Pyrolysis of Waste Biomass and Plastics for Production of Biochar and Its Use for Removal of Heavy Metals from Aqueous Solution

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Abstract

The aim of this work was to study the pyrolysis of waste biomass and plastics and use the produced biochar for the removal of heavy metals from aqueous solution. The batch experiments of Fe, Ni, Cu, Cr, Cd and Pb with biochars and plastic chars were carried for determining the effects of various experimental parameters (feedstock, contact time, adsorbent dose, pH and pyrolysis temperature). The isothermal sorption models demonstrated that the sorption capacities of biochars are higher in comparison to the plastic chars. The maximum removal efficiency shown by biochars and plastic chars at pH 4 was 99.86% and 99.93%, respectively. Both the carbon materials are thereby recognized as an environment-friendly and efficient pollutant control material at various studied parameters.

Keywords: Biochars; Plastic chars; Pyrolysis; Removal efficiency; Heavy metals

1. Introduction

Heavy metals emanating from various industries are perilous for wellbeing and life of the animal and human (**Zou et al., 2016**). In the past few years, industrial growth has introduced massive pollutant levels in the water bodies. Due to their bioaccumulative and toxic nature, heavy metals have become a major concern. Substantial pollution of heavy metals in river bodies may be caused either by natural processes, such as flooding, weathering, or by human activities like waste disposal, industrial processes, or mining (**Kaushik et al., 2009**). The wastewater streams typically incorporate nickel (Ni), copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb) and many more metals. They are non-biodegradable, and their concentrations regularly prompt bioaccumulation in living beings, causing health issues in human beings, animals and plants (**Argun et al., 2007**). For example, intemperate entry of Cu prompts extreme mucosal disturbance, hepatic damage and aggravation in the nervous system (**Rehman et al., 2017**). As indicated by an examination directed by the Central Water Commission (**CWC, 2018**), India's 42 rivers have at least two heavy metals beyond the safe limit. Ganga, the National river of India, was found to be contaminated with five heavy metals (i.e. iron (Fe), Ni, Cu, Cr, and Pb). Other rivers like Arkavathi, Orsang, Rapti, Sabarmati, Saryu and Vaitarna were found to have even higher concentrations of these metals. The highest concentration of six major heavy metals found in Indian river as reported was Cd (0.07 mg L^{-1}), Cr (0.45 mg L^{-1}), Cu (0.31 mg L^{-1}), Pb (0.37 mg L^{-1}), Ni (0.25 mg L^{-1}) and Fe (14.56 mg L^{-1}) (**CWC, 2018**). In India, major developmental activities depend on rivers, thereby making it very important to systematically study the removal techniques of heavy metals from water bodies (**Kaushik et al., 2009**).

Recently, there has been a high demand for sustainable solution to tackle the problem of river contamination due to heavy metals. Many traditional techniques including membrane filtration,

electrochemical treatment, reverse osmosis, precipitation, ion exchange, electrodialysis and adsorption were employed to extract metal ions from wastewater. Although most of these techniques suffer from high overhead and capital expenses, adsorption is far better option because of its versatility in design, ease of handling and operation. At the same time, it is also considered more effective and economical (**Ahmadi et al., 2014; Han et al., 2013**). From past few years, a considerable interest has been shown towards utilizing carbon and related materials as low-cost adsorbents for wastewater treatment (**Kumar et al., 2020a; Singh et al., 2020**). Heavy metal ions can be easily adsorbed by carbon materials because of their tunable surface functional groups. Existing studies have affirmed carbon materials as successful adsorbent of metal particles (**Sun et al., 2014; Tounsadi et al., 2016**). Char is a typical type of carbon-rich material and could be generated by the thermo-chemical processing (e.g., pyrolysis and carbonization) of biomass or carbonaceous waste under an oxygen-deficient condition. It has been prepared from different feedstocks like plastic waste, wood, forest and farming residues which are capable of adsorbing substantial metals (**Inyang et al., 2016; Johari et al., 2016**). The heavy metals sorption capacity of char is generally determined by the physico-chemical properties (e.g., specific surface area and surface functional groups) of char which are affected by the types and composition of feedstock as well the conditions of thermo-chemical processes (**Son et al., 2018**).

There have been limited studies on comparing the adsorption performance of heavy metals and the underlying mechanism of char derived from organic origin (e.g., biomass) with that from synthetic origin (e.g., plastic waste). The former is referred as biochar while the latter is plastic char in this work. Singh et al. (**2020**) synthesized low-cost plastic char using Polyethylene (PE), Polyethylene terephthalate (PET) and Polyvinyl chloride (PVC) waste plastics and investigated

the effects it shows towards the sorption of arsenic. It was found that plastic chars also have prospects for usage as a sustainable adsorbent material and proficient removal of pollutants from aqueous media. Kumar et al. (**2020a**) concluded that the chars derived from organic origin i.e. biomass materials were suitable for effective sorption of the volatile organic compounds (VOCs) with the mechanism of physical sorption and partitioning. However, the intake capacity differed with the changing VOC types. A comprehensive review by Yang et al. (**2019**) on various carbon sorbents clearly stated the role of their functional groups towards the exceptional removal efficiency of heavy metals from the aqueous solutions by enhancing the surface properties and structural stability of the sorbent materials.

This work deals with the use of two major carbon materials prepared from biomass and plastics towards purification of water bodies. It aimed to explain the role of these sorbents concerning their application for effective uptake of heavy metals from the polluted aqueous media. This work compared the compositions (proximate and ultimate), surface functional groups and surface morphology of biomass-derived chars (i.e. biochars) and plastic-derived chars (i.e. plastic chars). The metal ions uptake capacities between both the chars were also investigated in the current study. Although much work has been carried out using biochar towards the sorption of heavy metal ions, the use of chars derived from synthetic origin for the same remains understudied. The adoption of sustainable method for conversion of plastic and biomass wastes to chars for use as sorbent towards sorption of heavy metals as well as safeguarding the increasing loads of these waste warrant the present study.

2. Materials and Methods

2.1 Materials

Three biomass materials namely bamboo, sugarcane and neem were used for preparing biochar. The plastic char was prepared using PET, PE and PVC plastics. The biomass materials as well as plastic samples were washed, dried and then grinded using a mechanical grinder prior to pyrolysis. Pyrolysis was done using a fixed bed reactor comprising of a holder for placing the feedstock, a flow meter, gas collector, liquid collector and a water condenser. Moderate pyrolysis was performed in the presence of nitrogen (N_2) at a flow rate of 1 L min^{-1} at 450 °C and 550 °C at 8 °C min^{-1} of heating rate to convert each feedstock of 60 g of into char. The final temperature was held for 10 min, similar to that of Singh et al. (**2020**). The char was then sieved to achieve 0.5-1.0 mm size and dried at 105 °C for 18 hr and this was used for any further analysis. Both the chars were prepared in similar pyrolysis setups as followed in the previous works done by Kumar et al. (**2020a, b**) and Singh et al. (**2020**). The chars were named based on varying raw material, pyrolysis temperature and their applied dose for sorption as presented in **Table 1**.

Table 1

2.2 Characterization

Fourier transform infrared (FTIR) spectroscopy, BET (Brunauer-Emmett- Teller) surface area analyzer and Scanning Electron Microscopy (SEM) images were used to characterize biochar and plastic char. The thermogravimetric (TGA) analyzer (Model: DTG 60, PerkinElmer, USA) was used to assess thermogravimetric properties such as thermal stability and changes in weight with changing temperature. The elemental analyses of the char were done using Elemental Analyzer (Model: CHNS 628, Leco, UK). The SEM images were captured using Scanning Electron Microscope (Model: Vega 3, Tescan, Czech Republic). The FTIR analysis was done using FTIR spectrometer (Model: Vertex 70, Bruker, USA) at a room temperature for determining the functional groups on the prepared char's surface. The specific surface area of the

chars was determined using BET surface area analyzer (Model: Autosorb iQ_3, Quantachrome Instruments, USA) (**Ladavos et al., 2012**).

2.3 Batch Sorption of Heavy Metals

The batch sorption experiments of Fe, Ni, Cu, Cr, Cd and Pb with biochars and plastic chars were carried out in polypropylene tubes by batch technique for determining the effects of various parameters (contact time, adsorbent dose, pH and pyrolysis temperature). This was done by spiking Etalonmulti-element stock solution (Make: VMR Chemicals). Chars were prepared at two varying pyrolysis temperatures (450 and 550 °C). The solution was applied with 0.1 g and 0.5 g of char and the solution pH was held at 4.0, 6.0 and 8.0 for a time range of 5 min to 35 min (contact time). A 20-ppm working solution was used for setting the experiment, and solution pH was balanced using hydrochloric acid (HCl) and sodium hydroxide (NaOH). Different concentrations of these metals were taken at room temperature for evaluating the isotherms. The suspensions were shaken for varying time (5, 10, 15, 20, 25, 30, 35 minutes) to achieve equilibrium state and the solid was then separated using 0.45 μm syringe filters. Inductively Coupled Plasma-Optical Emission Spectrometer (Model: iCAP 6000 Series, Thermo Scientific, USA) was then used to analyze the heavy metal ions present in sample. A blank solution without adding the char put as a control, which corresponded to zero loss of heavy metals during the analysis. Each experimental set was performed in triplicates to reduce the error chances. The difference between the initial concentration (C_0 mol L^{-1}) and the equilibrium one (C_e mol L^{-1}) gave the adsorption percentage of ions.

2.4 Isotherm Study

Adsorption isotherm modelling is of fundamental importance while designing sorption-based system as they specify in what manner metals are partitioned between the aqueous medium and

the solid adsorbent as a function of concentration of the metal. When the char comes in contact with the liquid solution, concentration of metals on the surface of adsorbent will increase until the equilibrium is reached where there is an equal distribution of ions between solid-liquid phase. Initial ion concentration was fixed at 20 mg L^{-1} with two different doses (0.1g and 0.5g) of chars at three pH value cases (4, 6 and 8). The heavy metals sorption was calculated using the least squares regression approach. Langmuir isotherm's linear form is mentioned in equation 1 (**Miandad et al., 2018**):

$$C_e/q_e = C_e/q_m + 1/k_L q_m \quad \text{..... (1)}$$

Where, q_e (mg g^{-1}) is the amount of sorbed metal ions, C_e in (mg L^{-1}) is the metal absorption at equilibrium stage while q_m (mg g^{-1}) is the maximum uptake capacity of char and K_L is the Langmuir constant.

2.5 Kinetic Study

For determining the adsorption kinetics of the metals considered in the study, the kinetic parameters were studied for time ranging from 5 min to 35 min by periodically checking the percent elimination of the heavy metals. The obtained results were finally equated in Lagergren equation that represents a first order kinetic equation (2) and a pseudo-second order kinetic equation (3). The rate of heavy metals sorption on the char was calculated using pseudo-first-order equation (2) (**Jazini et al., 2017**):

$$\log(q_e - q_t) = \log q_e - (k_1 t/2.303) \quad \text{..... (2)}$$

Pseudo-second-order equation (3) is of the form as per the equation (3) (**Jazini et al., 2017**):

$$t/q_t = (1/k_2\, q_e^2) + t/q_e \quad \text{..... (3)}$$

Where, q_e and q_t (mg g^{-1}) signifies the metal ions sorbed at equilibrium and time t, whereas k_1 and k_2 signifies the rate constants.

3. Result and Discussion

3.1 Biochars and Plastic Chars Characterization

The data obtained from the proximate and elemental studies of the both chars (biochar and plastic char) are presented in Table 2. It is shown that the MC of biochars ranged from 0.36 wt.% to 2.15 wt.% while that of plastic chars ranged from 0.57 wt.% to 8.11 wt.%. The initial MC of biochars feedstock material ranged from 0.18 wt.% to 0.25 wt.%, while that of plastic chars feedstock material lied in between 0.60 wt.% to 2.01 wt.% (**Kumar et al., 2020a; Singh et al., 2020**). The MC of the plastic chars was found to increase with higher pyrolysis temperature (550 °C), while it decreased with increasing pyrolysis temperature in the case of biochars. The FC was found to be higher in bamboo-based biochar (85.4 wt.%) in comparison to that of plastic char (83.3 wt.%). The elemental analyses of the biochar showed lower content of nitrogen (0.47 to 1.0 wt.%) while the carbon content was found to be between 52.7 to 78.1 wt.%. Jazini et al. (**2017**) prepared barley straw-based biochar in similar range of pyrolysis temperatures (300 °C, 400 °C, 500 °C) and found the nitrogen content ranging from 0.48 to 0.87 wt.% and carbon content from 43.13 to 66.46 wt.%. The plastic chars showed 0.04 wt.% and 88.1 wt.% of nitrogen and carbon, respectively. With increasing pyrolysis temperature, an increase in the carbon content was observed, which is consistent with existing studies (**Fang et al., 2016; Suliman et al., 2016**). On increasing the temperature from 350 °C to 600 °C, the carbon fraction was found to increase from 70.5% to 87.8%, 69.9% to 83.1% and 66.1% to 78.1% in the case of Douglas fir wood biochars, poplar wood biochars and Douglas fir bark biochars, respectively in the study performed by Suliman et al. (**2016**). The obtained results were also found to resemble that obtained elsewhere (**Wang and Liu, 2017**). In the present work, it was found that with the rise of temperature from 450 °C to 550 °C, the carbon content increased from 72.8 to 78.1 wt.% and

63.1 to 66.1 wt.% in neem-based char and bamboo char, respectively. On the other hand, the plastic chars showed consistent decrease in their respective carbon contents (54.6 to 36.8 wt.%, 55.2 to 46.1 wt.% and 88.1 to 87.4 wt.% for PV, PE, PT chars, respectively) with the increasing pyrolysis temperatures.

Table 2

Plastic chars surface area ranged between 0.32-5.29 $m^2 g^{-1}$ while that of the biochar ranged between 1.04 - 43.9 $m^2 g^{-1}$. The specific surface areas are affected by the types of feedstock and pyrolysis temperature. Sun et al. (**2014**) observed in their study that the surface area of bamboo char increased from 1.3 to 10.2 $m^2 g^{-1}$ with a rise in temperature from 300 °C to 450 °C. The changes in feedstock type at fixed pyrolysis temperature also showed a similar rise in the surface area i.e. in bagasse 5.2 to 13.6 $m^2 g^{-1}$ while in bamboo, this was 1.3 to 10.2 $m^2 g^{-1}$. In the present work, the neem-based biochar (NC 1) had the highest specific surface area (43.9 $m^2 g^{-1}$) at 550 °C pyrolysis temperature. It was found that the plastic char (PE1) had highest specific surface area of 5.29 $m^2 g^{-1}$ which is almost eight times less than the highest area found in the case of biochar (NC 1) thereby confirming that the biochar to be more appropriate for use as adsorbent. The results validated the dependency of changing surface areas of the prepared chars on the raw material (feedstock) used along with the pyrolysis temperature. As pyrolysis temperature increased, the increase in the surface area of the biochar is possibly because of the decomposition of organic matters like lignin & cellulose and the formation of vascular bundles, channel structures and micro pores (**Zhao et al., 2017**). The destruction of aliphatic alkyls and ester groups as well as exposure to the lignin and cellulose available in the biomass feedstock at high pyrolysis temperature leads to the increased surface area (**Tomczyk et al., 2020**).

At low pyrolysis temperatures i.e. below 500 °C, lignin is not transformed to polycyclic aromatic hydrocarbon which makes the char more hydrophilic. At higher temperatures (>650 °C), the char formed is thought to be more hydrophobic and thermally stable (**Tomczyk et al., 2020**). Also, at higher temperatures, the pore-blocking substances thermally crack which increases the externally accessible surfaces and the release of higher volatile matter helps in formation of more pores (**Rafiq et al., 2016; Shaaban et al., 2014**).

The major functional group detected using FTIR showed that all the spectra obtained displayed powerful absorption band allocated to O-H bond at 3501 cm^{-1} for BC 1, 3565 cm^{-1} for PE 1 and 3544 cm^{-1} for PT 1 (**Li et al., 2013; Ren et al., 2013**). The peaks obtained at 1053 cm^{-1} and 1557 cm^{-1} in NC 1 is due to C-OH and C-O-C bonds. Peak at 1100 cm^{-1}, 1590 cm^{-1}, 3400 cm^{-1} indicates C-OH, C=C and -OH groups presence, which were also noticed in an earlier study conducted by Yang et al. (**2016**). New bands at 2359 cm^{-1} and 2883 cm^{-1} obtained for SC 1 have been given to symmetric and asymmetric CH_2 groups. The peaks obtained at 668, 1035, 871, 1053, 1416, 1539 cm^{-1} are given to the aromatic rings (**Machado et al., 2011**), C-H and C-H O-H vibration mode and bending mode, respectively (**Liu et al., 2010**). The peaks observed from the study can be correlated to those found on activated carbon and graphene oxide (**Ren et al., 2013**). It is shown that both biochar and plastic char contain oxygen containing functional groups and thus confirms the presence of adsorption sites for heavy metal ions (**Miandad et al., 2018**).

The morphology of NC 1, SC 1, PV 1 and PE 1 chars was studied using SEM. Plastic char showed rough surface with several cracks having spongy pores. This confirms that the char contains mesopores which is consistent with the study by Miandad et al. (**2018**). The cracked structures with pores also confirm the amorphous structure of the formed chars. This was

consistent with the results of the study performed using activated carbon for decontaminating copper by Ren et al. (2013). The biochar on the other hand showed smooth surfaces and long cylindrical structures having longer diameter. Furthermore, they were found to be curved and entangled among themselves. The interrelation among the pores of these biochars also predict better sorption capacity in comparison to the plastic chars. Similar morphological structure was found in the study conducted by Shaaban et al. (2013) using rubber wood sawdust-based chars prepared at 300 ℃ and 700 ℃ pyrolysis temperature. BET, SEM, FTIR, proximate and ultimate study described the structure of all the prepared chars. This research offered a qualitative and quantitative explanation of pyrolysis for sorption of heavy metals on the basis of char quality, quantity and its pore structures. These analyzes require time, and the measurements are mostly conducted after cooling down, which could result in a change in the char structure. Therefore, more sophisticated methods are required for analyzing the char performance to save time and money. The factors primarily responsible for adsorption are the specific surface area, contact time, feedstock content and pyrolysis temperatures.

3.2 Adsorption Studies

3.2.1 Influence of the Feedstock Material

Fig. 1 shows the uptake capacities of heavy metals of all the prepared biochars and plastic chars. Adsorption capacity is influenced directly with the changes in the raw samples being used. This happens due to the changing physico-chemical properties of the biomass and plastic samples. These changes in the properties of the feedstock are further responsible for the varying sorption performance for uptake of heavy metals. In the case of biochars, the highest sorption of Ni (99.01%), Cu (91.60%), Cd (99.24%), Fe (10.95%) and Pb (95.52%) was shown by SC 11 while Cr (99.06%) by BC 11. Meanwhile, in the case of plastic chars, the highest sorption of Ni

(43.32%) and Cu (90.96%) was shown by PV 11 while Cd (28.31%), Fe (4.0%), Pb (70.07%) and Cr (99.01%) by PT 11. The experimental data obtained fitted well for Langmuir isotherm in comparison to Freundlich isotherm. The value of correlation coefficient (R^2) for Pb sorption on different feedstocks was found to be 0.99 in case of Langmuir isotherm which inferred that the soprtion on these biochars and plastic chars is favorable in the studied conditions. Therefore, chars prepared from biomass feedstocks showed higher adsorption capacities for all the heavy metals considered when compared with the one prepared from synthetic plastics. In a study performed by Kongsuwan et al. (**2009**) using activated carbon from eucalyptus bark having specific surface area of approximate 1240 m^2 g^{-1} showed merely 0.45 and 0.53 mmol g^{-1} of Cu^{2+} and Pb^{2+} ions, respectively. Although the chars used in the present study are non-activated one still both plastic as well as biomass-based char clearly showed high removal efficiencies thereby confirming the positive role played as sorbent materials. Studies performed by various researchers showed the respective uptake sorption capacities of chars prepared at 400 to 600 °C pyrolysis temperature from varying feedstocks under similar conditions as in corn straw (12.5 mg g^{-1} of Cu, 11.0 mg g^{-1} of Zn), hardwood (6.8 mg g^{-1} of Cu, 4.5 mg g^{-1} of Zn), oak wood (0.3 mg g^{-1} of Cd, 3 mg g^{-1} of Pb), pine bark (0.4 mg g^{-1} of Cd, 2.6 mg g^{-1} of Pb), oak bark (5.4 mg g^{-1} of Cd, 13.1 mg g^{-1} of Pb) and rice husk (0.3 mg g^{-1} of Cu), respectively (**Inyang et al., 2016; Chen et al., 2011**). This confirms the varying uptake capacities of each sorbent formed from different feedstock materials irrespective of similar conditions of preparing them (**Wang et al., 2019a**). The obtained results in comparison with earlier studies confirmed the proficiency of the formed chars in efficiently removing heavy metals.

Fig. 1.

3.2.2 Influence of Pyrolysis Temperature

The chars obtained at 550 °C (NC 11, BC 11, SC 11, PV 11, PE 11, PT 11) exhibited a higher sorption ability in comparison to the chars pyrolyzed at 450 °C (NC 00, BC 00, SC 00, PV 00, PE 00, PT 00). The percentage of Cd removal using NC, SC, PV, PT was found to be 45.86%, 98.36%, 7.89% and 3.97% which increased to 66.40%, 99.24%, 24.58%, 28.31%, respectively with increasing pyrolysis temperature. This could be attributed to the lower specific surface areas of the char prepared at the lower temperature (450 °C). Wang et al. (**2019b**) reported a subsequent decrease in Cd removal efficiency using maize straw biochar from 97.1±0.8% to 90±2% at 500 °C and 600 °C pyrolysis temperatures, respectively. The uptake efficiency of all the chars used in the present study showed increased removal efficiency with increasing pyrolysis temperature. Among all the chars studied, SC showed the maximum increase in uptake efficiency of Cd ions from 98.36% to 99.24% on increasing the temperature from 450 °C to 550 °C. This shows the outstanding uptake efficiency of the prepared char in comparison to those reported in earlier studies (**Wang et al., 2019b**). Also, the results are noteworthy keeping in mind that the chars in the present study have not been modified by any means. The uptake capacities at different pyrolytic temperature of all the chars have been shown in **Fig. 2.** Analysis of Variance (ANOVA) was performed for studying the influence of different pyrolysis temperature on sorption capacity. The *p* value ($2.2\ E^{-5}$ for 450 °C, $3.4\ E^{-6}$ for 550 °C) obtained is very less than 0.05 thereby strongly confirming the rejection of null hypothesis. This low *p* value simply indicated the strong relationship between pyrolysis temperature (450 °C and 550 °C) and adsorption capacity.

Fig. 2

3.2.3 Influence of Char Dosage

Fig. 3 clearly showed that the adsorption of all the metals increased with an increase of char dosage from 0.1 to 0.5 g. All the other parameters i.e. pH, contact time, and temperature were kept constant for studying the effect of changing dosage of different chars on sorption capacity of heavy metals. Sorption of heavy metal ions was found to increase from 11.76 to 99.24%, 87.62 to 99.36%, 36.43 to 91.59%, 0.60 to 10.95%, 11.56 to 43.31% and 59.0 to 95.52% for Cd, Cr, Cu, Fe, Ni and Pb, respectively on rising the dose from 0.1 g to 0.5 g. The obtained results confirm inter-relationship between the dose of char and removal capacity and subsequent increase in the available sorption sites. The surface area increases with an increase in the dose of char, which subsequently increases the free sites available for sorption. This is possibly the reason behind increased sorption capacity of the prepared char. Kula et al. (**2008**) reported a change in sorption capacity of the char with the change in its dose and also reported maximum removal of Cd^{2+} at equilibrium time of 60 min, pH 6.0 and adsorbent dose of 1.0 g 50 mL^{-1}. Acharya et al. (**2009**) also obtained 97.74% maximum removal of Pb^{2+} at sorbent dose of 5g L^{-1}, while the char studied in the present work showed a maximum of 99.36% removal with increased dose. This confirms the quality and presence of high specific area of the char prepared in this study.

Fig. 3

3.2.4 Influence of pH

The variation in removal efficiencies of heavy metal ions by biochar and plastic char with respect to pH is shown in **Fig. 4.** The results clearly showed that the pH value significantly affects the removal efficiency of the char. At pH 4, the maximum removal was found to be

89.36%, 99.01%, 98.78%, 0.14%, 72.51% and 89.93% for Cu, Cd, Cr, Fe, Ni and Pb, respectively. The maximum removal efficiencies are 91.60% for Cu, 81.88% Ni, 95.52% Pb, 99.24% for Cd, 99.03% for Cr and 4.81% for Fe at pH 6 which later decreased to 34.03%, 72.10%, 58.64%, 61.07%, 49.08% at pH 8. Therefore, the removal efficiency of both the char was observed to increase with an increase in pH from 4 to 6. After pH 6, a significant decrease in the removal efficiency of the chars was observed. The influence of pH was also observed by Mousavi et al. (**2010**) while using waste tire rubber ash as an adsorbent to remove Pb^{2+} from waste stream. Mousavi et al. (**2010**) varied the pH from 4 to 6 and demonstrated that quantity of Pb^{2+} ions uptake from solution rises rapidly from 73.8% at pH 4 to 93.1% at pH 6. Pellera et al. (**2012**) also reported maximum Cu (II) uptake of 93.6%, 90.1%, 88.7% and 77.8% at pH 7 by the biochars prepared from compost, rice husks, orange waste and olive pomace, respectively. The results from the previous studies as well as the present study clearly demonstrated that the metal ions are better removed at higher pH range. The carbon content found in any char material studied acts mostly as a weak alkali that buffers the pH of the working solution. After the rise in pH, it becomes more difficult for the heavy metal ions present in the sample solution or the aqueous media to dissolve as it becomes less soluble. This thereby allows the sorption of the positively charged toxic heavy metal ions to be easily on the surface of the adsorbent which is then removed from the polluted stream. All the aquatic media are in general quite sensitive to pH and thereby special care needs to be taken while treating them. Hence, a pH neither alkaline nor acidic in nature is generally considered as the best for proper remediation. In this study, pH 6 has been found as the best one for removing heavy metals concentration.

Fig. 4

3.2.5 Influence of Contact Time

The sorption rate of Fe, Cu, Cd, Cr, Ni and Pb on all the chars regardless the carbon material used increased with change in the contact time. After the attainment of equilibrium condition at 20 min, the adsorption rate decreases progressively due to the limited free spaces available. This is because the adsorption efficiency of metal ions on the char is rapid during the first stage (0 to 20 min) for all the metal ions studied. The sorption rate also decreased after 20 min contact time and marginal changes occur till 35 min. Sorption of these metals onto the adsorbents (NC 11, PT 11, NC 00 and PT 00) also showed increasing uptake with increasing time during initial stage (0-20 min). After this, rate decreased and the equilibrium state was attained after 20 min. This is mostly due to the availability of well aligned free spaces of char for binding together the toxic heavy metal ions. After this stage, the sorption capacity of the char slowly decreases until the equilibrium condition is reached because of the saturation of all the available sites. Also, for studying the kinetics, pseudo first and second order models were applied. It was found that pseudo second order model fits better in comparison to pseudo first order model. The R^2 value in pseudo second order was 0.99. This confirms the that the sorption of heavy metals on both the chars is a chemical process. The obtained results were similar to those obtained from the experiment.

In adsorption experiment study conducted by Pellera et al. (**2012**), the reduction of Cu (II) was accomplished by increasing the contact time. In most of the cases, a slower adsorption rate followed the rapid initial adsorption rate within the first few min before reaching equilibrium. It is because of presence of ample amount of available biochar site, while as adsorption proceeded the depletion of these active sites also occurred over time.

3.2.6 Influence of Surface Area

A correlation evaluation of specific surface area of biochars and plastic chars was performed to analyze the effect on adsorption capacity on the basis of obtained results (**Fig. 1**). None of the six metals produced a line graph when their respective sorption capabilities were considered, which differed from those of other carbon materials (**Kumar et al., 2020a**). The sorption took place in accordance to the adsorption-partitioning processes. The interaction between sorption and surface area indicated that the adsorption of metals by char produced at 550 °C is primarily exothermic. Also, it is compatible with the adsorption-partition cycle. In the case of biochars prepared at higher temperatures, i.e. 550 °C with higher surface area and lower non-carbonized organic matter, adsorption is the dominant mechanism while partitioning remains a mechanism for chars prepared at lower pyrolysis temperatures with lower surface area and higher non-carbonized organic matter (**Kumar et al., 2020a**).

3.3 Statistical Analyses

Heavy metals sorption was done using ANOVA to obtain the basic data about the efficacy of parameters set for the sorption. The influence of independent variables on the dependent ones i.e. pH and sorption were studied. The statistically significant values were symbolized as p-values. It was found to be 0.012 for all the chars applied on different pH which indicated a positive relation between the sorption capacity, pH (4.0, 6.0, and 8.0), dose (0.1 g, 0.5 g) and contact time (35 min). F value was found to be 2.95 that is more than the F critical (2.21) for single way. This shows the rejection of null hypothesis and that the char dose plays a major role in its uptake capacity.

3.4 Isotherm Modeling and Kinetic Study

The data obtained from the sorption analysis were put to Langmuir adsorption isotherm using linear expression of the model similar to that used in the study performed by Miandad et al. (**2018**). The isotherm assumes homogenous surface and a continuous sorption potential. The sorption capacity of the biochar followed Langmuir isotherm with R^2 value being 0.99, thereby confirming the process of sorption being chemical. The increase in the sorption capacity of the char with increase in metal ion concentration is because of the high concentration gradient that resists the mass transfer from aqueous media to solid char. After a certain time, the efficiency of uptake of ions does not increase because the number of available sites is fixed. Son et al. (**2018**) also found Langmuir isotherm to fit better in the sorption study performed using marine macro algae for the uptake of Cu, Cd and Zn ions. Li et al. (**2013**) also demonstrated Langmuir model to be more suitable in comparison to Freundlich model to the obtained sorption data. Langmuir isotherm stated that monolayer sorption took place. The Langmuir model predicts the suitability/ favorability of the adsorption process to take place using both the chars. The linear form of the model suggests that the char prepared has high affinity towards the positively charged metal ions and would support the sorption process under the controlled experimental conditions. Biochars and plastic chars samples used in the present study presented moderately similar sorption by BC 11 and PV 11 which implied that chemical and physical sorption is involved in the entire adsorption procedure. Metal ions, amount of carbon material used, pH, contact time are accountable for the percentage removal of these metal ions. Even though the chars showed moderate surface areas, but because of high oxygen, it showed sorption of the metal ions on pore surface (**Mohan et al., 2014**).

The kinetic data in the present study was done with the help of some models. The models were verified by the fitness check of the lines obtained. The R^2 value clearly demonstrated that the data obtained during the study followed the retention kinetic of all the heavy metal ions. The first order kinetic model calculated qe value differs from the experimental values and obtained R^2 values also. The calculated qe values for second order model are somewhat near to the experimental value. The R^2 value was more in the case of pseudo second order kinetic model. This confirms the suitability of pseudo-second order model for better explaining the sorption of metal ions on different plastic char and biochar sorbents used in the study. Also, this confirms chemisorption being the fundamental mechanism behind the sorption of heavy metal ions on the biochar and plastic char surface by exchange of valence electron between adsorbate and adsorbent. The positive results for the sorption of six heavy metals found in Indian river using biomass and plastic-based chars thus suggested that both these chars serve as alternative sorbents to mitigate the heavy metals contamination. Large-scale field experiments will be required to examine the effects of char-based sorbents on reducing the heavy metals concentrations in river.

5. Conclusion

The study focused on synthesis of carbon materials from biomass and plastic wastes and comparing their performance as an economical heavy metals sorbent. It revealed the dependency of various factors like dose, pyrolysis temperature, feedstock type, contact time and pH on the sorption capacity. SC biochar was found to be most effective with sorption efficiencies ranging from 3.27-99.4%. Although, some challenges need to be addressed while implementing purification of aqueous media using these materials, the performance shown by biochars favorably suggested their use for better results. Carbon materials are thereby a proved sustainable solution towards purification of river water.

CRediT authorship contribution statement

Ekta Singh: Conceptualization, Methodology, Investigation, Writing -original draft, Writing - review & editing. **Aman Kumar:** Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Rahul Mishra:** Conceptualization, Investigation, Writing - original draft, Writing - review & editing. **Siming You:** Validation, Writing - review & editing. **Lal Singh:** Conceptualization, Validation. **Sunil Kumar:** Funding acquisition, Writing - review & editing, Supervision. **Rakesh Kumar:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

E-supplementary data for this work can be found in e-version of this paper online

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