Chromium (III) Removal from Synthetic Wastewater Using Biochar Produced from Vegetable Tanned Leather Shaving Dust

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Authors' contributions

This work was carried out in collaboration among all the authors. Author TRC designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors TRC, SA managed the analyses of the study. Author MSR designed and revised the manuscript. Authors BAB and UHBN managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

In recent years, the rapid industrialization leads to increase industrial discharges without any appropriate treatment. The present study deals with the removal of Cr (III) ions from aqueous solutions by $ZnCl_2$ treated biochar produced from vegetable tanned leather shaving dust. Effect of various process parameters like solution pH, adsorbent dose, adsorbent type, initial Cr (III) concentration and temperature have been studied in batch system. The thermal resistivity and scanning electron microscopy (SEM) analysis were engaged to perceive the surface morphologies of chemically treated and untreated biochar adsorbent. The experimental data was fitted well to the Langmuir adsorption isotherm model and the adsorption efficiency of chromium (III) was found to be maximum (70%) at low values of pH (around 3) for 0.75 g/50 mL dose of $ZnCl_2$ treated biochar

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adsorbent. The model matrix of 2^4 full factorial design approach has been applied at a 95% confidence level to find the impact of different variables on removal Cr(III) ions from waste water. This study revealed that three main factors: Adsorbent type ($p < 0.0001$; 66.39%), pH ($p < 0.001$; 16.01%) and adsorbent dose ($p = 0.032$; 12.15%) have significant impact on Cr (III) ions removal efficiency. For using $ZnCl_2$ biochar, Cr(III) ions removal efficiency was increased 66.39% compared to using untreated biochar. Subsequently, two interaction factors: pH-time and adsorbent type-time ($\alpha = 0.05$, $p < 0.05$) have shown statistically significant on Cr(III) ions removal efficiency. The $ZnCl_2$ treated biochar adsorbent prepared from vegetable tanned leather shaving dust is efficient and it is proposed that it can be conveniently employed as a low cost alternative in the treatment of industrial waste water.

1. INTRODUCTION

Toxic heavy metal ions discharged from different industrial activities are becoming a major environmental problem. Heavy metals are nonbiodegradable and probably may accumulate in microorganisms, aquatic flora and fauna, which in turn may enter into the human food chain and result in significant danger to human health [1,2]. Chromium is one of the heavy metals and found in the environment in three oxidation states: Cr(0), Cr(III) and Cr(VI), with the last two being most important and common forms [2]. The chromium form depends on the pH level. Cr (III) is more stable and less toxic than Cr(VI) and is considered an important trace element maintaining the normal metabolism of glucose, cholesterol and fat in human bodies [3,4,5]. However, in the presence of mild oxidizing agents, Cr(III) can be oxidized into Cr(VI), which is highly toxic, causing several forms of cancer, kidney diseases, liver, gastric damage and even death [6].

The leather processing industry is one of the most important economic sectors in many countries, representing an important remunerative field also in developing countries [7]. Tannery industries are among those industries, which required a large quantity of water for processing and discharge 90% of water as effluent. Nearly 40-45 liters of fresh water were required to process one kilogram of raw leather from hide or skin [8]. The wastewater from tannery industries loaded with a high percentage of various organic and inorganic substances, toxic metallic compounds. Among all these pollutants, chromium that is available in tannery effluent has significant health concerns due to high-ranking oxidizing properties [9]. Leather tannery industry is water intensive and originates highly polluted wastewater that contain various pollutants raising environmental and health concerns. Chromium is the principle threat among all the pollutants present in tannery waste water. The allowable limit of Chromium is 0.1 mg/L for surface water and 0.05 mg/L for potable water, according to world health organization [10]

Disposition of tanning effluents including chromium (Cr) modify the normal physiochemical properties of soil and water with many inauspicious outcomes. Cr can create extremely harmful effect to human kind, animals, vegetation as well as overall environment [11,12]. Exposure to chromium causes allergic skin irritation, dermatitis, irritation to mucous membranes and conjunctiva and gastro-intestinal ulcers. Excessive levels (50 ppm) of chromium have been associated with liver and kidney damage and depression in experimental animals [13]. In leather processing, 60-70% of total chromium salt reacts with hide/skin and 40-30% rest of it remains in wastewater [14]. Therefore it is necessary to remove chromium from waste water before discharging the chromium containing wastewater to mainstream water body for environment protection.

Different methods have been established to remove chromium from wastewater such as adsorption, membrane separation and electro dialysis, biological method [15], chemical or electrochemical precipitation, and ion exchange treatment [16]. Most of the methods are either expensive or not environment friendly. However, cost is a very important factor when considering materials for use as biosorbents. It is generally recognized that a material can be deemed 'low-cost' if it requires little processing, is abundant in nature, or is a byproduct or waste material from another industry [17,18]. Therefore, in this study a low cost biochar prepared from the by-product (vegetable tanned leather shaving dust) of leather industry was used for the removal of Cr (III) from synthetic waste water.

Mainly there are two methods of activation for producing biochar. They are chemical activation method and physical activation method [19]. In chemical treatment, different types of chemical agents such as alkaline chemicals (KOH, NaOH, Na_2CO_3 and $NaHCO_3$), acid chemicals (HCl, H_2SO_4 and $C_2H_4O_2$) and other chemicals ($ZnCl_2$, NaCl etc) are added for the purpose of improving the surface area or size of porous structure in biochar materials [20]. Physical activation involves carbonization of a carbonaceous material to eliminate the bulk of volatile matter. Then the resulting char is activated in the presence of activating agents, such as CO_2, steam, air, or some combination of these agents resulting in the release of carbon oxides from the carbon surface [20].

Shaving dust are small pieces of leather produced from the shaving process when the thickness of pelt (hide/skin after tanning process) is made uniform by a bladed cylinder [21]. Shaving process contains 35-40% of total solid waste of tanning operation [22]. Several attempts have been taken to utilize this solid waste. In this study biochar was produced from vegetable tanned leather shaving dust. The main aim of this research work is to remove chromium (III) metal ions from synthetic solution by the biochar produced from vegetable tanned leather shaving dust. The process parameters were optimized in batch technique. The adsorbent was characterized by scanning electron microscopy (SEM), and thermal analysis (TGA).

2. MATERIALS AND METHODS

2.1 Raw Material from Tannery Industry

Vegetable tanned leather shaving dust was collected from the tannery zone of Hemayetpur, Savar (23.7986°N, 90.2680°E). Shaving dust was shredded into rectangular pieces (2 cm × 1 cm) and then dried in an oven at 105°C to get constant weight.

2.2 Biochar of Shaving Dust

Carbonization of shaving waste was carried out in pyrolysis reactor. Pyrolysis reactor was of a fixed bed design and of stainless steel. Shaving waste of 50-60 g was placed into the reactor. The system was heated to the desired carbonization temperature of 450°C at a heating rate of 10°C/min. After the reactor temperature had reached at 450°C, it was hold at this temperature for 2 hours. This pyrolysis was carried out in vacuum condition. The reactor was cooled and biochar sample was collected.

2.3 Chemical Activation of Biochar Sample

The biochar sample was impregnated with 50% $ZnCl_2$ solution (1:1) at 85°C for 7 hrs and was allowed to dry. Then the biochar was washed with 0.1 N HCl and deionized water, the resulting biochar was dried overnight at 100°C and sieved. An average particle size biochar of 0.25 mm was used for adsorption study. For the production of biochar from vegetable tanned leather shaving dust by chemical activation method, $ZnCl_2$ was used as activating agent.

2.4 Characterization of Sample

Thermal stability of raw sample, untreated biochar sample (UTB) and treated biochar sample (TB) was recorded using Thermo gravimetric analyser (TGA) from 25 to 900°C at the rate of 10°C min^{-1}. The surface morphology was analyzed using scanning electron microscopy (SEM).

2.5 Adsorption Experiments

The adsorption capacity of prepared biochar sample was examined using standard reference chromium solution (1000 mg/L, Spectro-pure, USA) and then diluted to 0.5 mg/L. Batch adsorption studies were performed in a series of 250 ml stopper conical flasks containing 50ml of Cr (III) solution. Batch experiments were carried out to study the effect of parameters like contact time, pH, adsorbent dosage, initial Cr(III) concentration and temperature at a constant agitation speed of 100 rpm (revolutions per minute) for the removal of Cr(II) ions. Agitation of the solutions was provided by a thermostated shaking incubator (Labtech, Korea). After adsorption, the solution was filtered using filter paper (Whatman No. 41, Germany) in order to remove the adsorbent particles, and the Cr (III) ions concentration was determined in the filtrate using Atomic Absorption Spectrophotometer (Varian AA240 FS) at Analytical Chemistry Laboratory, Chemistry Division, Atomic Energy Centre, Dhaka. The chromium removal (%) at any instant of time was determined by the following equation:

$$Cr(III) removal \% = \frac{c_o - c_t}{c_o} x\ 100 \qquad (1)$$

Where, C_o and C_t are the concentration of Cr (III) in the sample solution before and after the treatment. Adsorption studies were carried out with different adsorbent doses ranging from 0.5 to 0.75 g/50 mL.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The effect of pH in percentage removal of Cr (III) is shown in Fig. 1. This study was conducted for the pH values from 3 to 8 and revealed that the removal percentage decreased with the increase of pH from 3 to 6 and then in stable condition for the pH value of 7 to 8 (Fig. 1), which indicate that Cr (III) removal percentage decreased from the acidic to basic media. It might be due to the reasons that at low pH value in solution as acidic environment, the main chromium species are $HCrO_4^-$; $Cr_2O_7^{2-}$ and H_2CrO_4 , while in basic medium CrO_4^{2-} predominates. In acidic solution, treated biochar adsorbent surface was protonated to a high extent. This phenomenon strongly increased the attraction between anionic species $HCrO_4^-$ and $Cr_2O_7^{2-}$ and positively charged the adsorbent surface. Hence the removal efficiency decreases with increase in pH. So it can be narrated that the treated biochar works better at low pH value. Finding of this study is consistent with the reported results in literature [23].

3.2 Effect of Dose

The removal of Cr (III) ions from synthetic waste water with respect to different adsorbent dose

from 0.25 g to 0.75 g in 50 mL solution was conducted and the Cr (III) ions removal percentage is graphically shown in Fig. 2. It can be observed that 0.75 g dose of adsorbent has maximum removal efficiency which is almost 70%. Removal percentage increased linearly with the increase of dose. The increase in adsorption with the increase in amount of TB dose is due to the fact that more surface area is available for adsorption or in other words more active sites are available at higher dose of adsorbent material [24].

3.3 Effect of Contact Time

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. The effect of contact time on removal of Cr (III) has been shown in Fig. 3. This study shows that contact time has very little effect on the percentage removal of chromium (III). The adsorption rate was high during the early adsorption period due to the availability of a large number of vacant sites, which increased the concentration gradient between the adsorbate in the solution and adsorbate on the adsorbent surface [25]. After 30 min, the metal ions are adsorbed into the surface that get almost saturated during the initial stage of adsorption and it can be said that after 1 h the adsorption phase reached to equilibrium. Subsequently, one way ANOVA test revealed that Cr(III) removal percentage was almost consistent with the increasing of time at a 95% confidence level with high probability value (p = 0.147). Finding of equilibrium time for this study is consistent with the reported results in literature [23].
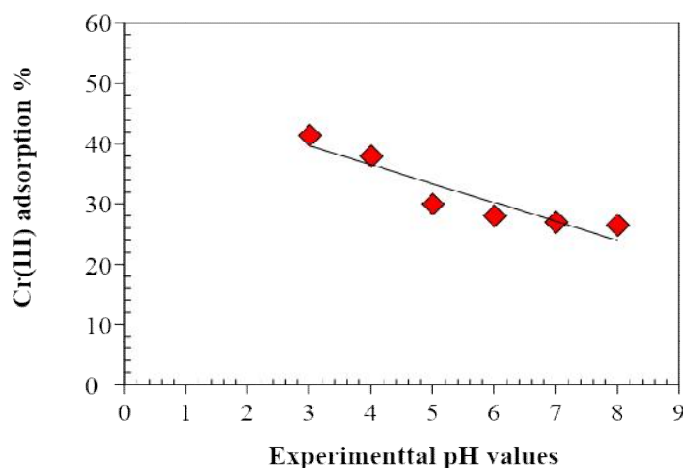

Fig. 1. Effect of pH (contact time: 1 h, dose: 0.50 g/50 mL, agitation speed: 100 rpm, initial concentration: 0.50 mg/L)
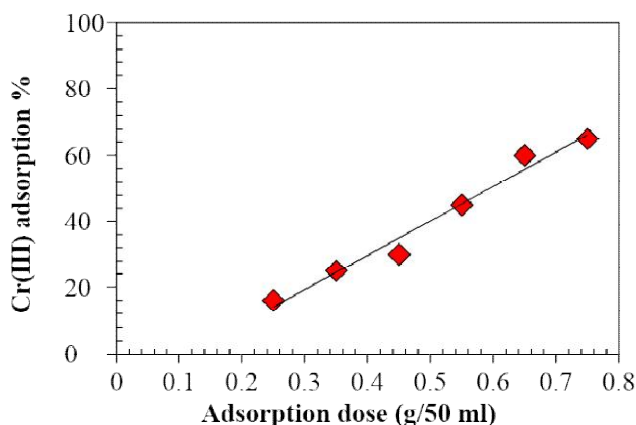
Fig. 2. Effect of adsorption dose on Cr (III) removal % (Contact time: 1 h, pH: 3, agitation speed: 100 rpm, initial concentration: 0.50 mg/L)
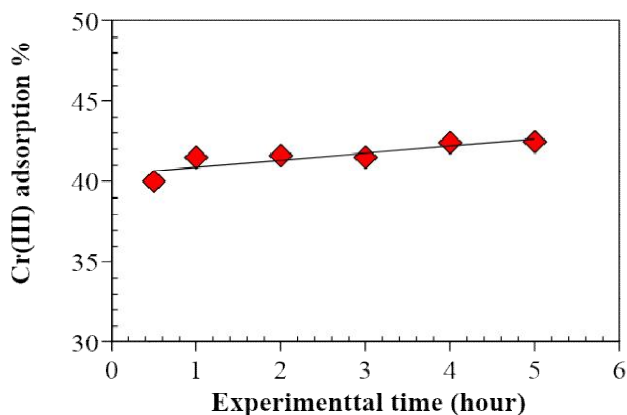

Fig. 3. Effect of contact time (pH: 3, Dose: 0.50 g/50 mL, agitation speed: 100 rpm, Initial concentration: 0.50 mg/L)

3.4 Effect of Adsorbent Type for Cr (III) Adsorption Process

Chromium removal study was conducted using the treated and untreated adsorbent and percentage of Cr(III) removal for both samples as shown in Fig. 4. The statistical analysis reveals that the percentage of Cr(III) removal is significantly higher in the presence of treated adsorbent in solution compared with the untreated adsorbent at a 95% confidence level ($p < 0.001$) following similar reaction conditions. The surface morphology is improved by activation of $ZnCl_2$. It has penetrated deeper into the body of carbonized sample to create internal pores. The breakage of the particles due to crushing has opened the external pores to the internal pores. As a result, the surface area of the particles increased [26].

3.5 Most Significant Factor on Removal of Cr (III)

The significant factors affecting the percentage of Cr(III) ions from synthetic waste water were determined following the model marix of 2^4 full factorial design approach (Table 1) at a 95% confidence level; and the results are presented in Table 2. This study demonstrated that two main factors, i.e., pH, adsorption dose and adsorption type were statistically significant ($\alpha = 0.05$, $p < 0.05$) for removing of Cr (III) ions from the waste water. However, two interaction factors: (a) pH and time ($\alpha = 0.05$, $p = 0.032$), and adsorption type and time ($\alpha = 0.05$, $p = 0.09$) have statistically significant effect on the increasing of Cr(III) ions removal percentage (Fig. 5). The effects of input parameters on the removal percentage (%) of Cr(III) ions are graphically

shown in Fig. 6 to access visually their impact on Cr(III) ions removal process.

Fig. 6 depicts that the change in solution pH values from a lower (pH 3.0) to a higher level (pH 8.0) have a sharp effect in increase of Cr(III) ions removal process having a positive slope of 0.519. However, when the adsorbent dose was changed from lower to higher level, the percentage of Cr(III) ions removal was increased with a slope factor of 4.079, but a reverse trend was observed to decrease the percentage of Cr(III) removal for using treated to untreated adsorbent with a negative slope of -9.0. Therefore, this study has suggested that type of adsorbent used has maximum variation on adsorption for lower pH values and higher adsorbent dose.
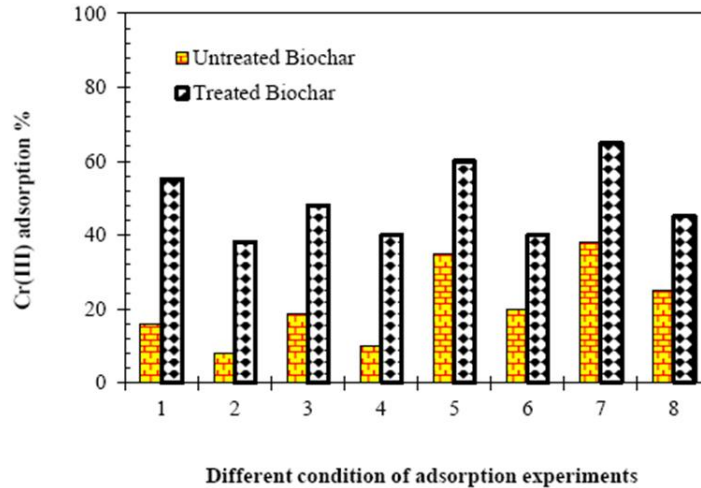

Fig. 4. Effect of adsorbent type on removal of Cr (III) ions from waste water

Table 1. Experimental range and level of different variables for Cr(III) ions removal study

Code	Variable	Unit	Level		
			Low level (-)	Center (+)	High level (+)
A	pH value.	unitless	3.0	5.5	8.0
B	Adsorption time	min	30	165	300
C	Adsorbent dose	g/50 mL	0.0	0.75	1.5
D	Adsorption type		Untreated	--	Treated

Table 2. Estimated effects, statistical significance and impact of single and interaction variables on Cr (III) ions adsorption process

| Source	DF	Adj	SS	Adj	MS	F-Value	*p*-Value	Impact %
One way factor								
pH	1	753.5	753.5	153.7	0	153.7	< 0.001	16.509
Time	1	19.8	19.8	4.04	0.101	19.8	0.101	0.434
Dose	1	554.6	554.6	113.13	0	554.6	< 0.001	12.151
Adsorbent Type	1	3030.5	3030.5	618.15	0	3030.5	0.032	66.397
2-Way Interactions factors								
pH*Time	1	6.5	6.5	1.33	0.302	6.5	0.032	0.142
pH*Dose	1	42.9	42.9	8.75	0.032	42.9	0.071	0.940
pH*Type	1	25.5	25.5	5.2	0.071	25.5	0.095	0.559
Time*Dose	1	20.7	20.7	4.22	0.095	20.7	0.419	0.454
Time*Type	1	3.8	3.8	0.78	0.419	3.8	0.009	0.083
Dose*Type	1	81.9	81.9	16.71	0.009	81.9		
Error	5	24.51	4.9			4.9		
Total	15	4564.24						
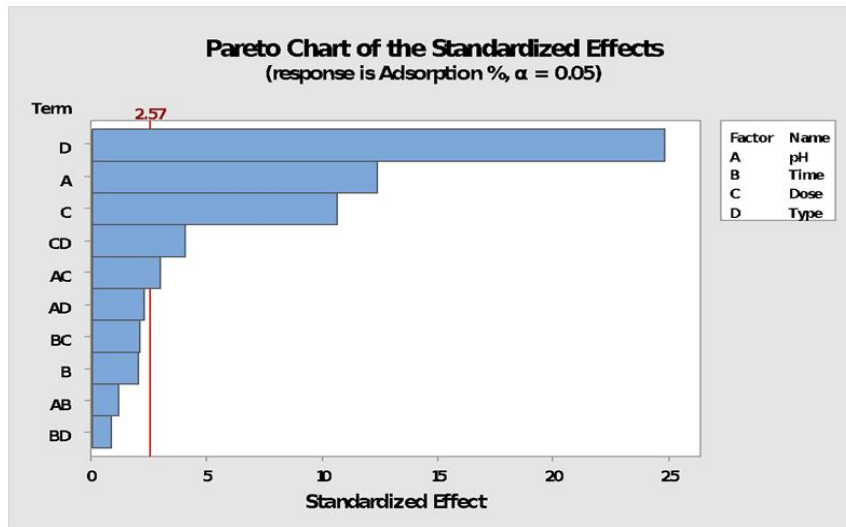
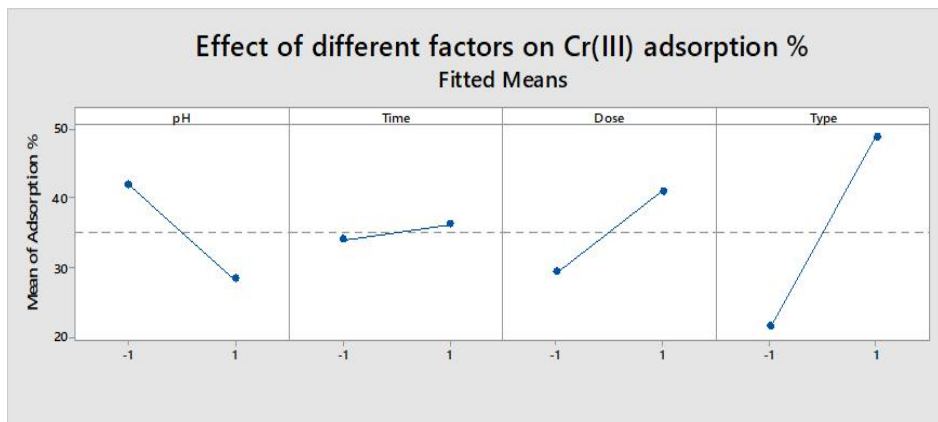**Fig. 5. Pareto chart of the standardized effects for removal (%) of chromium from waste water**

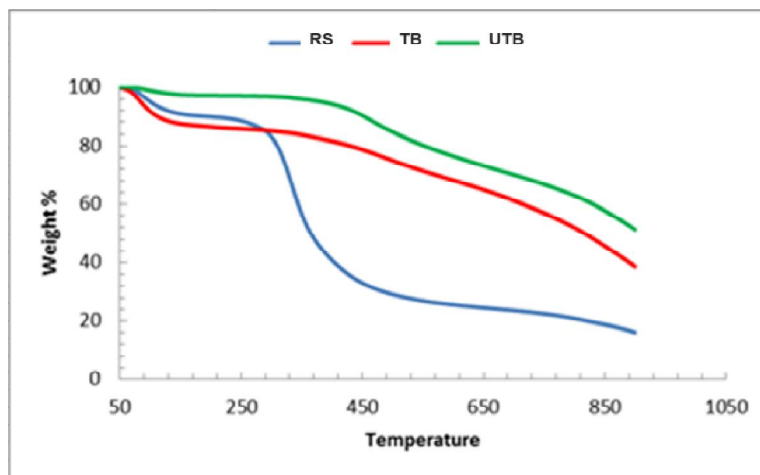**Fig. 6. One way interaction parameters (pH, time, dose, type) on adsorption**

Fig. 7. Thermo gravimetric analysis of raw sample (RS), TB, UTB

3.6 Thermo Gravimetric Analysis (TGA)

The thermal resistivity of $ZnCl_2$ treated biochar sample (TB), untreated biochar sample (UTB) and raw sample at different temperature was monitored by thermo gravimetric analysis which is shown in Fig. 7. From the figure it can be seen that thermal stability of raw sample is less than TB and UTB. From 50°C to 250°C temperature range there is around 20% weight loss for raw sample. Moisture content of raw sample is higher than TB and UTB. After 250°C raw sample starts to decompose. TB prepared at 450°C ascribes minor change in the initial stage which is around 10%. This is attributed to the loss of adsorbed water molecule present on the porous structure of TB. After initial moisture loss TB weight percentage gradually decreased with the increase of temperature. From temperature 200°C to 850°C there is around 60% weight loss. This steady state of weight loss indicates good thermal stability of TB. Fig. 7 showed that untreated biochar sample (UTB) has better thermal stability than TB in initial stage. That's because after carbonization the sample was treated with $ZnCl_2$ solution and HCl solution. So TB may contain moisture and there is no moisture in UTB sample. In the initial stage UTB had no weight loss from 50°C to 450°C. After 450°C it started to decompose and weight % gradually decreased. From 450°C to 900°C temperature range weight loss was around 50% which is similar to TB.

3.7 Adsorption Isotherms

The equilibrium adsorption isotherms are fundamental in order to examine the mechanism of Cr (III) adsorption onto the adsorbent and are also important in the designing of adsorption systems. The equilibrium data was applied to the isotherm models like Langmuir, Freundlich [25,2].

The Langmuir model is based on the assumption that the removal of metal ions occurs on an energetically homogenous surface through monolayer adsorption without any interactions between the adsorbate on adjacent sites [27,28,29,30]. This model provides information on adsorption capability and is capable of reflecting the usual equilibrium adsorption behavior.

Freundlichmodel [29,30,31] predicts no saturation of the adsorbent by the adsorbate, involving an infinite coating, indicating multilayer adsorption on the adsorbent surface.

The linearlized form of Langmuir (Equation 2) and Freundlich Isotherm (Equation 3) is given below:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \tag{2}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

Where q_{max} is the maximum adsorption capacity (mg/g), q_e is the equilibrium adsorption capacity (mg/g), K_L is the Langmuir Isotherm Constant (L/mg), C_e is the equilibrium concentration (mg/l) of chromium(III) solution, K_F is the Freundlich constant(L/g), n is the adsorption intensity exponent.

In the present work, the experimental data was plotted on the linear adsorption models of the Langmuir and the Freundlich adsorption isotherm. The results showed that the experimental data were better adjusted to Langmuir's isotherm model (R^2 = 0.9878) compared to the Freundlich isotherm model (R^2 = 0.774), which suggested that the adsorption occurred through a monolayer process. But The Freundlich model was not fitted well with the experimental in this study.

On the other hand, the main characteristic of the Langmuir isotherm is its dimensionless constant called separation factor (equilibrium parameter), R_L [32]. This separation factor (R_L) was calculated using the equation (4):

$$R_L = \frac{1}{1 + K_L C_o} \tag{4}$$

where, K_L is the Langmuir constant and C_o is the initial concentration of metal ion. The value of separation parameter R_L provides important information about the nature of adsorption (Table 3).

The values of the Langmuir separation parameter, R_L was calculated using Equation (4) and was shown in Fig. 9. The values of R_L between 0 to 1.0, indicates more favorable sorption of Cr(III) ions onto biochar treated by $ZnCl_2$. However the Langmuir separation parameter R_L is dependent on concentration and according to McKay et al. [33], this indicates that the sorption of Cr(III) ions onto biochar was also feasible at the concentrations studied.
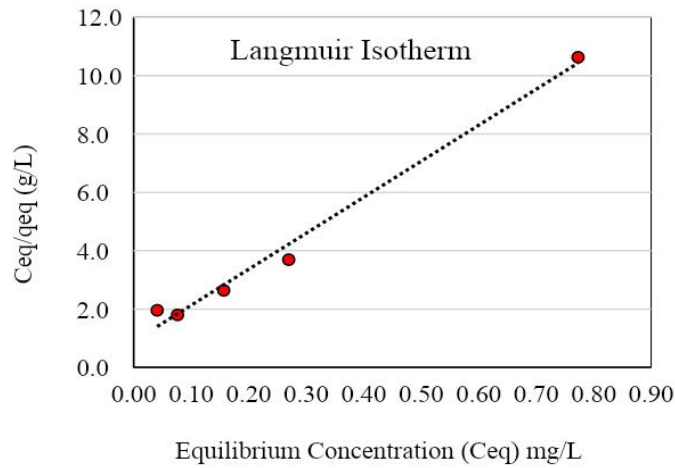
(a)
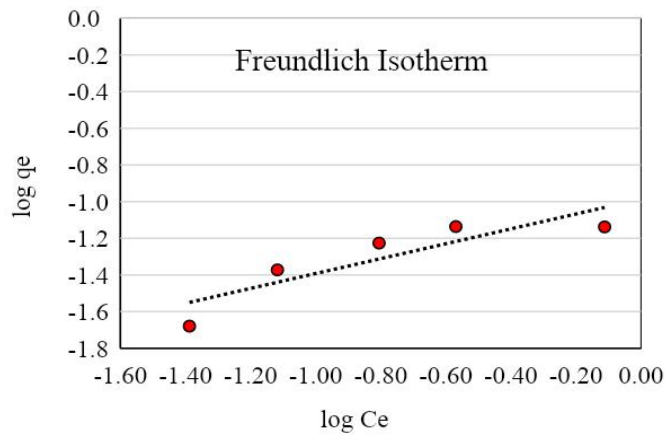
(b)

Fig. 8. The adsorption isotherm plots (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm for the adsorption of Cr(III) ions onto biochar treated by ZnCl$_2$
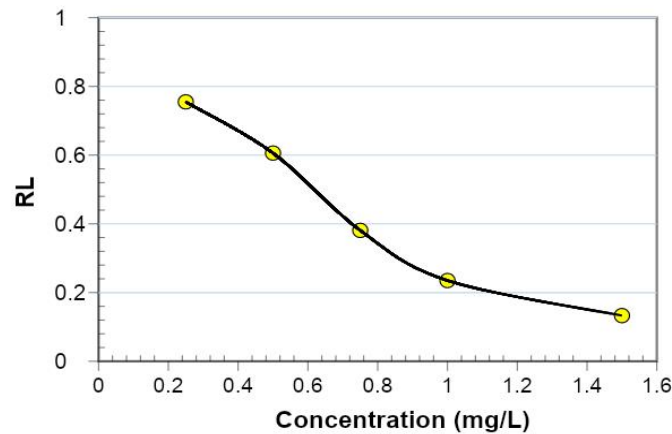

Fig. 9. The mean values of separation factor, *R$_L$* for the adsorption of Cr (III) ions onto ZnCl$_2$ treated biochar

Table 3. Use of separation parameter, R_L in getting information about the nature of adsorption [29]

| Serial No.	Value of R_L	Information about the adsorption
1.	$R_L > 1$	Unfavorable
2.	$R_L = 1$	Linear
3.	O< R_L <1	Favorable
4.	$R_L = O$	Irreversible

3.8 Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) analysis was employed to perceive the surface morphologies of prepared TB. Fig. 8(a) shows the SEM image of UTB and Fig. 8(b) shows the SEM image of TB. Pore size distribution has been used to describe the internal structures and adsorption capacities of Biochar. Due to varying methods of preparation, the pore sizes of the biochar can be categorized as being micropores (width < 2 nm), mesopores (width = 2–50 nm), or macropores (width > 50 nm); the differences in the size of their width openings being a representation of the pore distance. In Fig. 8(a) UTB gives the homogeneous surface whereas in Fig. 8(b) TB shows irregular pores.
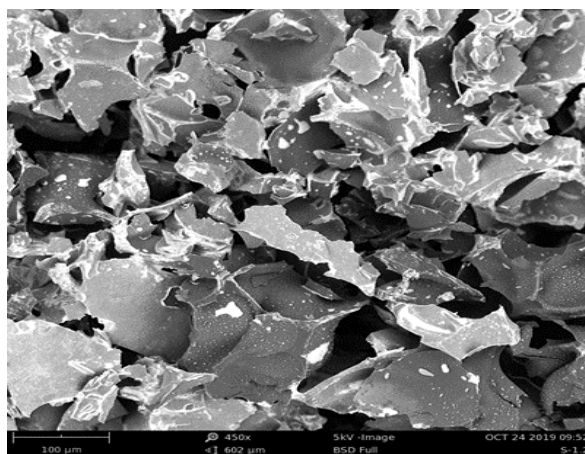
(a)
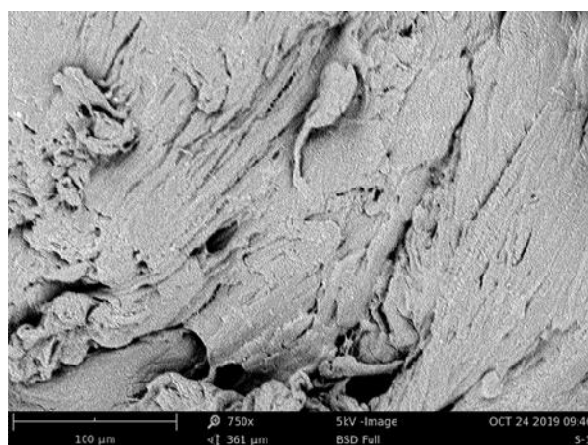
(b)

Fig. 10. Scanning electron microscopy (SEM) analysis for (a) UTB and (b) TB

4. CONCLUSION

This study highlights that biochar from the vegetable tanned leather shaving dust can be used as a low cost adsorbent for Cr(III) removal from waste water and also demonstrated that reasonably good adsorption capacity biochar has been prepared from this adsorbent with $ZnCl_2$ as an activating agent. The percentage removal of chromium is high with increasing contact time and the equilibrium time is nearly 1 hour. The removal percentage has been also increases with increased adsorbent dose as evident from the experiments that an adsorbent dose of 0.75 g / 50 mL removes 70% of the chromium. As the adsorbent is easily available and cost effective, it can be used in small amounts to obtain complete removal of Cr(III). The adsorption of Cr(III) is also affected much by the variation in pH of the solution and is found that the maximum adsorption of Cr(III) occur in pH 3. The adsorption equilibrium data were well fitted by the Langmuir isotherm model, this is indicative of monolayer adsorption by adsorbent. The one way ANOVA test stipulate that Cr(III) removal percentage was almost consistent with the increasing of time at a 95% confidence level with high probability value (p = 0.147) as well as other calculated parameters (pH, time, dose, type) are shown in Pareto chart of the standardized effects for removal (%) of chromium have been accepted. Therefore it can be concluded that vegetable tanned leather shaving dust which is a solid waste of leather industry can be employed as effective adsorbent for the removal of trivalent chromium from the aqueous solutions.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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