Chemical Engineering Journal Storage
homepage jurnal: https://ojs.unimal.ac.id/cejs/index
Chemical Engineering Journal Storage

Comparative Removal of Chromium Cr (VI) from Wastewater by Sawdust and Activated Charcoal Derived from Acacia and Sheesham Wood

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Abstract

This study investigates the removal of Chromium (VI) (Cr(VI)) ions from simulated wastewater using various adsorbents. The experiment employs unmodified sawdust (UMSD) and modified sawdust (MSD), along with activated charcoal (AC) derived from Acacia and Sheesham (Dalbergia Sissoo) wood. Batch experiments were conducted to assess the impact of several parameters including solution pH, adsorbent dosage (g/250 mL), contact time (minutes), and initial Cr(VI) concentration (ppm) on Cr(VI) adsorption at room temperature and pressure. SEM along with EDX as well as FTIR were used to analyze the adsorbent surface chemistry. The results revealed that AC exhibited the maximum Cr(VI) removal efficiency (90%) from the simulated wastewater due to its larger surface area as compared to UMSD (55%) and MSD (78%). Models of Freundlich and Langmuir isotherms were used to assess the adsorption process. Analysis of the model constants indicated that the Freundlich isotherm better described the experimental data for all adsorbents, as evidenced by the high correlation coefficient (R^2 = 0.99).

***Keywords**:* Activated Charcoal, Adsorption Isotherms, Modified Sawdust, Unmodified Sawdust

DOI : https://doi.org/10.29103/cejs.v4i6.19191

1. INTRODUCTION

Rapid population growth and industrialization have led to a significant increase in water pollution. Inorganic pollutants, particularly toxic heavy metals (HMs) like chromium (Cr), cadmium (Cd), zinc (Zn), and arsenic (As), represent a serious risk to human health and aquatic life (Cao et al., 2021) (Burant et al., 2018a). Because HMs do not biodegrade like organic contaminants do, they accumulate in living tissues and can lead to major health issues such harm to the

central nervous system, blood clotting, and organ damage (Burant et al., 2018a; Chandio et al., 2021). Their presence in industrial and natural wastewaters has become a critical environmental issue demanding immediate attention (Chandio et al., 2021).

Chromium (Cr) is a hard, lustrous metal found in various oxidation states, with Cr(III) and Cr(VI) being the most relevant. Cr(III) is by nature most stable form and poses minimal health risks (Alatabe & Hussein, 2021; Hashem et al., 2022). However, because of its detrimental effects on people, the International Agency for Research on Cancer (IARC) has designated Cr(VI) as a carcinogen . Studies in Pakistan reveal a worrying trend of Cr(VI) contamination in water sources (Waseem et al., 2014). Groundwater samples from specific areas show Cr(VI) concentrations exceeding safe limits, likely due to industrial activities like leather tanning. While surface water contamination appears lower, the overall situation necessitates effective treatment methods(Stasinakis et al., 2003) (Liu et al., 2024; Wan Ngah & Hanafiah, 2008). Chromium(VI) (Cr(VI)) contamination in wastewater is a significant environmental concern, prompting extensive research on effective removal methods. While various adsorbents have been explored, this study focuses on the potential of underutilized resources: MSD from Acacia and Sheesham wood, and their corresponding AC. These materials offer several advantages that includes least expensive, readily accessible, have a high carbon content as well as incredibly effective and non-toxic(Prasankumar et al., 2022) (Mukherjee et al., 2007; Üner et al., 2019a, 2019b). This research investigates the potential of these low-cost, eco-friendly adsorbents for Cr(VI) removal from wastewater, aiming to contribute to a more sustainable approach to wastewater treatment that can protect human health and preserve aquatic ecosystems(Farooq et al., 2010; Mohan et al., 2011; Yang & Chen, 2008).

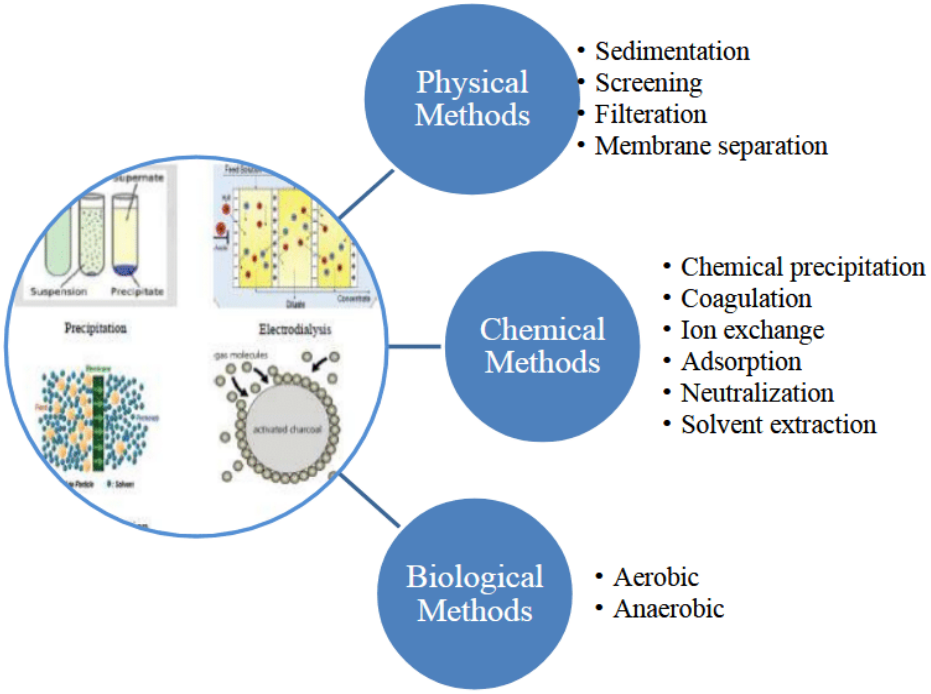

Figure 1: HMs removal techniques from wastewater (Stasinakis et al., 2003)

2. MATERIALS AND METHODS

2.1 Chemicals

Hydrochloric acid (MW. 36.46 g/mol) purchased from Sigma-Aldrich having CAS No. 7647-01-0 It is primarily used in maintaining the pH of solution while analyzing the impact of pH Sodium hydroxide (NaOH) is obtained from Sigma-Aldrich with CAS No. 1310-73-2 and molecular weight 40 g/mol. It is used to maintain pH of solution. Potassium dichromate ($K_2Cr_2O_7$) with MW. 294 g/mol is obtained from Sigma-Aldrich. It isutilized in preparation of stock solution.

2.2 Preparation of Cr (VI) Simulated Wastewater

To make the Cr (VI) stock solution with a concentration of 1000 ppm, 1L of distilled water was mixed with 2.826g of potassium dichromate ($K_2Cr_2O_7$). Dilution was used to provide sample solutions with the appropriate Cr(VI) concentrations (20–100 mg/L)(Hafiz Bilal Ahmad, 2020) (Kim et al., 2001). Throughout the experiment, 1M NaOH and 1M HCl solutions were employed to change the pH.

294 g (1 mole) of $K_2Cr_2O_7$ contains = 104 g of Cr (VI)

Quantity of $K_2Cr_2O_7$ that contains 1g of Cr (VI) = 294/104 = 2.826 g

The following relation is used to prepare the sample solution of Cr(VI) at various concentrations.:

$$C_1V_1 = C_2V_2 \qquad (1)$$

Figure 2: (a) Cr (VI) Stock Solution (b) Samples of Cr (VI) Solution with VariousConcentrations (c) Modified Mixed Sawdust

2.3 Modified Mixed Sawdust Preparation

The mixed sawdust made from Sheesham and Acacia wood was sourced domestically. Distilled water is used to clean it several times to get rid of any water-soluble and surface contaminants and later dried in an oven at 80 °C for 24 hours. The dry material was ground into a powder and sieved through mesh-70, which had a 0.2 mm opening. After adding 0.5M HCl solution tothe dry sawdust in a 1:10 (sawdust: acid w/v ratio), the mixture was magnetically agitated for two to three hours. Following stirring, the sawdust was filtered using filter paper and filtrate was repeatedly cleaned with distilled water until its pH was neutral... Following this, the sawdust was dried for 24 hours at 80 °C in an oven (Hafiz Bilal Ahmad, 2020) (Achak et al., 2009; Farhan et al., 2013; Mukherjee et al., 2007a, 2007b; Neolaka et al., 2020).

2.4 Activated Charcoal Preparation

The sawdust of mixed Acacia and Sheesham wood was heated to 400–600 ˚C in a muffle furnace for 60–90 minutes to produce charcoal. After being repeatedly cleaned with distilled water to eliminate contaminants and ash, it was dried at 80 °C in an oven for a predetermined amount of time. The dry charcoal was ground into a powder and sieved through mesh-70, which has a 0.2 mm size. Following that, a 0.5M HCl solution was used to activate it at a ratio of 1: 10 (charcoal: acid w/v). In this case, the activating agent is HCl. On a magnetic stirrer, it was also agitated for two to three hours. Following stirring, the activated charcoal was filtered through filter paper and the pH of the filtrate was then neutralized by washing it with distilled water. Activated charcoal was finally dried by placing it back in the oven at 80°C (Hafiz Bilal Ahmad, 2020) (Ali et al., 2014; Mukherjee et al., 2007a).

2.5 Adsorption Studies

The batch adsorption tests require various amounts of activated adsorbent to be added to 250 ml aqueous solutions containing 20, 40, 60, 80, and 100 mg/L concentrations of Cr (VI). These tests were conducted at room temperature across a range of time intervals (1-4 hours) using an orbital shaker. Throughout the experimental period, agitation at a constant speed of 200 rpm was applied to enhance mass transfer with a maximum interfacial contact area (Hafiz Bilal Ahmad, 2020) (Avola et al., 2023b; Chaiwon et al., 2017a; Yusuff et al., 2022) (Sinha et al., 2022). A UV-visible spectrophotometer was used to measure the amount of Cr (VI) that remained in the filtrate. A batch process does not require volume adjustment. Using the formula provided, the percentage removal [R %] of Cr (VI) was calculated.

$$R\ (\%) = [Co - Ce/Ci] \times 100 \qquad (2)$$

The following formula was used to determine the adsorbent's adsorption capacity at equilibrium for various Cr (VI) concentrations.

$$qe = V/W(Co - Ce) \qquad (3)$$

C_o is Cr (VI) solution initial concentration (mg/L), C_e is Cr (VI) solution equilibrium concentration (mg/L), q_e is Adsorbent’s Adsorption capacity (mg/g), V is Cr (VI) solution Volume (L) and W represents Adsorbent’s Weight (g).

3. RESULTS AND DISCUSSIONS

3.1. Effect of pH of Solution

The maximum adsorption of Cr (VI) ions is achieved at pH 4 for both UMSD and MSD, as shown in Figure 3. However, In the case of activated charcoal, the pH is 2 while keeping other parameters fixed, as shown in Figure 3. Adsorption of Cr (VI) for UMSD, MSD and AC of Acacia and Sheesham wood was determined at various pH values of solution that ranges from 2 to 10(Hafiz Bilal Ahmad, 2020) (Alatabe & Hussein, 2021; Barkat et al., 2009).

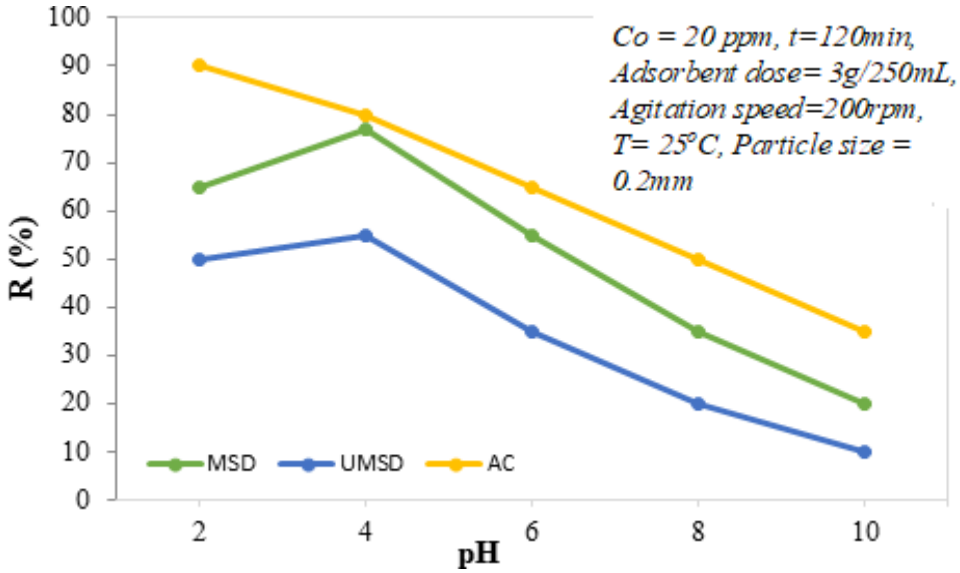

Figure 3: Effect of pH on the adsorption of Cr (VI) ions

3.2. Effect of Contact Time

The removal of Cr (VI) ions for UMSD, MSD and AC is highest at contact time of 120min. The adsorption of Cr (VI) ions was investigated as a function of time that ranges from 30 to 150 min, as shown in Fig 4. It is clearly reported that increase in contact time leads to an increase in adsorption. The values of the other parameters are preset (Avola et al., 2023c; Neolaka et al.,2020).

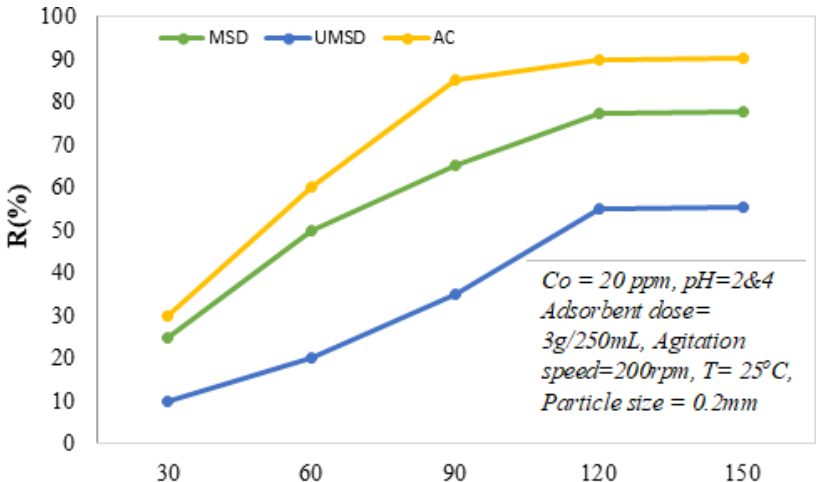

Figure 4: Effect of Contact Time on the adsorption of Cr (VI) ions

3.3 Effect of Adsorbent Dose

Since it determines the adsorbent capacity for a particular Cr (+VI) ion solution concentration, the adsorbent dosage is regarded as a crucial parameter in adsorption investigations. Figure 5 illustrates the investigation of Cr (+VI) adsorption for UMSD, MSD and AC of Acacia and Sheesham wood, with respect to adsorbent dose ranging from 1 to 5g/250mL. The Cr (+VI) ion adsorption onto the surface of all adsorbents is maximum at approximately 3g/250mL. It is noticed that the adsorption of Cr (VI) ions rises by increasing the adsorbent dosage. Other parameters' values, however, are not varying (Ajmani et al., 2019; Chaiwon et al., 2017b). The ability of the surface area of adsorbents to absorb Cr (+VI) ions is enhanced by increasing adsorbent dosage as shown in Figure 5.

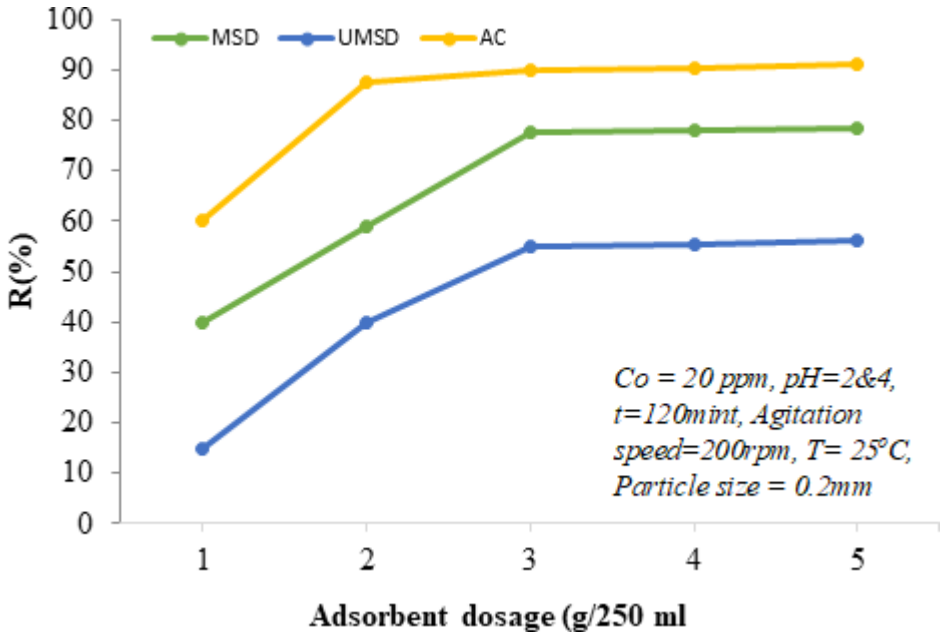

Figure 5: Effect of adsorbent dose on the adsorption of Cr (VI) ions

3.4 Initial Concentration of Cr (VI)

Adsorptive removal of Cr (VI) for UMSD, MSD and AC was examined as a function of concentration of Cr (+VI) that ranges from 20 to 100 ppm, as shown in Figure 6. when all parameters, including pH, particle size, temperature and agitation speed are held constant, the adsorption of Cr (VI) ions declines due to an uplift in concentration (Ahmad et al., 2014; Vo et al., 2019). For a 20ppm sample solution, the maximum amount of Cr (+VI) ions that may be adsorbed onto the surface of any adsorbent (UMSD, MSD, or AC) is found as disclosed in Figure 6.

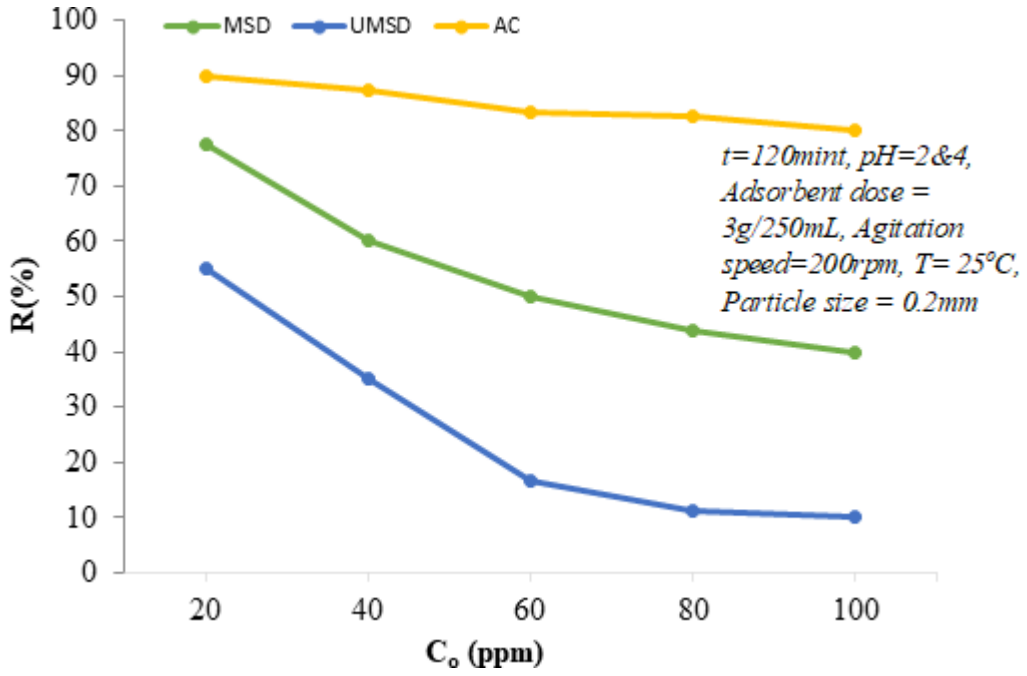

Figure 6: Effect of initial concentration of Cr (VI) on the on the adsorption of Cr (VI) ions

3.5 Adsorption Isotherms

The way in which adsorbate molecules are distributed in the liquid and solid phases in relation to pressure or concentration at constant temperature is mostly shown via adsorption isotherms. Freundlich and Langmuir isotherms are primarily used for solid-liquid systems (Al-Ghouti & Da'ana, 2020; Boparai et al., 2011; Neolaka et al., 2020). Isotherms of these models have been shown at room temperature (25 °C), based on equilibrium data acquired by varying the initial Cr (VI) concentrations for UMSD, MSD, and AC from 20 to 100 mg/L (Al-Asheh et al., 2000; Ayawei et al., 2017).

$$C_e/q_e = C_e/q_m + 1/bq_m \qquad (4)$$

When there is a Langmuir isotherm, all adsorbents provide linear plots between Ce and Ce/qe, as shown in Figures 7-9, and the values of correlation coefficient R^2, as shown in Table 2, depicts how closely the experimental equilibrium data match the Langmuir isotherm. The equation shown in the graph's slop (1/qm) and intercept (1/bqm) yield the values of "qm" and "b."

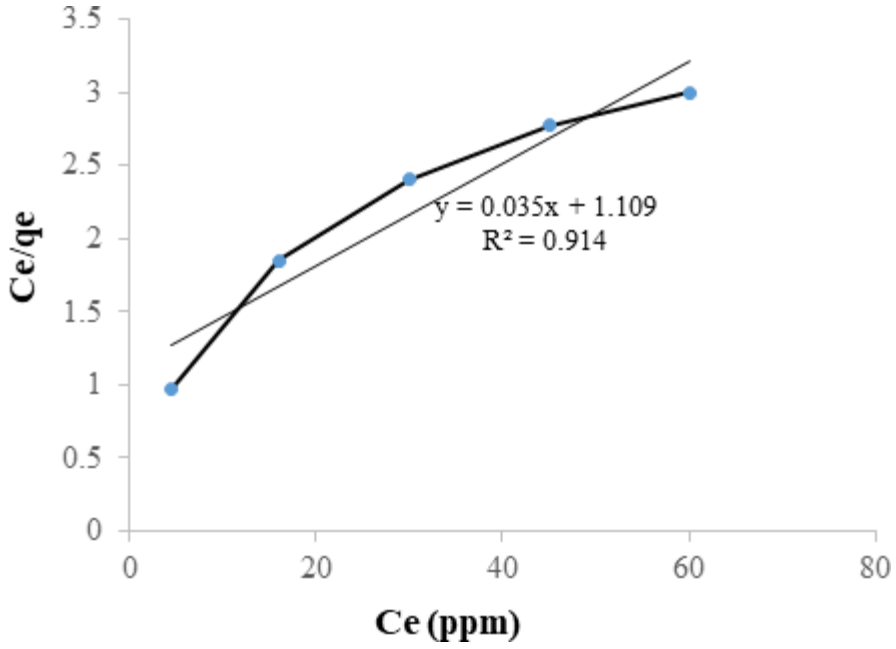

Figure 7: Langmuir isotherm in the case of MSD

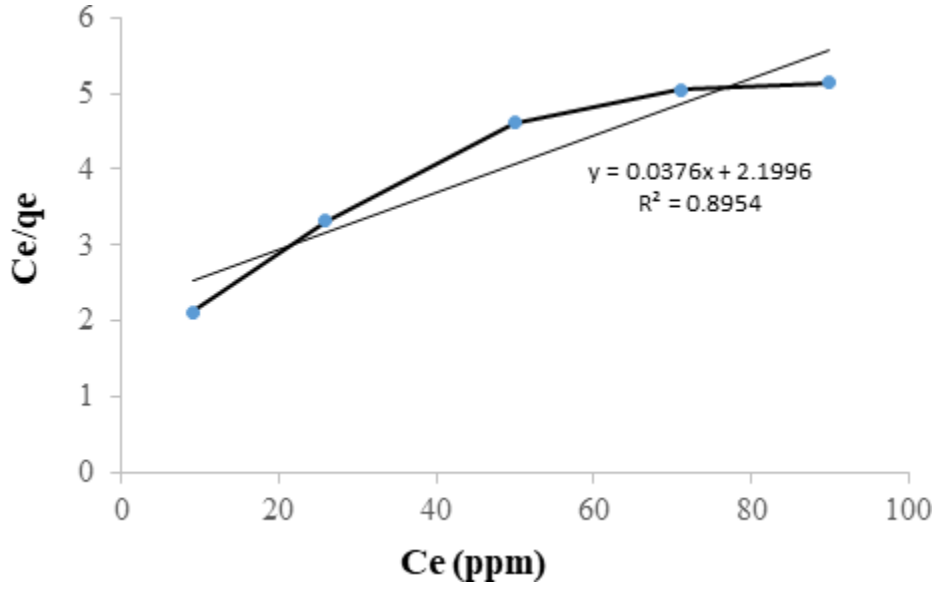

Figure 8: Langmuir isotherm in the case UMSD

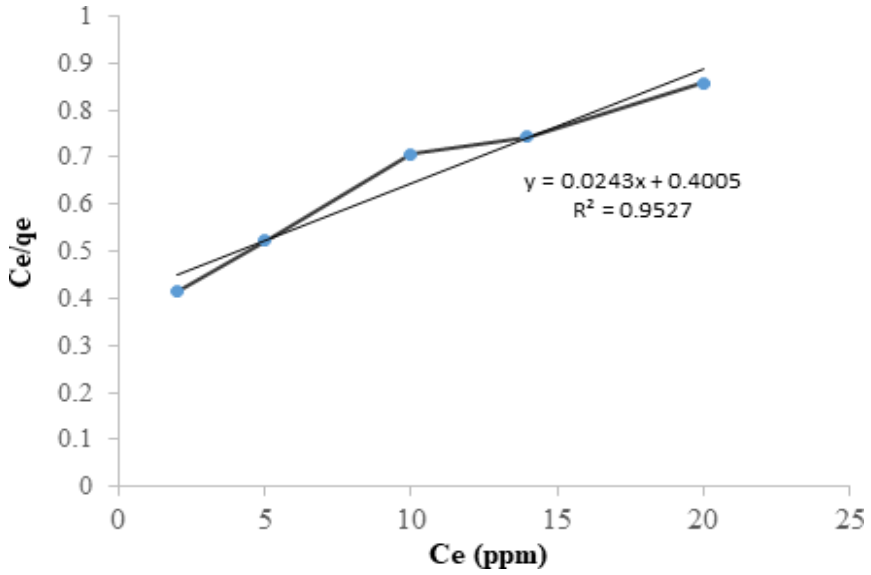

Figure 9: Langmuir isotherm in the case of AC

Table 2: Calculation of Langmuir parameters

Correlation Coefficient and Langmuir Constants			
	MSD	UMSD	AC
q_m	28.57	26.59	41.15
B	0.0316	0.0171	0.060
R^2	0.914	0.895	0.953

$$lnq_e = 1/n\ lnC_e + lnK_f \qquad (4)$$

In the event of a Freundlich isotherm, linear plots between lnCe and lnqe are also produced for all adsorbents as shown in Figure 10-12, and the values of correlation coefficient R^2 as shown in Table 4 depicts how closely the experimental equilibrium data match the Freundlich isotherm

(Al-Ghouti & Da'ana, 2020). In general, adsorption is advantageous for values in the range $1>1/n>0.1$. K_f values directly correlate with adsorption favorability (Ayawei et al., 2017; Boparai et al., 2011; Febrianto et al., 2009). The intercept (lnKf) and slop (1/n) from the graphed equation yield the values of 1/n and Kf

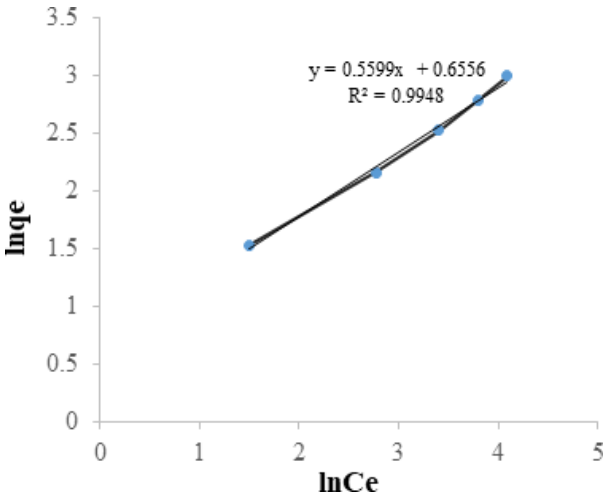

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Figure 10: Freundlich isotherm for MSD

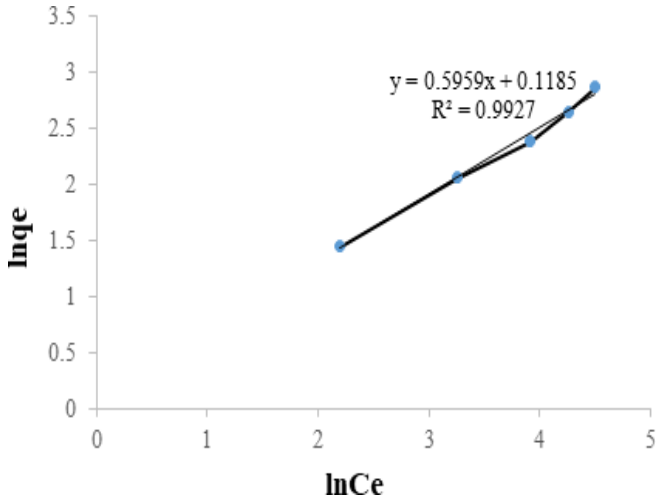

Figure 11: Freundlich isotherm for UMSD

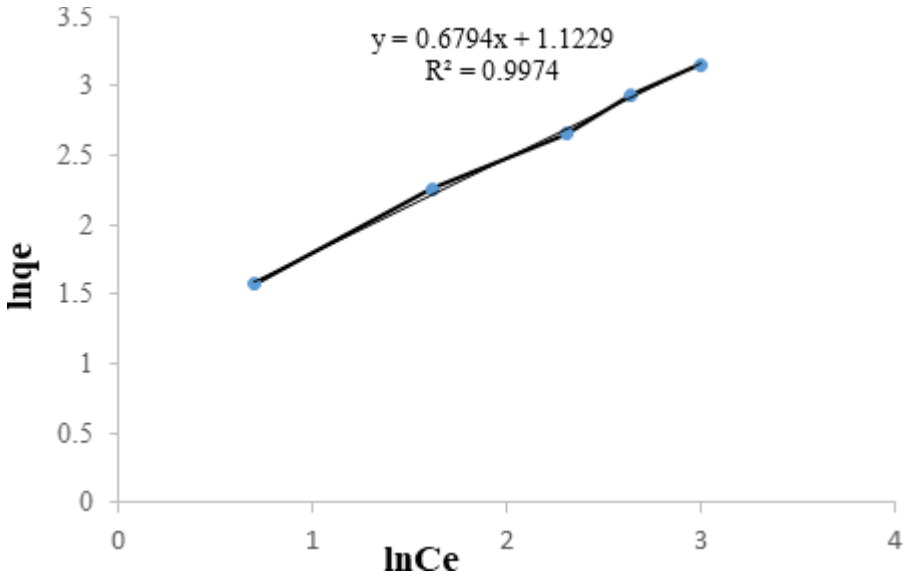

Figure 12: Freundlich Isotherm for AC

Table 3: Calculation of Freundlich Parameters

Correlation Coefficient and Freundlich Constants			
	MSD	UMSD	AC
K_f	1.926	1.126	3.074
1/n	0.5599	0.5959	0.6794
R^2	0.995	0.993	0.997

3.6 Characterization of Adsorbents

3.6.1 FTIR Analysis

Using an FTIR spectrophotometer, infrared spectra of UMSD, MSD and AC were obtained, revealing the chemistry of their surface in the wavenumber range of 4000 cm^{-1} to 500 cm^{-1}. The peak near 1000 cm^{-1} wavenumber indicates the presence of =C-H bond in all samples. Moreover, the slight peak around 2400 cm^{-1} presents the Carbon (C) in UMSD-1, MSD-2 and AC-1 as shown in Figure 13(Patel, 2018).

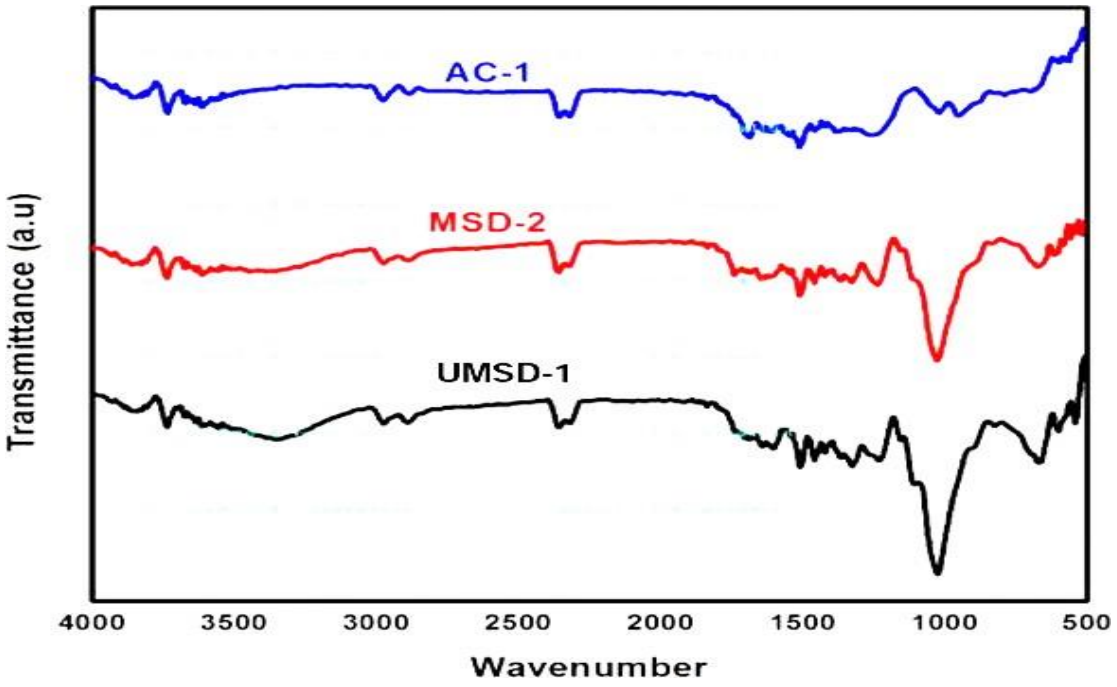

Figure 13: FTIR Analysis of AC, MSD and UMSD

3.6.2 SEM-EDX Analysis

Surface morphology of UMSD, MSD and AC was investigated by SEM analysis. According to SEM pictures, the activated charcoal and modified sawdust had distinct pores and holes because of the HCl activation as shown in Figure 14. This increased the adsorbents' surface area and allowed for the highest amount of Cr (VI) ions to be adsorbed. Therefore, AC have maximum adsorption performance among all adsorbents. Similarly, EDX analysis was usedto determine the elemental composition of MSD and AC, which are shown in Figure 15 and 16 respectively. Carbon have maximum Wt.% of 77.51 in the case of AC. Similarly, it is alsopresent in highest quantity in MSD that is 46.26 Wt.%. Meanwhile, Oxygen (O) and Silicon (Si) are present in 29.12 Wt.% and 1.96 Wt.% respectively in MSD. The results are shown in the Table 5 (Crini, 2006; Zhao & Xia, 2010) (Miao et al., 2022).

Table 4: Chemical Composition of AC

Elements	Wt.%	Atomic %	Net Int.
C	77.51	82.11	10112.83
O	22.49	17.89	1277.67

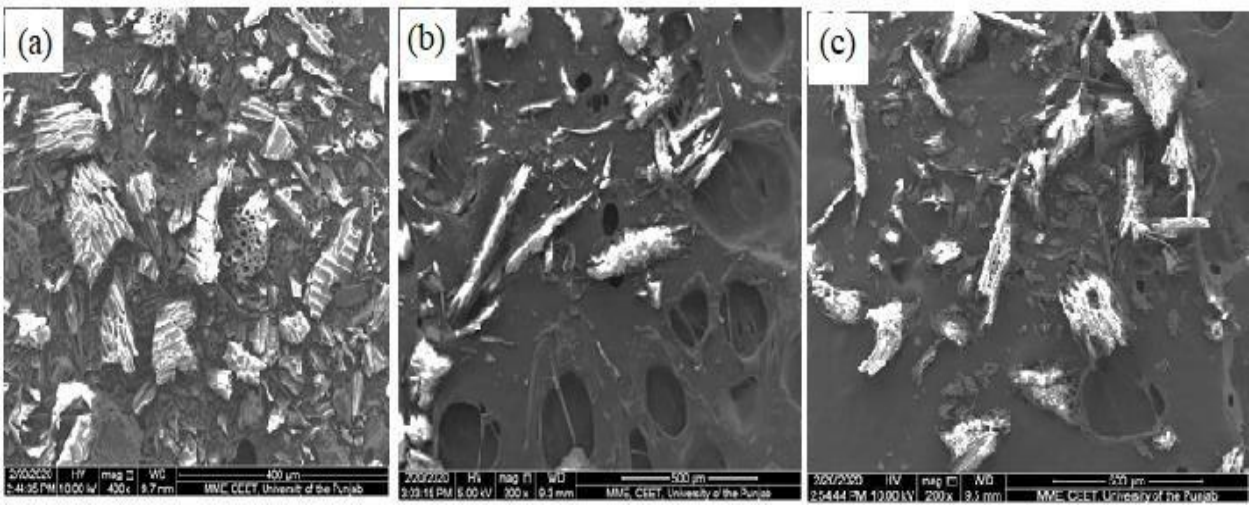

Figure 14: SEM Image of (a) AC (b) MSD (c) UMSD

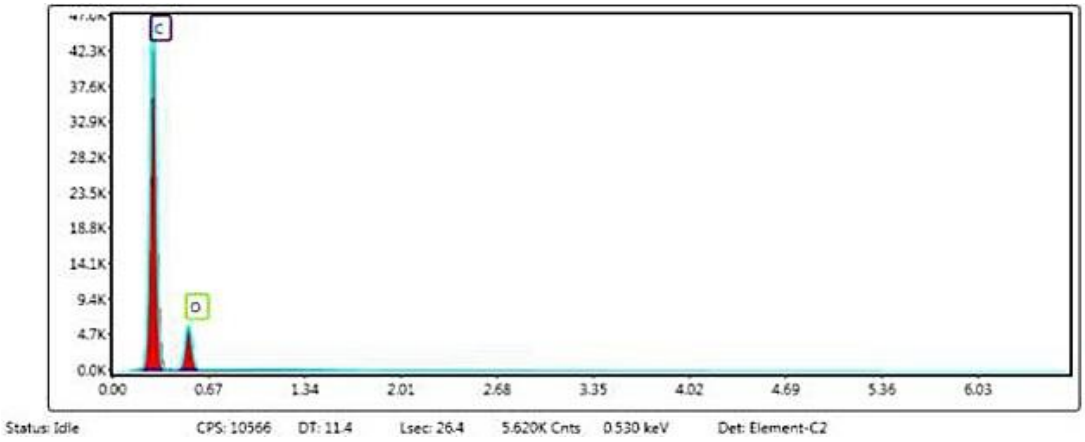

Figure 15: EDX Analysis of AC

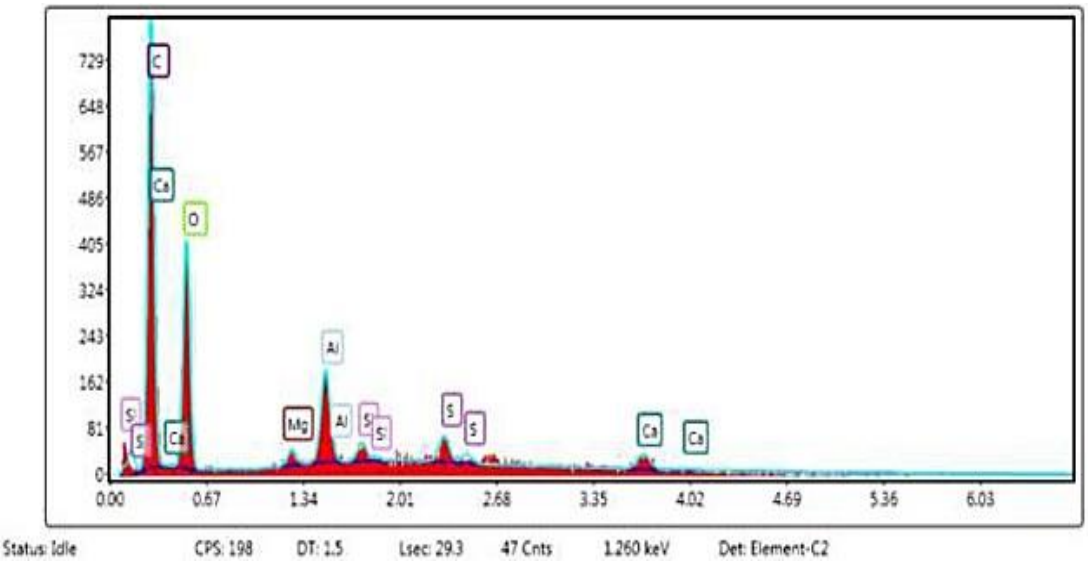

Figure 16: EDX Analysis of MSD

Table 5: Chemical Composition of MSD

Elements	**Wt.%**	**Atomic %**	**Net Int.**
C	46.26	59.54	134.02
O	29.12	28.14	80.84
Mg	1.28	0.81	6.27
Al	9.27	5.31	42.84
Si	1.96	1.08	8.41
S	4.57	2.2	14.37
Ca	7.55	2.91	10.07

CONCLUSION

In this study, UMSD and MSD were used in conjunction with AC made from Acacia and Sheesham wood to remove Cr(VI) ions from simulated wastewater. The results demonstrated that increased adsorbent dosage and contact time enhanced Cr(VI) removal, while higher initial Cr(VI) concentration and pH hindered it for all adsorbents. Evaluation using Langmuir and Freundlich isotherm models revealed that the Freundlich isotherm provided a significantly better fit for the experimental data (evidenced by a higher correlation coefficient, R^2) for all adsorbents. These findings suggest that MSD and AC derived from Acacia and Sheesham wood are promising, cost-effective adsorbents for Cr(VI) removal. Future research can explore their application in treating real industrial wastewater.

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