

# Low-Cost Biochar from *Parthenium hysterophorus* for Efficient Cr<sup>6+</sup> Removal: A Sustainable Wastewater Treatment Solution

## ABSTRACT

**Aims:** This study explores the development of innovative, cost-effective methods for removing Cr<sup>6+</sup> from wastewater, focusing on biochar derived from *Parthenium hysterophorus* shoots. The biochar was prepared using a conventional slow-pyrolysis process and evaluated for its potential to treat Cr<sup>6+</sup> in aqueous solutions.

**Study design:** Batch adsorption experiments are carried out in the study.

**Place and Duration of Study:** The study was conducted in the Department of Environmental Science, G B Pant University of Agriculture & Technology, between Feb 2024 and July 2024.

**Methodology:** *Parthenium hysterophorus* shoots were collected, reagents were purchased from Himedia, and Cr<sup>6+</sup> solutions were prepared and adjusted using NaOH and HCl. Shoots were washed, sun-dried, ground into powder and pyrolysed at 350°C for 180 minutes. Biochar yield was calculated, pH, proximal parameters (moisture, volatile matter, ash, fixed carbon) and ultimate analysis were measured, chemical functional groups by FTIR and morphology by XRD using Bruker D8 Advance was done. Cr<sup>6+</sup> removal was studied using biochar adsorbent under varying pH, initial Cr<sup>6+</sup> concentration, adsorbent dose and contact time, adsorption capacity (q) and removal percentage were then calculated.

**Results:** Characterization techniques such as Fourier Transform Infrared (FTIR) spectroscopy and X-Ray Diffraction (XRD) confirmed the presence of multiple functional groups and crystalline structures, which contribute to its adsorption efficiency. Batch adsorption experiments were conducted to investigate the influence of prepared biochar dosage, initial Cr<sup>6+</sup> concentration, pH and contact time. The optimal removal efficiency of 72.77% was achieved under conditions of pH 10, a biochar dose of 1 g/L, an initial Cr<sup>6+</sup> concentration of 30 mg/L and a contact time of 72 hours.

**Conclusion:** Although challenges remain in optimizing production and functionalization, this research highlights the potential of biochar for sustainable water treatment. Addressing production costs and practical challenges will further enhance its applicability, contributing to environmental sustainability efforts.

**Keywords:** adsorption, biochar, chromium, *Parthenium hysterophorus*, removal, sustainable.

## 1. INTRODUCTION

The increasing population and industrialisation are driving up the need for clean water. Water bodies in our ecosystem are under constant siege from industrial waste and human activities, threatening the delicate balance of life within them. A large quantity of organic and inorganic pollutants released from anthropogenic actions has defiled the nature of water resources at an exceedingly fast rate (Schweitzer and Noblet, 2018; Sivaranjane et al., 2022). Water pollution has become a major global concern, resulting in many areas lacking access to clean drinking water thus hindering to attain the goal number 6 of Sustainable Development Goals (SDGs) i.e. Clean Water of United Nations by 2030 (Carlsen and

**Comment [A1]:** "A large quantity of organic and inorganic pollutants released from anthropogenic actions" could be simplified to "Anthropogenic activities release large quantities of organic and inorganic pollutants," making the sentence more direct and clearer for your readers to understand.

Bruggemann, 2022). Water pollutants include various organic, microbiological and inorganic pollutants poses substantial environmental and human health risks (Mekonnen and Hoekstra, 2016). These pollutants are either man-made or naturally occurring compounds that enter the environment through freshwater sources and wastewater, mostly as a result of anthropogenic activities. The natural setting contains a wide range of pollutants, including antibiotics, pesticides, herbicides, microbes, steroid hormones, surfactants, pharmaceuticals, personal care products, food additives, preservatives, antibiotic resistance genes, industrial chemicals, detergents and heavy metals.

Rapid economic growth has raised concerns about heavy metal pollution, as industrial expansion and urbanization contribute to the heightened discharge of heavy metals into water bodies. These heavy metals, including lead, cadmium, arsenic, mercury, copper, zinc and chromium, in wastewater is well-known for their potential harm to human health due to their toxic nature (Grace-Pavithra et al., 2019; Lu et al., 2022). Among these heavy metals, chromium is extensively employed in industries (mining, leather tanning, textile dyeing, electroplating, aluminium conversion coating operations, plants producing industrial inorganic chemicals and pigments, and wood preservatives) contribute to water pollution which is known to be highly toxic even with low concentrations in water bodies and it is a potential mutagen (Costello et al., 2019; Lu et al., 2022; Swaroop et al., 2019; Udy, 1956). Chromium occurs most frequently as  $\text{Cr}^{3+}$  or  $\text{Cr}^{6+}$  in aqueous solutions. The two oxidation states have different chemical, biological and environmental properties.  $\text{Cr}^{3+}$  is relatively insoluble and an essential micronutrient (Saner, 1980), while  $\text{Cr}^{6+}$  is a primary contaminant because of its toxic effects to humans, animals, plants and microorganisms (Cieslak-Golonka, 1996). Chromium has widespread industrial applications; hence, large quantities of chromium are discharged into the environment and therefore the level of chromium in discharged wastewater should be reduced or recycled if possible (Dakiky et al., 2002).

Different treatment approaches have been developed and utilized for the treatment of  $\text{Cr}^{6+}$  contaminated wastewater which are broadly categorized under physio-chemical and biological approaches. The physio-chemical approach includes  $\text{Cr}^{6+}$  reduction via chemical precipitation, reduction, electro-chemical precipitation, solvent extraction, membrane separation, foam separation, freeze separation, cementation, evaporation, chemical precipitation, advanced oxidation processes, reverse osmosis, ion exchange, nano-filtration, adsorption, electrocoagulation, electrodialysis, etc. (Bibi et al., 2018; Chakravarti et al., 1995; Dahbi et al., 1999; Enaime et al., 2020; Fito et al., 2020; Kongsricharoern and Polprasert, 1996; Pagilla and Canter, 1999; Seaman et al., 1999; Tiravanti et al., 1997; Zhou et al., 1993) while the biological approach includes bio-sorption of  $\text{Cr}^{6+}$  using fungi, bacteria, algae, yeast, plant and other biological systems (Aksu and Kutsal, 1990; Ashraf et al., 2016; Pradhan et al., 2017; Shahid et al., 2017). The high expense of treatment, the massive amounts of toxic sludge produced, the high and expensive chemical requirements, the labour and energy-intensive nature of some of these procedures restrict the application of these methods (Bibi et al., 2018; Malaviya and Singh, 2016). Hence, the clean removal of  $\text{Cr}^{6+}$  from industrial wastewater treatment process is still a challenge due to improper technological selection from economical, technical and environmental aspects (GracePavithra et al., 2019). Therefore, it is imperative to employ low-cost, efficient and sustainable technologies for  $\text{Cr}^{6+}$  removal from wastewater.

Adsorption, in contrast to traditional techniques, is highly selective, practical and efficient approach and targets certain pollutants such as  $\text{Cr}^{6+}$ . This approach resolves the sludge disposal issues and increases the system's economic viability, particularly when low-cost adsorbents are employed (Bailey et al., 1999). It differs from other approaches due to its scalability and adaptability, simple processing and efficient removal of pollutants when compared to alternatives and therefore this technology is seen to be a suitable choice for

**Comment [A2]:** For clarity, goal 6 of the Sustainable Development Goals is often referred to as "Clean Water and Sanitation." Including "and Sanitation" would better reflect the official terminology and support the basis for your readers to understand the text.

**Comment [A3]:** This is a subject-verb agreement error. "Are" should be used

**Comment [A4]:** The phrase " $\text{Cr}^{3+}$  is relatively insoluble and an essential micronutrient" might be misleading, as  $\text{Cr}^{3+}$  is essential only in trace amounts, and excessive intake can still be harmful.

**Comment [A5]:** The term "physio-chemical" should be corrected to "physicochemical" (as "physio" relates to physical therapy rather than physical and chemical processes).

**Comment [A6]:** In the list of physicochemical approaches, "chemical precipitation" and "reduction" are mentioned twice, which is redundant.

**Comment [A7]:** The statement "Adsorption, in contrast to traditional techniques, is highly selective..." is inaccurate. Adsorption is typically *not* highly selective; it can adsorb a broad range of contaminants based on the adsorbent material's properties. Selectivity depends heavily on the type of adsorbent and may require further modification to target specific pollutants like

wastewater treatment, regardless of the size of the wastewater treatment project (Elwakeel et al., 2020; Gehrke et al., 2015; Kera et al., 2017). For the purpose of removing chromium from wastewater, a number of recent publications have used a variety of accessible and reasonably priced adsorbents. These include activated carbon, agricultural by-products, waste materials, charge minerals, iron-based adsorbents, zeolites, clay minerals, silica gel, biosorbents and biochar (Ahmed and Ram, 1992; Irshad et al., 2023; Leyva-Ramos et al., 1995; Namasivayam and Yamuna, 1995; Osias et al., 2019; Samantaroy et al., 1997; Singh et al., 1992). The kind of chromium present, the wastewater's pH, financial concerns and local availability are some of the factors that frequently influence the choice of adsorbent. Among these adsorbents, biochar is silver lining amid precarious Cr<sup>6+</sup> contamination of water when compared to the other contemporaries as it offers a high degree of viability in addition to a cheaper price and an easier-to-use functional plan.

**Comment [A8]:** "Charge minerals" is unclear terminology. It would be more precise to mention specific charged materials or ion-exchange resins if intended.

Biochar, a carbon-rich substance produced by pyrolysis of biomass in an inert environment has drawn interest as a potent wastewater adsorbent (Pokharel et al., 2020). Its unique properties which includes high surface area, porous structure, high adsorption capacity and high concentration of surface functionalities like -COOH, -OH, R-OH, phenols, quinones, etc., make it suitable for the removal of Cr<sup>6+</sup> ions from wastewater (Aichour et al., 2022; He et al., 2022). Biochar can be produced from a wide range of biomass feedstocks, including agricultural residues, forestry waste, organic sludge, tannery sludge, cauliflower stem waste, pinecone, banana peel, coffee husk and many other agro-residues (Chanda et al., 2024; Nguyen et al., 2021; Ihsanullah et al., 2022; Li et al., 2024; Masuku et al., 2024; Oyekanmami et al., 2019). Thus, there are lot of scopes for the study of low-cost biochar production and application for the treatment of wastewater contaminated by heavy metal particularly Cr<sup>6+</sup>. However, the literature is still insufficient to cover the Cr<sup>6+</sup> removal problem using biochar and therefore, more work and investigations are needed to deal with other locally available and cheap adsorbents to eliminate Cr<sup>6+</sup> from industrial wastewater samples with different compositions and characteristics.

The following study puts a projection of emphasis upon biochar obtained from *Parthenium hysterophorus* and their potential application in Cr<sup>6+</sup> adsorption from wastewater has not been studied so far. The invasive weed *P.hysterophorus* is a tropical and subtropical plant that is often regarded as a weed that hampers both the environment and biodiversity and is abundant and has no commercial value in most nations, creating global ecological, economic and agricultural issues. The allelopathic chemicals present in parthenium weed are mitigated during the conversion of the biomass into biochar (Kumar et al., 2013). According to studies, biochar made from *P.hysterophorus* has a high potential for absorbing a wide range of contaminants from wastewater. Few efforts have been undertaken to generate biochar from *P. hysterophorus* for industrial wastewater treatment, notably heavy metal such as Cr<sup>6+</sup> removal (Bapat and Jaspal, 2016; Singh et al., 2010). Conclusively, biochar derived from *P. hysterophorus* offer a dual-benefit approach for environmental remediation by tackling both invasive species management and wastewater treatment. They are viable candidates for sustainable practices that can contribute to the circular economy due to their significant pollutant absorption potential. Successfully integrating such innovative approaches could lead to more effective and environmentally friendly strategies for treating wastewater. Nevertheless, ongoing research is required to optimize synthesis processes and fully understand adsorption mechanisms, although initial findings are promising and could lead to future advancements in wastewater treatment.

**Comment [A9]:** The phrase "puts a projection of emphasis upon" is not too clear and not commonly used in scientific writing. A clearer phrasing could be "This study emphasizes" or "This study highlights."

**Comment [A10]:** The assertion that biochar from *P. hysterophorus* has a "high potential for absorbing a wide range of contaminants from wastewater" should be supported by specific data or references. General claims about high adsorption potential need quantitative backing or citation of studies demonstrating this capacity. Better still, add the citation to this claim.

The main objective of current study was to utilize the agro-waste *P.hysterophorus* to derive low-cost biochar adsorbent and apply it for the treatment of Cr<sup>6+</sup> in an aqueous solution. The specific objectives under the main objective were to (i) prepare biochar from *P.hysterophorus* by slow pyrolysis, (ii) investigate the properties, surface functional groups

and crystallinity of prepared biochar, (iii) assess the biochar performance to remediate  $\text{Cr}^{6+}$  from aqueous solution under various process conditions e.g. adsorbate concentration, pH, adsorbent dose and contact time.

## 2. MATERIAL AND METHODS

### 2.1 Chemicals and materials

Shoots of *Parthenium hysterophorus* was collected from different locations e.g. road sides, abandoned land, edges of unmanaged gardens within the premises of GBPUA&T, Pantnagar. All chemical reagents ( $\text{K}_2\text{Cr}_2\text{O}_7$ , HCl, NaOH, ethanol, etc.) are analytically pure and purchased from HiMedia Laboratories Private Limited. 2.83 g  $\text{K}_2\text{Cr}_2\text{O}_7$  salt was dissolved in deionised (DI) water to prepare 1000 mg/L of  $\text{Cr}^{6+}$ . All chromium solutions in this study were obtained by simulated solution dilution, and pH value of all solutions was adjusted with 0.1 N NaOH and 0.1 N HCl solutions.

### 2.2 Preparation of biochar from *Parthenium hysterophorus*

Initially, *Parthenium hysterophorus* shoots (PHS) were collected and washed with 70% (w/v) ethanol to remove out any organic contaminants. Then they were sun-dried for consecutive 20 days. The dried shoots were crushed into powered-sized particles by a mechanical grinder and put into a pyrolyser. The grounded shoots were pyrolysed at  $350^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . with 180 min. of residence time for biochar synthesis. The schematic preparation process of PHS-derived biochar is shown in Fig. 1.

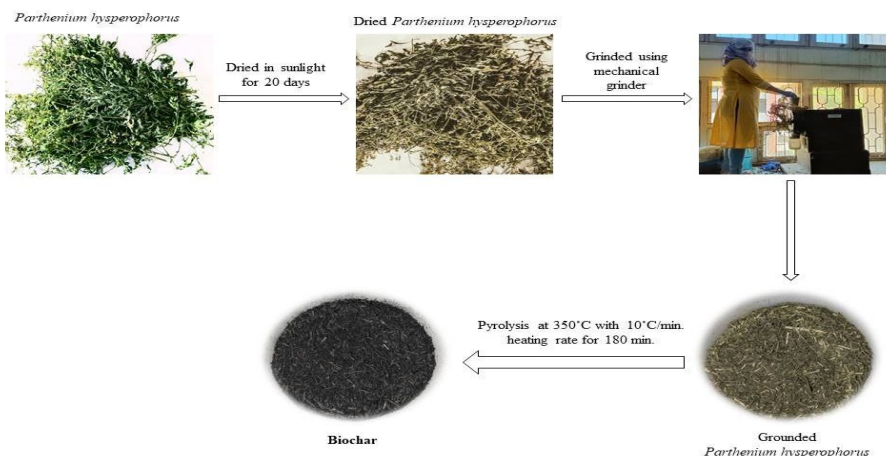


Fig. 1. Schematic diagram of the preparation of PHS-derived biochar.

### 2.3 Characterization of PHS-derived biochar

Yield of PHS-derived biochar was expressed as percentage weight of the amount of biochar obtained ( $W_B$ ) from the weight of the amount of grounded PHS feeded ( $W_F$ ) in the pyrolyser.

$$\text{Biochar Yield \%} = \frac{W_B}{W_F} \times 100 \quad (1)$$

The pH of the PHS-derived biochar was measured using Hach HQ4300 Portable Multiparameter, once oven-dried biochar was suspended in DI water (1:20) and shaken for three hours on a mechanical shaker (Rajkovich et al., 2011). The proximal parameters (moisture, volatile matter, ash and fixed carbon content all expressed in percentage) were measured using ASTM D1762-84 (2021). The ultimate analysis was done using a CHNS

elemental analyser (Model: VarioELcube). Chemical functional groups of PHS-derived biochar were evaluated by FTIR spectrum analysis. The spectra were recorded in the range of 4000-600  $\text{cm}^{-1}$  in transmission mode using FTIR-8400S spectrophotometer manufactured by Shimadzu. The morphology (crystalline or amorphous) of novel substances as well as the properties of crystals, such as the location, intensity, and number of diffraction lines, can be ascertained using X-ray diffraction (XRD) (Chen et al., 2003; Melamed et al., 2003). The test was carried out using a Bruker D8 Advance X-ray diffractometer that was equipped with a 2.2 kW Cu X-Ray source (40 kV/40 mA) and operated in the 10 to 90° angular theta range at a scan speed of 6°/min. Origin Pro 2024b was used to further examine the results.

## 2.4 Batch adsorption experiments

The batch adsorption studies for  $\text{Cr}^{6+}$  removal from wastewater through PHS-derived biochar adsorbent were done at the EIA laboratory of the Dept. of Environmental Science, GBPUA&T, Pantnagar (Uttarakhand, India). The prepared simulated solution of 1000 mg/L  $\text{Cr}^{6+}$  was used throughout the study to prepare the desired concentrations. Generally, the process of adsorption is affected by various parameters such as solution pH, initial concentration, adsorbent dosage, and contact time. Therefore, to obtain high adsorption performances, these parameters need to be well-optimized. Optimization in adsorption studies involves the change of one parameter at a time while keeping all other experimental parameters at fixed values. For the study, we first explored the effect of solution pH which was adjusted between 3 and 10 using either 0.1 M of HCl or 0.1 M NaOH which was followed by the biochar dose between 1 and 5 g/L. Thereafter, the influence of  $\text{Cr}^{6+}$  initial concentration and contact time was examined between 10 and 30 mg/L and 12 to 72 hrs, respectively. It is worth noting that throughout all the experiments, the agitation speed was maintained at 100 rpm. After completion of each parameter adsorption experiment, the solutions were filtered and the remaining solution of  $\text{Cr}^{6+}$  was analyzed at 540 nm by Thermo Scientific™ iCE™ 3500 AAS Atomic Absorption Spectrometer. Equation (2) was used to calculate the  $\text{Cr}^{6+}$  adsorption capacity (q) and Equation (3) was employed to determine the adsorbate removal percentage (%) (Masuku et al., 2024).

$$q = \frac{(C_o - C_e)V}{m} \quad (2)$$

$$\% \text{ Removal} = \frac{(C_o - C_e)100}{C_o} \quad (3)$$

Where,  $C_o$  is the initial  $\text{Cr}^{6+}$  concentration  $C_e$  is the final  $\text{Cr}^{6+}$  concentrations (mg/L), V is the volume of  $\text{Cr}^{6+}$  solution (L) and m is the mass of biochar (g).

## 3. RESULTS AND DISCUSSION

### 3.1 PHS-derived biochar properties

The biochar yield, pH, proximate and ultimate analysis of air dried sample of PHS-derived biochar as shown in Table 1 below. The pH of PHS-derived biochar is found to be slightly alkaline which is similar with confirms the findings of Irfan et al. in 2016 who explained this attribute because of the detachment of alkaline salts from organic compounds during pyrolysis. The volatile matter to fixed carbon ratio was calculated to be 1.05.

**Table 1. Characteristics of PHS-derived biochar.**

Biomass used	Pyrolysis conditions	Yield (%)	pH	Reference
PHS	350°C, 180 min.	36.35	8.9	This work

**Comment [A11]:** The phrase "prepared simulated solution of 1000 mg/L  $\text{Cr}^{6+}$ " should specify that this is a synthetic solution made to mimic wastewater conditions. Clarity on how this concentration was achieved (e.g., by dissolving a known quantity of a  $\text{Cr}^{6+}$  salt in a specific volume of water) would be beneficial. The use of "biochar dose" could be more clearly stated as "biochar dosage" or "amount of biochar used" to enhance clarity.

<i>Parthenium hysterophorus</i>		300°C, 30 min.			41	-	Kumar et al., 2013
Proximate analysis (% wt.)	Biomass used	Moisture content	Volatile matter content	Ash content	Fixed carbon content	Reference	
	PHS	8.33 ± 2	29.93 ± 3	33.21 ± 2	28.53 ± 3	This work	
	Geodae-Uksae 1	7.3	73.2	3.6	15.9	Lee et al., 2013	
Ultimate analysis (% wt.)	C	H	N	S	O	Equivalent to	Reference
	53.82	1.92	3.87	0.55	39.84	C <sub>1.00</sub> H <sub>0.04</sub> O <sub>0.74</sub> N <sub>0.07</sub> S <sub>0.01</sub>	This work
	47.6	5.5	0.8	-	46.1	C <sub>1.00</sub> H <sub>1.39</sub> O <sub>0.73</sub> N <sub>0.01</sub>	Lee et al., 2013

### 3.2 FTIR Analysis

The primary element influencing the adsorption of Cr<sup>6+</sup> in the PHS-derived biochar adsorbent is its surface functional groups (Zhou et al., 2020). Figure 2 displays the PHS-derived biochar's FTIR spectrum. According to Ozcimen and Ersoy-Mericboyu (2010) and Masuku et al. (2024), the peak at 624 cm<sup>-1</sup> and 678 cm<sup>-1</sup> band indicate the aromatic C–H deformation mode, indicating that the biochar was strongly carbonized. Bending vibrations of 775 cm<sup>-1</sup> and 865 cm<sup>-1</sup>, respectively, indicate the stretching of the C–O bond in the ether group and the pyridine group of heterocyclic nitrogen compounds (Qurat-ul-Ain et al., 2021). According to Qurat-ul-Ain et al. (2021) and Roy et al. (2022), the peak at 1006 cm<sup>-1</sup> indicates symmetric C–O stretching in aliphatic ether and alcohols or Si–O stretching. The lactone/carbonyl structure O=C–O vibration is shown by the peak at 1402 cm<sup>-1</sup> (He et al., 2018). According to Roy et al. (2022), the conjugated ketones and quinones' aromatic C=C and C=O stretching modes are represented by the peaks at 1550 cm<sup>-1</sup> and 1781 cm<sup>-1</sup>. Peak measured at 1975 cm<sup>-1</sup> corresponds to the functional group allene (–C=C=C). Another peak, which matches closely to the thiocyanate (–S–C≡N) functional group, was also seen at 2075 cm<sup>-1</sup>. For various aliphatic groups in the PHS-derived biochar, small absorption bands at 2360 cm<sup>-1</sup>, 2602 cm<sup>-1</sup>, 2699 cm<sup>-1</sup>, 2737 cm<sup>-1</sup>, and 2874 cm<sup>-1</sup> show the stretching vibration of the C–H out of the plain (Bhatlu et al., 2023; Liu et al., 2019). Peaks located at 3045, 3084, and 3162 cm<sup>-1</sup> respectively denote the =C–H functional group. O–H stretching vibrations of hydroxyl groups are responsible for the broad peaks seen at 3262 cm<sup>-1</sup>, 3343 cm<sup>-1</sup>, 3487 cm<sup>-1</sup>, 3524 cm<sup>-1</sup>, 3622 cm<sup>-1</sup> and 3661 cm<sup>-1</sup> (Roy et al., 2022).

**Comment [A12]:** The peak at 1006 cm<sup>-1</sup> is associated with C–O stretching in aliphatic ethers and alcohols or Si–O stretching. However, without additional analysis (e.g., SEM-EDX for elemental composition), it's speculative to confirm Si–O bonds, especially since silicon may not be present in biochar unless it is explicitly added or derived from silica-rich precursors.

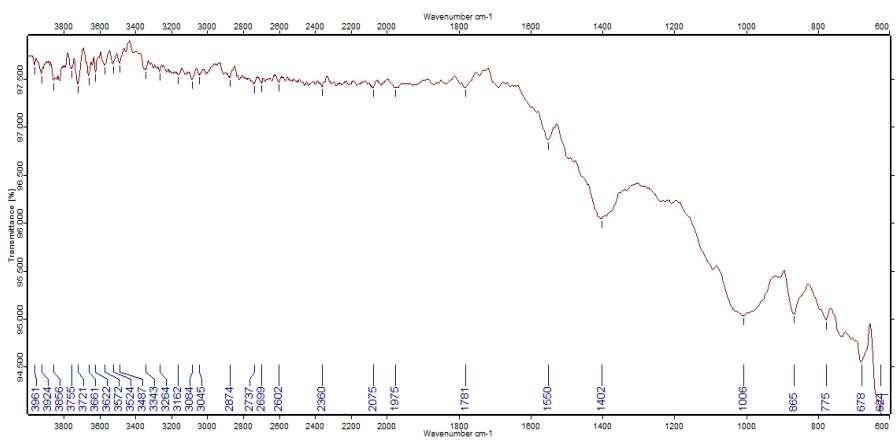


Fig. 2. The FTIR spectra of PHS-derived biochar.

### 3.3 XRD Analysis

Figure 3 displays 12 diffraction peaks at  $2\theta$  of  $\cdot 21.66^\circ$ ,  $\cdot 26.84^\circ$ ,  $\cdot 28.68^\circ$ ,  $\cdot 29.98^\circ$ ,  $\cdot 31.24^\circ$ ,  $\cdot 36.24^\circ$ ,  $\cdot 40.86^\circ$ ,  $\cdot 43.56^\circ$ ,  $\cdot 50.48^\circ$ ,  $\cdot 58.9^\circ$ ,  $\cdot 66.64^\circ$  and  $\cdot 73.92^\circ$ . Sylvite (KCl at  $2\theta = 28.68^\circ$ ,  $40.86^\circ$ ,  $50.48^\circ$ ,  $58.9^\circ$  and  $66.64^\circ$ ), arcanite ( $K_2SO_4$  at  $2\theta = 21.66^\circ$ ,  $29.98^\circ$ ,  $31.24^\circ$ ,  $43.56^\circ$ ), quartz ( $SiO_2$  at  $2\theta = 21.66^\circ$ ,  $26.84^\circ$ ,  $36.24^\circ$ ,  $50.48^\circ$ ), and calcite ( $2\theta = 29.98^\circ$ ) were identified in the XRD spectrum of PHS-derived biochar. High sylvite levels in the biochar are suggested by the strong peaks at  $28.68^\circ$  and  $40.86^\circ$  (Shafiq and Capareda, 2021).

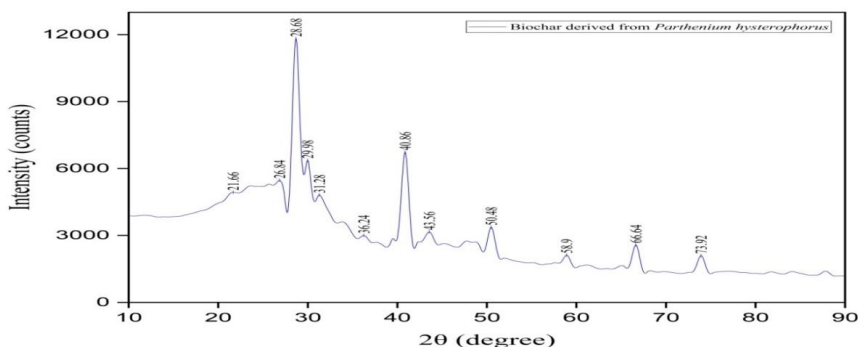


Fig. 3. The XRD spectra of PHS-derived biochar.

### 3.4 Adsorption of $Cr^{6+}$

#### 3.4.1 Effect of solution pH

Using the prepared PHS-derived biochar adsorbent for adsorption of  $\text{Cr}^{6+}$  from wastewater, the study investigated the pH from 3 to 10. During the pH investigation, all other parameters including initial concentration, biochar dose, temperature and contact time were kept constant constant at 20 mg/L, 1 g/L, 25°C and 24 hrs, respectively. Figure 4a demonstrates the uptake of  $\text{Cr}^{6+}$  onto the adsorbent and it was clear that adsorption was pH-dependent. In figure 4a, it is clear that adsorption capacity ( $q$ ) and % removal decrease with the increase in pH. It can be explained as in general,  $\text{Cr}^{6+}$  is an oxyanion in solution where the predominate species in solution are hydrogen chromate ( $\text{HCrO}_4^{2-}$ ) and chromate ( $\text{CrO}_4^{3-}$ ) between pH 1–6 and pH > 6, respectively (Herath et al., 2021) and therefore it is evident from figure 4a that the biochar adsorbent adsorbed well at a low pH (acidic pH) due to electrostatic attraction between the  $\text{H}^+$  ions and chromate ions. As the pH rises to 10 the biochar adsorbent removed less of the  $\text{Cr}^{6+}$  which could be because the biochar surface is more negatively charged ( $\text{OH}^-$  predominates) and repelling the  $\text{CrO}_4^{2-}$  anion. This outcome agrees with previously investigated chromium removal using other biochar adsorbents (Herath et al., 2021; Masuku, 2024; Qhubu et al., 2022).

### 3.4.2 Effect of $\text{Cr}^{6+}$ concentration

The adsorption of  $\text{Cr}^{6+}$  onto manufactured biochar adsorbent was tested in batch adsorption experiments, starting with concentrations of 10, 15, 20, 25 and 30 mg/L. The other variables, which included pH, the biochar dose, temperature, and contact duration, were all continuously maintained at 7, 3 g/L, 25°C and 48 hours, respectively. When the starting concentration of  $\text{Cr}^{6+}$  pollutant was increased from 10 to 30 mg/L, as shown in figure 4b, the percentage removal decreased from 7.31 to 56.93%. This result could be due to the more active sites (and therefore high surface area to volume ratio) on the surface of PHS-derived biochar than any other adsorbents which facilitates  $\text{Cr}^{6+}$  adsorption (Khamseh et al., 2023). However, when  $\text{Cr}^{6+}$  concentrations rises, fewer PHS-derived biochar active sites (adsorption sites are filled) are available to the  $\text{Cr}^{6+}$  ion; as a result, figure 4b shows a reduction in the percentage removal. The adsorption capacity rose from 0.24 to 5.69 mg/g when the initial  $\text{Cr}^{6+}$  concentration was raised from 10 to 30 mg/L. It is observed that raising the initial  $\text{Cr}^{6+}$  concentration can result in a larger amount of adsorption and an improvement in the adsorption rate. Masuku and colleagues saw a similar pattern, attributing the rise in adsorption capacity to the biochar adsorbent's increased availability of active sites for the adsorption of  $\text{Cr}^{6+}$  ions (Masuku et al., 2021; Masuku et al., 2024).

### 3.4.3 Effect of contact time

According to Hasan et al. (2023), contact time is one of the crucial elements that directly affect the  $\text{Cr}^{6+}$  adsorption. The following was the experimental setup for the study's time of contact: biochar dose: 1 g/L, pH 4, temperature: 25°C and variable contact time: 12–72 hrs. Three steps of adsorption were found when examining figure 4c. The first step lasted for 24 hrs where PHS-derived biochar adsorbent was found to quickly adsorb the  $\text{Cr}^{6+}$  ions because the adsorbent had more empty active sites and a higher chemical potential difference between the biochar dose and  $\text{Cr}^{6+}$  ions. Thus, the mass transfer was driven by a substantial concentration differential (Masuku et al., 2021; Staron et al., 2023). The second step is marked by steady increase in  $\text{Cr}^{6+}$  adsorption over the course of 24 to 48 hrs. This may be because of less interaction of PHS-derived biochar with  $\text{Cr}^{6+}$  and the adsorption may have only taken place by the top layers, leaving the buried layers out of the process. However, in the final stage, the biochar's absorption of  $\text{Cr}^{6+}$  increased rapidly after 48 to 72 hours (Isik et al., 2023; Lala et al., 2023). The % removal of  $\text{Cr}^{6+}$  increased steadily as contact time increased. The contact time increased, giving the  $\text{Cr}^{6+}$  ions sufficient time to interact with the PHS-derived biochar (Shafique et al., 2012).

**Comment [A13]:** The paragraph states that "adsorption capacity ( $q$ ) and % removal decrease with the increase in pH." This is accurate, but it lacks an explanation of why both values decrease. Typically, lower pH conditions favor the adsorption of Cr(VI) oxyanions due to increased positive surface charges on the biochar, which facilitates electrostatic attraction with negatively charged Cr(VI) ions.

**Comment [A14]:** The statement, "the percentage removal decreased from 7.31 to 56.93%" as  $\text{Cr}^{6+}$  concentration increased from 10 to 30 mg/L, appears to be incorrect based on typical adsorption behavior. Generally, percentage removal tends to decrease as initial concentration increases, not increase. If the percentage removal is indeed increasing, this should be clarified and supported, as it contradicts the usual trend due to limited active sites at higher concentrations.

**Comment [A15]:** The text first attributes high percentage removal to biochar's surface properties, but then says percentage removal decreases because of fewer available sites at higher  $\text{Cr}^{6+}$  concentrations. This is confusing and should be streamlined. The correct interpretation is that at lower concentrations, more  $\text{Cr}^{6+}$  ions can be captured by the available sites, resulting in high percentage removal. As concentration increases, the same fixed amount of biochar has relatively fewer active sites available per  $\text{Cr}^{6+}$  ion, so the percentage removal typically decreases.

**Comment [A16]:** The term "higher chemical potential difference between the biochar dose and  $\text{Cr}^{6+}$  ions" is incorrect. Adsorption does not occur due to a chemical potential difference between the "biochar dose" and  $\text{Cr}^{6+}$  ions but rather due to the concentration gradient between the solution and the biochar surface. The driving force for adsorption is typically the concentration difference between  $\text{Cr}^{6+}$  ions in solution and on the biochar surface.

**Comment [A17]:** The description implies that adsorption suddenly accelerates in the final stage, which contradicts typical adsorption kinetics. By this stage, adsorption usually tapers off as equilibrium is reached. Rapid adsorption in the later stages would be unusual and should be clarified if observed.

### 3.4.4 Effect of adsorbate dose

The impact of PHS-derived biochar adsorbent dose on the adsorption of  $\text{Cr}^{6+}$  from wastewater is depicted in figure 4d. The study included a range of biochar doses, ranging from 1 to 5 g/L. Other parameters i.e. initial  $\text{Cr}^{6+}$  concentration, temperature, pH and time, were held constant at 10 mg/L, 25°C, pH 10 and 48 hrs, respectively. As the biochar dose increased the value of  $q$  dropped from 3.40 to 0.81 mg/g, this is because the active sites are more exposed at low biochar dose and the  $\text{Cr}^{6+}$  ions may more readily occupy them, resulting in the reported adsorption capacity. However, while examining the percentage removal for  $\text{Cr}^{6+}$  by biochar adsorbent, it was found that the % removal rose from 34 to 40.63% when the biochar dose was increased. This could be because the amount of accessible active sites in the biochar was closely correlated with its adsorption capacity ( $q$ ). Watwe et al. (2023) and Mondal et al. (2016) showed similar outcomes when using biochar adsorbent to treat wastewater containing  $\text{Cr}^{6+}$  and ibuprofen, respectively.

**Comment [A18]:** The statement "As the biochar dose increased the value of  $q$  dropped from 3.40 to 0.81 mg/g, this is because the active sites are more exposed at low biochar dose and the  $\text{Cr}^{6+}$  ions may more readily occupy them" is misleading. The decrease in adsorption capacity ( $q$ ) with increasing adsorbent dose is typically due to a dilution effect. As the adsorbent dose increases, the number of available active sites increases, but the concentration of  $\text{Cr}^{6+}$  ions per gram of adsorbent decreases, resulting in a lower  $q$  value (adsorption capacity per gram of biochar).

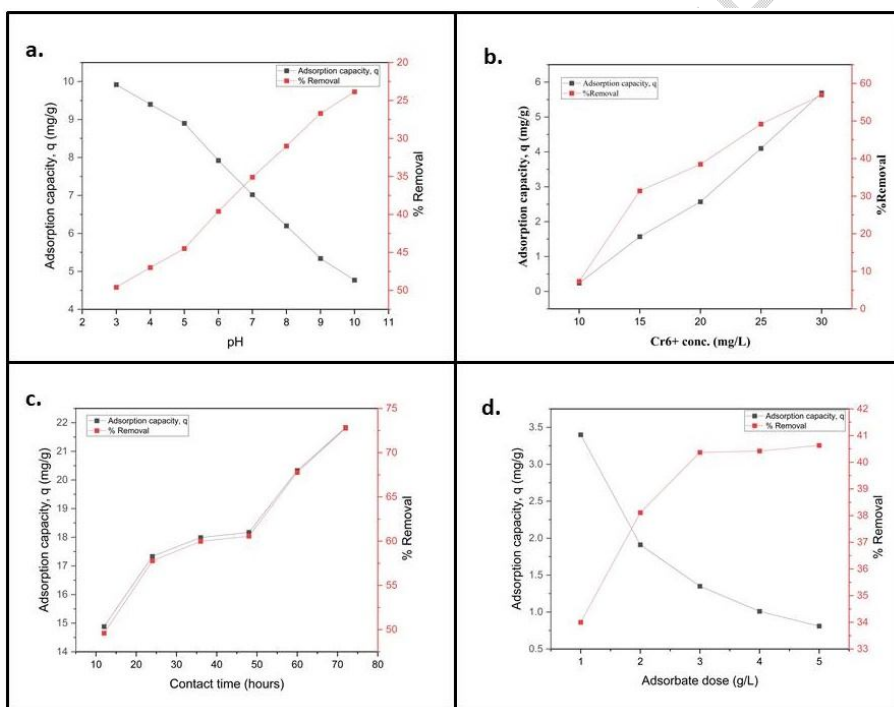


Fig. 4. The effect of (a) pH (b)  $\text{Cr}^{6+}$  conc. (c) contact time (d) adsorbate dose on  $\text{Cr}^{6+}$  adsorption onto prepared PHS-derived biochar.

## 4. CONCLUSION

The development of a green biochar and the use of low biochar mass in application studies can be economically feasible. PHS-derived biochar used in this study's slow-pyrolysis method. The biochar's balanced elemental makeup, slightly alkaline pH, and

considerable moisture, ash, and carbon content are all in line with findings from previous research on pyrolysis products. The varied surface functional groups of PHS-derived biochar are the main factor influencing the adsorption of  $\text{Cr}^{6+}$ , as demonstrated by FTIR spectrum. The presence of sylvite, arcanite, quartz and calcite is shown by XRD spectrum of PHS-derived biochar; the presence of strong sylvite peaks indicates high potassium content. The initial  $\text{Cr}^{6+}$  concentration and solution pH have a major impact on the adsorption of  $\text{Cr}^{6+}$  onto PHS-derived biochar; more electrostatic attraction leads to optimum adsorption at lower pH levels. Furthermore, adsorption capacity is initially increased when initial  $\text{Cr}^{6+}$  concentrations increases while % removal decreases due to active site saturation. Contact time affects the adsorption of  $\text{Cr}^{6+}$  by PHS-derived biochar; adsorption is quick during the first 24 hrs and then gradually increases, underscoring the need of having enough interaction time for efficient adsorption. Furthermore, the adsorption capacity drops as a result of active site saturation, even increasing the biochar dose increases the % removal of  $\text{Cr}^{6+}$ . This suggests that there is an ideal biochar dose for optimizing efficiency. This study shows that PHS-derived biochar has promising potential as an economical and effective adsorbent for removing  $\text{Cr}^{6+}$  from wastewater. The results highlight the PHS-derived biochar's potential as a sustainable option for enhancing water quality and assisting with environmental sustainable activities, even though more manufacturing and functionalization optimization is required.

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