APPLICATIONS OFBIOCHAR AS A SUSTAINABLE OPTION TO REMOVE HEAVY METALS FROM INDUSTRIAL EFFLUENT

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ABSTRACT: Application of biochar for the treatment of wastewater is found to be highly competent and innovative method. Natural adsorbents are formed by heating organic waste in the absence of oxygen at higher temperature.The aim of this study was to evaluate the efficiency of co-pyrolyzed biochar as an adsorbent for the mitigation of toxic effluents emitted from industrial wastewater.The proximate analysis of biochar revealed that the moisture, volatile, ashand fixed carbon content were found to be12%, 27%, 17.6% and 65.1%, respectively. The concentration of the heavy metals (Cr, Cu, Ni, As, Hg and Zn) were analyzed inwastewater samples by employing an atomic absorption spectrometer (AAS).Batch experiment was conducted for the adsorption process as a function for dosage concentration (0.1,0.5 and 1g), contact time (30, 60 and 90 minutes) and pH (3,5 and 7). AAS was employed for the determination of final concentration of heavy metals. The maximum removal of Cr (VI) (97.1%) and Pb (87.8%) was noticed with an adsorbent dose of 1g/L, at 90 minutes contact time and pH of the solution was 5.Based on experimental results, it can be established that biochar produced by co-pyrolysis of sugarcane bagasse and rice husk can be considered as an efficient and environment friendly adsorbent for the treatment of wastewater containing toxic heavy metals.

Keywords: Adsorption; heavy metals; lead and chromium, wastewater treatment, biochar.

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INTRODUCTION

Modern manufacturing is regarded as a sign of advancement, despite the fact that its everyday effects are sometimes concealed. As a byproduct of some production processes, industrial wastewater is invariably a mixture of contaminants(Aman et al., 2008).Lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr), nickel (Ni) and arsenic (As) are among the heavy metals that linger in environmental cycles and enter living things, influencing ecosystem structures and human well-being (Juturu et al., 2024).

Water scarcity, or the lack of sufficient water in a given area, is regarded as one of the most important issues facing contemporary society and is a global issue. The primary causes of water scarcity include insufficient rainfall brought on by climate change, as well as the frequent and careless use of water in homes, businessesand agriculture (Ezeonuegbu et al., 2021). To create practical and long-lasting solutions, governments, organizations and other stakeholders must work together to address the issue (Behera and Samal, 2022).

The process by which natural waters get contaminated with different substances is known as water pollution (Yang et al., 2021). It can be caused by a variety of sources, including oil and industries that deal with products that primarily contain a combination of oil and other substances, waste from mines and cities, and organic and inorganic wastes released into these water sources by industrial establishments, agricultural cultivators and home sewage systems(Juturu et al., 2024). Human health and well-being are negatively impacted by this pollution, which also disrupts the food chain and damages aquatic life and habitats. Diseases and illnesses are linked to this kind of pollution (Yang et al., 2021).

Many metal items, cables, pipes, paints and herbicides have been known to contain Pb. Amongthe metals, Pb heavy metal has the highest detrimental consequences on the health of people (Manyàet al.,2018). By upsetting the delicate antioxidant equilibrium of mammalian cells,Pbinduces oxidative stress and plays a role in the pathophysiology of Pb poisoning. Anemia, colic, headaches, brain damage and central nervous system disordersare all brought on by high levels of Pb buildup in the body HaqandAshraf (2023).

Agricultural waste is the byproduct produced during the cultivation and processing of a variety of agricultural goods, including dairy products, fruits, vegetables and crops. Agricultural waste produced depends on the agricultural practices and harvesting conditions that can affect how these wastes are made. Certain agricultural wastes are mostly made up of cellulosic compounds with essential oils and fatty acids; others are rich in lignocellulosic biomass, which contains carbohydrates, proteins and nitrogen (Urbina et al., 2021).The agricultural wastes are simple to decompose, and the end products promote soil porosity which helps improve soil aeration and water retention and also supplies vital nutrients for plants (Babu et al., 2022; Koul et al., 2022).

Pyrolyzing agricultural waste to produce biochar, is a beneficial strategy for long-term waste management. Producing biochar and using it in fields have several advantages for increasing food production, improving soil quality and environment (Li et al., 2019; Pal et al., 2021), waste handling and treatment to avoid adverse effects on the environment (Xia and Murphy, 2016).

For biochar production, biomass undergoes pyrolysis, a thermo-chemical breakdown process, when an oxidizing agent is absent or just partially available (Nyazika et al., 2019). Three products are obtained after pyrolysis process: gaseous and liquid products as well as charcoal known as biochar. To produce these products biomass material must be cracked, decarboxylate and decarbonylated(Nzihou et al., 2019). Biochar is a carbon rich substance with a thin matrix structure, has gained popularity as a pollution management option because of its outstanding adsorption capabilities and high specific surface area (Hadiya et al., 2022). The yield and quality including its mineral content, organic carbon content, pore structure and surface functional groups (Dhyani and Bhaskar, 2018; Jafri et al., 2018) of biochar, depends on the type of biomass feedstock and other factors including retention time, pyrolysis temperature rate of heating and pressure (Bai et al., 2020; Huang et al., 2021).

Biochar has drawn considerable attention as a potential remedy for addressing environmental problems due to its effectiveness in removing pollutants from soil and water. Various studies have analyzed the sorption abilities and mechanisms of biochar in removing pollutants from soils, particularly metals (Ahmad et al., 2014). The microporosity and high surface area of biochar play important role in sequestration of toxic chemicals by changing their bioavailability and lowering eco-toxicological effects. Theoccurrence of oxygenated groups on biochar directly relates to the adsorption mechanism of metal contaminant. Hydroxyl, carboxyl and phenolic functional groups have been found to act as a binding site for soil contaminants (Uchimiya et al., 2011).

Because of their multifunctional qualities, greater availability of active sites, efficiency in removing pollutants, reusability and less environmental load, biosorbents like biochar are considered advantageous for the removal of pollutants (Wang et al., 2019).Bridging the gap between environmental science and industrial practice, this study aims to promote a cleaner and safer world where technological development and environmental protection coexist harmoniously. Therefore, the aim of present study was to inspect the effectiveness and suitability of biochar produced from bio-residues in the removal of contaminants present in wastewater streams as a function of pH, time and adsorbent dosage.

MATERIALS AND METHODS

Biosorbent material collection and preparation: Both the raw materials namely sugarcane bagasse and rice husk were collected from private sector and washed with distill water thoroughly. The samples were then air dried followed by oven drying(105°C) leading to further processing (Biswas et al., 2017). The processed sugarcane bagasse and rice husk were subjected to slow pyrolysis under oxygen deprived environment (Wang et al., 2014),keeping the temperature and residence time 450°C and 60 minutes, respectively. The physical properties of biochar including pH and EC were measured by employing pH and EC meter, respectively (Orion Star A121 and A329, Thermo Scientific).

Characterization of wastewater: Wastewater was collected from chemical industries located near Hudiara drain, Lahore. The sterile plastic bottles were used for the collection of waste water samples and then mixed to form composite samples. Portable pH and EC meter was used for the measurement of pH and EC of wastewater sample.The water samples were preserved in ice containing boxes and transferred to laboratory for further analysis. After analysis, chromium and lead were found in higher concentration as compared to permissible limit established by WHO.

Characterization of biochar: The yield of biochar was calculated by formula given below. For determining moisture content, volatile content, ash content and fixed carbon content of biochar proximate analysis of biochar sample was conducted. The following formulas were used for the measurement of above-mentioned parameters.

$$\text{Biochar yield \%} = \frac{\text{mass of biochar}}{\text{mass of feedstock}} \times 100$$

$$\text{Moisture Content \%} = \frac{\text{weight of biochar} - \text{weight of oven dried biochar}}{\text{weight of biochar}} \times 100$$

$$\text{Volatile matter \%} = \frac{\text{weight of oven dried biochar} - \text{weight of biochar at 950°C}}{\text{weight of oven dried biochar}} \times 100$$

$$\text{Ash Content \%} = \frac{\text{weight of biochar at 950°C} - \text{weight of biochar at 750°C}}{\text{weight of biochar 950°C}} \times 100$$

$$\text{Fixed carbon \%} = 100 - \text{Volatile Matter \%} + \text{Ash Content \%}$$

Experimental set up for adsorption process

Effect of pH: Batch adsorption experiment was performed in Erlenmeyer flasks of 250 mL capacity at 25°C. HCL and NAOH (0.1M) solutions were employed for adjusting the pH of wastewater sample. The pH of the solution was varied from 3,5 and 7, keeping dosage concentration 1% at the agitation timeof90 minutes. The wastewater samples were then centrifuged at 120 rpm followed by filtration.The samples were stored for post analysis in order to determine the removal efficiency of biochar.

The percent Cr and Pb removal from samples was obtained by Eq. (2) (Prasad et al., 2013).

Removal percentage %= $\frac{Co-Ce}{Co} * 100$

where Co and Ce (mg L^{-1}) refer to original and equilibrium concentrations, respectively.

Effect of adsorbent dose: The optimum sorbent dose was determined and experiments were conducted at 0.1mg/L initial sorbent concentration, 60 minutes contact time and 3 pH level. Various sorbent doses, i.e., 0.1mg/L, 0.5mg/L and 1mg/L were applied and Cr and Pb concentrations in filtrate solution were analyzed using AAS (Atomic absorption spectrophotometer).

Effect of contact time: The influence of contact time was determined by varying contact time from 30,60 and 90 minutes. The adsorption solution pH was set at 3 while the applied adsorbent concentration was 0.5 mg/L. After centrifugation, the samples were filtered. The remaining Cr(VI) and Pb in the samples was analyzed by AAS.

RESULTS

Characterization of wastewater and biochar: Physiochemical characteristics of wastewater have been elaborated in the following Table 1.The real wastewater used in the following study has initial pollutant concentrations; 1.48mg/LCr, 1.04mg/LPb, 0.29mg/LNi, 0.4mg/LAs. The concentrations of Pb and Cr were found far above the WHO threshold values. The initial wastewater electrical conductivity was 580 dS/cm while initial pH of wastewater was 7.6. The total dissolved solid and total suspended solid values were 3210 mg/L and 275 mg/L, respectively. The values of chemical oxygen demand and biological oxygen demand were 189 mg/L and 97.8 mg/L, respectively.

The results of proximate analysis and physiochemical parameters of biochar are demonstrated in Table 1. It was observed that biochar yield was 48% at 40°C temperature. The pH and EC of biochar were 8.1 and 8.9±2.31dS/m, respectively. The proximate analysis results of biochar revealed the moisture content, volatile matter, ash and fixed carbon contents in biochar were 12%, 27%, 17.6% and 65.1%, respectively. The cation exchange capacity of biochar (40.89%) was also determined.

Table 1: Physiochemical characteristics of wastewater and biochar.

Parameters	Wastewater	Biochar	Units
pH	7.6	7.9	
EC	580	8.9	dS/m
COD	189	-	mg/L
BOD	97.8	-	mg/L
TDS	3210	-	mg/L
TSS	275	-	mg/L
Nickel	0.29	-	mg/L
Zinc	ND	-	mg/L
Copper	0.4	-	mg/L
Iron	-	-	mg/L
Lead	1.04	-	mg/L
Chromium	1.48	-	mg/L
CEC	-	40.89	cmol kg-1
Moisture content	-	12 ±0.69	%
Volatile content	-	27 ±1.2	%
Ash content	-	17.6 ±0.63	%
Fixed carbon	-	65.1±0.98	%

Factors affecting adsorption experiment

Effect of pH: Co-pyrolyzed biochar was analyzed with respect to different values of pH levels during Cr(VI) and Pb sorption. Cr(VI) removal percentage (%) for co-pyrolyzed biochar increased from 65.4% at the pH value of3 to 89.9% at the pH value of 5 and then decreased to 79.2% at the pH 7, whereas Pb removal percentage (%) had increased from 60.8 to 87.8% when pH varied from 3 to 5 and then decreased to 72.3% as pH was increased to 7 as shown in Figure 1.

Effect of dosage concentration: The effect of sorbent dosewas determined, keeping pH of solution 3 and 60-minutes contact time by varying dosage from 0.1, 0.5 and 0.1g/L, respectively. Results have revealed that with increase in dosage, the removal rate of Cr(VI) was increased from 76.1% to 95.7%, while the removal rate of Pb was increased from 68.4%.to 88.9%, respectively.The maximum removal rate (95.7%) of Cr and (88.9%) Pb was observed at 1g/L adsorbent concentration as shown in Figure 2.

Effect of contact time: The optimum sorption solution agitation time was determined for better performance of biochar in removing Cr and Pb. For Cr, it was observed that the removal rate was 75.3% at 30 minutes agitation time and improved a little (84.9%) at 60 minutes agitation

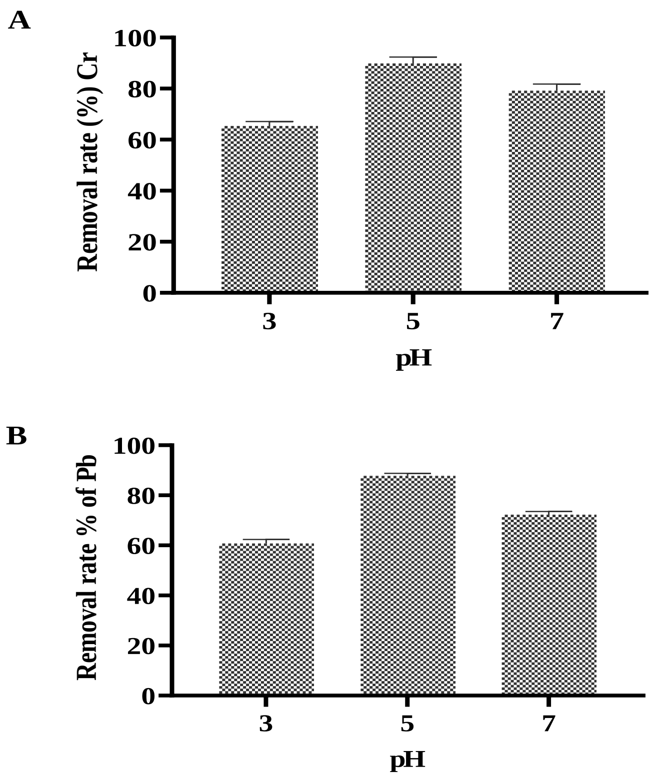

Figure 1: Effect of pH on (A) removal rate of Cr and (B) removal rate of Pb

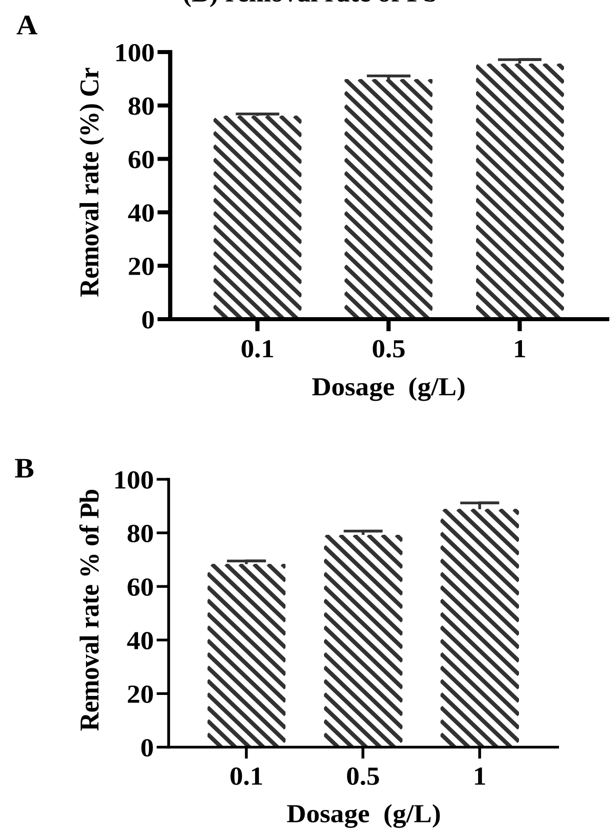

Figure 2: Dosage concentration effect on (A) removal rate of Cr and (B) removal rate of Pb

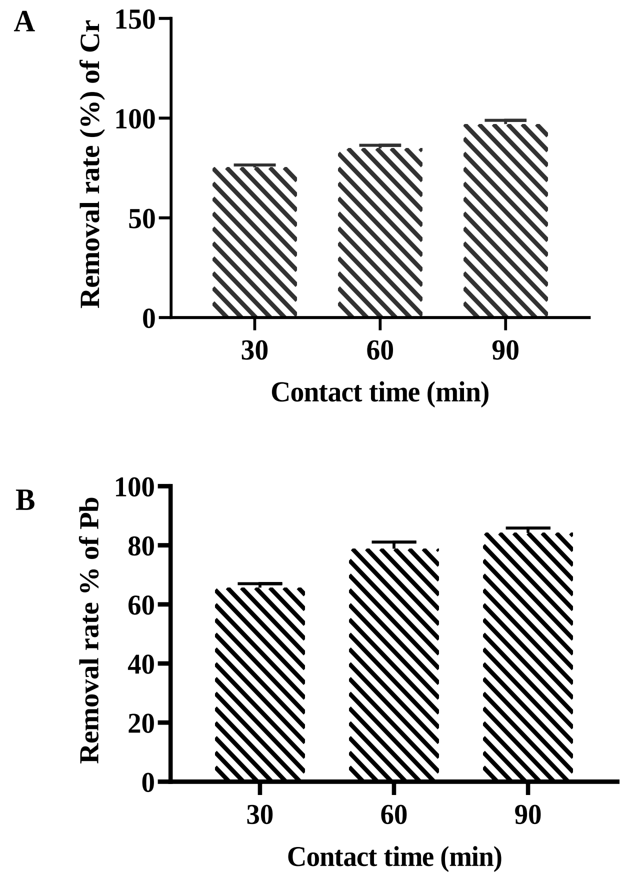

Figure 3: Effect of contact time on (A) removal rate of Cr and (B) removal rate of Pb

time, while maximum removal rate (97.1%) was observed at 90 minutes contact time.For Pb, it was observed that the removal rate was 65.7% at 30 minutes agitation time and improved a little (78.9%) at 60 minutes agitation time, while maximum removal rate (84.2%) was observed at 90 minutes contact time as shown in Figure 3.

DISCUSSION

The results of proximate analysis of biochar determines its constituents. It may be observed thatmaximum contribution was shown by volatile content whereas least contribution in biochar formation was shown by moisture level. High volatile content and high values of fixed carbon content are generally considered appreciable for biochar formation. It was also noticed that ash content decreased with increase in volatile content. The reason may be due to decomposition of cellulose and hemicellulose into volatile content. Similar trend of proximate analysis was also observed by Tadele Assefa Aragaw (2016) who conducted the proximate analysis of sugarcane bagasse and activated carbon, where moisture and ash content levels were low whereas volatile and fixed carbon contents were high.

Adsorption mechanism is affected by the pH of solution. The process of adsorption was carried out at different pH levels (3,5 and 7)where the agitation time and sorbent dose were kept constant. Highest removal rate was observed when the pH of solution was5. The increased removal at increased pH may be attributed to competing ions because at low pH there is more availability of H^+ and OH^- ions leading to less adsorption. Similar trend was also noticed byRoy and Bharadvaja, (2021) andGunatilake (2016) as they worked on the adsorption of Cr (III) using biochar made of saw dust and rice husk.

The influence of sorbent dose in adsorption of toxic metals was also determined by varying dosage from 0.1 to 1g/L, keeping pHand contact time constant. Maximum adsorption of Cr and Pb was noticed when the dosage was kept 1g/L. At higher sorbent concentration, there is increased availability of active sites and higher surface area leading to higher adsorption. Similar results were reported by Ezeonuegbu et al. (2021), they used sugarcane bagasse biochar for Pb removal from untreated wastewater.

The influence of contact time on removal rate of metals ions was elucidated at different agitation time (30, 60 and 90 minutes) keeping other factors constant. Maximum adsorption of Cr and Pb was observed when the agitation time was kept 90 minutes. The adsorption capacity increased linearly with contact time owing to the availability of free cavities leading to increased adsorption of detected heavy metals. Similar trend was reported by Khalil et al. (2021) as they worked on the removal of Cr (VI) using rice husk biochar where maximum removal was shown at 120 minutes contact time.

Conclusion: Formation of biochar by employing agricultural and garden waste leads towards achieving the objective of utilizing and managing waste and converting it into useful product. The proximate analysis results of biochar indicated varied distribution ofvolatile matter, ash, moistureand fixed carbon content. Co-pyrolyzed biochar prepared using sugarcane bagasse and rice husk can be used successfully in adsorption of various pollutants. The results showed that the maximum removal of Cr (97.1%) was observed when the pH of solution was kept 5, with 90 minutes agitation time and adsorbent dosage was kept 1g/L. Similar trend was observed in the removal of Pb, where the removal efficiency of (87.8%) was shown. Overall, agricultural waste biomass samples chosen as adsorbent were economic, environment friendlyand effective making the co-pyrolyzed biochar as a suitable alternative for the removal of wastewater pollutants.

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