

REMOVAL OF CHROMIUM LOAD FROM LEATHER INDUSTRY EFFLUENTS BY USING VEGETABLE TANNED LEATHER SHAVINGS AS ADSORBENT

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Abstract

In this study the possibility of using vegetable tanned leather shaving wastes as adsorbent for removing the chromium load in leather industry effluents was investigated. Optimum conditions were determined by investigating the effects of adsorbent amount, time, and pH on chromium adsorption. Additionally; isotherms, kinetics and thermodynamics of the adsorption were studied. According to findings the data fit to Langmuir isotherm with 0.10 L/g Langmuir constant and 10.24 mg/g maximum adsorption capacity. When adsorption kinetics was considered, the data fit Pseudo 2nd order kinetic rate model. According to thermodynamic findings, the adsorption was found to be endothermic, the randomness of solid/solution interface increased during the adsorption and the adsorption happened spontaneously. According to these findings chromium adsorption on vegetable tanned leather shavings is a complex process by taking place physically and chemically.

Keywords: Shavings, Chromium, Adsorption Isotherms, Adsorption Kinetics, Adsorption Thermodynamics

1. INTRODUCTION

Tanning is a process of converting raw skins and hides, which are unstable to microorganisms, hydration and heat, to leather with adequate material properties necessary for the place of use such as clothing, shoes, upholstery, automotive, bags, belts, etc. Various tanning materials are used for this conversion and maintain stability to collagen fibers of skins and hides. Among many available tanning materials chromium is used approximately more than 80% of leather production due to cost, ease of use and unique properties that it gives to leather.

World Leather tanneries process 16 to 17million tones of hides & skins per year and generate 600 million m³ of wastewater (Rajamani 2017). Chromium tanning is being carried out by using 8-10% of basic chromium sulphate over pelt weight. Since whole of the chromium used in process cannot be exhausted, approx. 1/3-1/4 of it (1500 – 5500 mg/L) remains in bath at the end of the process (R&D Dept. Seta Brazil 2000; Sreeram et al. 2006; Tao et al. 2014). Treatment, storage and disposal of this this chromium containing effluents and sludge poses a major challenge (Ozgunay et al. 2016).

The methods for removal of many heavy metals include precipitation, oxidation, reduction, ion exchange, filtration, electrochemical treatment, membrane technologies, reverse osmosis and solvent extraction (Cheung et al. 1997; Sternberg & Dom, 2002). Among these methods, adsorption is a well-established technique for heavy metal removal. The most effective adsorbent used in adsorption is active carbon due to its high surface area and enhanced porous structure. However, its disadvantage comparing to other adsorbents is high production cost. On the other hand, if any adsorbent is cheap and does not need any high cost pre-treatment, then adsorption process gets more economic. In recent years researches have focused on to find cheaper materials as potential adsorbents and made studies on using low cost and economic solid wastes for this purpose.

Due to their animal origin and individual nature, the hides and skins exhibit regional thickness variations on themselves. In leather processing, these hides and skins are passed through various mechanical processes to obtain homogenous thickness on overall their area. One of the important one among these processes is the shaving process. Shaving process is scraping leather substance from flesh

side into small pieces by a fast-rotating cylinder having a fitted spiral knife on it to obtain a certain and homogenous thickness. The solid wastes generated during shaving process are called shavings.

Shavings typically constitutes between 2 and 20% of the weight of the tanned hides. Shaving is generally minimised by accurate splitting. Where splitting is carried out very accurately, the amount of leather which needs to be shaved will be minimal and result in small leather particles. Shavings constitute solid waste, which has to be disposed of or can be sold as a raw material in manufacture of a wide range of products such as leather board and fertiliser or for the manufacture of hydrolysate following de-tanning (Black et al. 2013).

In this study, the possible use of vegetable tanned leather shavings as low-cost absorbent to decrease chromium load of leather industry effluents is researched. Adsorption process carried out under controlled conditions is investigated with isotherm, kinetic and thermodynamic studies.

2. MATERIAL AND METHODS

Vegetable tanned leather shaving wastes were used as the adsorbent material in the study. Shaving wastes have been obtained from a local business engaged in the production of vegetable tanned leathers. Unbound vegetable tanning materials in shaving wastes have been washed with pure water to homogenize and clean the material as they may affect the analysis results. For this purpose, shaving wastes were shaken with pure water for 8 hours, later dried by laying. In this study, a clear rinse water was observed in the 4th recycle. The dried shaving wastes were ground by a mill having a mesh with a diameter of 4 mm.

Commercial powder chromium tanning material was used to prepare the chromium solutions. The technical properties of the chrome tanning material used are given in Table 1.

Table 1. Technical Specifications of Used Chrome Tanning Material

Amount of Cr ₂ O ₃ (%)	25.5
Schorlemmer basicity (%)	33
pH (Solution of %10)	3.0

2.1. The Batch Adsorption Method

Adsorption experiments were carried out under batch-mode conditions. The adsorption experiments were carried out for desired time with chromium solutions (100 mL) whose concentrations were known. A certain amount of adsorbent and 100 mL of a known chromium solutions were mixed. Then the suspensions were agitated using a rotary shaker with a speed of 150 rpm at room temperature for the desired time. Prior to mixing, the pH of the solution was adjusted with pH-meter using dilute HCl and NaOH solutions.

At various time intervals, the adsorbent was separated from the mixture by filtration (Whatman black band). Taking into account the adsorption characteristics of the filter paper, filtration was continued after the first 40 mL of the filtrate was poured, and the next part of the filtrate was taken for the measurement. Here, 1000 µl of the micropipette solution was transferred to 25 ml volumetric flask and completed to 25 mL with ultra-pure water. Thus, these solutions were brought to the limit range (0.1-10 mg / L) used for calibration in the ICP OES instrument. The actual concentrations were calculated by multiplying the measured concentrations by 25 in the software. All experiments were repeated 3 times and mean results were given.

To determine the optimal contact time, 100 ppm of chromium solution and 0.1 g of adsorbent were shaken at constant pH and at room temperature with a speed of 150 rpm for different desired times.

The adsorbents weighed in different amounts between 0.1 and 10 grams were mixed with 100 mL of 100 ppm chromium solution prepared at pH 3 for 30 minutes at a rate of 150 rpm and at room temperature to find the optimum amount of adsorbent.

To find the optimum solution pH, 100 mL of 100 ppm chromium solutions prepared at different pHs and 0.2 grams of adsorbent were shaken at room temperature at 150 rpm for 30 minutes.

To obtain adsorption isotherms, 100 mL of chromium solutions prepared at various concentrations were mixed with the specified amount of adsorbent. The prepared suspensions were shaken at the optimum conditions preliminarily determined by the experimental method and at room temperature at the speed of 150 rpm on the orbital shaker after the pH values were set.

The adsorbents were then removed by filtration. The chromium concentration in the filtrate water was measured by ICP-OES.

For adsorption kinetics experiments, chromium amounts adsorbed by the adsorbent were determined at different time intervals. For each time interval, different baths but the same amount of material in the same condition was used.

In order to investigate the effect of temperature on adsorption capacity, the experiments were repeated at optimum temperature conditions according to the preliminary experiments at 25, 30, 35, 40 °±2 C temperature range.

2.2. Instrumental Method

The Perkin Elmer Optima 2100 DV ICP-OES system was used for the measurement of Cr^{+3} ions, the measurements were made at a wavelength of 267.716 nm and the instrument parameters used in the measurements are given in Table 2.

Calibration graph obtained by preparing 0.1, 0.3, 0.5 1, 3, 5 and 10 ppm (mg / L) standards of Cr^{+3} ion to be measured is given in Fig.1.

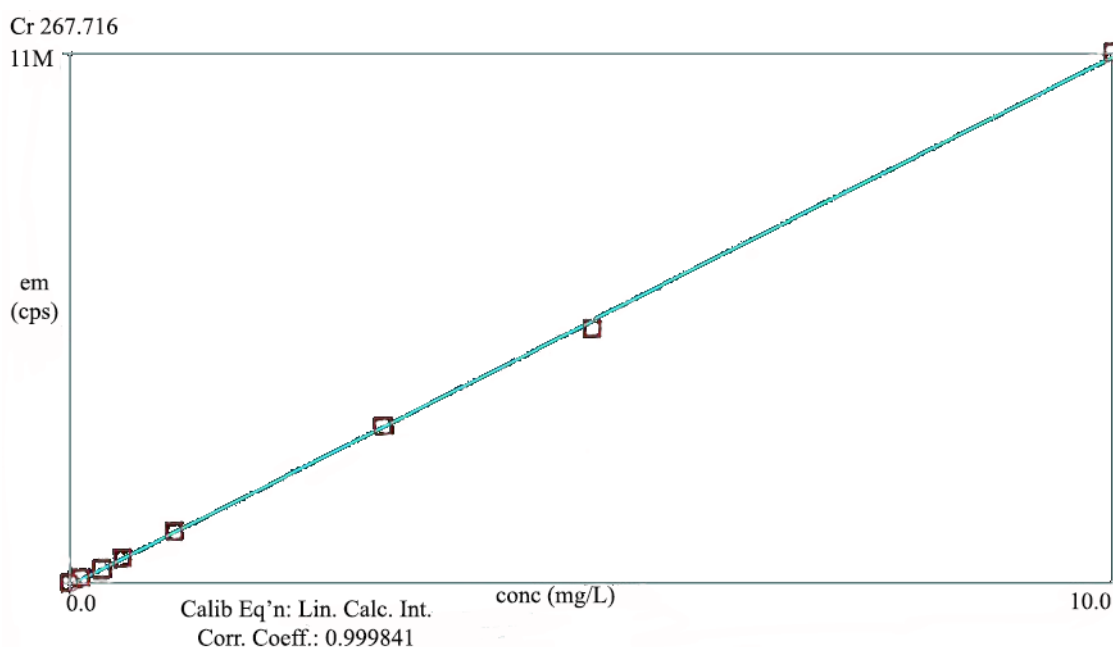


Fig. 1. Standard Calibration Curve for Chromium III Solutions with Known Concentrations.

Table 2. The parameters of ICP-OES

View	Axial view
Optical system	Echelle
Pump rate	1.5 ml/min.
Plasma gas	17 L/min.
Auxiliary gas	0.2 L/min.
Nebulizer	0.8 L/min.
RF power	1450 W

Approximately 100 ppm stock chromium solutions were prepared as adsorbate. ICP measurements of stock solutions were performed to find their true concentrations. Absorption calculations were carried out at 100 ppm.

3. RESULTS AND DISCUSSION

The adsorbed chromium amount (q_e , mg g^{-1}) on the adsorbent was calculated using the following equation:

$$q_e = (C_0 - C_e)V/W$$

C_0 : Initial metal concentration (mg L^{-1})

C_e : Residual metal concentration in solution after adsorption (mg L^{-1})

V : The volume of the solution (L)

W : Adsorbent amount (g).

3.1. Effect of the Contact Time

Contact time is an important parameter for the removal of the metal ions by adsorption. 0.1 gr of adsorbent and 100 mL 100 ppm of the metal solution were shaken by the shaker at 150 rpm for different contact times. As seen in the Figure 2 the removal of chromium ions increased during the first 30 minutes and did not change significantly between 30 and 60 minutes. Desorption began between 60 minutes and 480 minutes and after 24 hours the adsorption started again. For this reason, optimum contact time was chosen for 30 minutes.

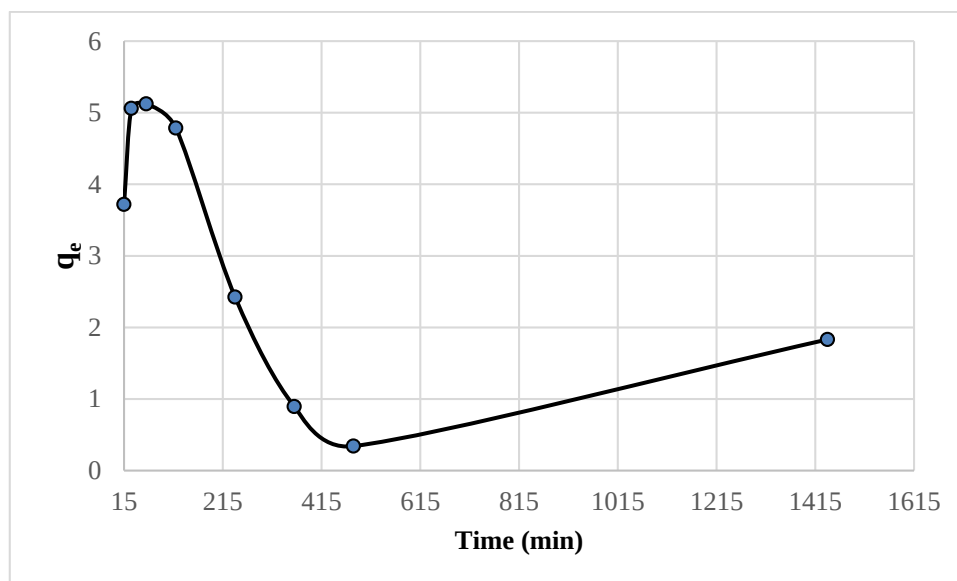


Fig. 2. Effect of contact time on chromium removal

3.2. The Effect of the Adsorbent Amount

In order to investigate the effect of adsorbent amount on chromium removal, the adsorption experiments were repeated by taking the adsorbent in varying amounts of 0.1-10 grams and mixing with 100 ppm chromium solution for 30 minutes. In these experiments, the pH of the solution was 3. The removal of the chromium ions increased as the amount of the adsorbent increased from 0.1 to 0.2 grams. But the adsorption decreased after 0.2 grams. So, the optimum adsorbent amount is 0.2 grams (Figure 3).

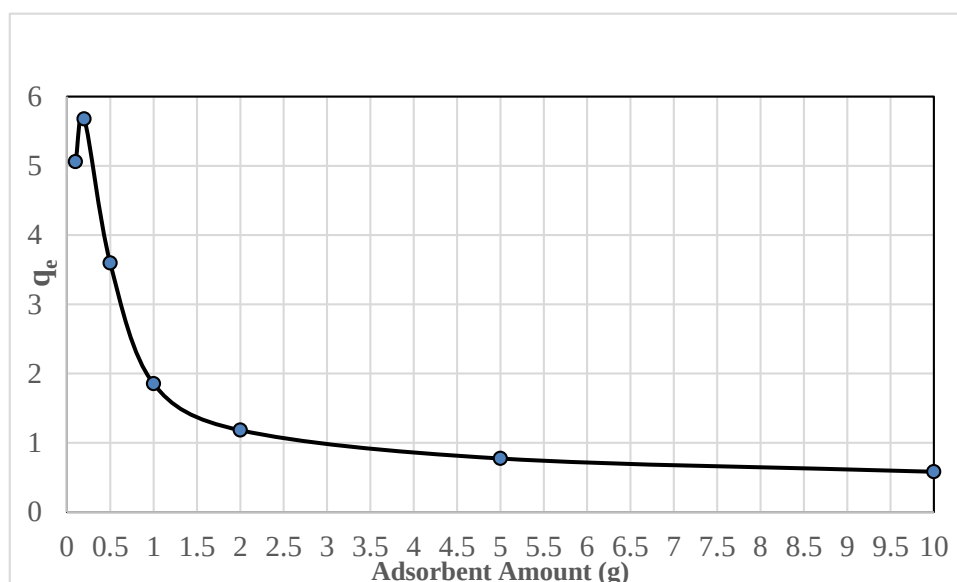


Fig. 3. Effect of adsorbent amount on chromium removal

3.3. The Effect of the pH of the Solution

To investigate the effect of pH on chromium removal, 0.2 grams of adsorbent was mixed for 30 minutes at a shaking speed of 150 rpm on a shaker with 100 mL of 100 ppm chrome solution prepared at different pHs. The pH of the solution ranged from 2.0 to 4.0. After pH 4.0, the chromium ions precipitated with hydroxide ions, so they were not tested at higher pH. Covington (2009) states that any substance capable of raising the pH of the tanning solution from 4.0 to above is a candidate for a basification material. He mentions the risk of chromium collapse at pH above this point. Chromium sulphate in solution has a strong interaction with hydroxyl ions, and hydroxyl ions are included in the molecule by substitution with one or more sulphate ions. As the pH increases, the hydroxyl ions enter the chromium sulphate molecule and increase the reactivity of the molecule to collagen. However, when it rises above pH 4.3 all the sulphate radicals are removed and chromium hydroxide is formed. Chromium hydroxide is insoluble and there is no tanning power (Dewhurst 1999). pH is one of the most important factors in the adsorption. This is due pH effects the surface load of the adsorbent and the species of the chromium metal. The maximum chromium removal in this study was observed at pH 4. As the pH increased, the amount of chromium adsorbed increased (Figure 4). When the pH is high, the surfaces of the adsorbents are more negative and chromium has a positive effect on the metal removal due to the electrostatic attraction because of the plus valence.

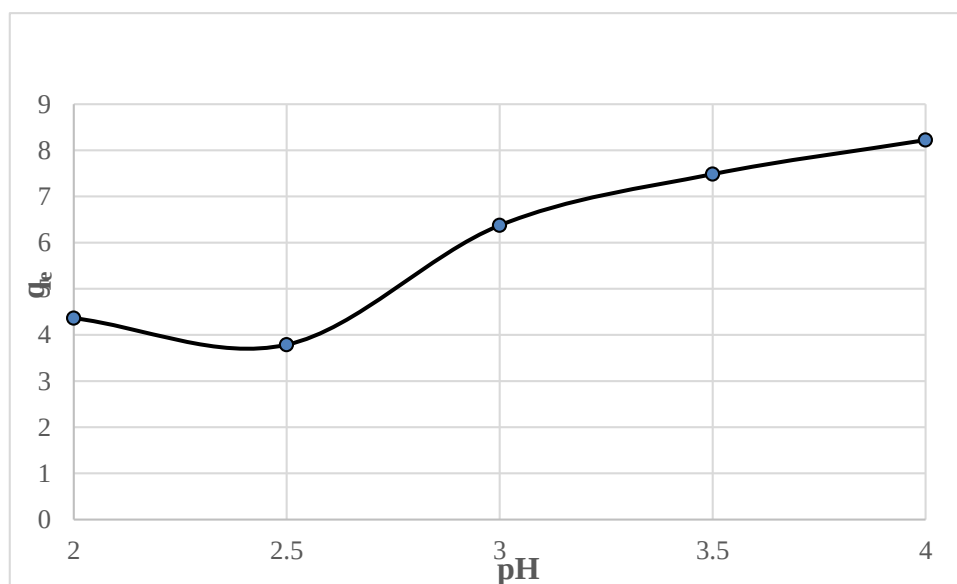


Fig. 4. Effect of pH on chromium removal

3.4. Adsorption isotherms

Adsorption isotherm studies are important because they provide information about the interaction between adsorbent and adsorbed matter. Experimental studies to obtain adsorption isotherms are used to test the compatibility of the data obtained with different isotherm models. The most widely used models are Langmuir and Freundlich models. It provides information on the compatibility of experimental results with adsorption isotherm models, the mechanism of adsorption and the heterogeneity of the adsorbent surface. Langmuir and Freundlich isotherms were applied in this study. For this, the metal solutions in different concentrations prepared at pH 4 are shaken with 0.2 grams of adsorbent at a speed of 150 rpm for 30 minutes. Isotherms are obtained by determining the metal concentrations remaining in the solution after adsorption. According to the Freundlich model, the regression coefficient obtained for the line graph drawn between $\log C_e$ and $\log q_e$ is very low (0.51) and the obtained adsorption does not comply with Freundlich isotherm. The obtained data were tested for compatibility with Langmuir isotherm and the adsorption was determined to be in accordance with Langmuir isotherm. The regression coefficient of the graph drawn between C_e/q_e and C_e is quite high

(0.98). The Langmuir isotherm adsorption assumes a homogeneous surface which is formed by single layer adsorption. For this reason, we can say that the adsorption mechanism is walking on a single layer.

The maximum adsorption capacity according to the Langmuir isotherm is 10.24 mg /g and the Langmuir constant is 0.100 L / g.

In Table 3 example adsorption capacities of the adsorbents for the removal of Cr(III) from some previous studies are given. Looking at the work done in the literature, adsorption capacities of chromium removal with adsorbents developed in recent years but expensive or difficult to prepare or requiring modification with various harmful chemicals are higher than in this work. However, it is the value that can be compared with the work done using waste or cheap adsorbents. Additionally, when various modifications are made to such adsorbents, an increase in adsorption capacities is observed. The adsorbent used in this study made an acceptable removal without any modification and without a very acidic / basic environment.

This adsorbent can also be evaluated in terms of its use in metal removal by evaluating a waste since it is an existing waste.

Table 3. Adsorption Capacities of the Adsorbents for the Removal of Cr(III)

Activated carbons/adsorbents	Adsorption capacity (mg/gram)	References
ATFAC	12.23	Mohan et al. 2006
ACF	39.56	
Activated carbon, GAC-S	13.31	Aggarwal et al. 1999
Activated carbon, GAC-E	10.52	
Activated carbon, ACF-307	7.08	
Activated carbon, ACF-310	3.52	
Carbon F	7.33	Rivera-Utrilla and Sanchez-Polo 2003
Carbon F10	10.27	
Carbon 120	19.23	
Activated Carbon	2.7	Bautista-Toledo et al. 1994
Activated Carbon oxidized with HNO ₃	25.3	
Chrome sludge	24.0	Low et al. 1995
Aminated polyacrylonitrile fibers	~5	Deng & Bai 2004
Pinus pinaster bark	19.45	Teles de Vasconcelos and Gonzalez Beca 1993
Treated Pinus sylvestris bark	9.77	Alves et al. 1993
Untreated Pinus sylvestris bark	8.69	
Rice Straw	15.6	Tan et al. 1989
Moss	15.1	Low et al. 1997
Wine processing waste sludge	13.45	Li et al. 2004
Brown seaweed (Turbinaria spp.)	31	Arvindhan et al. 2004
Peat	22.36	Ma and Tobin 2004
Lignin	17.97	Wu et al. 2008
Vegetable tanned leather shavings	10.24	This study

3.5. The Adsorption Kinetics

A 100 ppm chromium solution at pH 4 was mixed with 0.2 g of adsorbent in the shaker at small time intervals at room temperature. The adsorbent was then removed by filtration and the remaining chromium ion concentration in the solution after adsorption was determined from the remaining filtrate. Pseudo 1st and 2nd order velocity equations were applied to the obtained data to clarify the adsorption rate mechanism.

Pseudo 1st order reaction rate equation:

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303) t$$

k_1 : Pseudo 1st order adsorption velocity constant (min^{-1})

q_t : the amount of adsorbed matter at time t (mg / g)

q_e : The amount of adsorbed matter in any small-time interval (mg / g)

Pseudo 2nd order reaction rate equation:

$$t / q_t = [1 / k_2 q_e^2] + (1 / q_e) t$$

k_2 : Pseudo 2nd order adsorption velocity constant (g/mg.min)

The regression coefficient of the $\text{Ln} (q_e - q_t)$ - t graph plotted according to the Pseudo 1st order mechanism is very low (0.34) and chromium adsorption does not conform to the Pseudo 1st order velocity equation.

Pseudo 2nd order velocity equation was applied to the adsorption data. The regression coefficient of the graph drawn between t / q_t and t is very high (0.99).

This indicates that the chromium adsorption of vegetable tanned leather shavings is compatible with the 2nd order reaction model.

The q_e value calculated from kinetic data is 7.62. The velocity constant in the 2nd order (k_2) was $0.0436 \text{ g mg}^{-1} \text{ min}^{-1}$. The predominance of 2nd mechanics suggests that chemical adsorption may be the rate determining step in the biosorption process (Allen et al. 2005).

3.6. Thermodynamic Parameters

Investigating the thermodynamic adsorption process is important for the applicability of the process. Using 0.2 g of adsorbent, 100 mL of 100 ppm chromium solution at pH 4 was prepared and mixed for 30 minutes at four different temperatures (25, 30, 35, 40 °C) on a thermostat shaker. The effect of temperature on chromium removal has been investigated. In order to calculate the thermodynamic parameters, the free energy change was calculated using the slope (ΔH°) and cut-off point (ΔS°) of graph drawn between $\text{Ln } K_C$ and $1 / T$ (Figure 5) and using this equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

K_C : The adsorption equilibrium constant is calculated by the following equation;

$$K_C = q_e / C_e$$

As the temperature increased, the chromium adsorption showed a small increase due to the increase of the surface activity and the kinetic energy of the chromium ions. Positive ΔH° indicates that the adsorption between vegetable tanned skin shaving wastes and chromium ions is endothermic (Table 4).

That is, in order for the adsorption to take place, the system must be supplied with heat from the outside. The positive value of ΔS° indicates that the irregularity at the solid / solution interface increases during adsorption onto the chrome vegetable tanned leather shavings. The free energy value of the adsorption process is negative at all temperatures. A negative value of ΔG° indicates that chromium adsorption occurs spontaneously (Mittal et al., 2006). The values of ΔG° are smaller than -20 kJ mol^{-1} , indicating that the adsorption mechanism is generally physical (Wu, 2007). From here, adsorption of chromium ions occurs physically. On the other hand, according to kinetic calculations, the adsorption process is proceeding at Pseudo 2nd order. This indicates that the adsorption is by

chemical route. These results show that chromium adsorption on leather waste can be a very complex process (Wu 2007). Wu [2007] suggested that the thermodynamic analyses were more appropriate for determining whether the adsorption was a physisorption or a chemisorption process.

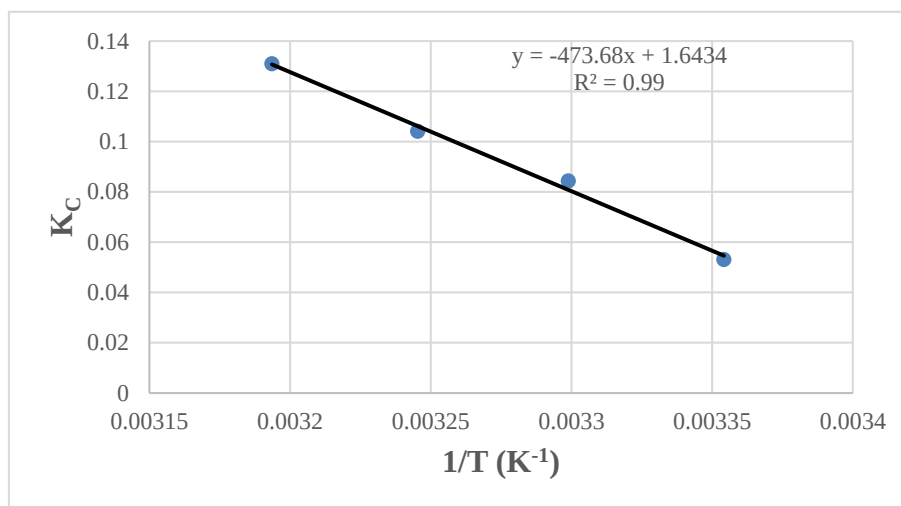


Fig. 5. Effect of Temperature on Chromium Removal

Table 4. Thermodynamic Parameters of Chromium Adsorption

T(K)	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° J K ⁻¹ mol ⁻¹
298	-0.13	3.94	0.014
303	-0.20		
308	-0.27		
313	-0.34		

4. CONCLUSIONS

The isotherm of adsorption between vegetable tanned leather shaving wastes and chromium ions fit well to Langmuir isotherm. Thus, we can say that the adsorption mechanism was mono layered. According to Langmuir isotherm, maximum adsorption capacity was found to be 10.24 mg/g and Langmuir constant was 0.10 L/g.

When the adsorption kinetics was investigated, regression constant of the line was higher than 0.95 which shows that chromium adsorption of vegetable tanned leather shaving wastes fit to Pseudo 2nd order rate equation.

Considering the adsorption thermodynamics, the positive ΔH° value (3.94 kJ mol⁻¹) shows that the adsorption is endothermic. Positive ΔS° value (0.014 J K⁻¹mol⁻¹) shows that disorder increased between solid/solution interface during adsorption of chromium on vegetable tanned leather shaving. Gibbs free energy (ΔG°) values of adsorption process were negative for all temperatures and they show that chromium adsorption takes place spontaneously. When ΔG° values are lower than -20 kJ mol⁻¹, that shows that adsorption mechanism is generally physical (Wu, 2007). So, the adsorption of chromium ions to vegetable tanned leather shavings was by physical ways. On the other hand, according to kinetic calculations, Pseudo 2nd order shows that the adsorption was by chemical way.

Consequently, these results show that chromium adsorption on vegetable tanned leather shavings is a complex process taking place physically and chemically.

As a conclusion, by lightening up the adsorbent properties of vegetable tanned leather shaving wastes with isotherm, kinetic and thermodynamic studies, it was found that they can be used as a cheap alternative adsorbent for removing chromium from effluents of leather industry.

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