

**BIOSORPTION OF CHROMIUM (VI) BY USING SULPHONATED BIOMASS OF
STALKS OF PRUNUSCERASUS****Anandrao A. Kale***

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anandraoakale@gmail.com.**ABSTRACT**

The sulphonated biomass prepared from stalk of *Prunuscercasus* was used for investigation of biosorption of Cr (VI). It was found that the biosorption process is dependent on pH value of solution, adsorbent mass, contact time, temperature and initial Cr (VI) concentration. Data of biosorption of Cr (VI) on Sulphonated biomass of Stalks of *Prunuscercasus* were applied to three adsorption isotherm models. The maximum adsorption capacity was determined from the Langmuir isotherm as 21.0 mg/g. Adsorption process of Cr (VI) ions onto Sulphonated biomass of Stalks of *Prunuscercasus* (S-III) was found to obey the second-order kinetic equation. The n value obtained from the Freundlich isotherm indicates that the sorption of Cr (VI) ions onto Sulphonated biomass of Stalks of *Prunuscercasus* (S-III) is favourable. Thermodynamic parameters proved that the adsorption process is spontaneous and endothermic. Investigation Kinetic, isotherm and thermodynamic studies on biosorption of chromium (VI) by using activated carbon from Sulphonated biomass of Stalks of *Prunuscercasus* was conducted in batch conditions. The effect of different parameters such as contact time, sorbent dose, pH and temperature has been studied. Adsorption kinetic modelling data were found out. The kinetics of biosorption results shows that sorption process is well explained by pseudo-second order model with determination coefficients higher than 0.96 for sorbent under all experimental conditions. Thermodynamic parameter via KD , ΔG has also been calculated to determine the spontaneity of the process. The value K_p is found to be 0.825 to 2.50 for initial and final concentrations. The low value of activation energy indicates that sorption is an activated and physical process. Thus Kinetic, isotherm and thermodynamic studies on biosorption of chromium (VI) by using activated carbon from Sulphonated biomass of Stalks of *Prunuscercasus* is a low cost and easily available efficiently used as an excellent sorbent for the removal of chromium (VI) from wastewater.

KEYWORDS: E.D.T.A., biosorbent, adsorbent, adsorption, Chromium (VI) Sulphonated biomass, Stalks of *Prunuscercasus* (S-III).

INTRODUCTION

The activities of industrial sectors has showed a considerable spread and development, but concurrently the natural environment has been contaminated. The toxicity of hexavalent chromium from the discharge of various industrial wastes is well studied by D.K. Singh.^[1] A number of industries are causing heavy metal pollution e.g. battery manufacturing processes, mining and metallurgical engineering, dyeing operations, electroplating, nuclear power plants, tanning, production of paints and pigments.^[2] Heavy metals are one of the most widespread pollutants which contaminate the environment and cause serious damage to the ecosystem and also may be a reason for various dangerous diseases suffered by animals and human beings.^[3] Chromium [Cr] compounds are among the most common environmental contaminants because of their widespread and extensive use in industrial applications.^[4] Chromium (VI) is more

toxic than chromium (III) and as such receives more attention. Strong exposure to chromium (VI) has been linked to various types of cancer and may cause epigastric pain, nausea, vomiting, severe diarrhea and haemorrhage.^[5] Chromium (VI) is one of the most poisonous contaminants which cause severe diseases and very harmful environmental complications. When chromium (VI) accumulates at high levels, it may lead to serious problems and even be fatal when concentrations reach 0.10 mg/g of body mass.^[6] The removal of toxic metals from wastewater has been achieved using various methods sedimentation,^[7] ion exchange,^[8] biological operations,^[9] solid phase extraction.^[10] and adsorption by chemical substances.^[11] Several conventional physical, chemical, and biological methods have been developed to remediate Cr (VI)-contaminated wastewater and water, and thereby avoid or reduce the adverse effects of highly toxic Cr (VI) on human health and the environment.^[12] All these techniques suffer from

multiple drawbacks such as high capital and operational costs and disposal of residual metal sludge.^[13] The pH is considered the most important experimental parameter that controls the biosorptive removal of chromium ions from aqueous solution because of its strong influence on the degree of dissociation of functional groups from the biosorbent surface as well as on the charge, chemical speciation, and solubility of the chromium compound in aqueous solution and on the competition with coexisting ions in solution.^[14] In contrast, the bio-sorption method has become one of the most favoured ways to remove heavy metals because it is environmentally friendly, highly efficient and has low associated costs. Various parts of plants are commonly used as biomass adsorbent for Cr (VI) adsorption from drinking water and wastewater. These include rice bran,^[15] gooseberry seeds,^[16] Cupressus lusitanica Bark,^[17] Activated carbon derived from procumbens,^[18] oil palm shell charcoal.^[18] The biosorption of cadmium and lead ion from artificial aqueous solution using waste baker's yeast biomass.^[19] was investigated by Goksungur et al. Choy and McKay studied the rate of adsorption of cadmium,^[20] copper and zinc ions onto bone char in three single component systems using an agitated batch adsorbent Rice straw soybean hull, sugar baggase. Adsorption behaviour of Cd²⁺, Pb²⁺, Ni²⁺ Cd²⁺ and Zn²⁺ from aqueous solutions by mangifera indica.^[21] seed shell was reported by Mohammad Ajmal and et al., Tsunetaka Sasaki and et al. has been worked on adsorption of dyes, chromate and metallic ions by poly(ethyleneimine)^[22], Removal of Fe²⁺, Zn²⁺ and Mg²⁺ from polluted water using thioglycolic modified oil-palm fibre^[23] was done by J.O.Akaniwor and et al. Mazahar Farooqui reported that the use leaves of Cauliflower^[24] for removal of iron from waste water. Badie S. Girgis and et al has been worked on activated carbon from cotton stalks^[25] by impregnation with phosphoric acid. A Sorption study of Al³⁺, Co²⁺ and Ag⁺ in aqueous solutions by Fluted Pumkin^[26] waste biomass was carried out by Michael Horsfull Jnr and Ayebeaemi I. Spiff. The uptake capacity of Chromium (VI) by nitrated and Sulphonated Coconut Shell carbon^[27] was studied by V. Selvi and G.P. Jeyanthi, A batch study was carried out by Mohamed Chaker Ncibi and et al. on biosorption of textile dyes^[28] from aqueous solutions using Posidonia oceanic leaf sheath fibers. The present study deals with Kinetic, isotherm and thermodynamic studies on biosorption of chromium (VI) by using activated carbon from Sulphonated biomass of Stalks of Prunuscerasus (S-III).

Table 1:

Adsorbent	Bulk density g / cc	Moisture content %	Ash Content %	Volatile material %
S-III	0.32	2.75	3.23	5.9

I R spectrum data for Sorbent Sulphonated biomass of Stalks of Prunuscerasus (S-III) indicate 3350 cm⁻¹ broad

MATERIALS AND METHODS

Preparation of biosorbent

The stalks of Stalks of Prunuscerasus were thoroughly washed with distilled and deionized water, dried at room temperature for 3 days. This is further ground in an electric mill and then mixed with concentrated sulphuric acid then the mixture was filtrated and the obtained activated carbon was rinsed thoroughly with deionised water to remove the acid residue and dried for 6 h at 105 °C The dried material was then passed through 0.63 mm mesh get particles of uniform size. The present work deals with the study of adsorption of heavy metals Cr (VI) ion solutions on chemically treated biomass of Sulphonated biomass of Stalks of Prunuscerasus (S-III).

Preparation of Cr (VI) solutions

Stock solution of potassium dichromate of 1000 mg/L concentration was prepared by dissolving the appropriate weight in 1.0 L of deionised water. The required concentrations were then prepared by taking adequate volumes from the stock solution (All Chemicals used Merck Chem.).

Batch bio-sorption experiments were carried out by mixing bio-sorbent with Cr (VI) ion solutions of chosen concentration in 250 mL glass Stoppard flask. A temperature controlled shaker at a speed of 120 rpm/min was used throughout all runs. The effect of pH on the adsorption of chromium (VI) ions was studied by using HCl and/or NaOH. The amount of bio-sorption was determined based on the difference between the preliminary and final concentrations in each flask as shown in Eq. (1)

$$q_e = (C_o - C_e)V/M \quad (1)$$

Where q_e is the metal uptake capacity (mg/g), V is the volume of the Cr (VI) solution in the flask (L) and M is the dry mass of bio-sorbent (g). Percent removal (% R) of Cr (VI) ions was determined by using of Eq. (2)

$$\%R = (C_o - C_e) 100/V \quad (2)$$

RESULT AND DISCUSSION

Characterization of biosorbents

The physical parameter and I R spectrum data of Sulphonated biomass of Stalks of Prunuscerasus (S-III) as Sorbent is described in Table-1.

–OH, 3025 cm⁻¹ –NH, 1720 cm⁻¹ COOH

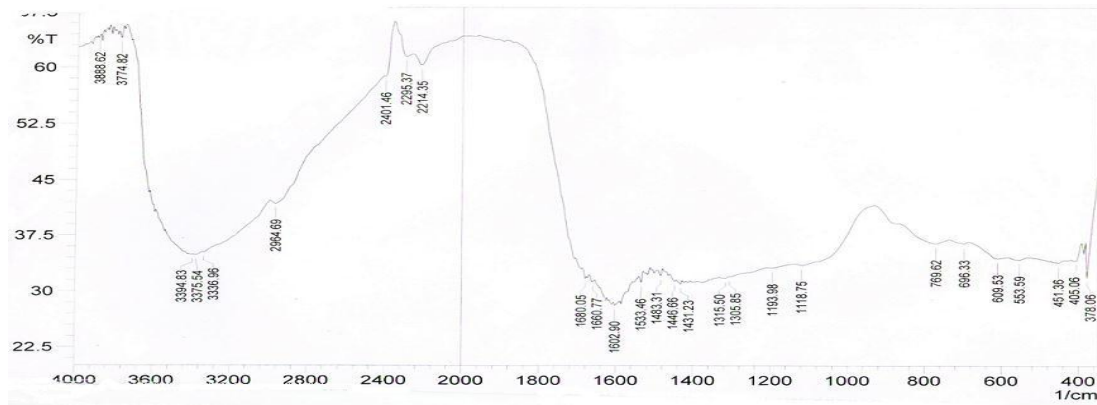


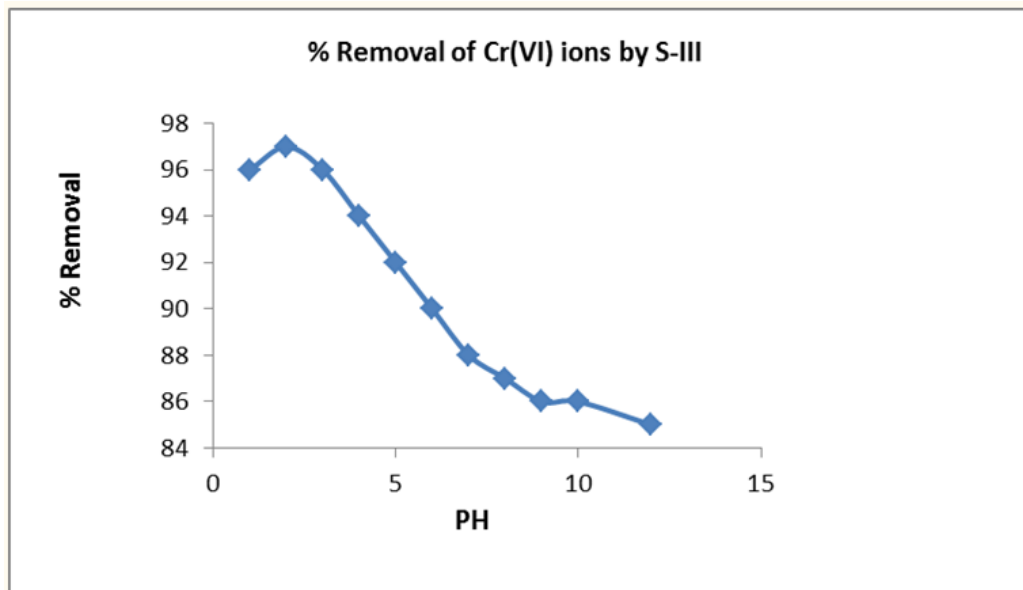
Fig. 1: Infra Red Spectrum of biosorbent.

A number of parameters i.e., linearity, LOD, LOQ, RSD were determined in order to check the reliability of results.

Effect of pH

The pH of the solution is one of the factors that may affect bio-sorption of heavy metals. Figure 1 shows that bio-sorption of Cr (VI) onto Sulphonated biomass of Stalks of *Prunuscerasus* (S-III) is dependent on the pH of the solution. Maximum removal of Cr (VI) ions from aqueous solution was achieved at acidic pH range. The optimal pH range for Cr (VI) removal was from 1.50 to

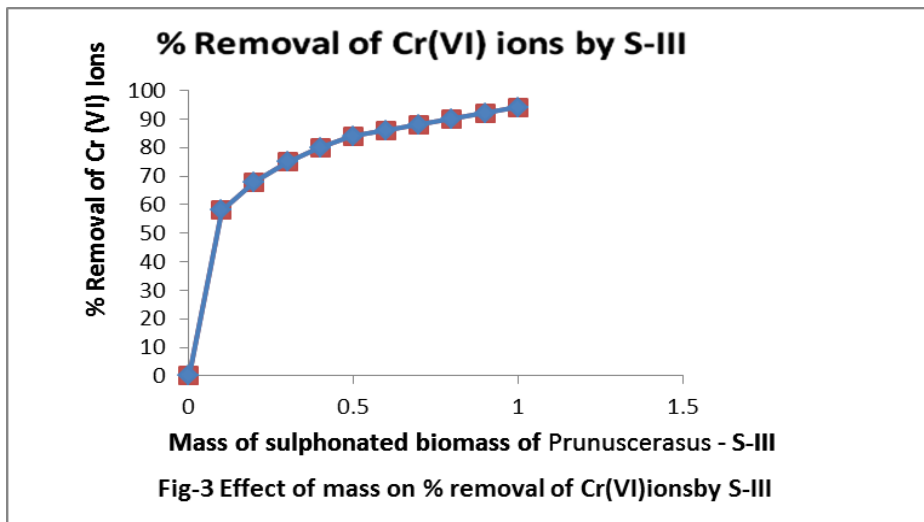
4.00. When the pH value is greater than 6.00 it is likely that Cr (VI) ions were precipitated as a result of the formation of hydroxides and thus removal efficiency decreased sharply. At lower pH values, protons exist in high concentration and binding sites of metals became positively charged and this has a repelling effect on the Cr (VI) cations. As the pH value increases, the density of negative charge on Sulphonated biomass of Stalks of *Prunuscerasus* (S-III) rises because of deprotonation of the binding sites in the metals hence is increasing metal uptake. This is in good agreement with the previous explanations.^[17]



Effect of biomass weight

The bio-sorbent quantity is a significant factor because it may control the metal uptake capacity of a bio-sorbent for a given concentration. The bio-sorption effectiveness for Cr (VI) ions as a function of bio-sorbent amount was examined. A number of solutions were prepared with the adsorbent dose of 0.10, 0.20, 0.40, 0.60, 0.80 and 1.00 g/100 mL of chromium (VI) solution (50 mg/L). Figure 2 shows that the percentage of the metal bio-sorption clearly increases with the bio-sorbent mass up to 0.80 g/100 mL. Therefore, the optimum bio-sorbent dosage was taken as 0.80 g/100 mL for further experiments. This

result can be attributed to the fact that the bio-sorption sites remain unsaturated for the period of the bio-sorption process, whereas the number of sites available for bio-sorption site increases by increasing the bio-sorbent dose. Furthermore when the bio-sorbent ratio is small, the active sites available for binding metal ions on the surface of Sulphonated biomass of Stalks of *Prunuscerasus* (S-III) are less, so the bio-sorption effectiveness is low. As the bio-sorbent quantity increased, more active sites to bind Cr (VI) ions are available, thus it results an increase in the bio-sorption efficiency until saturation.



Effect of contact time

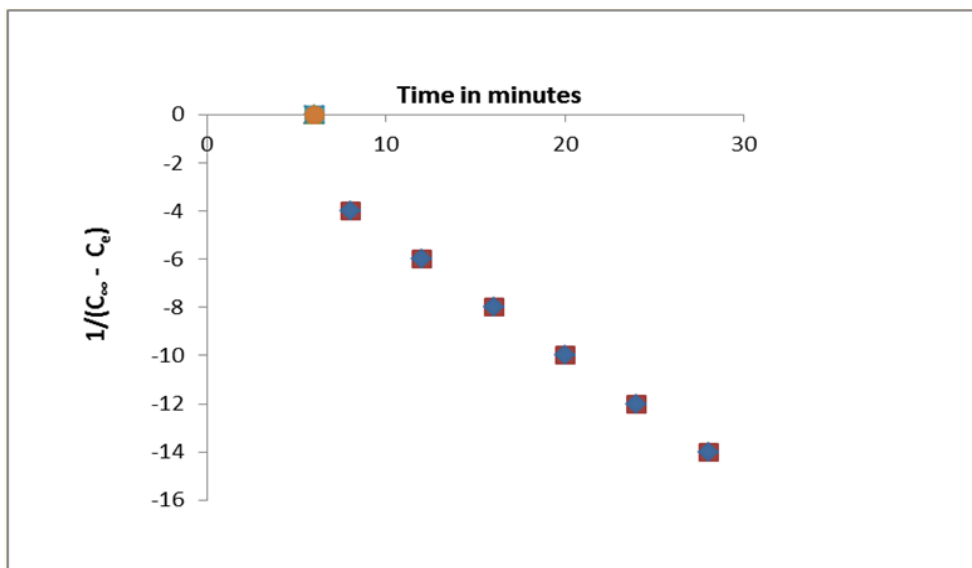
The impact of contact time on the removal of 50 mg/L of Cr (VI) ions from aqueous solutions was also investigated. Results revealed that the metal ions removal increases linearly with time up to 25 min and then remains at the same level. The rate of metal ion removal is higher in the beginning because of the large surface area of the adsorbent available for the adsorption of the Cr (VI). Furthermore, no major changes were observed in the removal of Cr (VI) ions from the

aqueous solution after 24 h of equilibration.

Kinetic calculations

Kinetics of bio-sorption of Cr (VI) ions onto activated carbon of leaves of Sulphonated biomass of Stalks of Prunuscercasus (S-III) was studied. It is obvious from the results (Fig.4) that the bio-sorption behaviour follows Eq. 3 indicating second order kinetics.

$$1/(C_{\infty} - C_t) = kt + 1/C_0 \quad 3$$



Results showed that after 30 min of shaking time, 96 % of Cr (VI) ions were removed from the aqueous solution indicating that the interfering ions have almost no effect on the efficiency of Sulphonated biomass of (S-III) to remove Cr (VI) ions. Furthermore very small quantities of the interfering ions were removed demonstrating that Sulphonated biomass of Stalks of Prunuscercasus (S-III) may be used as selective bio-sorbent for Cr (VI) ions. This may be attributed to the fact that the experiment was carried out at the optimal conditions for Cr (VI) removal.

Effect of Cr (VI) concentration

The effect of initial concentrations of Cr (VI) ions on its adsorption on the was Sulphonated biomass of (S-III) investigated by varying the initial concentration from 50 to 200 mg/L. Results revealed that the removal percentage is inversely proportional to the initial Cr (VI) concentration. This may be attributed to coverage of active sites of adsorbent as the concentration of Cr (VI) increases. Adsorption of Cr (VI) ions onto Sulphonated biomass of Stalks of Prunuscercasus (S-III) was studied using three models of adsorption isotherm: Langmuir, Freundlich and Temkin isotherms. The aim of adsorption

isotherms is to explain the relation between the remaining concentration of the adsorbate and the adsorbed quantity on the sorbent surface.

Langmuir isotherm

The Langmuir isotherm postulates monolayer adsorption on a uniform surface with a limited number of adsorption sites. Once a site is filled, no additional sorption can occur at that site. The linear equation of the Langmuir isotherm model is described by Eq. (4).

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (4)$$

Where Q_m is the maximum adsorption capacity (mg/g) and b is the Langmuir constant which related to

adsorption rate. Values of q_m and b are shown in Table 1. The attraction between sorbent and sorbate can be deduced by using separation factor, b , as shown in Eq.^[5]

$$R_L = \frac{b C_0}{1 + b C_0} \quad (5)$$

R_L value provides significant evidence about the adsorption nature. Langmuir isotherm is considered to be irreversible when R_L is equal to zero, favourable when $0 < R_L < 1$, linear when $R_L = 1$ or unfavourable when $R_L > 1$. R_L values were determined as 0.10, 0.07, 0.05, 0.04, 0.03 and 0.02 for concentrations 50, 70, 100, 120, 150 and 200 mg/L of Cr (VI) ions indicating favourable adsorption.

Table 2: Constants of different adsorption isotherm models.

Isotherm	Value	Isotherm	Value	Isotherm	Value
Langmuir		Frenudlich		Temkin	
q_m , mg/g	23.0	n	2.70	A , L/g	2.84
b , L/g	0.20	K_f , mg/g (L/mg) ^{1/n}	5.20	B	3.33
R^2	0.985	R^2	0.9443	R^2	0.98

Freundlich isotherm

This model is applied to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules. Application of the Freundlich equation suggests that adsorption energy exponentially decreases on completion of the adsorption centres of sorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems as shown in Eq. (6).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

Where K_f is the adsorption capacity of sorbent, n value determines the degree of non-linearity between solution concentration and adsorption in this manner: if $n = 1$, then adsorption is linear; if $n > 1$, then adsorption is a chemical process; if $n < 1$, then adsorption is a physical process. K_f and n values were listed in Table 1. The n value lies between one and ten indicating the physical adsorption of Cr (VI) onto Sulphonated biomass of Stalks of *Prunus cerasus* (S-III).

Temkin isotherm

Temkin isotherm^[30] takes into consideration the indirect interaction between adsorbate molecules and assumes that the heat of adsorption of all molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to a maximum binding energy. The Temkin isotherm model has been used in the linear form as shown in Eq. (7).

$$q_e = B \ln A + B \ln C_e \quad (7)$$

Where $B = RT/b$, b is the Temkin constant associated to heat of adsorption (J/mol), A is the Temkin isotherm

constant (L/g), R is the universal gas constant (8.314) J/mol. K, and T is the absolute temperature (K). The constants B and A are listed in Table 1. The determination coefficients higher than 0.96 for sorbent under all experimental conditions. The value KP is found to be 0.825 to 2.50.

Effect of Temperature

The effect of temperature on bio-sorption of Cr (VI) on Sulphonated biomass of Stalks of *Prunus cerasus* (S-III) was studied at temperature range of 25.0–50.0 °C. Equations (8–12) were used to calculate some thermodynamic parameters.

$$\Delta G^\circ = -RT \ln K_D \quad (8)$$

K_D is defined as:

$$K_D = C_o / C_e \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

Equations (8) and (10) can be written as:

$$RT \ln K_D = \Delta H^\circ - T \Delta S^\circ \quad (11)$$

on rearrangement $\ln K_D = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (12)$

Enthalpy and entropy change of activation were calculated from Eq. (12), while values of free energy change of activation ΔG° were determined from Eq. (8).

Table 2 showed that (ΔG°) has negative values indicating that the bio-sorption process is spontaneous. It is also observed that the negative values of free energy change, increases with increasing temperature. This may be ascribed to activation of more sites on the surface of Sulphonated biomass of Stalks of *Prunus cerasus* (S-III) with a rise in temperature or that the energy of bio-sorption sites has an exponential distribution band at higher temperature enabling the energy barrier of bio-

sorption to be overcome. When the free energy change (ΔG°) ranges between -20 and 0 kJ/mol, adsorption is classified as physical adsorption, while in chemical adsorption values of free energy change range from -80 to -400 kJ/mol. ΔG° for Cr (VI) bio-sorption onto w Sulphonated biomass of Stalks of *Prunus cerasus* (S-III) as in the range of $(-5.02$ to $-13.52)$ kJ/mol and so the adsorption was predominantly physical bio-sorption. This is in agreement with results derived from the n value calculated with the Freundlich isotherm. Results showed that the value of ΔS° is 343.72 J/mol K. This positive value showed that there is an increased randomness at the solid solution interface during the adsorption of Cr (VI) ions onto Sulphonated biomass of Stalks of *Prunus cerasus* (S-III) Results in Table 1 also showed that the bio-sorption is an endothermic process.

Table 3: Thermodynamic parameters of the biosorption of Cr (VI) ions onto Sulphonated biomass of (S-III).

T, K	K_d	ΔG° (kJ/mol)
298	150.61	-12.52
303	60.98	-9.74
313	14.67	-0 5.93
323	6.59	-0 4.02

CONCLUSIONS

Biosorption of Cr (VI) ions onto activated carbon prepared from leaves of Sulphonated biomass of (S-III) was investigated and found to be dependent on pH value of solution, adsorbent mass, contact time, temperature and initial Cr (VI) concentration. Data of biosorption of Cr (VI) on were applied to three adsorption isotherm models. The maximum adsorption capacity was determined from the Langmuir isotherm as 21.0 mg/g. The n value obtained from the Freundlich isotherm indicates that the sorption of Cr (VI) ions onto Sulphonated biomass of Stalks of *Prunus cerasus* (S-III).

is favourable. Adsorption process of Cr (VI) ions onto Sulphonated biomass Stalks of *Prunus cerasus* of (S-III) was found to obey the second-order kinetic equation. Thermodynamic parameters proved that the adsorption process is spontaneous and endothermic. Investigation Kinetic, isotherm and thermodynamic studies on biosorption of chromium (VI) by using activated carbon from Sulphonated biomass of Stalks of *Prunus cerasus* was conducted in batch conditions. The effect of different parameters such as contact time, sorbent dose, pH and temperature has been studied. Adsorption kinetic modelling data were found out. The kinetics of biosorption results shows that sorption process is well explained by pseudo-second order model with determination coefficients higher than 0.96 for sorbent under all experimental conditions. The value K_p is found to be 0.825 to 2.50 for initial and final concentrations. The Weber and Morris intraparticle diffusion model show liquid-film, mass transfer is effective sorption mechanism. Thermodynamic parameter via KD , ΔG has

also been calculated to determine the spontaneity of the process. The low value of activation energy indicates that sorption is an activated and physical process. Thus Kinetic, isotherm and thermodynamic studies on biosorption of chromium (VI) by using activated carbon from Sulphonated biomass of Stalks of *Prunus cerasus* is a low cost and easily available efficiently used as an excellent sorbent for the removal of chromium (VI) from wastewater. It can be safely concluded that biomass of Stalks of *Prunus cerasus* is much economical effectual, viable and can be an alternative to more costly adsorbents.

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