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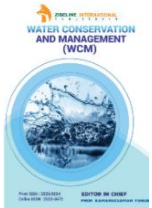

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RESEARCH ARTICLE

OPTIMIZING THE REMOVAL EFFICIENCY OF CHROMIUM FROM TANNING PLANT EFFLUENT BY ADSORPTION METHOD WITH ACTIVATED CARBON CHAT STEMS (CATHA EDULIS) USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Due to the high-water consumption of tanning plants, which produce many pollutants such as wastewater and heavy metals (chromium) as by-products enter the water bodies and pollute or harm the environment. This study investigated the removal of hexavalent chromium (VI) from wastewater using activated carbon Chat-Stem. Adsorption is a common treatment method using activated carbon because these heavy metals can be removed inexpensively, profitably, and efficiently. The approximate analysis of the moisture content of the chat stem is 6%, ash content of activated carbon is 17.35%, the volatile matter is 20.12%, fixed carbon content is 56.53%, and the bulk density of activated carbon is 0.392 g/cm^3 at 360 ° C, which is in good agreement with the standard quality of activated carbon. As the process parameters changed, the increase of chromium removal efficiency was from 62.5% to 97.03%. The Maximum conditions of chromium removal efficiency were observed at the adsorbent dosage of 30 g/L, at pH of 4, and contact time at 180 minutes using the activated carbon chat stem to remove Cr from wastewater was found to be 97.03% with the desirability of 1 and the corresponding chromium removal efficiency optimized to 97.50%. The selected optimal conditions at the adsorbent dosage of 29.155 g/ml, at a PH of 3.32, and contact time of 174.651 min increasing the chromium removal efficiency to 97.83% with desirability 1 at Run 1. The surface of the chat stem before and after adsorption was characterized by FTIR. For short contact times, Langmuir and Freundlich's adsorption isotherms were 0.9839 and 0.9995, respectively.

KEYWORDS

Adsorption; Chromium (Cr); Chat stems activated carbon; Response Surface Methodology; Wastewater treatment

1. INTRODUCTION

Now a day the health problem connected with water pollution is the major and primary issue throughout the world (Raizada, 2020). Thus, the main cause of water pollution is, directly and indirectly, related to human activities that lead to the poor control of wastewater generated from different factories. Due to the higher water consumption of tanning plants, water pollution, and excessive release of heavy metals from wastewater are increasing rapidly into the environment due to urbanization, unprecedented population growth, and rapid industrialization at an unexpected rate because of the fast industrial development, mechanized agricultural development, and progress of development in the previous few decades (Fito et al., 2019; Shakir et al., 2012; Beksissa et al., 2021). Since various industries frequently discharge a huge amount of potentially toxic metals and untreated waste into water bodies (Vo et al., 2019). Contamination of water bodies with Cr (VI) comes from natural and anthropogenic sources, the latter with increasing pollution. The main anthropogenic sources of Cr (VI) include metallurgy, electroplating, and the production of chromium-containing compounds such as pigments, paints, catalysts, chromic acid, and tanning agents (Alemu et al., 2018).

Currently, the most common techniques for removing or eliminating chromium from wastewater are adsorption, reverse osmosis, and chemical reactions involving its removal and precipitation (Husen and Khwairakpam, 2021). However, these methods have some drawbacks, such as low efficiency, high operational and maintenance costs, sludge production that causes disposal problems, or secondary pollutant production that limits their application in real-world situations. In comparison, adsorption processes are superior to other techniques for wastewater recycling in terms of being cost-effective, easier to design and use, and an effective process for removing Cr (VI) and other heavy metals from aqueous solutions (Alemu et al., 2017). Treatment of wastewater containing heavy metals is necessary as a practical alternative to removing trace amounts of chromium from wastewater (Alemu et al., 2017). Activated carbons are more effective in the removal of heavy metals (i.e. such as lead, arsenic, mercury, and chromium) due to their non-biodegradability and sustainability in the environment that enhance the use of activated carbon for removal of both organic and inorganic contaminants including heavy metals from water supplies and wastewater (Husen and Khwairakpam, 2021; Fahim et al., 2006).

The presence of hexavalent and trivalent chromium is two of the most common causes of chromium to the environment and causes a variety of known toxic effects (Chemistry, 2008). For this reason, the main causes of chromium leaks that are widespread in the industry are: textile manufacturing, metallurgical operation, mining, tanning, wood

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preservation, cement industry, dye use, electroplating, steel production, photographic material, corrosive paints are considered as a major environmental toxin (Rahaman et al., 2016; Chen et al., 2014; Brar et al., 2019). Among all the industrial sectors, effluent released from tanneries is categorized as a major contributor of chromium pollutants all over the world (Chowdhury et al., 2015; Neelam, 2018). Since the tanning process consumed, 60-70% of total Chromium, whereas the rest of the 30-40% remains unconsumed.

This unconsumed chromium goes away with the industrial pollution, due to the tanning process with Cr-salt and consequently, large quantities of Cr are being discharged by polluting surface waters, soil, air, land, and groundwater (Neelam, 2018). The surface of the adsorbent particles can be updated to improve the ability to adsorb chromium, and the adsorption process can be developed according to economic cost, high adsorption capacity, effectiveness, technical, efficiency, and low time (Nur-E-Alam et al., 2018; Jumean et al., 2015). The purpose of this study is to investigate the removal of Cr present in tanning to treat wastewater by adsorption techniques and its reuse in the tanning process by using activated carbons chat stem under different parameters. We investigated the effects of adsorbent dose, contact time, and pH value of activated carbons made from chat stem on the adsorption process.

2. MATERIAL AND METHOD

2.1 Materials and Reagents

The samples of Chat stem were collected from Jimma city, Ethiopia. All used chemicals were analytical reagent grade. Sulfuric acid (H_2SO_4), Nitric acid (HNO_3), Potassium dichromate ($K_2Cr_2O^7$), and hydrochloric acid (HCl) were purchased from Chem-Supply Kirkos Ltd. in Addis Ababa, Ethiopia. The FTIR (Perkin Elmer, USA) used to identify the functional group of chat stem before and after adsorption of Cr (VI) removal prepared and the experiments were used the Langmuir and Freundlich equations to explain the nature of adsorption of the heavy metal (Cr (VI) on the adsorbent removal (Jumean et al., 2015).

2.2 Methods

Chat stem was first cleaned with water to remove any impurities from dirt, sand, clay, and small stones, and then manually washed to completely remove the impurities. The samples are then cut into 5 mm-sized pieces that can be easily dried in an oven at 105 °C for 24 hours until completely dry (Fito et al., 2019). Crush the dried sample with a jaw crusher and sift through a sieve to even out the particle size of the sample. As the particle size decreases, internal diffusion decreases, and it is easy to achieve mass transfer limitation on the permeation of adsorbents affected by absorptivity. Such an effect is due to the small particle size that increases the total surface area, and the ability of Cr to penetrate or penetrate the entire internal pore structure of carbon is very high.

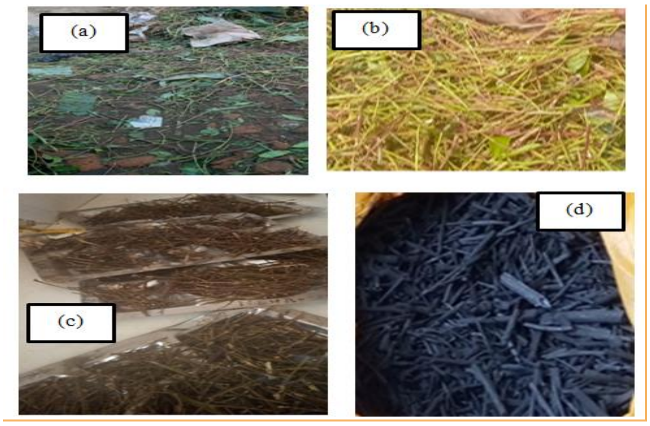

Figure 1: (a) collection of chat stem around Jimma city, (b) after washing the chat stem sample collected, (c) chat stem drying in an oven, (d) Chat stem after pyrolysis.

Based on the prescreening, the powder sample was carbonized in a furnace using H_2SO_4 at 600°C, which was selected, because it has a superior fixed carbon composition and higher surface areas associated with the others. Then, the samples procedure of the selected activated by 0.5M HCl was started by soaking the sample with concentrated H_2SO_4 for 24 h to achieve a good carbon structure and a large surface area, to remove impurities. Then, the soaked sample was washed with 1% HNO_3 to remove residual acid content and make it neutralize the acid and further washing was done using deionized water until pH 7 of the activated carbon was achieved. After that, the samples will be dried at 105 ^{0}C for 12 hours in an oven (Fito et al., 2019). Finally, the samples will be kept for the adsorption experiment.

Adsorption studies were carried out in a Standard solution of Cr (VI) was prepared by dissolving an appropriate amount of $K_2Cr_2O^7$ in distilled water. This solution was diluted to obtain a standard solution containing 10 to 30 gm/l. Based on this, known amounts of activated carbon chat stem were added and solution pH was adjusted using dilute 0.5 M HCl hydrochloric acid. The solution was agitated at 500 rpm placed in the flasks and shakes for 3hr at 30 ºC, were prepared by dissolving in deionized water until pH 7 of the activated carbon was achieved (Chen et al., 2014). After that, the samples dried at 105 ^{0}C for 12 hours in an oven (Fito et al., 2019). Finally, the samples will be kept for the adsorption experiment. After centrifuging the solution, the amount of Cr (VI) was measured by using an atomic absorption spectrometer. Adsorption isotherms were carried out with different initial concentrations of Cr (VI), while the carbon dosage was fixed for the effect of pH. The percentage of Cr (VI) adsorption from the prepared solution was calculated by the following equation:

$$Adsorption\ (\%) = \frac{C_I - C_F}{C_I} \times 100 \quad (1)$$

Where; C_I and C_F are the initial and final chromium (VI) concentrations. In this study, the contact time was varied between 30 to 180 min, the solution pH of 1.0 to 7.0, and the initial chromium (VI) concentration varying from 10 to 30 mg/L.

2.3 Adsorbent Characterization

The chat stem activated carbon (CAC) was analyzed for the operating adsorption process are; the moisture content of the chat stem, ash content, volatile matter, and fixed carbon of the adsorbent was investigated.

2.3.1 Determination of moisture content

The moisture (water) contents of the chat stem are affected the adsorption abilities of the activated carbon. A weight of 2 g of samples was added to the crucible and weighed. The samples will be kept in the oven at 105 ^{0}C for 12 hr. After that, the samples will be taken out and kept in the desiccators. The weights sample will be recorded before and after drying and burnt the samples into the oven and furnace respectively. Then the weight will be measured and the moisture content will be calculated as follow;

$$Moisture\ content\ (\%) = \frac{M_0 - M}{M_0} \times 100 \quad (2)$$

Where M_0 = mass of crucible plus sample

M = mass of crucible plus dried sample

2.3.2 Determination of Ash Content

Chat stem essential modified physically and chemically to improve its adsorptive properties concerning, organic and inorganic molecules, and metal ions routinely found in water and wastewater. This preparation is accomplished by altering the chat stem to activated carbon as a suitable resource (Husen and Khwairakpam, 2021). 2 g of samples will be weighed. The samples will be kept in a muffle furnace for one and half hours at a temperature of 650 ^{0}C. Then, the samples will be taken out and kept in desiccators for half-hour to cool down. Then, again, the weight of samples will be measured, and ash content calculated by the same formula from equation (2).

2.3.3 Determination of Volatile Matter

A 2g sample was added to the crucible and weighed. The samples were kept in a furnace at a temperature of 800 ^{0}C for 10 minutes. Then, the samples will be taken out and kept in the desiccators for half-hour to cool down. The weight of the samples in the crucible will be measured again. The Percentage volatile matter is then calculated as;

$$V = \frac{100(B-F) - M(B-G)}{(B-G)(100-M)} \times 100 \quad (3)$$

Where, V = volatile matter (%), B = mass of crucible plus sample, F = mass of crucible plus dried sample, G = mass of empty crucible, M = moisture content of the samples.

2.3.4 Determination of fixed Carbon Content

Depending on the sample, the fixed carbon contents can be calculated by using the formula;

$$\% \text{ Carbon } = 100 - (\% \text{ moisture content } + \% \text{ volatile content} + \% \text{ ash content}) \tag{4}$$

2.4 Adsorption isotherms

The adsorption isotherms describe the mathematical models of the distribution of adsorbate species among liquid and solid phases (Bonilla-Petriciolet et al., 2017). To construct adsorption isotherm for chat stem, an experiment was carried out by varying the initial concentration of metal ions as 8, 14, and 18 mg/L in 2 g of dose with 100 mL solution of the metal ions. Other parameters were kept constant. The representation of Langmuir isotherm is described by the equation (Ghosal and Gupta, 2017):

$$q_e = \frac{q_m k_a C_e}{1 + k_a C_e} \tag{5}$$

Where; q_e is amount removal to adsorbent (mg/g), at concentration equilibrium of C_e (adsorbate) in (mg/L), q_m is the maximum adsorption for monolayer complete capacity (mg/g), Ka is constant adsorption equilibrium (L/mg). The linearized Langmuir isotherm allows the adsorption calculation capacities, and Langmuir constants and is given according to the equation (Ghosal and Gupta, 2017).

$$\frac{C_e}{q_e} = \frac{1}{(q_m k_a)} + \frac{C_e}{q_m} \tag{6}$$

When, Ce/qe is plotted vs Ce, with linear equation at slope 1/qm and intercept of $1/q_m K_a$, were gained. According to, the necessary features equation of Langmuir isotherm can be explained in terms of a constant dimensionless called separation equilibrium parameter factor (K_L).

$$k_L = \frac{1}{1 + k_a C_0} \tag{7}$$

Where, C_o is the initial adsorbate concentration, and K_a is the Langmuir constant (L/mg). The parameter K_L indicates the adsorption process nature [$K_L > 1$; Unfavorable; $K_L = 1$; Linear; $0 < K_L < 1$: Favorable; $K_L = 0$: Irreversible]. The representation of Freundlich is equation (Jumean et al., 2015).

$$q_e = K_F C_e^{\frac{1}{n}} \tag{8}$$

Where, n and K_F were incorporating constants parameters that affect the adsorption intensity and capacity respectively and calculated from the plot slope and intercepts. The isotherm Freundlich linear function is also represented as below equation:

$$\log(q_e) = \frac{1}{n}\log(C_e) + l\,og(K_F) \tag{9}$$

2.5 Analysis of variance (ANOVA)

The experimental Design-Expert software (7.0 Portable), by using Response Surface Methodology was used to determine the influences of three operating variables for adsorption and maximum percentage removal efficiency of chromium from tannery wastes. A BBD with three numerical factors on three levels was used. They consisted of 17 randomized runs. Effects of dosage of the adsorbent 10 to 30 g/ml, the effect of contact time from 30 to 180 min, and effects of pH from 1 to 7 were investigated as independent variables (Jumean et al., 2015).

3. RESULTS AND DISCUSSION

3.1 Chat stem activated carbon characterization

3.1.1 The moisture content of chat stem

In this section, the moisture content of the chat stem had a great influence on the adsorption capacity of activated carbon. The percentage moisture content of the chat stem prepared for activated carbon according to Equation 2 is 6%, which shows good quality. In this regard, the low moisture content of the activated carbon was preferable when related to that of commercial activated carbon almost the same (7.8%) (Husen and Khwairakpam, 2021).

3.1.2 Ash content

The ash percentage content of the prepared activated carbon was calculated using equation 2 was 17.35%, which verified that the inorganic content was insignificant. A large amount of ash content is not favorable for activated carbon, which in turn can lower the adsorption capacity and efficiency. Hence, adsorbent with low ash content is one of the critical concerns waged on water and wastewater purification processes through adsorption treatment methods. Relatively the chat stem ash content, which was much lower than that of activated carbon prepared, compared with other raw materials (Fito et al., 2019; Husen and Khwairakpam, 2021).

3.1.3 Determination of Volatile Matter

The Percentage of volatile matter of the adsorbent or chat stem activated carbon was determined according to equation 3 and was 20.12%.

3.1.4 Determination of fixed Carbon Content

Fixed carbon was one the most important parameters determined using equation (4) was 56.53%, a significant amount of carbon. The prepared activated carbon from the chat stem was a higher carbon material, good quality compared to other studies, and was a good sign of an adsorbent that has done more to purify water and wastewater on an industrial scale (Fito et al., 2019).

Table 1: Summarized Proximate analyses of chat stem activated carbon for adsorbent

Proximate analysis contents	Mass in %
Moisture	6.0
Volatile matter	20.12
Ash content	17.35
Fixed carbon	56.53

3.1.5 Bulk density

The bulk density of the prepared activated carbon chat stem determined based on the mass of the adsorbent in the specific volume is ($0.392 g/cm^3$), which is comparable with that of commercial activated carbon ($0.387 g/cm^3$).

3.2 Factors affecting the Adsorption parameters

3.2.1 Effects of Dose of the Adsorbent

The effect of the dose of the adsorption is primarily associated with the surface of the adsorbent which is interrelated to the amounts of the adsorbent and hence adsorption increases with increase in surface or amounts of the adsorbent (Husen and Khwairakpam, 2021; Nur-E-Alam et al., 2018). The activated carbon chat stem doses from 10 to 30 gm/L were studied to see the effect on chromium adsorption keeping other parameters at optimum conditions Figure 2 (a). The results showed that with an increase in activated carbon chat stem dose, the percentage removal efficiency of chromium was decreased due to increased surface area of the adsorbent that increases the number of available binding sites for the adsorption process. Moreover, the maximum chromium removal efficiency was observed at 30 gm/L activated chat stem dose of the aqueous solution containing 100 mg/L chromium concentration.

3.2.2 Effects of PH

The pH measures a weak acid or basis of the degree of ionization of a species is affected by the pH, this in turn affects adsorption (Husen and Khwairakpam, 2021; Nur-E-Alam et al., 2020). Cr (VI) removal was studied as a function of pH over a range of 1–7, for an activated chat stem at an aqueous solution containing100 mg/L chromium concentration. The result in Figure 2 (b) shows that optimal Cr (VI) removal efficiency was obtained at pH 1.0 for 180 min contact time. The chromium (VI) removal efficiency increases with a decrease in pH. This is due to excess hydrogen ions being neutralized the negative changes on the surface of the adsorbent by forming the diffusion of the hydrogen chromate ion (HCr_2O^{7-}) in the solution at lower pH for a dominant anionic form of Cr (VI) between pH 1.0 and 4.0.

3.2.3 Effect of Contact Time

The result shown in Figure 4.1c, the contact time investigations needed to reach the equilibrium point is dependent on the initial and final concentrations of the solution contents at different times was found to increase rapidly in the initial stage (Husen and Khwairakpam, 2021; Nur-E-Alam et al., 2018). Figure 2(c) depicts the effect of contact time on the adsorption of chromium on activated chat stem carbon from an aqueous solution. Clearly, increasing the contact time increases the removal efficiency but further increase in contact time did not make any change in removal and adsorption capacity. This is due to always when the adsorption process starts the availability of the large active binding site occurred but as time further increased the process slows down due to the active binding sites are filled by the metal ion. As shown in Figure 4.1c, the percentage removal of chromium by activated carbon chat stem at a contact time of 5min was 70.7% this was increased with time until equilibrium is achieved for the samples of the same concentration to 97.8% as time increases to 150 min.

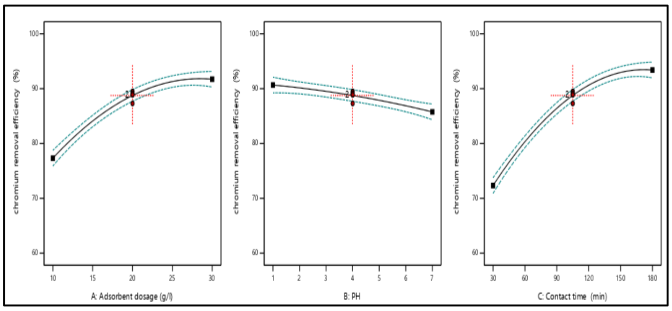

Figure 2: (a) Effect of adsorbent dose on Cr removal, (b) Effect of pH on Cr removal, and (c) Effect of contact time on Cr removal.

3.3 Variables Effect on the removal of chromium

Based on the ANOVA analysis the parameter that significantly affected the removal efficiency of chromium from wastewater was shown in Table 1. The Model F-value of 178.50 implies the model is significant; P-values less than 0.0500 show model terms and all process parameters and the interaction effects are significant and the Lack of Fit F-value of 1.90 implies the Lack of Fit is not significant.

Table 1: ANOVA analysis for process parameter of Cr (VI) removal

Source	Sum of square	df	Mean square	F- value	P- value	
Model	1618.80	9	179.87	178.50	< 0.0001	significant
A-dosage	415.15	1	415.15	411.99	< 0.0001	
B-PH	48.02	1	48.02	47.65	0.0002	
C-Contact time	886.84	1	886.84	880.08	< 0.0001	
AB	18.06	1	18.06	17.92	0.0039	
AC	5.13	1	5.13	5.09	0.0586	
BC	7.02	1	7.02	6.97	0.0334	
Residual	7.05	7	1.01			
Lack of Fit	4.14	3	1.38	1.90	0.2715	not significant

3.4 Interaction's effect

The response surface curves representing the interaction effects of two variables, i.e. adsorbent dosage with pH and pH with contact time on the adsorption of chromium were plotted as shown in Figure 3. Figure 3a shows that maximum adsorption of chromium was attained at a high adsorbent dosage (30 g/L), and considerably low pH. On the other hand, Figure 3b shows maximum adsorption of chromium at relatively low pH and at contact time. The adsorption equilibrium of chromium compounds was obtained after 105 min contact time and 25 g adsorbent dose with adsorption of approximately 96% of chromium compounds. Practically, no remarkable improvement was observed after a longer contact time and high adsorbent dose. This can explain the decrease of adsorption rates which is well illustrated by the plateau line (red shaded area) after 140 min and 25 g adsorption. In general, at sufficient contact time and low particle size, the increment in adsorbent dose from 10 to 30 g/l results in an increment of chromium removal efficiency, from 62.5 % to 93.03%, whereas the adsorption capacity decreased from 4.26 to 1.55 mg/l.

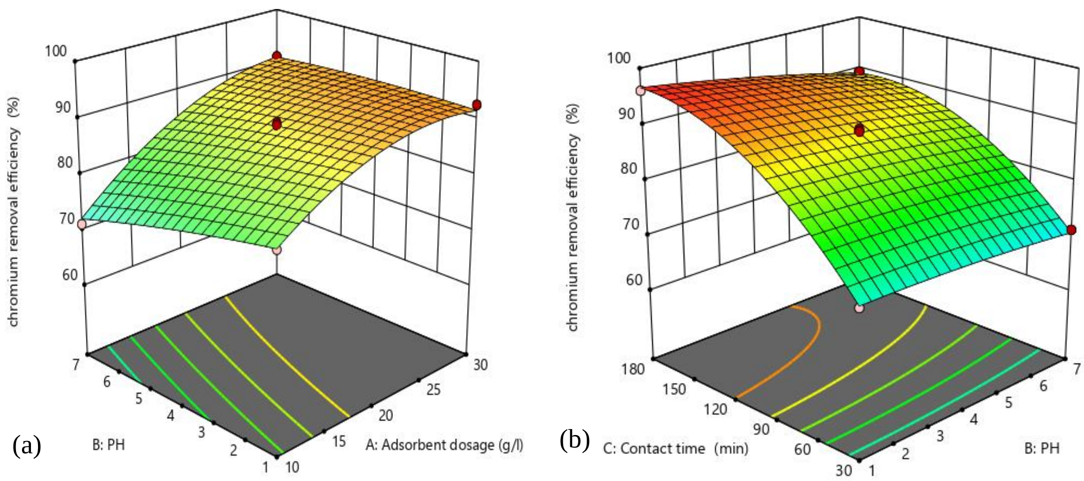

Figure 3: Interaction effects between (a) adsorbent dosage and pH; (b) pH and contact time interaction's effect result for chat stem

3.5 Optimization of chromium removal efficiency using ANOVA

In this study, optimization of the chromium removal efficiency was achieved by varying its operating independent variables. The overall optimized chromium removal efficiency was obtained at a dosage of 30 g/ml adsorbent, at pH of 4, and the contact time at 180 minutes of using the activated chat stem to remove Cr from wastewater was found to be 97.03%. The predicted chromium removal efficiency was 97.50%. This means that the experimental values obtained are very close to the predicted values calculated from the model 0.47% of error. Therefore, we concluded that the model created had reasonable predictability and accuracy for the chromium removal efficiency under the experimental conditions used.

Table 2: Model fit Statistics			
Std.Dev.	1.00	**R^2**	0.9957
Mean	83.74	**Adjusted R^2**	0.9901
C.V. %	1.20	**Predicted R^2**	0.9564
		Adeq Precision	46.0643

The Predicted R^2 of 0.9564 is in reasonable agreement with the Adjusted R^2 of 0.9901; i.e. the difference is less than 0.2. The Predicted R^2 indicates that the error value used to estimate the current model value and the sum of the squares is defined by the sum of the squares and the numerical value differs between 0 and 1. The closer the number to 1 is the more valid the proposed model. The R-squared value in this study was 0.9957, demonstrating the strength and high adaptability of the proposed model for chromium removal efficiency using an activated carbon chat stem. Design-Expert sorts the results from the most desirable to the least desirable, as shown in Figure 4. In Figure 5, the optimal chromium removal efficiency of the predicted run is selected and preferable to other observed desirable (1) run from constraint solutions. Therefore, in the predicted practice, the optimal chromium removal efficiency was selected.

Table 3: Constraints for optimization						
Variables	**Goal**	**Lower limit**	**Upper limit**	**Lower weight**	**Upper weight**	**Importance**
Dosage (g/mL)	In range	10	30	1	1	3
pH	In range	1	7	1	1	3
contact time (min)	In range	30	180	1	1	3
removal efficiency of Cr (VI)	Maximize	62.5	97.03	1	1	3

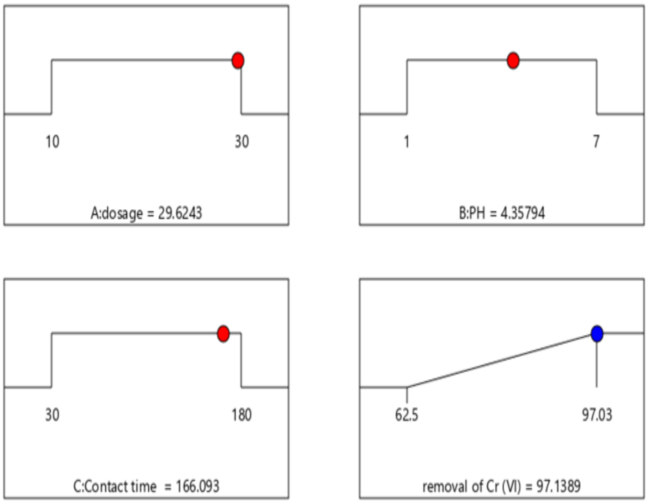

Figure 4: Optimizing the removal efficiency of ramp's function

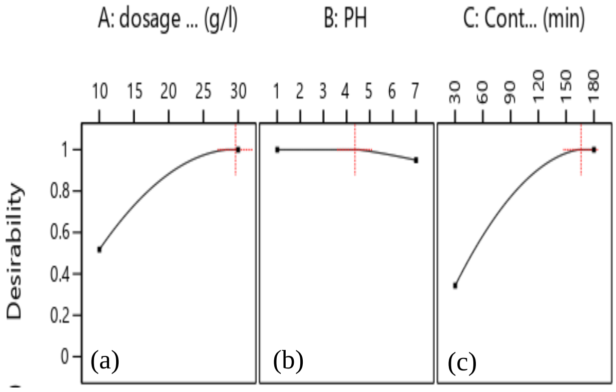

Figure 5: Constraint's solutions; (a) desirability vs effect of adsorbent dosage (g/L), (b) desirability vs effects of pH, and (c) desirability vs effects of contact time (min).

The optimization of process parameters such as effects of dosage of the adsorbent, effects of contact time, and effects of pH was under RSM with a CCD. As shown in Table 4, the main criteria for process parameters have maximized the yield of chromium removal efficiency and keep the coefficient values within the range.

Numerical optimization design experts offer 100 different solutions. Therefore, the optimum point of the independent variable that can maximize the response solution with 100% desirability selects the optimum value condition. Design experts have selected the optimal conditions at an adsorbent dosage of 29.155 g/ml, at a PH of 3.32, and contact time of 174.651 min increasing the chromium removal efficiency to 97.83% with desirability 1, at Run 1 by Design Expert Software.

3.6 FTIR Analysis

Fourier transforms infrared (FTIR) transmission spectra were obtained to characterize and to identify the occurrence of certain functional groups on the chat stem before and after adsorption, as shown in Figures 4 (a) and (b), respectively. Broadband noticed from 3650-3120 cm^{-1} corresponds to the hydroxyl functional group (OH stretching vibration), and the weak bands at 2920 cm^{-1} are assigned to asymmetric C-H stretching. The bands observed in the region between 1700 cm^{-1} and 1490 cm^{-1} were attributed to C=C symmetrical stretching of pyrone groups and C=O of carboxylic groups, and the band observed at 1,632 cm^{-1} was assigned to carbonyl C–O present in carbonyls (Jumean et al., 2015). The bands in the region 450-800 cm^{-1} were also suggested to be due to alkaline groups of cyclic ketones and their derivatives, the in-plane and out-of-plane aromatic ring deformation vibrations, and the out-of-plane C-H bending mode.

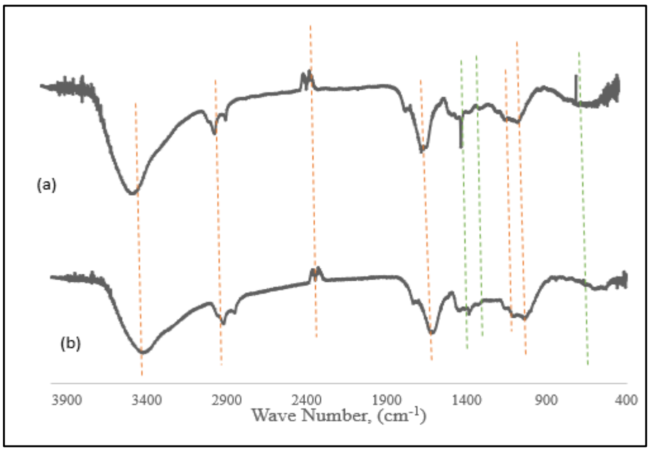

Figure 6: FTIR graph of the raw chat stem (a) before and (b) after adsorption

After adsorption, a significant reduction was observed for a series of complex bands for bio sorbent. Figure 4 (b) shows that many functional groups shifted to different frequency levels or disappeared after adsorption, indicating the possible involvement of those groups for uptake of the adsorbate. It can be observed that the sharp and intense peak at around 3,434 cm^{-1} was shifted to a lower frequency level of 3,423 cm^{-1} and after adsorption, it was broad, which represented that the hydrogen-bonded -OH group was involved for binding adsorbate from wastewater. The peak at 1632 cm^{-1} corresponds to carbonyl C–O present in carbonyls, ketones, aldehydes, or ester groups, and C–C present in olefinic vibrations in the aromatic region was slightly decreased to 1616 cm^{-1} after adsorption. However, the minor peak of 1030 cm^{-1} shifted to a slightly higher wavenumber of 1038 cm^{-1} after adsorption. The minor peaks at around 1270 cm^{-1} were disappeared after adsorption, which confirms that the adsorption of chromium by both adsorbents was highly effective. The large perturbation of the absorption band in the range of 720 cm^{-1} to 400 cm^{-1} was observed on the bio sorbent before adsorption and that may be due to the inside structure was become weaker after adsorption. In general, shifts in adsorption bands of functional groups to lower or higher energies show that there was a binding process taking place at the surface of the bio-sorbent.

3.7 Isotherm Adsorption

The graph plotted using the Langmuir equation can show the relationship between Ce (in X-axis) and Ce/qe (in Y-axis), while the graph drawn based on the Freundlich equation shows the relationship between log Ce (in X-axis) and log qe (in Y-axis).

Table 4: Adsorption isotherm of Cr (VI) ions

Initial concentration (C_0 (mg/L))	**Final conc. C_e (mg/L)**	**Adsorption capacity (q_e) (mg/g)**	$\frac{C_e}{q_e}$	**Log C_e**	**Log q_e**
7	4.24	0.45	6.7	0.5	-0.3
13	5.532	0.76	8.0	0.85	-0.1
17	7.659	0.95	9.5	0.95	-0.03

As the result has shown in Figure 5, and using equation 2.6, the empirical constants q_m and K_a were found to be 2.083 mg/g and 0.0925, respectively. The value of q_m show, one gram of the chat stem activated carbon can adsorb 2.083 mg chromium. The value of K_L indicates a favorable adsorption, i.e. $(0 < 1/\ (1+0.0925C_o) < 1)$. This means that chat stem activated carbon is a favorable adsorbent for the removal of Cr (VI) ions from wastewater. The adsorption Freundlich model equation is widely used in the description of the mathematical adsorption equation for an aqueous system. From equation 2.9, K_F and n, show the capacity of adsorption and intensity of adsorption, respectively.

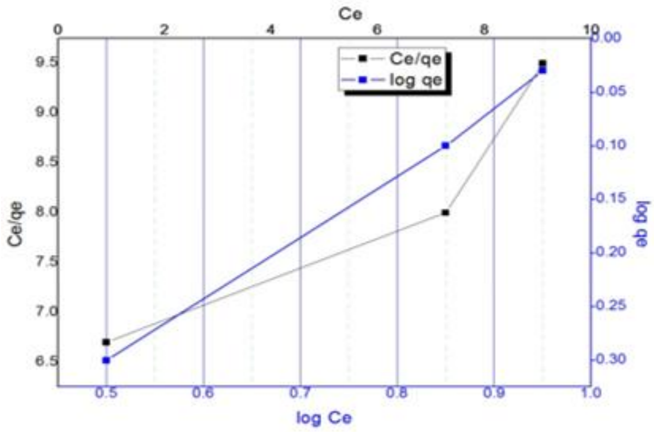

Figure 7: Langmuir adsorption isotherms and Freundlich adsorption isotherm for Cr (VI) ions

The equation of Freundlich fits with experimental data was examined, from this graph of log q_e versus log C_e was employed to generate the intercept value of log K_F and the slope of 1/n. Figure 5, and equation 2.9, the Freundlich constants K_F and n were found to be 0.2218 and 1.503, respectively. The value of 1/n shows the concentration of solute adsorption. If the value of 1/n is an approach to 1, just shows that the little concentration change can relatively affect the adsorption. If n is more than 1, means the adsorbent can effectively adsorb the solute. Since the values of 1/n (0.6653) lie between 0 and 1 and n > 1, it indicates that the chat stem can adsorb Cr (VI) ions effectively. The chromium adsorption on chat stem fitted to both Langmuir and Freundlich adsorption isotherms since the correlation coefficients (R^2) are 0.9839 and 0.9995 respectively. Therefore, each site of a chat stem can accommodate first-order reactions (one chromium ion), it is characterized by heterogeneity of surfaces of chat stem.

4. Conclusion

Chromium (Cr) is a heavy metal, which is very harmful to human health, animals, humans, animals, and the environment, and if the absorption standard value is exceeded, the environmental stability of the surrounding will be affected extremely when its absorption standard level goes beyond the permissible level. If the chromium effluent is not properly treated at the beginning, then it finally blends with the surrounding water bodies and contaminates the water due to this the released wastewater must be reused in a controlled manner or it is recycled and processed for other purposes. The activated carbon chat stem was used as an adsorbent to remove chromium from wastewater since adsorption is a real treatment method based on the requirement of highly efficient, economical, simple, environmentally friendly, highly effective adsorbent, and versatile.

Proximate analysis of the moisture content of chat stem is 6%, activated carbon ash content of 17.35%, volatile materials of 20.12%, fixed carbon content of 56.53%, and activated carbon bulk density at 360 ° C was 0.392 g/cm^3. It is in good agreement with current research on the quality of activated carbon. Factors influencing the adsorption parameters are the effect of adsorbent dose of 10 - 30 g/L, extraction time of 30-180 minutes, and the effect of pH 1- 7, which are investigated as independent variables using response surface methodology. Therefore, the maximum removal efficiency of chromium from tannery wastewater using the adsorption method was 97.03% observed at 30 g/L dosages of the adsorbent, pH 4, and at 180 min contact time, and at the minimum dosage of 10 g/L, the removal efficiency was 62.5 %. The selected optimal conditions by Design experts Software from 100 different run at an adsorbent dosage of 29.155 g/ml, at a PH of 3.32, and contact time of 174.651 min increasing the chromium removal efficiency to 97.83% with desirability 1 at Run 1. Investigational data were acceptable by Langmuir and Freundlich adsorption isotherm. The chromium adsorption on chat stem fitted to both Langmuir and Freundlich adsorption isotherms, since the correlation coefficients (R^2) are 0.9839 and 0.9995 respectively, which obeyed with no detectable change in the oxidation state.

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Availability of Data and Materials

All data generated or analyzed during this study are included in this published article.

Declarations

Competing interests

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Ethics approval and consent to participate are not applicable for this study.

Consent for publication

Consent for publication is not applicable for this study.

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