Bio-sorption for Effective Removal of Chromium (VI) from Wastewater Using *Moringa Stenopetala* Seed Powder (MSSP) and Banana Peel Powder (BPP)

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**Abstract:** Chromium is an extremely toxic heavy metal that causes severe environmental and health problems. Therefore, the aim of this study was to remove chromium ions from wastewater by using cost effective and environmentally friendly bio-sorbents; (MSSP) and (BPP) and to evaluate adsorption capacities of the bio-sorbents. FT-IR characterization of the adsorbents showed that there was a change in the functional groups of the structure of both adsorbents before and after the adsorption processes confirming that there was effective adsorption of chromium on both adsorbents. Adsorption experiments were carried out as batch studies at different contact times, pH, adsorbent dose, initial metal concentration and temperature. Results showed maximum removal efficiency for Cr (VI) at 120 minutes contact time, adsorbent dose of 20 g/L and pH 2 by MSSP and pH 4 by BPP. Percentage removal of Cr(VI) increased with increasing adsorbent dose (from 5g/L to 20 g/L) and contact time (from 60 min to 120 min). Freundlich isotherm model showed a better fit to the equilibrium data than the Langmuir model. The result of thermodynamic parameters showed negative values of $\Delta G^\circ$ and $\Delta H^\circ$ confirming spontaneous and exothermic nature of the sorption of Cr(VI) ion onto both adsorbents. A positive value of $\Delta S^\circ$ indicates the increase in randomness of Cr(VI) ion at the solid-liquid interface of the adsorbents during the sorption process. The kinetics of adsorption for chromium was well represented by pseudo-second order kinetic model and the calculated equilibrium sorption capacity of the model showed good agreement with the sorption capacity obtained from experimental results.

**Keywords:** *Moringa stenopetala*, Banana peel, Chromium (VI), FT-IR, Adsorption Isotherms
1. Introduction

Water is crucial for all aspects of life and it is the defining feature of our planet. As water is extracted and used along the supply chain, both the quality and quantity of water is reduced [1]. Societies that are able to use their water resources in an efficient and sustainable manner have succeeded in being food self-sufficient, reducing the incidences of water-borne diseases and minimizing adverse effects of the resource. But nowadays, industrialization and urbanization gained momentum in all developing countries at the cost of environmental degradation. In many developing countries, more than 70% of industrial wastes are dumped untreated into waters where they pollute the usable water supply [2]. An estimated 90% of all wastewater in developing countries is discharged untreated directly into rivers, lakes or the oceans [3]. In particular, Ethiopia has used 18% of 49 million m$^3$ of its generated wastewater in volume per annum without treatment for agricultural production and other purposes, while the remaining wastewater is discharged into nearby water bodies such as rivers, springs, streams, and lakes [4-5]. In many instances, wastewater from industries not only drains directly into rivers and lakes, it also seeps into the ground contaminating aquifers and wells. This discharging of wastewater to the water source can cause environmental pollution. If water is polluted, it may contain dissolved impurities like toxic heavy metals, organic pollutants, radioactive nuclides, etc. [6].

Heavy metals such as chromium, Cr are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity [7]. They are stable and persistent environmental contaminants since they cannot be degraded or destroyed [8]. Therefore, they can cause health problems in humans and animals ranging from irritation to cancers [9]. Increasing quantity of heavy metals in our resources is an area of great concern, especially since a large number of industries are discharging their metal containing effluents into fresh water without any adequate treatment [10]. Unlike organic pollutants, heavy metals are non-biodegradable in the environment and can accumulate in living tissues, particularly in human bodies, causing significant physiological disorders such as damage of central nervous system and blood composition, production of energy and irreversible damage of vital organs of body. Hence the presence of heavy metals and their removal in natural or industrial wastewater is a
subject of great interest in environmental science which is one of the most serious worldwide environmental problems [11-12].

Cr-containing compounds are widely used in industries such as leather, electroplating, textile dyeing, and metal fabrication and finishing. Cr-containing wastewaters are one of the major pollutants of the environment. It is essential that industries treat their effluents to reduce the Cr ions concentration in water and wastewater to acceptable levels before releasing it into the natural environment. Various conventional treatment methods have been employed for the removal of Cr ions from water and wastewater. These include chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and activated carbon adsorption. However, these conventional technologies are expensive due to non-regenerable materials used, generation of toxic sludge and often ineffective, particularly for the removal of Cr ions at low concentrations as below as 50 mg/L [13-15].

Therefore, needs for cost-effective and eco-friendly alternative technologies are essential. Accordingly, it is crucial to explore locally available materials for the treatment of Cr ions from wastewater. For this purpose, cost effective adsorption technology, simple to design and operate using locally available materials is the focus of current work. Therefore, *Moringa Stenopetala* Seed Powder and Banana peel powder have been investigated and compared for their adsorptive removal efficiency of Cr(VI) ions from aqueous solutions under various operating variables (contact time, solution pH, initial Cr concentration and temperature).

### 2. Materials and Methods

#### 2.1 Preparation of *Moringa Stenopetala* Seed Powders (MSSP)

Matured and fresh seeds of *Moringa stenopetala* were collected from Arba Minch University main campus and specimen identification of the seed was done at Addis Ababa University National Herbarium. Then the seeds (Fig.2.1) were separated from their cover or shell manually. They were, air dried and ground using a grinding mill and sieved through a mesh. Finally, the fine powder of the seed shown in Fig. 2.1 B, was collected and kept in a clean bottle until experiments were done.
2.2 Preparation of banana peel Powders (BPP)
Banana was collected from the local market of Arba Minch. The peel shown in Fig. 2.2 was separated from bananas and cut into smaller pieces while still wet, washed thoroughly with tap and distilled water to remove dirt particles. Finally the wetted banana peel was air dried, ground into powder and kept in a clean airtight bottle; until experiments were done.

2.3 Preparation of Adsorbate
A 1000 ppm of Cr(VI) stock solution was prepared (2.827 g of K$_2$Cr$_2$O$_7$ in 1000 mL distilled water) [16]. Other working solutions of different concentrations were prepared by appropriate dilution of the stock solution.

2.4 Batch Experiments
All experiments were carried out in batch mode to obtain both the equilibrium and rate data. The experiments were run in different Erlenmeyer flasks of 250 ml capacity each containing 100 mL of the test solution. The studies were carried out at the desired contact time, pH value and adsorbent dosage. Before adding the adsorbent, the solution pH was adjusted by using 0.1 M NaOH/HCl solution. To ensure equal mixing, all the experiments were performed with an orbital shaker with a constant agitation speed (150 rpm). The equilibrium study was conducted using Langmuir and Freundlich isotherm models. The kinetics experiments were made using pseudo- first order and pseudo-second order models. After completing the batch experiment, the solution was separated from the adsorbent by gravity filtration using Whatman no.1 filter.
paper, the supernatant solution of chromium was digested in a microwave digester and the concentration was determined by GFAAS. All experiments were carried out in triplicate and the mean value was used for further calculation. The adsorption efficiency (%) and capacity at a given contact time for the selected adsorbents were determined using the following equations:

\[
\% \text{ Removal} = \frac{(C_0 - C_f)}{C_0} \times 100
\]

\[
q = \frac{(C_0 - C_f)V}{m}
\]

where \(C_0\) = initial concentration, \(C_f\) = concentration after adsorption, \(q\) = metal removal in mg/g, \(m\) = adsorbent mass in gram and \(V\) = volume of wastewater used during the experiment.

### 2.5 Adsorption Isotherm

Adsorption isotherm is a graphical representation expressing the amount of solute adsorbed per unit mass of adsorbent as a function of equilibrium concentration in bulk solution at constant temperature. The experiments were carried out under different adsorbent dose that ranged from 0.5g - 2g with an interval of 0.5g by keeping the previously determined parameters at the optimal level in 100 mL solution of the metal ion with an agitation speed of 150 rpm. The adsorption equilibria between the adsorbate and adsorbent were described using Langmuir and Freundlich adsorption isotherm models and the data obtained were fitted in to the two models for the analysis.

Langmuir isotherm model involves an assumption that the energy of sorption is the same for all surface sites and not dependent on degree of coverage. The Langmuir sorption isotherm equation is represented as [23]:

\[
q_e = \frac{(q_m b C_e)}{(1 + b C_e)}
\]

where \(C_e\) is the equilibrium concentration of the ion (mg/L); \(q_e\) is the amount of ion adsorbed (mg/g); \(q_m\) is \(q_e\) for a complete monolayer (mg/g); and \(b\) is bio-sorption equilibrium constant (L/mg).

The linear form of Langmuir isotherm model can be represented by using equation (4):

\[
\frac{C_e}{q_e} = \left(\frac{1}{q_m b}\right) + \left(\frac{C_e}{q_m}\right)
\]

The essential characteristics of the Langmuir isotherm can be explained by the equilibrium separation factor \(R_L\), defined as:
\[ R_L = \frac{1}{1 + bC_o} \] (5)

where \( b \) is the Langmuir constant and \( C_o \) is the highest metal concentration (mg/L).

Depending on the value of \( R_L \) (Table 1) the shape of the isotherm and whether the bio-sorption is favourable or not, can be determined.

**Table 1: Type of isotherm for various \( R_L \)**

| \( R_L \)   | Type of isotherm | Source |
|------------|------------------|--------|
| \( R_L = 1 \) | Linear           | [24]   |
| \( R_L > 1 \) | Unfavourable     | [24]   |
| \( R_L \) between 0 & 1 | Favourable     | [25]   |
| \( R_L = 0 \) | Irreversible     | [26]   |

Freundlich isotherm model describes a multi-layer bio-sorption based on adsorption on heterogeneous surface and adsorption capacity which is related to the concentration of the adsorbent. The model can be presented as [27]:

\[ q_e = K_f C_e^{1/n} \] (6)

where \( q_e \) is the amount of ion adsorbed (mg/g); \( C_e \) is the equilibrium concentration (mg/L); \( K_f \) and \( 1/n \) are empirical constants, indicating the adsorption capacity (Freundlich constant) and adsorption intensity (which varies with the heterogeneity of the material), respectively.

The two Freundlich parameters \( K_f \) and \( 1/n \) can be determined graphically by plotting the experimental data and then using the Freundlich equation in the following form

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \] (7)

where \( K_f \) and \( 1/n \) are evaluated from the intercept and slope of the plot of \( \ln q_e \) vs \( \ln C_e \). For values in the range 0.1<\( 1/n \)<1, bio-sorption is favourable. The greater the values of \( K_f \), better is the favourability of bio-sorption.

### 2.6 Adsorption Kinetics

The effect of time on the removal rate of Cr(VI) ion from the solution were investigated using kinetic study. Adsorption kinetics shows a large dependence on the physical and/or chemical characteristics of the adsorbent material. The experiment was conducted in a separate 250 mL Erlenmeyer flask by keeping pH, adsorbent dose and metal ion concentration at the optimum level in different time intervals (30 min., 60 min., 90 min., 120 min. and 150 min.) by adjusting the agitation speed at 150 rpm. Finally the experimental data were analyzed using pseudo first-order [21] and pseudo-second order [22] kinetics models.
Pseudo-first order kinetics model was based on adsorption capacity of adsorbent and suggests that there are no interactions between ions and each ion sorbs on a local site. The model approves that the coverage does not influence on the adsorption energy and the concentration of a substance is constant. The model also designs that bio-sorption process as a monolayer of adsorbate on the adsorbent surface and expressed as follows [21]:

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]

(8)

Where \( q_e \) and \( q_t \) are the amounts (mg/g) of adsorbed pollutant on the adsorbent at equilibrium and time \( t \); and \( k_1 \) is the rate constant (min\(^{-1}\)) of Lagergren’s first-order adsorption.

After integration and applying boundary conditions \( t=0 \) to \( t=t \) and \( q_t=0 \) to \( q_t=q_e \), the integrated form becomes:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
\]

(9)

Plot of \( \log (q_e - q_t) \) versus \( t \) gives a straight line for first order adsorption kinetics which allows computation of the rate constant \( k_1 \) and \( q_e \) from the slope and intercept of the plot.

The pseudo-second order kinetics model is based on the assumption that the bio-sorption follows a second order mechanism and occupation rate of adsorption site is proportional to the square of the number of unoccupied sites. The rate equation can be represented in the following form [22]:

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2
\]

(10)

where \( k_2 \) is rate constant (g/mg min) of second-order adsorption.

The integrated form of the equation (10) becomes:

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t
\]

(11)

The linear form of equation (11) is as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{(q_e) t}
\]

(12)

The \( k_2 \) and \( q_e \) values of the pseudo-second-order kinetic model can be determined from the intercept and slope of the plots of \( t/q_t \) versus \( t \).

2.7 Thermodynamic Study

Thermodynamic parameters provide in-depth information of inherent energetic changes that are associated with adsorption. The thermodynamic parameters such as standard Gibbs free energy change \( \Delta G^\circ \), standard enthalpy change \( \Delta H^\circ \), and standard entropy change \( \Delta S^\circ \) gives better understanding about the effect of temperature on adsorption. These parameters were determined using the following equations [28].
\[ 
\Delta G^o = -RT \ln K_c 
\]  \hspace{1cm} (13)

\[ 
K_c = \frac{C_a}{C_e} 
\]  \hspace{1cm} (14)

The Gibbs free energy change (\( \Delta G^0 \)) is related to the entropy change (\( \Delta S^0 \)) and enthalpy change (\( \Delta H^0 \)) at constant temperature by the following equation:

\[ 
\Delta G^0 = \Delta H^0 - T \Delta S^0 
\]  \hspace{1cm} (15)

By combining the above two equations we get the following equation:

\[ 
\ln K_c = \frac{\Delta S^0}{R} \frac{\Delta H}{RT} 
\]  \hspace{1cm} (16)

where \( K_c \) is the equilibrium constant, \( T \) is the absolute temperature (K), \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( C_a \) (mg/L) is the amount of metal ion adsorbed at equilibrium, \( C_e \) (mg/g) is the amount of metal ion left in the solution at equilibrium. The values of \( \Delta H^0 \) and \( \Delta S^0 \) were calculated from the slope and intercept of the Van’t Hoff plot of \( \ln K_c \) versus \( 1/T \) equation (16).

3. Results and Discussion

3.1. FT-IR result for BPP and MSSP

The FT-IR spectra before and after adsorption of chromium were given for both BPP and MSSP in which the absorption peaks were appeared in wavenumber range of 3500 cm\(^{-1}\) to 625 cm\(^{-1}\). The Fig. 3.1a shows the absorbance spectra of BPP and MSSP before adsorption and Fig. 3.1b indicates the absorbance spectra of BPP and MSSP after adsorption of chromium taken place.

The spectra containing weak bands in both figures represent the absorbance spectra of BPP before and after adsorption where as the one containing stronger bands in both figures are indicating the absorbance spectra of MSSP before and after adsorption.

Figure 3.1 FT-IR Spectra of a) BPP and MSSP Before adsorption b) BPP and MSSP after adsorption

The FT-IR spectra in Fig. 3.1a show that broad bands at 3337 cm\(^{-1}\) and 3310 cm\(^{-1}\) indicate that O-H stretching vibration of carboxylic acid for both BPP and MSSP. These bands disappeared.
(decreased highly in intensity) in Fig. 3.1b, which confirms that the adsorption of chromium by both adsorbents was highly effective. In the same way a medium bands at 1654 cm\(^{-1}\) in both figures indicate that stretching vibration of C=O group in carboxylic acid. In Fig. 3.1b these bands for both BPP and MSSP were also decreased in intensity that confirms adsorption of chromium was taken place effectively. Therefore, FT-IR spectra of both BPPand MSSP show that both absorbents were effective for the removal of chromium from wastewater.

### 3.2 Effect of Contact Time

The percentage removal of Cr(VI) ions and the adsorption capacity of MSSP and BPP as a function of contact time was conducted at 60, 90, 120 and 150 minutes using different pH and dose at a constant initial concentration, agitation speed and temperature. The experimental results shown in Fig. 3.2 indicate that the percentage removal of Cr(VI) ion increases with increasing contact time up to 120 minutes. Further increase in contact time did not make any change in removal and adsorption capacity. Higher removal efficiency and adsorption capacity was observed at 120 minutes for both the adsorbents. Hence, 120 min was chosen as the equilibrium time. Because at the beginning of the process, adsorption is fast due to the availability of large active binding site but as the time has gone, the process slow down as active binding sites are filled by the molecules.

![Figure 3.2. Effect of contact time on % removal of: A/ Cr(VI) by MSSP and B/ Cr(VI) by BPP (concentration 30mg/L, contact time 60, 90, 120 & 150 minutes, adsorbent dose 5, 10, 15 & 20 g/L solution, agitation speed 150 rpm and pH = 2 for MSSP, pH = 4 for BPP)](image)

### 3.3 Effect of pH

Cr(VI) adsorption was studied as a function of pH over a range of 2 - 8 on MSSP and BPP at initial concentration of 30mg/L wastewater. The results of the experiment shown in Figure 3
indicate that optimal metal removal efficiency occurs at pH 2.0 (92.77%) for Cr(VI) by MSSP at 120 min contact time. Results of the study conducted by Bhatti, et al confirmed this result as follows: At pH 2.0, the maximum sorption of Cr was observed to be 97.77% which indicates pH 2 is optimum for sorption of chromium [31]. On the other hand, the maximum adsorption of Cr(VI) ion by BPP is obtained at pH 4.0 (90.82%). Therefore pH 4.0 was selected as optimum pH for chromium ion adsorption onto BPP. Maximum adsorption of Cr(VI) ion by MSSP is 5.75 mg/g which is observed at pH 2.0 and 120 min contact time. On the other hand maximum adsorption of Cr(VI) ion by BPP is 5.45 mg/g at pH 4 and 120 min contact time.

Chromium removal in mg/g by MSSP and BPP increases with increasing contact time from 60-120 min. for all pH values; this is because the solution pH is directly related to the large availability of positively charged active sites on the surface of the adsorbent to bind with the metal ions. As solution pH decreases, the surface of the adsorbents exhibits increasing positively charged active sites. As pH decreases, the removal efficiency becomes increasing that was shown in Fig. 3.3. The maximum adsorption of Cr(VI) was observed at the acidic range because, at lower pH, there is an increase in H⁺ ions on the adsorbent surface, and the presence of HCrO₄⁻ ions result in significantly strong electrostatic attraction [29].

![Figure 3.3](image)

**Figure 3.3. Effect of solution pH on % removal of: a/ Cr(VI) by MSSP and b/ Cr(VI) by BPP (concentration 30mg/L, pH, 2, 4, 6 & 8 and contact time 60, 90, 120 & 150 minutes, agitation speed 150 rpm)**

### 3.4 Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of Cr(VI) ions onto MSSP and BPP was conducted by using 5, 10, 15 and 20 g/L of adsorbent dose under variable pH and contact time on keeping agitation speed and initial concentration constant. Fig.3.4 shows that the percent removal of chromium by MSSP increases from 24.85% to 90.96% and by BPP from 20.06% to 89.62% with an increase in adsorbent dose from 5 to 20 g/L at all pH values. The increase in adsorbent dose generally increases the percent removal of the metal ion to be removed due to the
increased surface area of the adsorbent which increases the number of binding sites available for the adsorption process. On the other hand, the quantity of adsorbate metal ion per unit weight of the adsorbent decreases with increase in the adsorbent dose and this may be due to, at high adsorbent concentration, the available metal ion to be sorbed is not sufficient to completely cover the available active sites leading to the reduction of metal ion uptake [30].

![Figure 3.4. Effect of adsorbent dose on % removal of: a/ Cr(VI) by MSSP and b/ Cr(VI) by BPP (concentration 30 mg/L, agitation speed rpm, adsorbent dose 5, 10, 15 and 20 g/L solution, pH 2, 4, 6 & 8).](image)

On the other hand, adsorption capacity in mg/g decreases with increasing adsorbent dose for all pH values. Higher metal removal was observed at 5 g/L of adsorbent. Adsorbent dose has also its own effect on the removal efficiency at various contact time. Higher adsorption was obtained at 20 g/L for all contact times but at this dose percent removal variations among different contact times were small. This may be explained by the presence of screening effect when the adsorbent dose increases [31]. Thus, the removal efficiencies of chromium ions at optimal adsorbent concentration were selected as 20 g/L [32]

### 3.5 Effect of Initial Concentration of chromium

The experiment was carried out under optimal conditions and different initial concentration ranging from 30 mg/L up to 60 mg/L with an interval of 10 mg/L. As shown in Fig.3.5, the increasing of the initial concentration of chromium increases adsorption capacity of the adsorbents but decreases percentage removal of the metal. Maximum % removal of chromium by MSSP is 92.17% and by BPP is 90.07 at 30 mg/L. The decrease in percentage removal of the metal ion with increasing initial concentration may be due to the saturation of adsorption sites on the adsorbent surface. This can be explained by the fact that, at low concentration, the metal ions interact with the binding sites and result in maximum adsorption. This is because,
at low concentration, the ratio of available surface to the initial metal ion concentration is larger, so the removal is higher [33]. On the other hand, maximum Cr(VI) ion adsorption capacity of MSSP is 1.71 mg/g and that of BPP is 1.63 mg/g at initial concentration of 50 mg/L. The increase in adsorption capacity with increasing initial concentration is due to the fact that, at fixed adsorbent dose with increasing the metal concentration, all the available active sites of the adsorbent would be fully exposed to get occupied by the metal ions that are in excess saturating and yielding a higher adsorption capacity [34].

![Figure 3.5. Effect of initial concentration on % removal of Cr (VI) by MSSP and by BPP. (dose 20 g/L, contact time 120 min. and pH 2 for Cr(VI) by MSSP and pH 4 for Cr(VI) by BPP)](image)

3.6 Effect of Temperature

The effect of temperature on adsorption capacity of Cr(VI) onto MSSP and BPP was studied at a temperatures of 293k, 313k, 333k and 353k at the optimal conditions of the solution. As shown in Fig.3.6, an increase in temperature from 293k to 353k decreases the percentage removal from 91.40% to 37.93% that contains MSSP and from 90.03% to 33.80% for chromium solution that contains BPP respectively. Similar to percent removal, adsorption capacities of MSSP and BPP on the adsorption of Cr(VI) ion decreased from 1.37 mg/g to 0.57 mg/g and 1.35 mg/g to 0.51 mg/g with increasing temperature from 293k to 353k. This falls of metal uptake capacity of the adsorbents during the rise in temperature might be due to desorption caused by an increase in the available thermal energy. Higher temperature induces higher mobility of the adsorbate causing desorption or the damage of active binding sites in the biomass [35]. The decrease in adsorption capacity with increasing temperature indicates that adsorption process is exothermic in nature.
3.7 Adsorption Isotherm

The Langmuir plot between $1/q_e$ vs $1/C_e$ for the sorption of Cr(VI) ion by MSSP and BPP are drawn in Fig. 3.7. It was found that the values of maximum adsorption capacity of MSSP and BPP were 9.709 mg/g and 7.353 mg/g, respectively (Table 2). The essential characteristics of the Langmuir isotherm can be explained by the equilibrium separation factor $R_L$. The $R_L$ values for sorption of Cr(VI) ion by MSSP and BPP in this study were 0.325 and 0.275, respectively. This indicates that MSSP and BPP are favourable adsorbents for the removal of chromium.

The Freundlich adsorption model is based on adsorption on heterogeneous surface and adsorption capacity related to the concentration of the adsorbent. The value of Freundlich constant $1/n$ and $K_f$ for the sorption of Cr(VI) ion by MSSP and BPP were obtained from the slope and intercept of the plot log$q_e$ vs log$C_e$. $K_f$ is an indicator of adsorption capacity of adsorbent and the higher the maximum capacity, the higher the value of $K_f$. On the other hand, $1/n$ is a measure of intensity of adsorption. Therefore, the $K_f$ value for the sorption of Cr(VI) ion by MSSP and BPP are 0.685 and 0.635 whereas the $1/n$ values for the sorption of Cr(VI) are 0.792 and 0.779 respectively. This indicates that both MSSP and BPP have high chromium sorption capacity and are favourable adsorbents from wastewater. The values of correlation
coefficients (R²) of the Freundlich model given in Fig. 3.8, which were 0.993 and 0.983 for MSSP and BPP respectively and these values are larger than the R² values of the Langmuir model (0.983 and 0.976). This indicates the Freundlich model fits better to the adsorption data and thus it is more suitable to be used to describe the relationship between the amounts of Cr(IV) ion adsorbed by MSSP and BPP.

![Figure 3.8](image)

**Figure 3.8** Freundlich adsorption isotherms for: A/ Chromium by MSSP and B/ Chromium by BPP

| Table 2. Parameters of Langmuir and Freundlich adsorption isotherms of chromium |
|---------------------------------|------------------|------------------|------------------|------------------|
| Metal ion | qₘₑ | b | R<sub>L</sub> | R<sup>2</sup> | K<sub>f</sub> | 1/n | R<sup>2</sup> |
|----------|------|----|------------|---------|---------|-----|---------|
| Cr(VI)-MSSP | 9.709 | 0.0692 | 0.325 | 0.983 | 0.685 | 0.792 | 0.993 |
| Cr(VI)-BPP | 7.353 | 0.0879 | 0.275 | 0.976 | 0.635 | 0.779 | 0.983 |

**3.8 Adsorption Kinetics**

From the experimental data shown in Table 3, the calculated and experimental equilibrium adsorption capacity, qₑ(cal) & qₑ(exp), of pseudo-second-order kinetic model was close to each other than the pseudo-first-order kinetic model. This indicates that the pseudo-second order kinetics is the best kinetic model that fits to the experimental data for sorption of Cr(VI) by MSSP and BPP. The correlation coefficients (R²) of pseudo-second-order kinetic model of chromium by MSSP and BPP (0.998 & 0.994) are closer to unity compared to the pseudo-first-order kinetic model (0.939&0.897). This indicates pseudo-second-order kinetic model is better model to the kinetics of adsorption onto the adsorbents it is indicated in Fig. 3.9 and 3.10.
3.9 Thermodynamics Study

The values of the thermodynamic parameters for adsorption of Cr(VI) ion onto MSSP and BPP are shown in Table 4. The increase in temperature made the values of $\Delta G^0$ more positive. A negative value of Gibbs free energy change ($\Delta G^0$) confirms the feasibility of the process and spontaneous nature of the sorption of Cr(VI) ion onto MSSP and BPP. The change in Gibbs free energy decreases with increasing temperature which indicates that a lower temperature favours adsorption.
The adsorption process involves energy changes that could result in a positive or negative value of $\Delta H^0$. The negative values of $\Delta H^0$ in this study indicates adsorption of Cr(VI) ion onto MSSP and BPP is exothermic in nature. If enthalpy change, $(\Delta H^0)$ of an adsorbent is higher than 40 kJ mol$^{-1}$, the process is said to be chemisorption which includes strong electrostatic chemical bonding between the metal ions and adsorbent surface. On the other hand, enthalpy change less than 20 kJ mol$^{-1}$ indicate the physical nature of the adsorption process. In this study, all the values of $\Delta H^0$ are greater than 40 kJ mol$^{-1}$ revealing that chemisorption was responsible for the adsorption Cr(VI) ion onto MSSP and BPP. The positive values of entropy, $(\Delta S^0)$, indicate the increase in randomness of Cr(VI) ion at the solid-liquid interface of MSSP and BPP during the adsorption process.

Table 4: Thermodynamic parameters for Cr(VI) ion adsorption onto MSSP and BPP at different temperatures.

| T (K) | Cr-MSSP | Cr-BPP |
|-------|---------|--------|
|       | $K_c$   | $\Delta G^0$ | $\Delta H^0$ | $\Delta S^0$ | $K_c$   | $\Delta G^0$ | $\Delta H^0$ | $\Delta S^0$ |
| 293   | 1.88    | -1.535  | -43.44  | 0.152    | 2.21    | -1.924  | -42.57  | 0.151    |
| 313   | 4.02    | -3.617  | -43.44  | 0.152    | 5.57    | -4.476  | -42.57  | 0.151    |
| 333   | 26.05   | -9.026  | -9.275  | 28.45    | 38.94   | -10.742 | -10.423 | 0.151    |

4. Conclusions

From the present study, it is concluded that without giving any chemical treatment, the seed powders of Moringa stenopetala and banana peels can be used to remove Cr(VI) ion from wastewater. FT-IR characterization of the adsorbents showed that there was a change in the functional groups on the structure of both adsorbents before and after the adsorption processes taken place confirming that there was an effective adsorption of chromium on both adsorbents. Operational parameters such as pH, contact time, adsorbent dose, initial concentration and temperature affect the sorption of Cr(VI) ion. Percentage removal of Cr(VI) ion increases with decreasing pH (from 8 to 2), increasing adsorbent dose (from 5 g/L to 20 g/L) and contact time (from 60 min to 120 min). Adsorption isotherm were described using the Langmuir and Freundlich models, show that the Freundlich model fits better to the adsorption
The kinetics study reveals that the sorption of Cr(VI) ions are faster in the pseudo-second order kinetics than pseudo first order kinetics. Thermodynamic study was investigated using $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ and the results show that the negative values of $\Delta G^0$ (confirming the spontaneous nature of the sorption process), negative values of $\Delta H^0$ indicates the exothermic nature of the sorption process and positive value of $\Delta S^0$ (showing the increase in randomness of Cr(VI) ion at the solid-liquid interface of MSSP and BPP during the sorption process). The greener bio-sorption process using MSSP and BPP adsorbents are very good for the removal of Cr(VI) ions from wastewater. When comparing the two adsorbents, the removal efficiency of MSSP is higher than BPP.

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**Availability of data and materials**

The authors declare that the manuscript contains the minimal dataset that is required to interpret, replicate, and build upon the methods and findings reported in the article. Raw data can be shared via correspondence upon reasonable request.

**Ethics approval and consent to participate**

Not applicable.

**Consent for publication**

Not applicable.

**Competing interests**

The authors declare that we have no competing interests
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