* at 10 mg/L initial sample, pH 2 and 10 minutes contact time. Based on the values of separation factor (R_L) and heterogeneity factor ($1/n$), the experimental data fit well to Langmuir adsorption isotherms indicating monolayer homogeneous surface conditions. Pseudo-second-order kinetics was found to explain the kinetics of adsorption most effectively based on the agreement of calculated and experimental adsorption capacities and regression coefficients. The efficiency of the biosorbents towards removal of Cr(VI) ions from real waste effluent was tested and a satisfactory result was obtained.
Key words: Adsorption isotherm, adsorption of Cr(VI) ions, biosorbents, sorption kinetic, tannery wastewater.

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Introduction

There is growing attention to the health risks on humans and animals due to the existence of heavy metals in the environment. The accumulation of which in living tissues throughout the food chain poses a serious health problem. Even though some of these heavy metal ions in traces play a significant role in human metabolic system, their higher concentrations are toxic which can cause severe physiological or neurological damage.[1] Heavy metal is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water.[2] The most familiar metals are cadmium (8.65 g/cm^3), chromium (7.19 g/cm^3), cobalt (8.90 g/cm^3), copper (8.95 g/cm^3), lead (11.34 g/cm^3), mercury (13.53 g/cm^3), nickel (8.91 g/cm^3) and zinc (7.14 g/cm^3).[3]

Among the different heavy metals, chromium is a common and very toxic pollutant introduced into natural waters from a variety of industrial wastewaters.[4] Such for example, from electroplating metal corrosion resistance, leather tanning, metal finishing, chromate preparation[5], cement, dyeing, wood preservatives, paint and pigments, textile dyeing and steel fabrication industries.[3] Most tanneries adopt chromium tanning process (particularly chromium sulphate) because of its processing speed, low costs, light color of leather, greater stability of the resulting leather,[5] and the resulting hides tanned with chromium salts have a good mechanical resistance, an extraordinary dyeing suitability and a better hydrothermic resistance in comparison with hides treated with vegetable substances.[6] In the chromium tanning process, the leather takes up only 60–80% of the applied chromium, and the rest is usually discharged into the sewage system causing serious environmental impact. Chromium ions in liquid tanning waste occurs mainly in trivalent form, which gets further oxidized to hexavalent chromium form, due to the presence of organics.[7] The latter form is of particular concern due to its greater toxicity.[5]

The Cr(VI) compounds are extremely toxic to human, animals and plants. The continuous discharge of Cr(VI)-containing wastewater from industries, such as electroplating, tanning or pigment, has already caused severe pollution of Cr(VI) in environment.[1] Chromium occurs most frequently as Cr(VI) or Cr(III) in aqueous solutions. Both valences of chromium are potentially harmful but hexavalent chromium poses a greater risk due to its carcinogenic properties. Hexavalent chromium, which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), poses significantly higher levels of toxicity than the other valency states.[4] The tolerance limits for Cr(VI) based on the US EPA are 0.05 and 0.1 mg/L in drinking water and inland surface waters and 5 mg/L for Cr(III) in drinking water.[7,8]

Conventional methods for removing metal ions from industrial effluents include evaporation [9], chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion–exchange and adsorption. Most of these methods suffer with high

capital and regeneration costs of the materials. Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Bio-sorption is an effective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewater. [10] This process includes the selective transfer of solute components in the fluid phase onto the surface or onto the bulk of solid adsorbent materials.[11] The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. Their advantage over conventional treatment methods include: low cost, high efficiency, minimization of chemical and/or biological sludge regeneration, no additional nutrient requirement, and the possibility of metal recovery. [12]

The sawdusts of *A. albida* and leaves of *C. africana* are type of plants that grow in most part of Ethiopia and used mainly for fire wood. These biosorbents did not yet used for any adsorption process. Thus, in this study, saw dusts of *A. albida* and leaves of *C. africana* had been used for chromium (VI) ions removal from aqueous solution. These were sampled from Adekney village located in Eastern Tigray, Ethiopia, latitude 14°23′02.71''N, longitude 39°15′01.94''E, elevation 1967 m above sea level. The aims of this study were to 1) investigate the chromium (VI) adsorption from aqueous solution by these biosorbents 2) study the effect of different parameters such as pH, contact time, adsorbent dose and initial chromium concentration on adsorption process.

Material and Methods
Chemicals and reagents

Analytical reagent grade potassium dichromate ($\geq$ 99.8%; Riedel-de Haen, Seelze, Germany), diphenylcarbazide (DPC) (> 99.5%; Riedel-de Haen), distilled deionized water, sulphuric acid (95-97%; Riedel-de Haen), potassium permanganate (97%, Sigma-Aldrich, St. Louis, MO, USA), nitric acid (70%, Riedel-de Haen), sodium hydroxide, and acetone (99.5%; Riedel-de Haen) were used.

Preparation of Adsorbent

The collected sawdusts of *A. albida* and leaves of *C. africana* were cut in to small pieces and dried in sun light for about two days. Then crushed and pounded manually. Then sieved using 500 - 355 μm size analyzer (FRITSCH, 55743, ldar-Oberstein, Germany). There after the adsorbents were kept in air tight plastic container for further use.

For characterization of the sorbents, 5 mg of each were placed in a mortar, four to five drops of paraffin was added, and the whole was mixed using a pestle to form a mull. The mull was analyzed by Fourier transform infrared spectrometry (Spectrum 65 FT-IR, Perkin Elmer, Waltham, MA, USA) in the range of 4000 - 400 cm^{-1} using KBr pellets for the original and the metal loaded adsorbents.

Calibration curve

A stock solution of Cr(VI) was prepared by weighing (CP124S, Sartorius, Göttingen, Germany) 2.283 g potassium dichromate into a 1-L volumetric flask, dissolving it in distilled water and dilution up to the mark.

A series of standard solutions for five-point calibration at 0.0, 0.05, 0.2, 0.8 and 1.6 mg/L were prepared by further diluting the stock solution with distilled water. A calibration line exhibiting linearity with an intercept of 0 and a correlation coefficient of 0.9995 was obtained.

Sampling site, sample collection and pretreatment of the wastewater samples

Tannery effluents were collected from Sheba Tannery, Wukro Village, Eastern Tigray, Northern Ethiopia, latitude 13°47'00''N, longitude 39°36'00''E, elevation 1992 m above sea level. Two samples of the wastewater were collected from the line into the chromium pond in 1-L plastic containers, the latter previously soaked for 24 h with a 1:1 (*v/v*) mixture of conc. H_2SO_4 and HNO_3, followed by thorough washing with tap water four times and final rinsing with distilled water. The pH of the samples was immediately adjusted to 2.0 with 70% nitric acid, and the samples were packed in ice boxes and transported to the quality control and physicochemical laboratory of the Addis Pharmaceuticals Factory, latitude 14°16'26.22'N', longitude 39°27'43.92''E, elevation, 2458 m. The analyses were carried out within 24 h, as Cr(VI) is not stable for longer periods.[13]

For determination of the concentrations of Cr(VI) in the tannery effluent, 50 mL aliquots were transferred into 250-mL conical flasks and 5 mL each of conc. HNO_3 were added. The mixtures were digested using a hot plate (FALC Instruments s.r.l., Treviglio, Italy) to dryness by heating to 100 °C for about 40 min. The flasks were cooled to room temperature, another 5 mL each of conc. HNO_3 were added, and the contents were again heated to 100°C for 15 min. The solutions were cooled to room temperature, quantitatively transferred to 100-mL volumetric flasks, and diluted to the mark with distilled water repeatedly rinsing of the digestion flasks. The solutions were filtered using Whatman No 541 filter paper, 3 mL each of an aqueous solution of 0.02 molar $KMnO_4$ were added for oxidation of any Cr(III) to Cr(VI), and the mixtures were heated until the pink color had faded and disappeared.[14] Upon addition of 2 mL of an aqueous solution of 5 g/L diphenylcarbazide, a reddish violet colored complex formed within 10 min, resulting from the reaction with Cr(VI); absorbance was measured at 540 nm using a double beam UV-Vis spectrophotometer (UV-1700, Shimadzu, Kyoto, Japan) against reagent blank.

Batch sorption experiments

All experimental works were carried out at 25°C. The effects of various parameters on analyte adsorption were studied by varying contact time, t (10, 20, 30, 60, 90, and 120 min), initial concentration of Cr(VI), C_o (10, 40, 70, 100, 130 and 160 mg/L), sorbent quantities, w (5, 10, 15, 20, 25 and 30 g/L per 100 mL) and pH (2, 3, 5, 7, 9 and 11). Measurement of pH was performed using a microprocessor based pH meter (MP220, Mettler Toledo, Greifensee, Switzerland). The solution volume was kept constant at 100 mL. [15] Each experiment was carried out in triplicate and the measured values were used for evaluation of precision and other relevant analytical parameters.

Data analysis

The experimental results were processed utilizing Microsoft excel 2007 for all statistical calculations including the calibration plots. The results of the optimization process were subjected to analysis of variance (ANOVA) in order to check whether they were significantly different from each other or not. [16]

Results and discussion

Characterization of the adsorbents

FT-IR spectra of the finished biosorbents and the metal ion loaded form were taken showing signals for the –OH, C-H, C=O and C-O functionalities. [17] The spectral signal of the raw and Cr(VI) loaded biosorbents were then compared. Accordingly, after loading the sorbents with the metal ions, changes in the intensity of the peaks were noted. The intensity of the broad peak around 3400 cm^{-1} was decreased, to a great extent, which suggests that the surface-OH groups could be responsible for adsorption of Cr(VI) on both adsorbents. There was also band shifts for the C-H, C=O and C-O functional groups, for both the adsorbents, as a result of Cr(VI) loading. All the changes in the spectral characteristics may be due to the possible reaction that took place between Cr(VI) and the respective functional groups of the adsorbents.[18] The FT-IR spectra of the raw and Cr(VI) loaded sawdust of *A. albida* are given in Figures 3.1 and 3.2.

The pattern of sorption of metals onto the plant materials can be associated to the presence of the active groups and bonds. Plant cell walls consisting of mainly polysaccharides, proteins and lipids offering several functional groups such as carboxyl, carbonyl, hydroxyl, amino, aromatic, nitro, silicate, sulphonate which may be involved in the metal binding.[11,19]
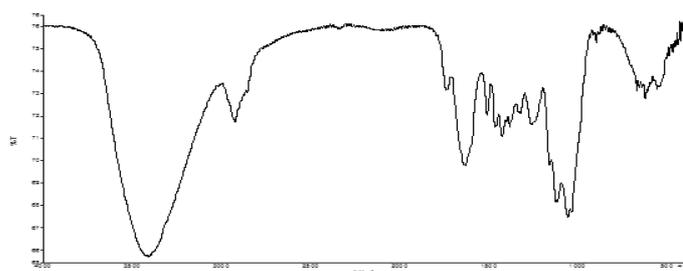

Figure 3.1 Sawdust of *A. albida* unloaded with Cr(VI)(raw, initial sawdust)
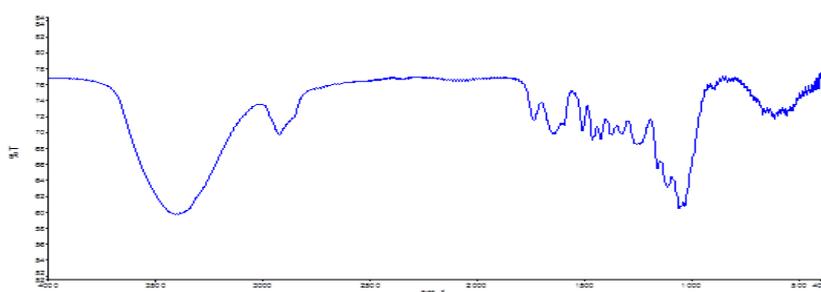

Figure 3.2 Sawdust of *A. albida* loaded with Cr(VI) ions

Optimization of Factors Affecting Chromium Adsorption

The parameter such as pH, contact time, adsorbent dosage , initial Cr(VI) concentration which affect the removal of Cr(VI) ions by using biosorbents were optimized by varying each at a time and keeping the remaining parameters constant. The results were presented below:
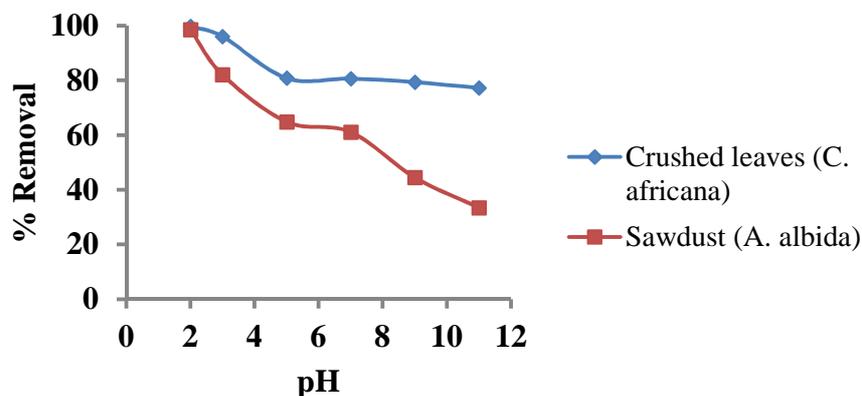
Effect of pH

In order to establish the optimum pH, it was varied from 2 to 11. The adsorption capacity (q_e) was found to be maximum at pH 2 and significantly declined with increase in pH, Figure 3.3. At pH 2 and 11 the corresponding uptake yield values were found to be 98.67% and 33.42 % for sawdust of *A. albida* and 99.79 % and 77.23 % for leaves of *C. africana* respectively. It

was noted that efficient adsorptions could be attained at lower pH, i.e., pH 2.

The predominant form of Cr(VI) in aqueous solution at pH < 6.0 is $HCrO_4^-$,[20] which is thus preferentially adsorbed at pH 2.0. At lower pH, the surface of sorbent is positively charged due to the protonation with H^+, which as a result promotes binding of the negatively charged $HCrO_4^-$ ions. Consequently, the uptake of Cr(VI) increased markedly with decreasing pH. At higher pH, the sorbent undergoes deprotonation which may lead to a decrease in electrostatic force of attraction between the sorbent and sorbate ions.[19] The decrease in adsorption, at higher pH, may be due to the competitiveness of the oxyanion of Cr(VI) and OH^- ions in the bulk.[21] Similar pH was also found optimum for the uptake of Cr(VI) from aqueous solutions by tamarindus indica,[4], sawdusts of neem and mango, wheat shell, sugarcane bagasse and orange peel mango and neem sawdust[21] and treated oil palm fiber.[20]
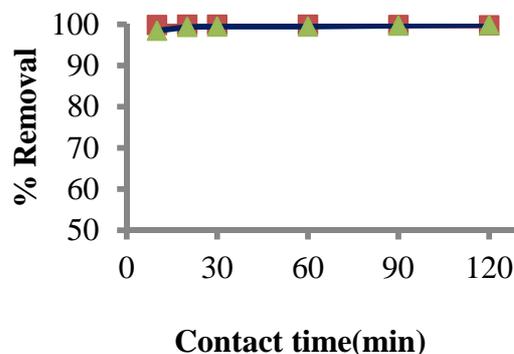

Figure 1.3 Effect of pH on biosorption of chromium (VI). Initial Cr (VI) conc. = 10 mg/L, Biosorbent dosage = 10 g/L, Contact time = 30 minutes.

Effect of Contact Time

In the process of analyte adsorption equilibrium is established at the surface of the adsorbent after certain time or instantaneously. [22] The equilibrium uptake, in this study, was about 99.84 % for leaves of *C. africana* and 98.44 % for sawdust of *A. albida,* respectively, during 10 min equilibration time which was also chosen as the optimum equilibration time for both the sorbent materials. The adsorbents considered here have demonstrated better Cr(VI) removal efficiency than the efficiency reported for wheat bran[15], which was 87.6% for equilibrium uptake of Cr(VI) during 60 min contact time.
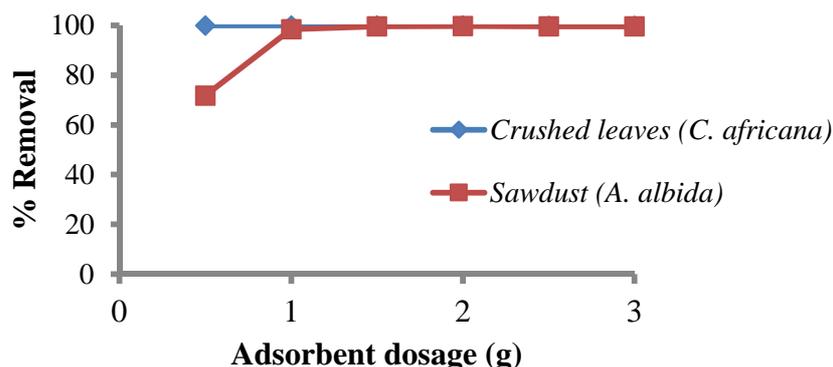

Figure 3.2 Effect of contact time on biosorption of chromium (VI). Initial Cr (VI) conc. = 10 mg/L, Biosorbent dosage = 10 g/L, pH = 2.

Effect of Adsorbent Dosage

An increase in biomass dosage generally increases the amount of biosorbed metal ions due to an increase in surface area of the biosorbent, which consequently increases the number of binding sites. [19] As it can be seen from Figure 3.5, adsorption of Cr(VI) was found to increase from about 72% to 99.6% with increase in adsorbent dose from 5 to 30 g/L using the sawdust of *A. albida* which was then remained nearly constant and considered as the optimum dose. Utilizing 5 g/L of the leaves of *C. africana,* on the other hand, about 99.99% of Cr(VI) was removed, which may be because the physically available active sites are well exposed to the metal ions in the solution, and also used as optimum dose. Further increase in the adsorbent dose, however, hasn't shown any significant change in adsorption, may be due to the overlapping of the adsorption sites.[23]

Adsorption capacity was found to drop from 1.4 to 0.3 mg/g for the sawdust of *A. albida* and 2.0 to 0.3 mg/g for the leaves of *C. africana* as the adsorbent dosage was increased, may be due to saturation of the

Figure 3.3 Effect of adsorbent dosage on biosorption of chromium (VI). Initial Cr (VI) conc. = 10 mg/L, Contact time = 10 min, pH = 2.

available adsorption sites with fixed metal ions as has also been observed by [24] for Neem leaves.

Effect of Initial Metal ion Concentration

In the presented work, the removal efficiency was found to decrease with an increase in the metal ion concentrations as can be seen from Figure 3.6. This is may be due to inadequate surface area available to accommodate much more metallic ions.[19] At lower concentrations of the metal ions, the ratio of the sorptive surface area to the total metal ions available is high and thus higher possibilities for the metal ion removal could be obtained. As a result, removal capacity of the adsorbent may be higher at lower initial metal ion concentrations. Other workers have also reported similar findings for the root bark of Indian Sarsaparilla [25] and wheat bran. [15]

It was also observed that adsorption capacity increased from 1.0 to 15.2 mg/g for sawdust of *A. albida* and 2.0 to 29.0 mg/g for the leaves of *C. africana,* as the initial metal ions varied from 10 to 160 mg/L. This may be due to the increase in the initial metal ion concentration which possibly enhances the interaction between the metal ions in the aqueous phase and the adsorbents. Similar studies, conducted by[22], on maize tassel for adsorption of Cr(VI), have also shown the adsorption capacity in the range from 1.8 to 10 mg/g, as the initial metal ion concentrations varied from 25 to 500 mg/ L.

The results obtained in all of the optimization processes for Cr(VI) ions removal are significantly different when checked using ANOVA single factor at 95 % confidence level.
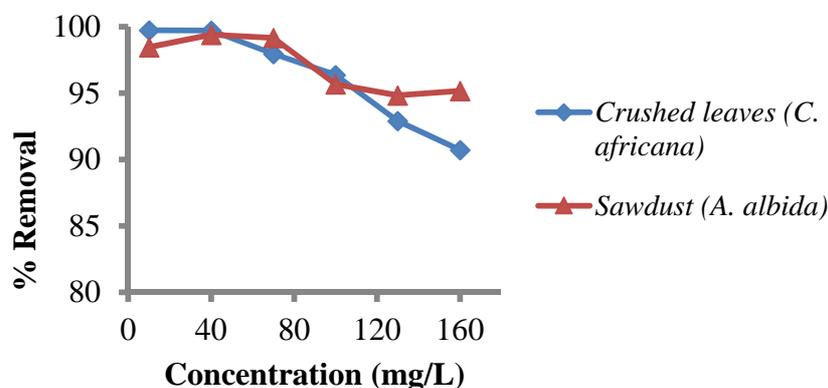
Figure 3.4 Effect of initial Cr(VI) ions concentration on the biosorption process: Contact time = 10 min, pH = 2, adsorbent dosage = 5 and 10 g/L for *C. africana* and *A.albida* respectively.

Application to the industrial effluent

The optimized conditions, pH 2, contact time 10 minutes, 5 and 10 g/L for leaves of *C. africana* and sawdust of *A. albida* respectively, were applied to the wastewater samples collected from the effluents of the Sheba Tannery. The results obtained are depicted in Table 3.1, where remarkable removal efficiencies were observed for both the plant materials utilized in the study. It was also noted that the quantities of Cr(VI) significantly reduced in the filtrate analyzed. The plant materials investigated can thus be used as reliable

alternatives for efficient and maximum removal of Cr(VI) from contaminated wastewaters in the tannery effluents.

In this factory, they did not treat the waste effluent that contains Cr(VI) ions. Simply they collect in a pond, only sun light is evaporated the water and the metal is expected to be precipitated reacting with different compounds like with sulfate ions. But this has different side effects since a large sludge is accumulated at the end and which is much cost to remove or eradicate the metal ions from the sludge. Thus, the current

biosorbents can be used as an effective means to remove this metal from such tannery areas. To obtain a satisfactory result, consecutive analysis can be performed until the concentration of the metal ions is reduced to an acceptable limit depending upon the purpose for which the wastewater is used.

Table 3.1 Real sample analysis after treating with the adsorbent (10 minutes contact time, pH 2, 5 and 10 g/L leaves of *C. africana* and sawdust of *A. albida* respectively).

| Adsorbent	Initial conc.(mg/L)	C_f (mg/L)	% Removal
C. africana	8.4(0.0091)	0.218(0.0012)	97.42 (0.0115)
A. albida	8.4(0.0091)	0.322(0.0036)	96.17 (0.0436)

C_f = final concentration in the filtrate

Adsorption isotherms

Experiments for adsorption isotherms were carried out with a fixed adsorbent dose and varying adsorbate concentrations and applicability of the data to the Langmuir and Freundlich adsorptions were evaluated at room temperature. [24, 26, 27]

The separation factor (R_L) values for the adsorption of Cr(VI) onto the adsorbents were calculated based on equation 1 below:

$$R_L = \frac{1}{1 + K_L C_i} \quad …..(1)$$

The result obtained is indicated in Figure 3.7. All the results are between 0 and 1 which implies favorable adsorption.[19] Higher R_L values at lower ion concentrations showed that adsorption was more favorable at lower concentration. Similar result was obtained using Pine needles powder as a biosorbent for Cr(VI) removal from aqueous solution.[3]
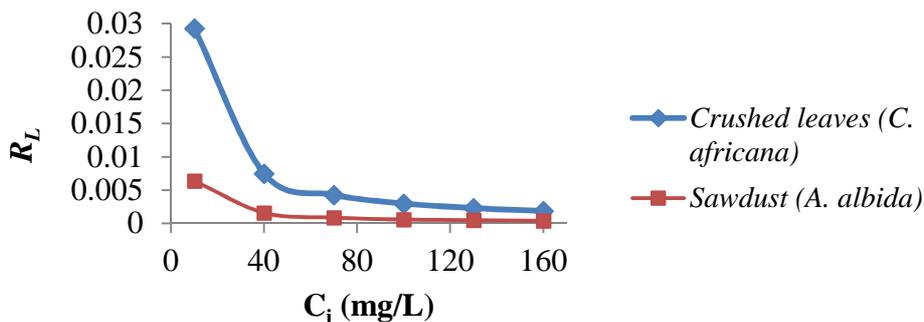
Figure 3.5 Separation factor R_L for adsorption of Cr(VI) using leaves of Cordia africana and sawdust of Acacia albida

The Langmuir parameters (q_{max}, K_L) were calculated from the intercepts and slopes of the linear plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ based on equation 2:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} \cdot \frac{1}{C_e} \quad …….(2)$$

Similarly, Freundlich parameters (n, K_f) were calculated from slopes and intercepts of the linear plot of $\log q_e$ versus $\log C_e$ based on equation 3:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad …(3)$$

The results indicate that there is a linear relationship between the amounts (mg) of Cr(VI) ions sorbed per unit mass (g) of the adsorbents against the concentration of Cr(VI) ions remaining in solution (mg/L). The values of the regression coefficients obtained from these models were used as the fitting criteria to find out these isotherms. It was observed that the experimental data fitted well to Langmuir adsorption isotherms, indicating monolayer homogeneous surface conditions. The adsorption capacities and values of regression coefficients are also indicated in Table 3.2.

The values of $1/n$ obtained from Freundlich model were 0.5 for the sawdust of *A. albida* and 0.4 for the leaves of *C. africana* which lied between 0.0 and 1.0 indicating favorable sorptions.[19] However, close evaluation of the values of the regression coefficients, (R^2), given in Table 3.2, the equilibrium data seemed to fit better to the Langmuir isotherm model than the Freundlich adsorption model for both adsorbents.

Table 3.2 Linear regression data for Langmuir and Freundlich isotherm models using leaves of *C. africana* and sawdust of *A. albida*

Biosorbents	Langmuir parameters			Freundlich parameters		
	q_{max} (mg/g)	$K_L(L/mg)$	R^2	$1/n$	K_f	R^2
C. africana	23.8	3.3	0.993	0.4	11.3	0.925
A.albida	126.6	15.6	0.822	0.5	5.2	0.796

Sorption Kinetics

The kinetics of the parameters for adsorption process were studied from variation of the contact times and analyzed using two simple kinetic models; *viz.*, the pseudo-first order and pseudo-second order models. [15, 21] The first-order rate expression of Lagergren was calculated using equation 4.

$$\log(q_e - q_t) = \log q_e - 0.4342 k_1 t \qquad (4)$$

A graph was drawn by plotting $\log(q_e - q_t)$ versus 't'. The slope and intercept of this graph were used to obtain the first-order rate constant, k_1, and equilibrium adsorption capacity, q_e. The calculated q_e, k_1 and regression coefficient, R^2, values are summarized in

Table 3.3. On the other hand, calculation of parameters for the second order kinetics followed equation 5 given below.

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \qquad (5)$$

For both adsorbents the plots of t/q_t against 't' displayed linear relationships, as shown in Figure 3.8 for sawdust of *A. albida*. The intercept and slope of the plot were used to determine the numerical values of the rate constant, k_2, and the equilibrium adsorption capacity, q_e, respectively. The calculated values of q_e, k_2 and the regression coefficient, R^2, are also presented in Table 3.3.

Table 3.3 Regression parameters for the kinetic models using leaves of *C. africana* and sawdust of *A. albida*

Kinetic model		*C. Africana*	*A. albida*
$q_{\exp erimental}$		0.9992	0.9979
Pseudo-first-order	k_1	0.0196	0.0212
	q_e	0.0003	0.0094
	R^2	0.4690	0.7306
Pseudo-second-order	k_2	7.0091	17.4011
	q_e	0.9985	0.9954
	R^2	1.0000	1.0000

Based on the determined experimental values indicated in Table 3.3, for various parameters, it has been observed and concluded that pseudo-second-order

equation which exhibited significantly better regression coefficient (R^2) was noted to be in good agreement with the calculated q_e values, suggesting that chemisorption is

y = 1.0015x + 0.1431
R² = 1
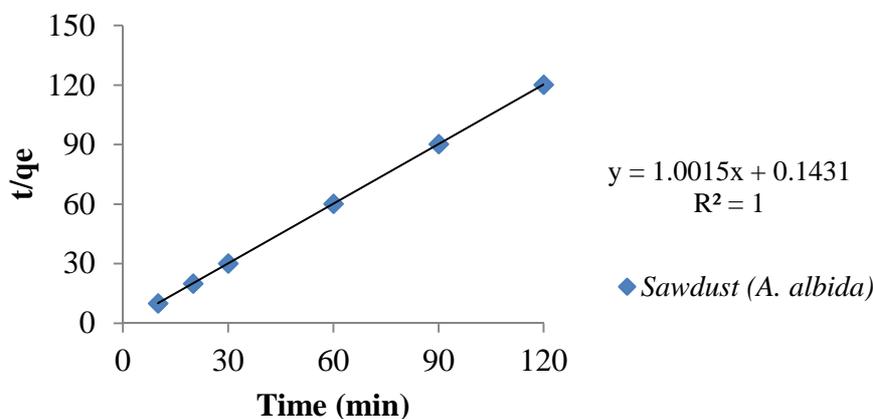
◆ *Sawdust (A. albida)*

Figure 3.8 Pseudo- second order reactions for the adsorption of Cr(VI) ions onto sawdust of *A. albida*

the rate-determining step in the adsorption of Cr(VI) ions on the sorbents obtained from the plant materials.[23, 28] Similar results have also been observed in the adsorption of Cr(VI) onto the Neem leaf powder [5] and Neem sawdust.[21]

Comparison of adsorption capacities of the biosorbents studied with other biosorbents

Direct comparison of the adsorbents with other similar sorbent materials was found difficult, owing to the differences in experimental conditions and the respective

applications. Nevertheless, comparison based on the maximum adsorption capacity was preferred as some general qualitative as well as quantitative information, concerning the performances of the adsorbents, could be described more clearly. Accordingly, performances of the biosorbents employed in the presented study have been compared with others similarly used biosorbents based on their maximum adsorption capacity, as shown in Table 3.4.

Table 3.4 Comparison of adsorption capacities (q_{max}) of leaves of *C. africana* and sawdust of *A. albida* with other adsorbents.

Adsorbent	solute	q_{max}(mg/g)	C_o(mg/L)	reference
Almond Green Hull	Cr(VI)	2.04	10-50	[8]
Wheat bran	Cr(VI)	0.942	2.5-25	[15]
Potato Peel Waste	Cr(VI)	8.012	20-120	[19]
Orange peel	Cr(VI)	19.80	10-150	[21]
Neem leaves	Cr(VI)	10.40	20-200	[24]
Isarog ash soil	Cr(VI)	0.864	5-25	[29]
Mandalagan ash soil	Cr(VI)	0.171	5-25	[29]
Aspergillus niger	Cr(VI)	6.970	25-100	[30]
C. africana	Cr(VI)	23.75	10-160	present study
A. albida	Cr(VI)	126.58	10-160	present study

The sorbents utilized in the current study are found to demonstrate significantly improved removal of Cr(VI) ions from aqueous solution as compared to the other sorbents reported in the literature (Table 3.4). The overall findings of the presented study may also signify the potential candidacy of the sorbents of the plant materials for further practical applications in removal of Cr(VI) from industrial wastewater discharges and other similar toxic metals, of similar chemical and physicochemical properties, from different sources greatly contaminated with the metal ions. However, for extending their applications at industrial scale, special structural design of the waste receiving ponds, in which the sorbents could be added and stirred and the parameters related to the wastewater flow conditions, among others, needed to be investigated.

Conclusions

In this study, two types of sorbents, *viz.*, sawdust of *A. albida* and the leaves of *C. africana* have been investigated for their performances in removing Cr(VI) ions from contaminated aqueous solutions. The method was also applied to the wastewater effluents of the leather industry. Effects of the different experimental parameters, influencing the efficiencies of the sorbent materials, have been evaluated and optimized. The investigation revealed that almost a complete removal of Cr(VI) (> 99 %) was obtained with 5 g/L of leaves of *C. africana* and greater than 98 percentage removal using 10 g/L sawdusts of *A. albida* at 10 mg/L initial sample,

pH 2 and 10 minutes contact time. The experimental data obtained was also found fit well to the Langmuir adsorption isotherm model indicating monolayer homogeneous surface conditions. Pseudo second-order kinetics was found to explain the kinetics of adsorption most effectively on the basis of the agreement of the calculated and experimental adsorption capacities. The regression coefficients are indicative and thus suggestive for the chemisorption to be considered as the rate-determining step in the adsorption process. The results adequately confirmed successful application of the developed for efficient removal of Cr(VI) from the effluents of the leather industries.

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