

Low-Cost Biochar from *Partheniumhysterophorus* for Efficient Cr⁶⁺ Removal: A Sustainable Wastewater Treatment Solution

ABSTRACT

Aims: This study explores the development of innovative, cost-effective methods for removing Cr⁶⁺ from wastewater, focusing on biochar derived from *Partheniumhysterophorus* shoots. The biochar was prepared using a conventional slow-pyrolysis process and evaluated for its potential to treat Cr⁶⁺ 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: *Partheniumhysterophorus* shoots were collected, reagents were purchased from HiMedia, and Cr⁶⁺ 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. Cr⁶⁺ removal was studied using biochar adsorbent under varying pH, initial Cr⁶⁺ 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 Cr⁶⁺ 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 Cr⁶⁺ 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, *Partheniumhysterophorus*, 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 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 Cr^{3+} or Cr^{6+} in aqueous solutions. The two oxidation states have different chemical, biological and environmental properties. Cr^{3+} is relatively insoluble and an essential micronutrient (Saner, 1980), while 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 Cr^{6+} contaminated wastewater which are broadly categorized under physio-chemical and biological approaches. The physio-chemical approach includes 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; Kongsricharoen 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 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 Cr^{6+} from industrial wastewater treatment process is still a challenge due to improper technological selection from economical, technical and environmental aspects (Grace-Pavithra et al., 2019). Therefore, it is imperative to employ low-cost, efficient and sustainable technologies for Cr^{6+} removal from wastewater.

Adsorption, in contrast to traditional techniques, is highly selective, practical and efficient approach and targets certain pollutants such as 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 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 Cr⁶⁺ 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.

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 Cr⁶⁺ 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 Cr⁶⁺. However, the literature is still insufficient to cover the Cr⁶⁺ removal problem using biochar and therefore, more work and investigations are needed to deal with other locally available and cheap adsorbents to eliminate Cr⁶⁺ 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 Cr⁶⁺ 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 Cr⁶⁺ 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.

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 Cr⁶⁺ 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 Cr⁶⁺ 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 *Partheniumhysterophorus* 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 (K₂Cr₂O₇, HCl, NaOH, ethanol, etc.) are analytically pure and purchased from HiMedia Laboratories Private Limited. 2.83 g K₂Cr₂O₇ salt was dissolved in deionised (DI) water to prepare 1000 mg/L of Cr⁶⁺. 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 Partheniumhysterophorus

Initially, *Partheniumhysterophorus* 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°C at a heating rate of 10°C/min. with 180 min. of residence time for biochar synthesis. The schematic preparation process of PHS-derived biochar is shown in Fig. 1.

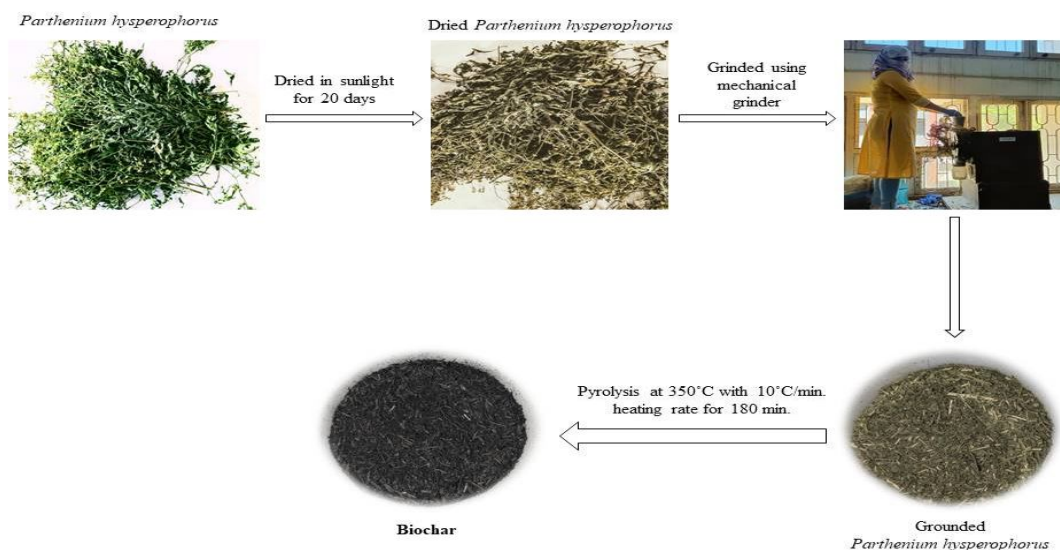


Fig. 1. Schematic diagram of the preparation of PHS-derived biochar.

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 fed (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 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 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 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 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 Cr^{6+} was analyzed at 540 nm by Thermo Scientific™ iCE™ 3500 AAS Atomic Absorption Spectrometer. Equation (2) was used to calculate the Cr^{6+} adsorption capacity (q) and Equation (3) was employed to determine the adsorbate removal percentage (%) (Masuku et al., 2024).

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

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

Where, C_o is the initial Cr^{6+} concentration C_e is the final Cr^{6+} concentrations (mg/L), V is the volume of 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

<i>Partheniumhyster ophorus</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 _{1.00} H _{0.04} O _{0.74} N _{0.07} S _{0.01}	This work
	47.6	5.5	0.8	-	46.1	C _{1.00} H _{1.39} O _{0.73} N _{0.01}	Lee et al., 2013

3.2 FTIR Analysis

The primary element influencing the adsorption of Cr⁶⁺ 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⁻¹ and 678 cm⁻¹ band indicate the aromatic C–H deformation mode, indicating that the biochar was strongly carbonized. Bending vibrations of 775 cm⁻¹ and 865 cm⁻¹, 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⁻¹ 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⁻¹ (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⁻¹ and 1781 cm⁻¹. Peak measured at 1975 cm⁻¹ 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⁻¹. For various aliphatic groups in the PHS-derived biochar, small absorption bands at 2360 cm⁻¹, 2602 cm⁻¹, 2699 cm⁻¹, 2737 cm⁻¹, and 2874 cm⁻¹ show the stretching vibration of the C–H out of the plane (Bhatlu et al., 2023; Liu et al., 2019). Peaks located at 3045, 3084, and 3162 cm⁻¹ respectively denote the =C–H functional group. O–H stretching vibrations of hydroxyl groups are responsible for the broad peaks seen at 3262 cm⁻¹, 3343 cm⁻¹, 3487 cm⁻¹, 3524 cm⁻¹, 3622 cm⁻¹ and 3661 cm⁻¹ (Roy et al., 2022).

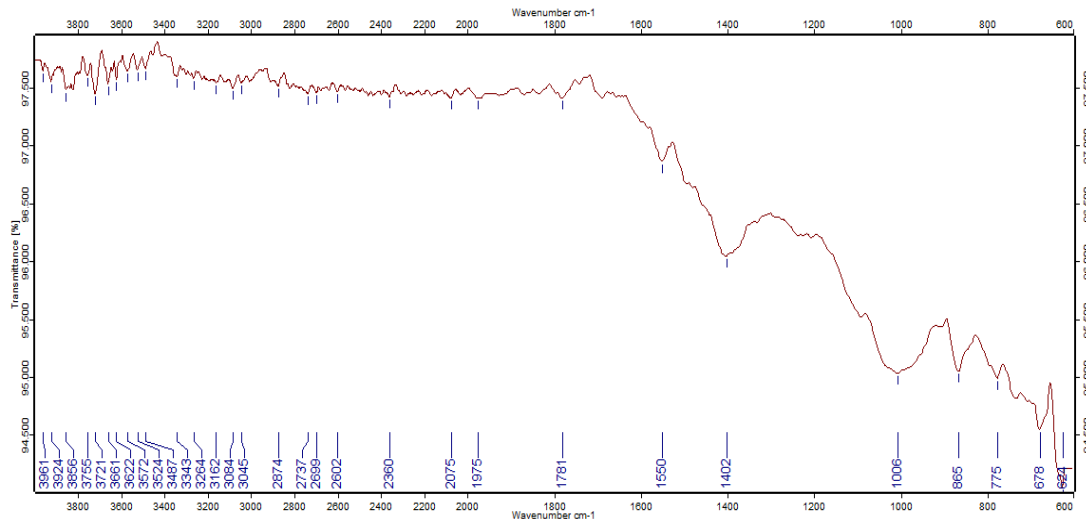


Fig. 2.The FTIR spectra of PHS-derived biochar.

3.3 XRD Analysis

Figure 3 displays 12 diffraction peaks at 2θ 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° , 50.48° , 58.9° and 66.64°), arcanite (K_2SO_4 at $2\theta = 21.66^\circ$, 29.98° , 31.24° , 43.56°), quartz (SiO_2 at $2\theta = 21.66^\circ$, 26.84° , 36.24° , 50.48°), 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° and 40.86° (Shafiq and Capareda, 2021).

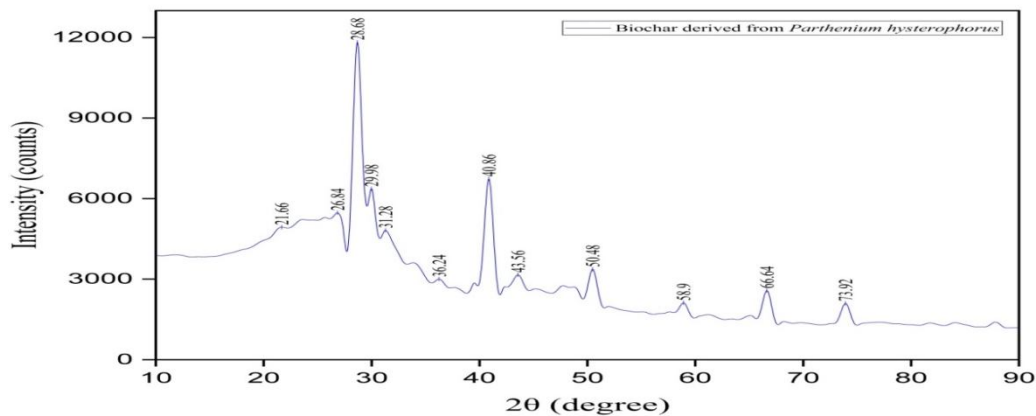


Fig. 3.The XRD spectra of PHS-derived biochar.

3.4 Adsorption of Cr^{6+}

3.4.1 Effect of solution pH

Using the prepared PHS-derived biochar adsorbent for adsorption of 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 at 20 mg/L, 1 g/L, 25°C and 24 hrs, respectively. Figure 4a demonstrates the uptake of 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, Cr^{6+} is an oxyanion in solution where the predominate species in solution are hydrogen chromate (HCrO_4^{2-}) and chromate (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 H^+ ions and chromate ions. As the pH rises to 10 the biochar adsorbent removed less of the Cr^{6+} which could be because the biochar surface is more negatively charged (OH^- predominates) and repelling the 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 Cr^{6+} concentration

The adsorption of 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 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 Cr^{6+} adsorption (Khamseh et al., 2023). However, when Cr^{6+} concentrations rises, fewer PHS-derived biochar active sites (adsorption sites are filled) are available to the 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 Cr^{6+} concentration was raised from 10 to 30 mg/L. It is observed that raising the initial 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 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 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 Cr^{6+} ions because the adsorbent had more empty active sites and a higher chemical potential difference between the biochar dose and Cr^{6+} ions. Thus, the mass transfer was driven by a substantial concentration differential (Masuku et al., 2021; Staro'n et al., 2023). The second step is marked by steady increase in Cr^{6+} adsorption over the course of 24 to 48 hrs. This may be because of less interaction of PHS-derived biochar with 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 Cr^{6+} increased rapidly after 48 to 72 hours (Isik et al., 2023; Lala et al., 2023). The % removal of Cr^{6+} increased steadily as contact time increased. The contact time increased, giving the Cr^{6+} ions sufficient time to interact with the PHS-derived biochar (Shafique et al., 2012).

3.4.4 Effect of adsorbate dose

The impact of PHS-derived biochar adsorbent dose on the adsorption of 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 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 Cr^{6+} ions may more readily occupy them, resulting in the reported adsorption capacity. However, while examining the percentage removal for 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 Cr^{6+} and ibuprofen, respectively.

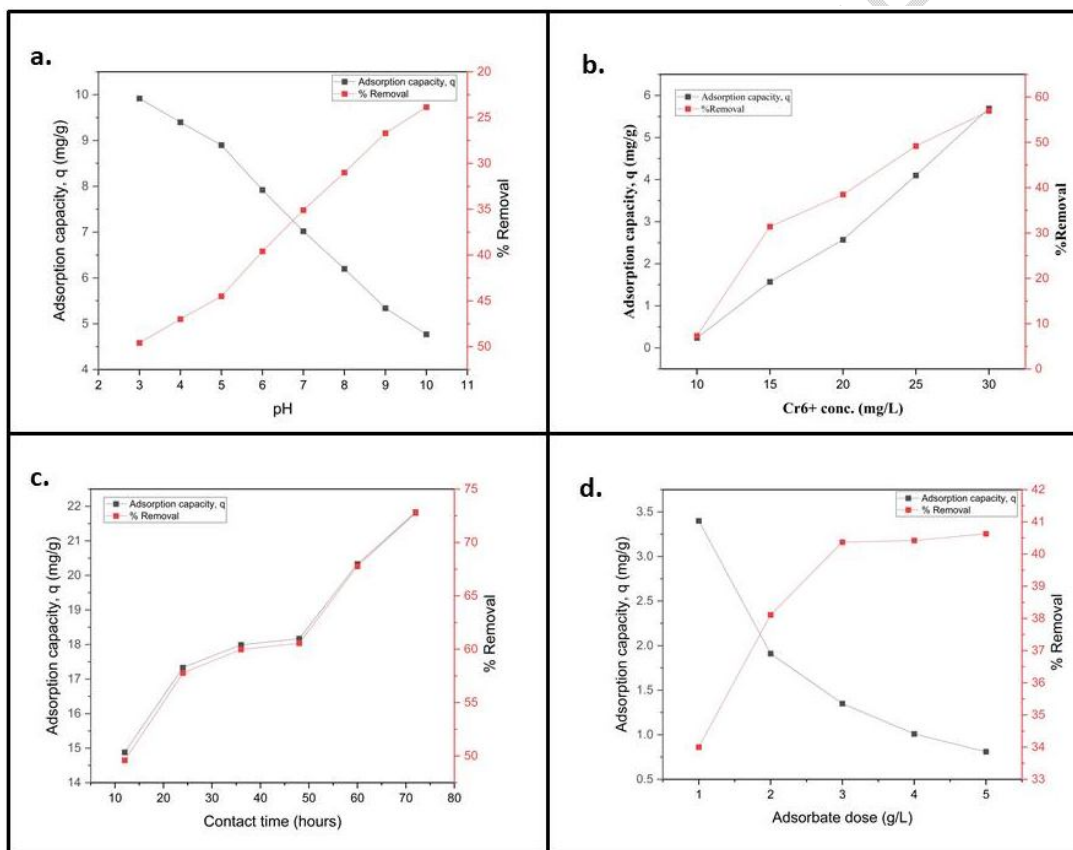


Fig. 4. The effect of (a) pH (b) Cr^{6+} conc. (c) contact time (d) adsorbate dose on Cr^{6+} adsorption onto prepared PHS-derived biochar.

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 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 Cr^{6+} concentration and solution pH have a major impact on the adsorption of 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 Cr^{6+} concentrations increases while % removal decreases due to active site saturation. Contact time affects the adsorption of 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 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 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.

Disclaimer (Artificial intelligence)

Author(s) hereby declare that no generative AI technologies and text-to-image generators have been used during the writing or editing of this manuscript: "Nishtha Naudiyal declares that there is no use of generative AI technologies and text-to-image generators such as large language models (chatGPT, copilot, etc.)"

REFERENCES

Schweitzer, L., & Noblet, J. (2018). Water contamination and pollution. In B. Torok & T. Dransfield (Eds.), *Green Chemistry* (pp. 261-290). <https://doi.org/10.1016/B978-0-12-809270-5.00011-X>.

Sivaranjane, R., Kumar, P. S., & Mahalaxmi, S. (2022). A review on agro-based materials on the separation of environmental pollutants from water system.

Chemical Engineering Research and Design, 181, 423-457. <https://doi.org/10.1016/j.cherd.2022.04.002>.

Carlsen, L., & Bruggemann, R. (2022). The 17 United Nations' sustainable development goals: A status by 2020. *International Journal of Sustainable Development & World Ecology*, 29(3), 219-229. <https://doi.org/10.1080/13504509.2021.1948456>.

Mekonnen, M. M., & Hoekstra, A. Y. (2016). Four billion people facing severe water scarcity. *Science Advances*, 2(2), e1500323. [10.1126/sciadv.1500323](https://doi.org/10.1126/sciadv.1500323).

Grace Pavithra, K., Jaikumar, V., Kumar, P. S., & SundarRajan, P. (2019). A review on cleaner strategies for chromium industrial wastewater: present research and future perspective. *Journal of Cleaner Production*, 228, 580-593. <https://doi.org/10.1016/j.jclepro.2019.04.117>.

Lu, Y., Cai, Y., Zhang, S., Zhuang, L., Hu, B., Wang, S., et al. (2022). Application of biochar-based photocatalysts for adsorption-(photo) degradation/reduction of environmental contaminants: mechanism, challenges and perspective. *Biochar*, 4(1), 45. <https://doi.org/10.1007/s42773-022-00173-y>.

Costello, R. B., Dwyer, J. T., & Merkel, J. M. (2019). Chromium Supplements in Health and Disease. In J. B. Vincent (Eds.), *The Nutritional Biochemistry of Chromium (III)* (2nd ed., pp. 219-249). <https://doi.org/10.1016/B978-0-444-64121-2.00007-6>.

Swaroop, A., Bagchi, M., Preuss, H. G., Zafra-Stone, S., Ahmad, T., & Bagchi, D. (2019). Benefits of chromium (III) complexes in animal and human health. In J. B. Vincent (Eds.), *The Nutritional Biochemistry of Chromium (III)* (2nd ed., pp. 251-278). <https://doi.org/10.1016/B978-0-444-64121-2.00008-8>.

Udy, M. J. (1956). Recovery of chromium from its ores. *Chromium*. New York, USA: Reinhold-USGS (United States Geological Survey), 3-4.

Saner, G. (1980). *Chromium in nutrition and disease*. Alan R Liss Inc, New York.

Cieslak-Golonka, M. (1996). Toxic and mutagenic effects of chromium (VI): a review. *Polyhedron*, 15(21), 3667-3689. [https://doi.org/10.1016/0277-5387\(96\)00141-6](https://doi.org/10.1016/0277-5387(96)00141-6).

Dakiky, M., Khamis, M., Manassra, A., & Mer'Eb, M. (2002). Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. *Advances in environmental research*, 6(4), 533-540. [https://doi.org/10.1016/S1093-0191\(01\)00079-X](https://doi.org/10.1016/S1093-0191(01)00079-X).

Bibi, I., Niazi, N. K., Choppala, G., & Burton, E. D. (2018). Chromium (VI) removal by siderite (FeCO₃) in anoxic aqueous solutions: an X-ray absorption spectroscopy investigation. *Science of the Total Environment*, 640, 1424-1431. <https://doi.org/10.1016/j.scitotenv.2018.06.003>.

Chakravarti, A. K., Chowdhury, S. B., Chakrabarty, S., Chakrabarty, T., & Mukherjee, D. C. (1995). Liquid membrane multiple emulsion process of chromium (VI) separation from waste waters. *Colloids and surfaces A: Physicochemical and engineering aspects*, 103(1-2), 59-71. [https://doi.org/10.1016/0927-7757\(95\)03201-N](https://doi.org/10.1016/0927-7757(95)03201-N).

Dahbi, S., Azzi, M., & De la Guardia, M. (1999). Removal of hexavalent chromium from wastewaters by bone charcoal. *Fresenius' journal of analytical chemistry*, 363, 404-407. <https://doi.org/10.1007/s002160051210>.

Enaime, G., Baçaoui, A., Yaacoubi, A., & Lübken, M. (2020). Biochar for wastewater treatment—conversion technologies and applications. *Applied Sciences*, 10(10), 3492. <https://doi.org/10.3390/app10103492>.

Fito, J., Abrham, S., & Angassa, K. (2020). Adsorption of methylene blue from textile industrial wastewater onto activated carbon of *Parthenium hysterophorus*. *International Journal of Environmental Research*, 14, 501-511. <https://doi.org/10.1007/s41742-020-00273-2>.

Kongsricharoern, N., & Polprasert, C. (1996). Chromium removal by a bipolar electrochemical precipitation process. *Water Science and Technology*, 34(9), 109-116. [https://doi.org/10.1016/S0273-1223\(96\)00793-7](https://doi.org/10.1016/S0273-1223(96)00793-7).

Pagilla, K. R., & Canter, L. W. (1999). Laboratory studies on remediation of chromium-contaminated soils. *Journal of Environmental Engineering*, 125(3), 243-248. [https://doi.org/10.1061/\(ASCE\)0733-9372\(1999\)125:3\(243\)](https://doi.org/10.1061/(ASCE)0733-9372(1999)125:3(243)).

Seaman, J. C., Bertsch, P. M., & Schwallie, L. (1999). In situ Cr (VI) reduction within coarse-textured, oxide-coated soil and aquifer systems using Fe (II) solutions. *Environ Sci Tech*. 33(6), 938-944. <https://doi.org/10.1021/es980546+>.

Tiravanti, G., Petruzzelli, D., & Passino, R. (1997). Pretreatment of tannery wastewaters by an ion exchange process for Cr (III) removal and recovery. *Water Science and Technology*, 36(2-3), 197-207. [https://doi.org/10.1016/S0273-1223\(97\)00388-0](https://doi.org/10.1016/S0273-1223(97)00388-0).

Zhou, X., Korenaga, T., Takahashi, T., Moriwake, T. & Shinoda, S. (1993). A process monitoring controlling system for the treatment of wastewater containing chromium (VI). *Water Research*, 27(6), 1049-1054. [https://doi.org/10.1016/0043-1354\(93\)90069-T](https://doi.org/10.1016/0043-1354(93)90069-T).

Aksu, Z., & Kutsal, T. (1990). A comparative study for biosorption characteristics of heavy metal ions with *C. vulgaris*. *Environmental Technology*, 11(10), 979-987. <https://doi.org/10.1080/09593339009384950>.

Ashraf, A., Bibi, I., Niazi, N. K., Ok, Y. S., Murtaza, G., Shahid, M., et al. (2017). Chromium (VI) sorption efficiency of acid-activated banana peel over organo-montmorillonite in aqueous solutions. *International journal of phytoremediation*, 19(7), 605-613. <https://doi.org/10.1080/15226514.2016.1256372>.

Pradhan, D., Sukla, L. B., Sawyer, M., & Rahman, P. K. (2017). Recent bioreduction of hexavalent chromium in wastewater treatment: a review. *Journal of Industrial and Engineering Chemistry*, 55, 1-20. <https://doi.org/10.1016/j.jiec.2017.06.040>.

Shahid, M., Shamsad, S., Rafiq, M., Khalid, S., Bibi, I., Niazi, N. K., et al. (2017). Chromium speciation, bioavailability, uptake, toxicity and detoxification in soil-plant system: a review. *Chemosphere*, 178, 513-533. <https://doi.org/10.1016/j.chemosphere.2017.03.074>.

Malaviya, P. & Singh, A. (2016). Bioremediation of chromium solutions and chromium containing wastewaters. *Critical Reviews in Microbiology*, 42(4), 607-633. <https://doi.org/10.3109/1040841X.2014.974501>.

Bailey, S. E., Olin, T. J., Bricka, R. M., & Adrian, D. D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water research*, 33(11), 2469-2479. [https://doi.org/10.1016/S0043-1354\(98\)00475-8](https://doi.org/10.1016/S0043-1354(98)00475-8).

Elwakeel, K. Z., Elgarahy, A. M., Khan, Z. A., Almughamisi, M. S., & Al-Bogami, A. S. (2020). Perspectives regarding metal/mineral-incorporating materials for water purification: with special focus on Cr (VI) removal. *Materials Advances*, 1(6), 1546-1574. [10.1039/D0MA00153H](https://doi.org/10.1039/D0MA00153H).

Gehrke, I., Geiser, A., & Somborn-Schulz, A. (2015). Innovations in nanotechnology for water treatment. *Nanotechnology, science and applications*, 8, 1-17.

Kera, N. H., Bhaumik, M., Pillay, K., Ray, S. S., & Maity, A. (2017). Selective removal of toxic Cr (VI) from aqueous solution by adsorption combined with reduction at a magnetic nanocomposite surface. *Journal of Colloid and Interface Science*, 503, 214-228. <https://doi.org/10.1016/j.jcis.2017.05.018>.

Ahmed, M. N., & Ram, R. N. (1992). Removal of basic dye from waste-water using silica as adsorbent. *Environmental pollution*, 77(1), 79-86. [https://doi.org/10.1016/0269-7491\(92\)90161-3](https://doi.org/10.1016/0269-7491(92)90161-3).

Irshad, M. A., Sattar, S., Nawaz, R., Al-Hussain, S. A., Rizwan, M., Bukhari, A., et al. (2023). Enhancing chromium removal and recovery from industrial wastewater using sustainable and efficient nanomaterial: a review. *Ecotoxicology and Environmental Safety*, 263(115231), 10-16. <https://doi.org/10.1016/j.ecoenv.2023.115231>.

Leyva-Ramos, R., Fuentes-Rubio, L., Guerrero-Coronado, R. M., & Mendoza-Barron, J. (1995). Adsorption of trivalent chromium from aqueous solutions onto activated carbon. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental and Clean Technology*, 62(1), 64-67. <https://doi.org/10.1002/jctb.280620110>.

Namasivayam, C., & Yamuna, R. T. (1995). Adsorption of chromium (VI) by a low-cost adsorbent: biogas residual slurry. *Chemosphere*, 30(3), 561-578. [https://doi.org/10.1016/0045-6535\(94\)00418-T](https://doi.org/10.1016/0045-6535(94)00418-T).

Osias, J. M. L., Chen, Y. C., Lin, D. Y., Shih, Y. C., Caparanga, A. R., & Chen, B. H. (2019, October). Degradation of methylene blue utilizing cobalt-impregnated zeolite beta via sulfate radical-based advanced oxidation process. In *IOP Conference Series: Earth and Environmental Science* (344(1), pp. 012041). IOP Publishing.

Samantaroy, S., Mohanty, A. K., & Misra, M. (1997). Removal of hexavalent chromium by Kendu fruit gum dust. *Journal of Applied Polymer Science*, 66(8), 1485-1494. [https://doi.org/10.1002/\(SICI\)1097-4628\(19971121\)66:8<1485::AID-APP9>3.0.CO;2-A](https://doi.org/10.1002/(SICI)1097-4628(19971121)66:8<1485::AID-APP9>3.0.CO;2-A).

Singh, D. B., Rupainwar, D. C., & Prasad, G. (1992). Studies on the removal of Cr (VI) from waste-water by feldspar. *Journal of Chemical Technology & Biotechnology*, 53(2), 127-131. <https://doi.org/10.1002/jctb.280530204>

Pokharel, A., Acharya, B., & Farooque, A. (2020). Biochar-assisted wastewater treatment and waste valorization. Applications of biochar for environmental safety, 19. <https://doi.org/10.5772/intechopen.92288>.

Aichour, A., Zaghouane-Boudiaf, H., & Khodja, H. D. (2022). Highly removal of anionic dye from aqueous medium using a promising biochar derived from date palm petioles: Characterization, adsorption properties and reuse studies. *Arabian Journal of Chemistry*, 15(1), 103542. <https://doi.org/10.1016/j.arabjc.2021.103542>.

He, M., Xu, Z., Hou, D., Gao, B., Cao, X., Ok, Y. S., et al. (2022). Waste-derived biochar for water pollution control and sustainable development. *Nature Reviews Earth & Environment*, 3(7), 444-460. <https://doi.org/10.1038/s43017-022-00306-8>.

Chanda, R. K., Jahid, T., Hassan, M. N., Yeasmin, T., & Biswas, B. K. (2024). Cauliflower stem-derived biochar for effective adsorption and reduction of hexavalent chromium in synthetic wastewater: A sustainable approach. *Environmental Advances*, 15, 100458. <https://doi.org/10.1016/j.envadv.2023.100458>.

Nguyen, X. C., Nguyen, T. T. H., Nguyen, T. H. C., Van Le, Q., Vo, T. Y. B., Tran, T. C. P., et al. (2021). Sustainable carbonaceous biochar adsorbents derived from agro-wastes and invasive plants for cation dye adsorption from water. *Chemosphere*, 282, 131009. <https://doi.org/10.1016/j.chemosphere.2021.131009>.

Ihsanullah, I., Khan, M. T., Zubair, M., Bilal, M., & Sajid, M. (2022). Removal of pharmaceuticals from water using sewage sludge-derived biochar: A review. *Chemosphere*, 289, 133196. <https://doi.org/10.1016/j.chemosphere.2021.133196>.

Li, Z., Yu, D., Wang, X., Liu, X., Xu, Z., & Wang, Y. (2024). A novel strategy of tannery sludge disposal—converting into biochar and reusing for Cr (VI) removal from tannery wastewater. *Journal of environmental sciences*, 138, 637-649. <https://doi.org/10.1016/j.jes.2023.04.014>.

Masuku, M., Nure, J. F., Atagana, H. I., Hlongwa, N., & Nkambule, T. T. (2024). Pinecone biochar for the Adsorption of chromium (VI) from wastewater: Kinetics, thermodynamics, and adsorbent regeneration. *Environmental Research*, 258, 119423. <https://doi.org/10.1016/j.envres.2024.119423>.

Oyekanmi, A. A., Ahmad, A., Hossain, K., & Rafatullah, M. (2019). Adsorption of Rhodamine B dye from aqueous solution onto acid treated banana peel: Response surface methodology, kinetics and isotherm studies. *PLoS One*, 14(5), e0216878. <https://doi.org/10.1371/journal.pone.0216878>.

Kumar, S., Masto, R. E., Ram, L. C., Sarkar, P., George, J., & Selvi, V. A. (2013). Biochar preparation from *Parthenium hysterophorus* and its potential use in soil application. *Ecological Engineering*, 55, 67-72. <https://doi.org/10.1016/j.ecoleng.2013.02.011>.

Bapat, S. A., & Jaspal, D. K. (2016). *Parthenium hysterophorus*: Novel adsorbent for the removal of heavy metals and dyes. *Global Journal of Environmental Science and Management*, 2(2), 135-144. doi: 10.7508/gjesm.2016.02.004.

Singh, B., Singh, B. P., & Cowie, A. L. (2010). Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Research*, 48(7), 516-525. <https://doi.org/10.1071/SR10058>.

Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A. R., & Lehmann, J. (2012). Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and fertility of soils*, 48, 271-284. <https://doi.org/10.1007/s00374-011-0624-7>.

Chen, M., Ma, L. Q., Singh, S. P., Cao, R. X., & Melamed, R. (2003). Field demonstration of in situ immobilization of soil Pb using P amendments. *Advances in Environmental Research*, 8(1), 93-102. [https://doi.org/10.1016/S1093-0191\(02\)00145-4](https://doi.org/10.1016/S1093-0191(02)00145-4).

Melamed, R., Cao, X., Chen, M., & Ma, L. Q. (2003). Field assessment of lead immobilization in a contaminated soil after phosphate application. *Science of the Total Environment*, 305(1-3), 117-127. [https://doi.org/10.1016/S0048-9697\(02\)00469-2](https://doi.org/10.1016/S0048-9697(02)00469-2).

Irfan, M., Chen, Q., Yue, Y., Pang, R., Lin, Q., Zhao, X., & Chen, H. (2016). Co-production of biochar, bio-oil and syngas from halophyte grass (*Achnatherum splendens* L.) under three different pyrolysis temperatures. *Bioresource Technology*, 211, 457-463. <https://doi.org/10.1016/j.biortech.2016.03.077>.

Zhou, R., Zhang, M., Li, J., & Zhao, W. (2020). Optimization of preparation conditions for biochar derived from water hyacinth by using response surface methodology (RSM) and its application in Pb²⁺ removal. *Journal of Environmental Chemical Engineering*, 8(5), 104198. <https://doi.org/10.1016/j.jece.2020.104198>.

Özçimen, D., & Ersoy-Meriçboyu, A. (2010). Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renewable energy*, 35(6), 1319-1324. <https://doi.org/10.1016/j.renene.2009.11.042>.

Qurat-ul-Ain, Shafiq, M., Capareda, S. C., & Firdaus-e-Bareen. (2021). Effect of different temperatures on the properties of pyrolysis products of *Parthenium hysterophorus*. *Journal of Saudi Chemical Society*, Volume 25, Issue 3, 101197. <https://doi.org/10.1016/j.jscs.2021.101197>.

Roy, H., Prantika, T. R., Riyad, M. H., Paul, S., & Islam, M. S. (2022). Synthesis, characterizations, and RSM analysis of Citrus macroptera peel derived biochar for textile dye treatment. *South African Journal of Chemical Engineering*, 41, 129-139. <https://doi.org/10.1016/j.sajce.2022.05.008>.

Laxmi Deepak Bhatlu, M., Athira, P. S., Jayan, N., Barik, D., & Dennison, M. S. (2023). Preparation of breadfruit leaf biochar for the application of Congo red dye removal from aqueous solution and optimization of factors by RSM-BBD. *Adsorption Science & Technology*, 2023, 7369027. <https://doi.org/10.1155/2023/7369027>.

Liu, X., Liao, J., Song, H., Yang, Y., Guan, C., & Zhang, Z. (2019). A biochar-based route for environmentally friendly controlled release of nitrogen: urea-loaded biochar and bentonite composite. *Scientific reports*, 9(1), 9548. <https://doi.org/10.1038/s41598-019-46065-3>.

Shafiq, M., & Capareda, S. C. (2021). Effect of different temperatures on the properties of pyrolysis products of *Parthenium hysterophorus*. *Journal of Saudi Chemical Society*, 25(3), 101197. <https://doi.org/10.1016/j.jscs.2021.101197>.

Herath, A., Layne, C. A., Perez, F., Hassan, E. B., Pittman Jr, C. U., & Mlsna, T. E. (2021). KOH-activated high surface area Douglas Fir biochar for adsorbing aqueous Cr (VI), Pb (II) and Cd (II). *Chemosphere*, 269, 128409. <https://doi.org/10.1016/j.chemosphere.2020.128409>.

Qhubu, M. C., Methula, B., Xaba, T., Moyo, M., & Pakade, V. E. (2022). Iron-zinc impregnated biochar composite as a promising adsorbent for toxic hexavalent chromium remediation: kinetics, isotherms and thermodynamics. *Chemistry Africa*, 5(6), 1797-1807. <https://doi.org/10.1007/s42250-021-00273-5>.

Masuku, M., Ouma, L., & Pholosi, A. (2021). Microwave assisted synthesis of oleic acid modified magnetite nanoparticles for benzene adsorption. *Environmental Nanotechnology, Monitoring & Management*, 15, 100429. <https://doi.org/10.1016/j.enmm.2021.100429>.

Hasan, M. M., Salman, M. S., Hasan, M. N., Rehan, A. I., Awual, M. E., Rasee, A. I., et al. (2023). Facial conjugate adsorbent for sustainable Pb (II) ion monitoring and removal from contaminated water. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 673, 131794. <https://doi.org/10.1016/j.colsurfa.2023.131794>.

Staroń, P., Kuciakowski, J., & Chwastowski, J. (2023). Biocomposite of hydrochar and Lindnerajadinii with magnetic properties for adsorptive removal of cadmium ions. *Journal of Environmental Chemical Engineering*, 11(3), 110270. <https://doi.org/10.1016/j.jece.2023.110270>.

Isik, B., Avci, S., Cakar, F., & Cankurtaran, O. (2023). Adsorptive removal of hazardous dye (crystal violet) using bay leaves (*Laurus nobilis* L.): surface characterization, batch adsorption

studies, and statistical analysis. *Environmental Science and Pollution Research*, 30(1), 1333-1356. <https://doi.org/10.1007/s11356-022-22278-4>.

Lala, M. A., Ntamu, T. E., Adesina, O. A., Popoola, L. T., Yusuff, A. S., & Adeyi, A. A. (2023). Adsorption of hexavalent chromium from aqueous solution using cationic modified rice husk: Parametric optimization via Taguchi design approach. *Scientific African*, 20, e01633. <https://doi.org/10.1016/j.sciaf.2023.e01633>.

Shafique, U., Ijaz, A., Salman, M., uzZaman, W., Jamil, N., Rehman, R., & Javaid, A. (2012). Removal of arsenic from water using pine leaves. *Journal of the Taiwan Institute of Chemical Engineers*, 43(2), 256-263. <https://doi.org/10.1016/j.jtice.2011.10.006>.

Watwe, V., Kulkarni, S., & Kulkarni, P. (2023). Development of dried uncharred leaves of *Ficus benjamina* as a novel adsorbent for cationic dyes: Kinetics, isotherm, and batch optimization. *Industrial Crops and Products*, 195, 116449. <https://doi.org/10.1016/j.indcrop.2023.116449>.

Mondal, S., Bobde, K., Aikat, K., & Halder, G. (2016). Biosorptive uptake of ibuprofen by steam activated biochar derived from mung bean husk: equilibrium, kinetics, thermodynamics, modeling and eco-toxicological studies. *Journal of environmental management*, 182, 581-594. <https://doi.org/10.1016/j.jenvman.2016.08.018>.

UNDER PEER REVIEW