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# TANNERY WASTES WATER TREATMENT USING *MORINGA STENOPETALA* SEED EXTRACT

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## ABSTRACT

High amount of heavy metal ions like Cr in the environment has been harmful for animal and human health. Bioadsorption of Cr from tannery wastes would be an alternative method to the chemical treatment in tannery industries. Hence, in this study the efficiency of Moringa stenopetala seed extract to adsorption Cr from tannery waste water was investigated. The influence of solution pH, adsorbent concentration, initial concentration of Cr, contact time and temperature on the efficiency of Moringa stenopetala seed extract for the adsorption of Cr from tannery effluent was studied. Results obtained revealed that in strongly acidic condition Moringa stenopetala seed extract was less efficient to remove Cr. However, the result of the present study showed that Moringa stenopetala seed extract at a concentration of 1g/100 ml and pH of 9.5 decreased the concentration of Cr in tannery waste by 99.86%. In addition, the adsorption data was correlated using the Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models. Among models studied Dubinin-Radushkevich isotherm was the best fit with correlation coefficient of 0.958. Moreover, thermodynamics parameters, such as Gibbs free energy ($\Delta G^o$), enthalpy ($\Delta H^o$), and entropy ($\Delta S^o$) were calculated. Results indicated that the bioadsorption of Cr by Moringa stenopetala seed extract was spontaneous, feasible and endothermic. The results of this study proved that Moringa stenopetala seed extract can be used to remove Cr from tannery effluent.

**KEYWORDS:** *Moringa stenopetala*, Cr, tannery, pH, temperature, concentration

## INTRODUCTION

Heavy metal ions are great concern not only among chemist but also among the general population, who are affected with some of the disadvantages associated with them. Although some heavy metal ions play important roles in living systems, they are very toxic and hence capable of causing serious environmental health problems. Chromium (Cr) is a heavy metal used in various industrial processes like in chrom-plating, wood preserving, textile dyeing, pigmenting, chromium chemical production, pulp and paper industrial and tanning. The wastewater resulting from these processes contains high amount of chromium metal which is harmful for environment and human health (Zayed and Terry, 2003). Tanning process with chromium compounds is one of the most common methods for processing of hides. Several reports have shown that the values for Cr in tannery effluent are considerably higher than the safe limits prescribed by international standards (Shanker et al., 2005). In the tanning process about 60%-70% of chromium reacts with the hides the remaining about 30%-40% of the chromium amount remains in the solid and liquid wastes (especially spent tanning solutions) (Abdulla et al., 2010). The concentration of chromium ion in the tanning waste water varies from 1300 to 2500 ppm (Abdulla et al., 2010).

A wide range of physical and chemical processes are available for the adsorption of heavy metals including chromium from water. These methods include electro-chemical precipitation, ultrafiltration, ion exchange and reverse osmosis. A major drawback with precipitation is sludge production. Ion exchange

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is considered a better alternative technique for such purpose. However, it is not economically appealing because of high operational cost. Adsorption using commercial activated carbon (CAC) can remove Cr from wastewater. However, CAC remains an expensive material for heavy metal adsorption (Nomanbhay and Palanisamy, 2005). Hence, recently there has been increased interest in the subject of natural coagulants for treatment of water and wastewater. Our aim was to investigate the potential of seed extract of *Moringa stenopetala* in removing total chromium from tannery liquid wastes.

M. *stenopetala* grows naturally in well-drained soils at altitudes of 900-1200 m. The species is quite drought resistant. In southern Ethiopia, it has been found in areas of mean annual rainfall ranging from 500-1400mm. Cold temperatures are limiting factor for the cultivation of the species (Orwa et al., 2009).The water soluble Moringa seed proteins possess coagulating properties. The active agents in *Moringa oleifera* (other species of Moringa) extracts responsible for coagulation were suggested as the cationic polypeptides (Jahn, 1986). Although the water clarifying properties of *M.stenopetala* have not been as extensively studied as those of *M. oleifera*, Jahn (1986) reported that 100-150 mg/l of *M. stenopetala* was as effective in water clarification as 200 mg/l of *M. Oleifera.* However, no work has been reported previously on the potential of seed extracts of *M. stenopetala* to remove different pollutants like chromium.

Material derived from microbial biomass, seaweed or plants that exhibit adsorptive properties are inexhaustible, low-cost and non-hazardous materials, which are specifically selective for different contaminants and easily disposed by incineration (Nascimento et al., 2012). *Moring Stenopetala* seed extract was used as biosorbent to remove total chromium from tannery wastes. Adsorption is an important process that describes the interaction between adsorbent and metal ion to develop design model for wastewater industrial treatment.

Adsorption results in the adsorption of solutes from solution and their concentration at a surface, until the amount of solute remaining in solution is in equilibrium with that at the surface. This equilibrium is described by expressing the amount of solute absorbed per unit weight of adsorbent qe, as a function of Ce, the concentration of solute remaining in solution. An expression of this type is termed an adsorption isotherm. The Langmuir equation, the Freundlich equation, Dubinin-Radushkevich model used for describing adsorption isotherms for water and wastewater treatment applications (Nascimento et al., 2012, Reddy et al., 2012 and Mataka et al., 2010).

The percentage of adsorption and the amount of metal ion sorbed onto the biosorbent were calculated as (Reddy et al, 2010): Biosorption (%) = $\frac{Co-Ce}{Ce}\boldsymbol{x100}$ (1) qe = $\frac{\mathbf{V}}{\mathbf{m}}\mathbf{x}(\mathbf{Co}-\mathbf{Ce})$ (2) Where C*o* and C*e* are concentrations of the metal ions in the solution initially and after biosorption. Also, *v* and *m* are solution volume and mass of biosorbent, and *q*e is the amount of metal ions adsorbed on the biomass (mg/g), respectively.

## MATERIALS AND METHODS

Seeds of *Moringa stenopetala* were collected from South Ethiopia and deshelled, air dried and grinded in grinding mill untill a consistant powder obtained. Defatted cakes were prepared by cold solvent extraction of the powdered seed with hexane fraction and then dried in a vacuum oven at 40 $^0$C for 24h (Ibrahim, 2008).Tannery effluent samples were collected from ELICO-Awash Tannery, Addis Ababa, Ethiopia Liquid waste samples were collected from three different sites using plastic sample bottles. The first site was as soon as the sample released from the industrial plant. The second point was the waste sample ready for treatment (Inlet) and the third point is the treated discharge (outlet), which is released to the environment. The samples were centrifuged using centrifuge machine, and the supernatant were used for analysis after digestions.

### Sample Digestion

25 ml of the sample was digested by mixing with 5 ml mixture of (1:1) conc. $H_2SO_4$ and conc. $HNO_3$. The solution was boiled on a hot plate at 120°C until dense white fumes of $SO_3$ just appeared. Aliquots of 5 ml conc. $HNO_3$ were added and the heating was continued until the solution is clear and no brown fume is observed. 15 ml of 0.5% v/v $HNO_3$ was added and the solution was boiled to dissolve the soluble salts. Five drops of potassium permanganate was added for complete oxidation of Cr (III) to Cr (IV). The excess of $KMnO_4$ was reduced by adding sodium azide, 1 ml. After cooling, the solution

was transferred into a 50 ml flask and the volume was made up with 0.5% v/v $HNO_3$ (Ibrahim, 2008).

**Chromium adsorption**

Different mass of powdered *Moringa stenopetala,* 1.0 g, 1.5 g, 2.0 g and 2.5 g, was added to 100 ml effluent wastes and the mixtures were stirred for 1 h. The mixtures were filtered by gravity through filter paper and the chromium concentrations of the filtrates were determined using Flame atomic absorption spectrometry (FAAS) (Mataka, et al., 2010 and Reddy et al, 2012).

**Effect of pH on chromium adsorption**

Effluent samples of pH 2.5, 4.5, 5.5, 6.5 and 9.5 were prepared by adjusting the pH of 100 ml tannery waste solution using 0.1 M sodium hydroxide and 0.1M hydrochloric acid. The resulting solutions were treated with 1 g powdered *Moringa stenopetala seed extract* and stirred for 1 h. After 1 h the mixtures were filtered through Whatman filter paper and the chromium concentrations of the filtrate were quantified using FAAS (Mataka et al., 2010 and Reddy et al, 2012).

**The effect of contact time on chromium adsorption**

100 ml of tannery waste solutions and 1.0 g of *Moringa stenopetala* seed extract was mixed and stirred at 60 minutes, 90 minutes, 120 minutes, 150 minutes and 180 minutes intervals. The mixture was filtered by gravity through Whatman No.1 filter paper and the concentrations of the filtrates were determined using FAAS (Mataka, et al., 2010 and Reddy et al, 2012).

**Effect of temperature on chromium adsorption**

100 ml tannery waste water was treated with 1.0 g *Moringa stenopetala* seed extract at various temperatures from 20 $^0$C to 80 $^0$C. The *Moringa stenopetala* suspension was immersed in a constant temperature water bath with shaking for 1 h. After 1 h the mixtures were filtered through Whatman filter paper and the chromium concentrations of the filtrate were quantified using FAAS (Mataka, et al., 2010 and Reddy et al, 2012).

**Adsorption Isotherm Study**

1.0 g *Moringa stenopetala* seed extract was weighed into centrifuge tubes to which 100 ml of tannery waste solution with varying initial Cr concentrations (100 mg/l, 105 mg/l, 110 mg/l, 115 mg/l and 120 mg/l) were added. The sample tubes were then shaken at a constant speed using the shaker for 2 h. The suspensions were filtered using Whatman No.1 filter paper. The filtrates were collected in separate clean sample bottles and the metal content was determined using FAAS (Mataka et al., 2010).

## RESULT

**Adsorption of Cr using *Moringa stenopetala* seed extract**

*Moringa stenopetala* seed extract removed 18.47% of total Cr at a concentration of 1 g/100 ml and as the concentration increased to 2.5 g/100 ml, the adsorption efficiency of *Moringa stenopetala* seed extract was raise to 79.35%. The result showed that concentration and Cr adsorption efficiency has a linear relationship (figure 1). As the concentration of *Moringa stenopetala* seed extract increases, many active sites are available to adsorb the metal ions present in the tannery waste. Chromium adsorption efficiency of *Moringa stenopetala* seed extract was highly dependent on pH values (figure 2). At more acidic condition (pH = 2.5) the percent adsorption of Cr was very low. However, as the pH of the solution changes to 4.5 there was sharp increase on percent adsorption of Cr (97.897%). Moreover, as the pH changed to basic medium (pH = 9.5) the percent adsorption of Cr increased to 99.864%

**Figure 1**

When the acidic nature of the waste solution decreases, the Cr adsorption efficiency of *Moringa stenopetala* seed extract was increase. Studies on the bark of *Moringa oleifera* for the adsorption of Cd (II) and Cu (II) showed similar result (Reddy, et al, 2012). Lower adsorption efficiency at low pH is apparently due to the presence of a higher concentration of $H^+$ in the solution, which competes with metal ions for the adsorption sites of the *Moringa stenopetala* seed extract. The adsorption of Cr using *Moringa stenopetala* seed extract was not significantly affected as the initial concentration of Cr was changed.

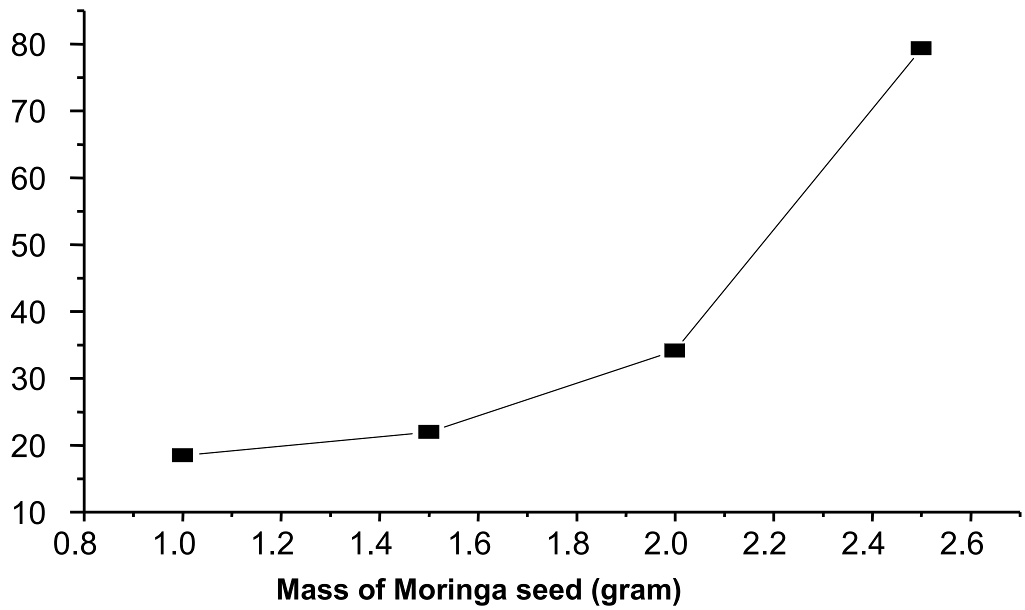


**Figure 1**: Effect of *Moringa stenopetala* seed powders on adsorption of Cr at initial total Cr ion concentration of 1323.20 ppm.

When the initial Cr concentration was 170.33 ppm the percent adsorption was 99.777%. As the initial concentration of Cr was raised to 1703.33 ppm the adsorption efficiency was increased to 99.913%. Hence, at the optimum pH the initial concentration of Cr did not affect the efficiency of *Moringa stenopetala* seed extract to remove Cr from tannery wastes. Adsorption of Cr from tannery wastes using *Moringa stenopetala* seed extract showed slight change as the contact time was changed. As the contact time changed from 60 minutes to 120 minutes the percent adsorption showed slight increase and started to show a bit decline after 120 minutes (figure 3). The slight decreasing of percent adsorption as contact time increased was due to as the agitation time increased the metal ions were go back to the bulk solution. Generally, *Moringa stenopetala* seed powder was very effective to remove Cr from tannery effluents in all contact times studied in basic medium.

**Figure 2**

The adsorption of Cr from tannery waste using *Moringa stenopetala* seed extract was not significantly affected as the temperature increased from 293 K to 373 K. However, the percent adsorption was a bit higher at 333 K

(99.910%). The effect of temperature on biosorption of Cr using *Moringa stenopetala* is similar to the influence of contact time. The percent adsorption is slightly declined (99.881%) at 373 K. The slight decreasing of percent adsorption as temperature increased may be due to the damage of some of active binding sites of *Moringa stenopetala* seed extract.

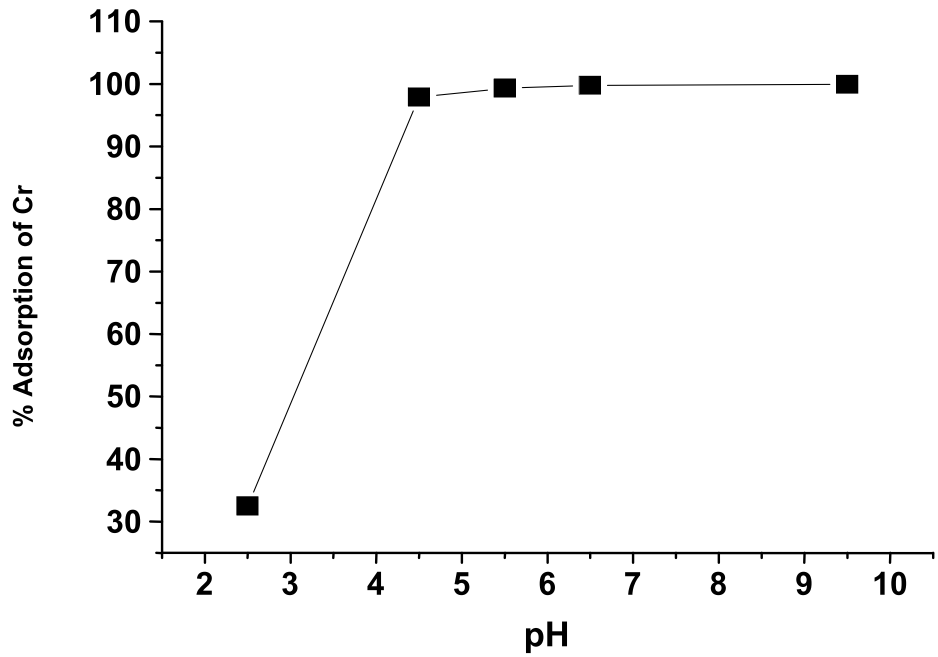


**Figure 2**: The effect of pH on adsorption of Cr at initial Cr concentration of 647.80 mg/l

**Table 1:** Dubinin-Radushkevich Isotherm constants for the adsorption of Cr unto *Moringa stenopetala* seed extract at pH 9.5.

| Dubinin-Radushkevich constant | Qm(mg/gm) | $K_{DR}$ ($mol^2/kJ^2$) | $E$ (KJ/mol) |
|---|---|---|---|
| Calculated value | 316.916 | $2.8566 \times 10^{-7}$ | 1.323 |

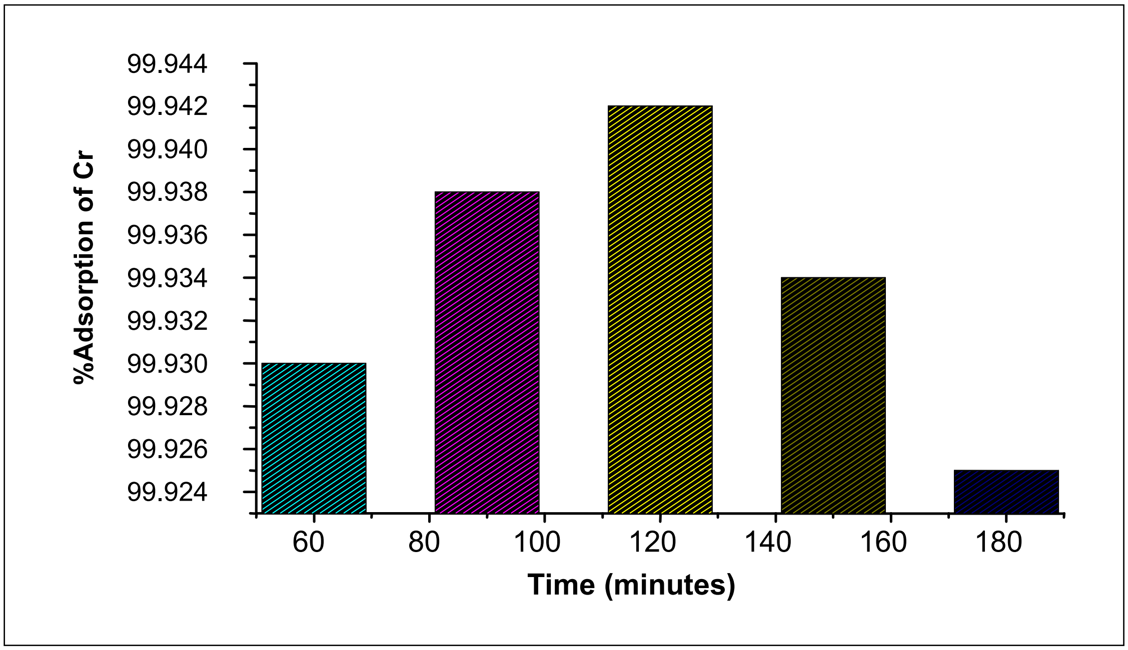


**Figure 3:** The effect of contact time on adsorption of Cr at initial total Cr ion concentration of 17303.33 ppm and pH 9.5.

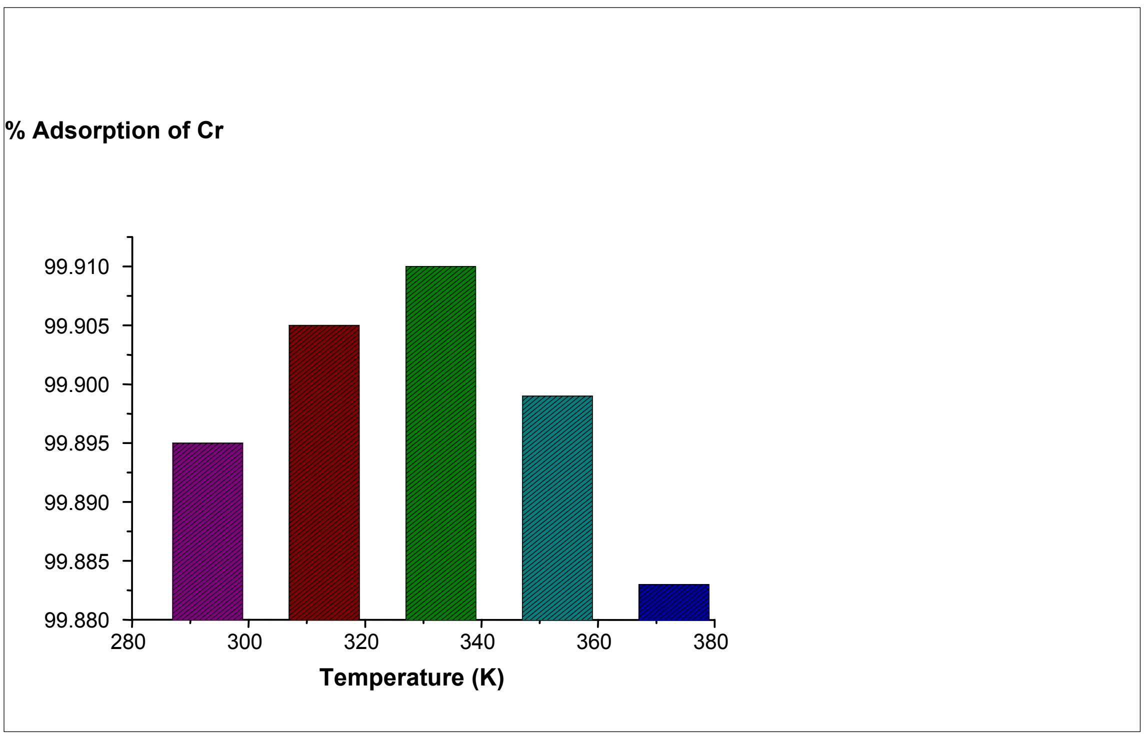


**Figure 4:** The effect of temperature on adsorption of Cr at initial total Cr ion concentration of 17303.33 ppm and pH 9.5

**Adsorption Isotherms**

The equilibrium biosorption of Cr by Moringa stenopetala seed extract was described by fitting the experimental data with models which were used to represent the equilibrium adsorption isotherm. Hence, the results were tested using Freundlich, Langmuir, Dubinin-Radushkevich, and Temkin isotherms models. In all models equilibrium was described by expressing qe (the metal ion uptake per unit weight of Moringa powder) as a function of Ce (the concentration of metal ions in solution at equilibrium).

Isotherm models considered in this study gave $R^2 > 0.916$.The value of the Correlation coefficient ($R^2$) of Langmuir Isotherm plot for adsorption of Cr unto Moringa stenopetala seed extract was 0.9196 (figure 5). This confirmed that the Langmuir isotherm fits less with the experimental data and this may be due to the active sites on Moringa stenopetala seed extract surface has not homogeneous distribution, since the Langmuir equation assumes that the surface is homogenous (Hameed et al., 2008).

The maximum theoretical adsorption capacity of Moringa stenopetala seed extract and the constants related to adsorption energy was 29.069 (mg/g) and 1.003 L/g, respectively. Moreover, the value of the separation factor (RL) was in between 0 and 1, which indicated that adsorption is favorable process to remove Cr from tannery waste using Moringa stenopetala seed extract. The values of Freundlich isotherm constants Kf and n shows the biosorption capacity and intensity of Moringa stenopetala, respectively (Reddy, et al, 2012). The Kf and n values are 162.181 mg/g and 0.452, respectively. The value of n is less than 1, which indicates the change in adsorbed dye concentration is greater than the change in the dye concentration in solution (Theivarasu and Mylsamy, 2010).The experimental data was fitted with Freundlich model and linear plot of ln (qe) and ln (Ce) (Figure 6). It was found that the correlation coefficient (R2) of Dubinin-Radushkevich model gave very good description for biosorption of Cr by Moringa stenopetala seed extract (Figure 7)

The maximum amount of the metal ion that could be sorbed onto a unit weight of sorbent (Qm) and Dubinin- Radushkevich isotherm constants ($K_{DR}$) (Table 1) was obtained from the linear plot of ln(qe) versus $P_o^2$( figure 7). The high value of Qm (mg/g) shows the high efficiency of *Moringa stenopetala* seed extract to remove Cr metal from tannery effluents. Results obtained showed that the mean free energy of sorption per mole of the sorbate ($E$ (KJ/mol)) was less than 8 KJ/mol which illustrate that the sorption process is physical in nature (Mataka et al., 2010). Temkin adsorptionfitting for adsorption of Cr from tannery effluents using *Moringa stenopetala* seed extract showed linear correlation coefficient (Figure 8). It is the best fit next to Dubinin-Radushkevich isotherm.

The change in Gibb's free energy for the biosorption was negative. The negative value of $\Delta G^0$ at the studied temperatures indicates that the biosorption process is spontaneous (Table 2). The calculated value of $\Delta H^0$ is positive, which confirms the bioadsorption of Cr by *Moringa stenopetala* seed extract is spontaneous. Moreover, high positive value of $\Delta S^0$ verified that there is increased randomness of solid-liquid interface during adsorption of Cr on *Moringa stenopetala* seed extract surface.

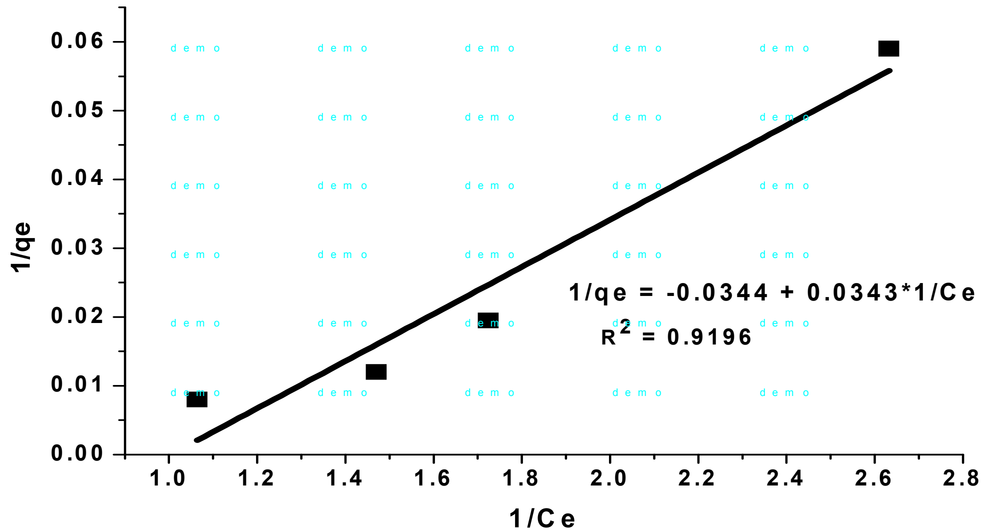


**Figure 5:** Langmuir adsorption isotherm plot of Cr using 1g/100 ml of *Moringa stenopetala* seed powder at pH 9.5

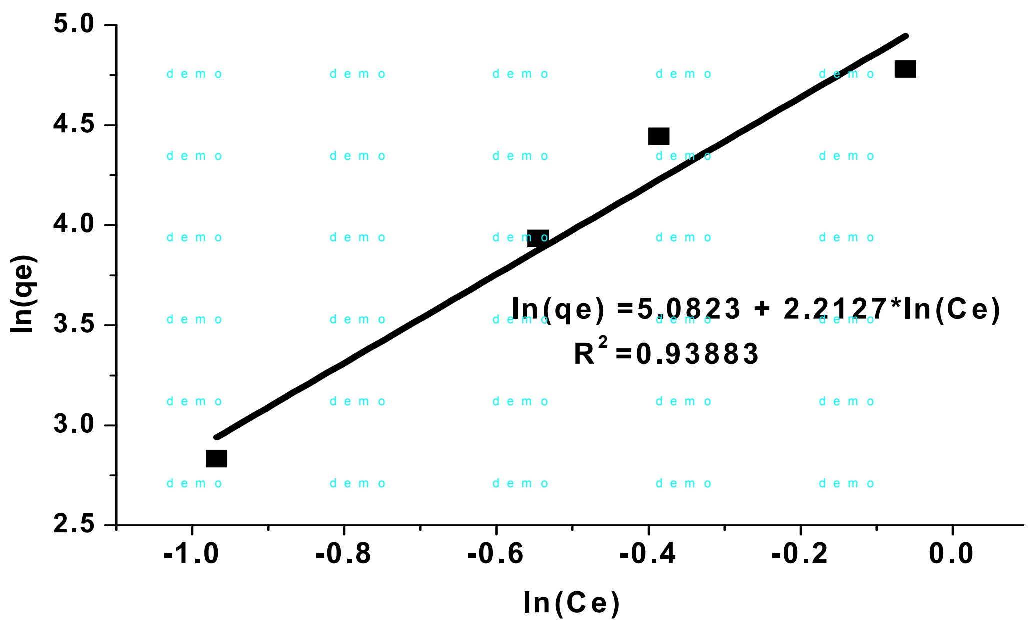


**Figure 6:** Freundlich adsorption isotherm plot of Cr using 1g/100 ml of *Moringa stenopetala* seed powder at pH 9.5.

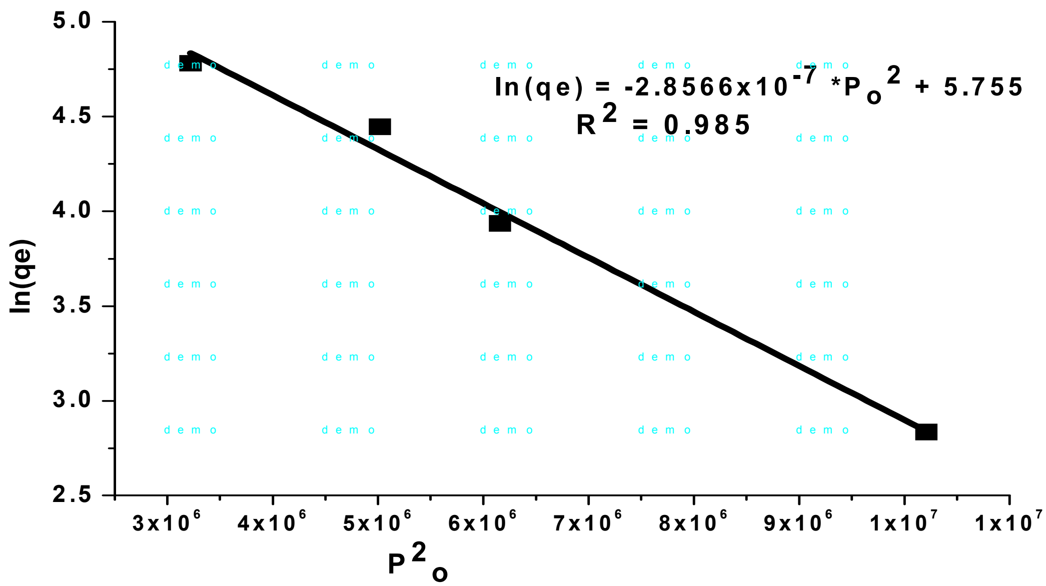


**Figure 7:** Dubinin-Radushkevich adsorption isotherm plot of Cr using 1 g/100 ml of *Moringa stenopetala* seed powder at pH 9.5.

**Table 2:** Thermodynamics parameters for the adsorption of Cr onto *Moringa stenopetala* seed extract at pH 9.5

| T (K) | $\Delta G^0 (kJmol^{-1})$ | $\Delta H^0 (kJmol^{-1})$ | $\Delta S^0 (Jmol^{-1})$ |
|---|---|---|---|
| 293 | -16.718 | | |
| 313 | -18.104 | 3.139 | 67.784 |
| 333 | -19.482 | | |

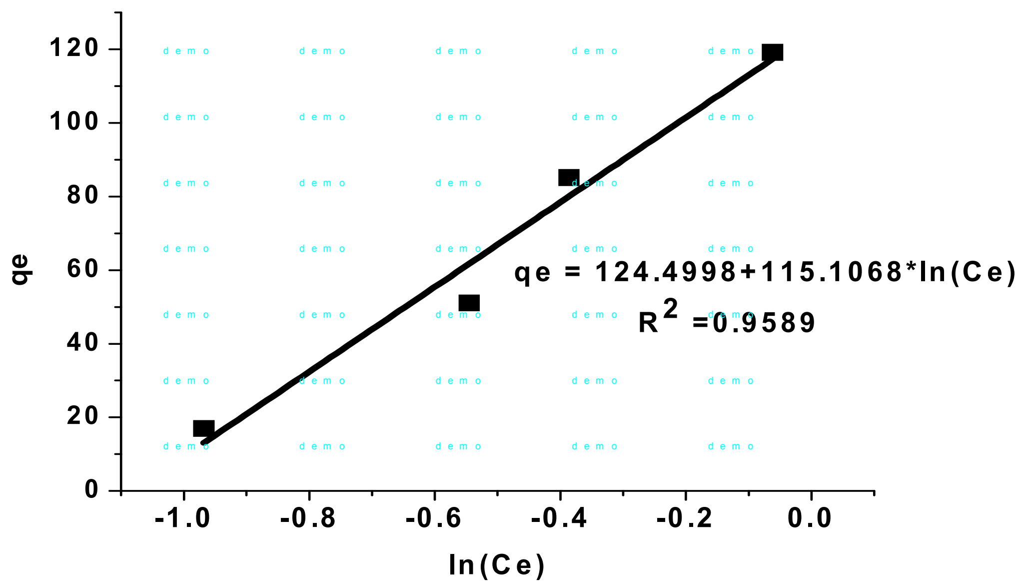


**Figure 8:** Temkin adsorption isotherm plot of Cr using 1 g/100 ml of *Moringa stenopetala* seed powder at pH 9.5.

**DISCUSSION**

The adsorption of Cr from tannery waste water using *Moringa stenopetala* seed extract is highly dependent on the pH and best adsorption was obtained at pH value of 9.5. Concentration of seed extract and Cr adsorption effeciency has showed linear relationship. However, temperature and contact time has less significant effect on the adsorption of Cr. The isotherm study showed that the adsorption data was well fitted with Dubinin-Radushkevich model. Furthermore, the energy of adsorption calculated from Dubinin-Radushkevich model confirms that adsorption process is physical in nature. In addition, the adsorption thermodynamic study revealed that the adsorption process of Cr using *Moringa stenopetala* seed extract was spontaneous and endothermic. *Moringa stenopetala* seed extract has equivalent effeciency with chemicals used to remove heavy metals from tannery waste water. On top of it the seed extract is less costly and environmental friendly than other heavy metal treatment methods. However further detail research is needed to recover chromium from the sludge and to reuse it.

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