Remediation of Cadmium Contaminated Soil using Biochar Derived from Wheat Straw, Rice Husk and Bagasse

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Abstract. Improper waste disposal has resulted in rapid deterioration of the environment and the advent of fatal diseases. Carcinogenic substances that percolate into the ground deteriorate the quality of groundwater and soil. Moreover, pollution from large scale burning of agricultural waste each time after the harvest season, makes the goal of a healthy environment of utmost importance. Toxins, such as polycyclic aromatic hydrocarbons (PAH) and heavy metal contaminants, have several pathways to enter into the environment and bioaccumulate within living organisms. The objective of this study is to synthesize a substance that will break the source-receptor pathway resulting in cleaner water and soil. Biochar, through ion exchange or physical adsorption, has the capacity to adsorb heavy metal ions such as those of Cadmium. The biochar was synthesized from biomass consisting of wheat straw, rice husk, and bagasse. The biomass was then heated to temperatures ranging from 300°C to 700°C using the process of slow pyrolysis, in an environment in which the oxygen supply was limited. The samples were then subjected to fourier transform infrared spectroscopy (FTIR) to ascertain the functional groups present followed by powder x-ray diffraction (XRD) to determine the elements or form of metal oxides present in the samples. The samples were mixed with a known amount of cadmium solution and the final testing was performed using atomic absorption spectroscopy (AAS). The final testing directly showed the heavy metal ion adsorption efficiencies of biochar derived from different types of biomass, giving an insight into the future scope of using biochar has a remediating agent

Keywords: Biochar, Heavy Metal, Soil Remediation.

1 Introduction

The use of burnt agricultural material as a means to enrich the soil has been used for the past several years. Farmers have the knowledge that using this burnt material from cook stoves etc. and applying it to the soil makes it more suitable for cultivation. This process releases large amounts of pollutants into the atmosphere. However, burning in limited oxygen conditions produces liquid, gasses and solid matter. This solid matter, biochar, is the end product that effectively removes contaminants present in the soil that are generally bio-available for uptake by plants.

The property of biochar to bind carcinogens to its surface is governed by properties such as the feeder material and the temperature of synthesis. Variation in these properties result in changes in surface area available to adsorb toxins, pH changes in the soil, and the amount of different toxic substances taken up by the biochar through a series of differing surface chemical reactions. Biochar is the substance that breaks the source-receptor pathway through cation exchange, the physical processes of electrostatic attraction, pH increasing properties, etc.

These properties of biochar make it a highly researched into substance. Its applications could benefit several people and have a global impact in the reduction of soil and atmospheric pollutants. The objective of this study is to determine the effect of biochar derived from three different raw materials on the uptake and removal of cadmium heavy metal ion. The ideal temperature and the that the maximum amount of contaminant is to be determined for further research.

1.1 Mechanics of Remediation by Biochar

The properties of biochar such as the chemical process of chemisorption and the physical process of physisorption make it ideal for the removal of organic and inorganic contaminants. According to Gomez-Eyles et. al (2013) the cation exchange capacity at low temperatures of pyrolysis takes place due to the presence of a high number of oxygen containing functional groups. A higher temperature results in the increase in surface area of the biochar, making more sorption points available on the biochar surface. (Gomez-Eyles et. al, 2011) It also results in the presence of a greater number of aromatic compounds available (Jindo et. al, 2014).

Physical adsorption is the main phenomenon responsible for the binding of metal contaminants to the surface of the biochar. High temperatures increase the aromaticity of the biochar resulting in the polarisation of the electron cloud and consequent attraction of positive metal ions to the pi-pi bonds of the aromatic group. (Gomez-Eyles et. al, 2011). pH plays an important role in the removal of heavy metal ions since a high negative value results in competition for sorption points on the surface of biochar by hydrogen ions while a positive pH prevents the dissociation of compounds into ions following the Le Chatelier’s principle (Sizmur et. al, 2015; Bolzan, 2017). This ensures that harmful compounds formed with the heavy metals on the surface of the char remain insoluble and are not bioavailable for uptake.

1.2 Properties of Biochar

Various research has provided insight into the composition of chars from different sources.

Bagasse. According to the study conducted by Figuerdo et. al (2017), the detectable elements in sugarcane biochar were potassium, phosphorous, magnesium, zinc, copper, silicon and aluminium. The presence of manganese in bagasse biochar increased in the temperature range of 450-550℃ while the percentage of sulphur and phosphorous decreased in the same temperature range. (El-Gamal et. al, 2017). The carbon content of the bagasse biochar decreases with an increase in temperature after a maximum temperature of 500℃ and the highest phosphorous content is achieved at a temperature of 400℃ (Nwajiaku et. al, 2017). Phosphorus, silicon and sulphur are responsible for the removal of Zinc, mercury and lead.

Rice Husk. . Biochar synthesised from rice husk has a high phosphorous content (Windeatt et. al, 2014). The highest percentage of silicon, about 31%, is present in chars synthesised at lower temperatures of 400℃. (Sandhya et. al, 2015). Rice husk biochar has a high carbon content, production potential and carbon storage potential (Zu et. al, 2012). A direct correlation exists between carbon content and an increase in temperature, the highest yield of carbon, 74%, was found at a temperature of 525℃ (Ahmad et. al, 2015).

Wheat Straw. An increase in temperature results in an increase in carbon content and a lower H/C ratio which showcases and increase in aromaticity of biochar (Gai et. al, 2014). There is an increase in phosphorous and manganese content of the char at a temperature range of 300℃ to 500℃ (Naeem et. al, 2017). The highest potassium content and phosphorous content of 1g/kg was found at a temperature of 550℃ (Windeatt et. al, 2014).

2 Experimental Section

2.1 Material

Rice husk, bagasse and wheat straw are the raw materials obtained from the farms in the Dadri, Uttar Pradesh and from Bulandshahr, Uttar Pradesh.

2.2 Instrumentation

A muffle furnace B1410M-33 Furnace was used to synthesize the biochar. For ATR, Samples were directly analyzed after synthesis using the Thermo Nicolet iS5 with the software — Ominic Diamond. The results were plotted using Origin. The Bruker D8 discover was used for XRD testing.

2.3 Raw material preparation

Each of the raw materials were prepared in a different way to remove impurities that may have been present. The rice husk and wheat straw were sieved to remove traces of soil, animal droppings and plastic. The bagasse was thoroughly washed by distilled water, to remove soil dust and prevent the formation of molasses at high temperatures. Bagasse was then dried in an oven for 48 hours at a temperature of 60°.

2.4 Synthesis of Biochar via Pyrolysis process

For the synthesis of biochar: 2 grams of rice husk and wheat straw were placed in silicon crucibles and the temperature was slowly increased up to a starting temperature of 200°C. The samples were carefully placed within the furnace for one hour. Fresh samples were then placed into the furnace for temperatures of 300°C, 400°C, 500°C, 600°C and 700°C for a residence time of 1 hour each (Zhu et. al 2016). The bagasse biochar was prepared at temperature of 300° and 400° according to the FTIR data of the study by (Li et. al 2016) the resulting biochar at these temperatures has the highest heavy metal ion removal efficiency. The resultant products were analysed by ATR mode FT-IR and XRD technique. After performing ATR and XRD samples were shortlisted for further testing.

2.5 Removal of Cd (II)

Due to the presence of microscopic particles, AAS method was used for testing. The sample was prepared by introducing a set amount of 81 ppm cadmium solution to the biochar. Four samples were prepared using 25 mg, 50 mg, 75mg and 100 mg of each type of biochar. 16 samples were selected based on maximum removal efficiency, after ATR and XRD, for further testing. These samples were placed in a shaker for 6 hours, after which, they were centrifuged. The centrifuge was set at 10,000 rpm for the span of 20 minutes. After this process, the supernatant was extracted and placed in 10ml containers and allowed to rest so that the suspended particles settle to the bottom of the container. The solution was then filtered for further testing.

3 Result and Discussion

3.1 FTIR

Findings. The characteristic peaks in all three kinds of biochar at various temperature comes at 1630, 1410, 1058 and 630 cm^{-1} showed the functional groups mainly including aromatic ring –C=C-, carboxyl, phosphate and aromatic -C-H-, and intensity of these peaks decreases by increasing the pyrolysis temperature (Li et al 2018). Figure 1, 2 and 3 shows the intensity of respective function group at various temperature.

Bagasse. Figure 1 shows FTIR spectra of the biochar synthesised from bagasse, the sample synthesized at 500°C shows the presence of peaks in Zone 5 indicating the presence of benzene ring and whereas the sample at 400°C shows no such peak. The sample at 400°C however shows the presence of oxygen containing functional groups in Zone 4 such as acid and amines. Thus, the most favourable condition for the synthesis of the product would be at 400°C.

Wheat Straw. Based on the FTIR graph in Figure 2, the wheat straw char shows the most favorable conditions at a temperature of 300°C. This is due to the presence of aromatic hydrocarbon benzene indicated by the double peaks at approximately 1500

cm^{-1} and 1600 cm^{-1}. The peaks at zone 4 (1850-1650 cm^{-1}) indicate the presence of oxygen containing functional groups.

Rice Husk. On the basis of the FTIR analysis of rice husk in Figure 3, the sample synthesized at 300°C has the formation of slight double peak at Zone 5, 1680-1450 cm^{-1}, indicating the presence of aromatic hydrocarbons such as benzene ring and alkenes. Thus, the product synthesized at 300°C will be most efficient.

3.2 XRD

Findings. Distinct peaks were observed in two of the XRD graphs. The rice husk graph has not been included as the graph obtained contained no distinct peaks.

Bagasse. The XRD graph of bagasse (fig. 4) shows two distinct peaks which were found using the peak analyser software on Origin Lab. The graph look similar to the one studied during the literature review and using the mineralogy database the first peak at the two-theta value of 26.547 is indicative of silicon dioxide and the second peak indicated the presence of silicon dioxide, graphite, copper carbonate. Smaller peaks with lesser intensity could indicate the presence of copper oxide and calcium hydroxide.

Wheat Straw. The XRD graphs of wheat straw (fig 5.) shows 17 peaks using peak analysis on origin lab. The peaks of potassium chloride, calcium carbonate, magnesium chloride and silicon dioxide were found from the XRD graph.

Rice Husk. The XRD graph of rice husk complies with the literature review however no peaks were observed from the graph. The peaks of manganese dioxide, silicon dioxide, calcium oxide and aluminium oxide were to be observed for the samples.

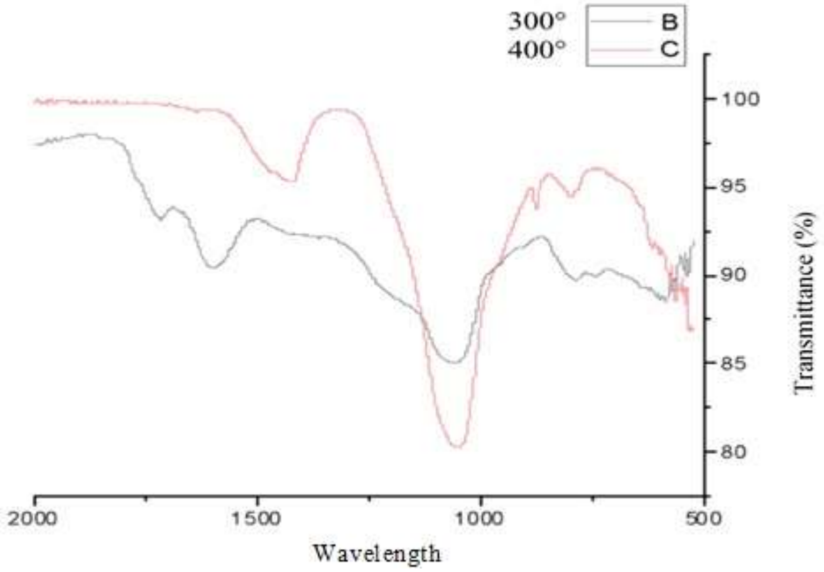

Fig. 1. Bagasse FTIR

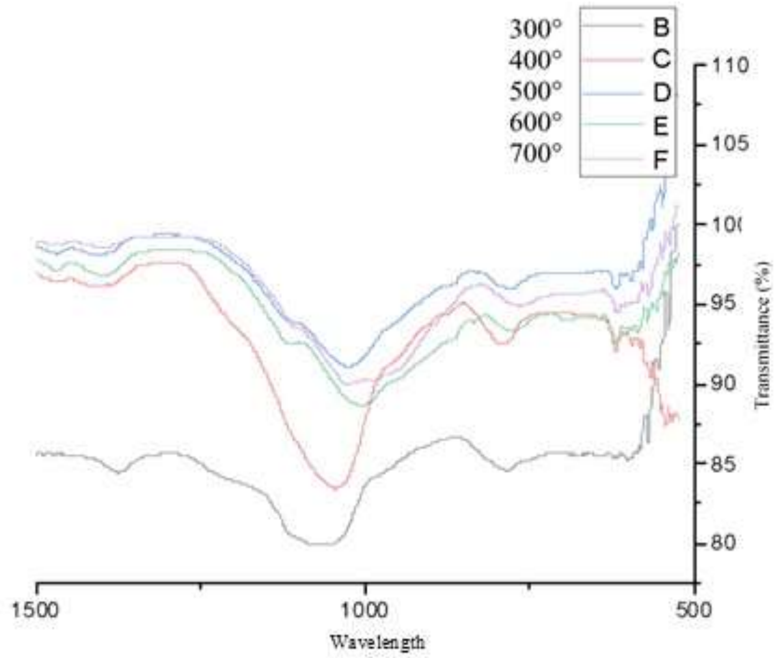

Fig. 2. Wheat Straw FTIR

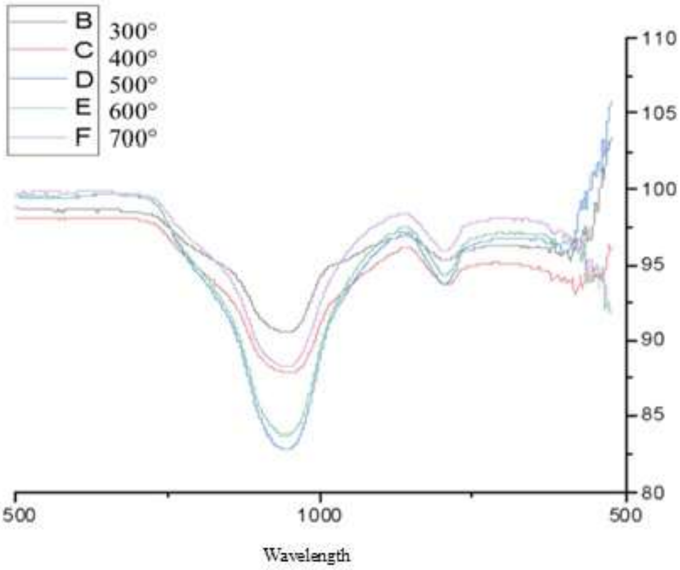

Fig. 3. Rice Husk FTIR

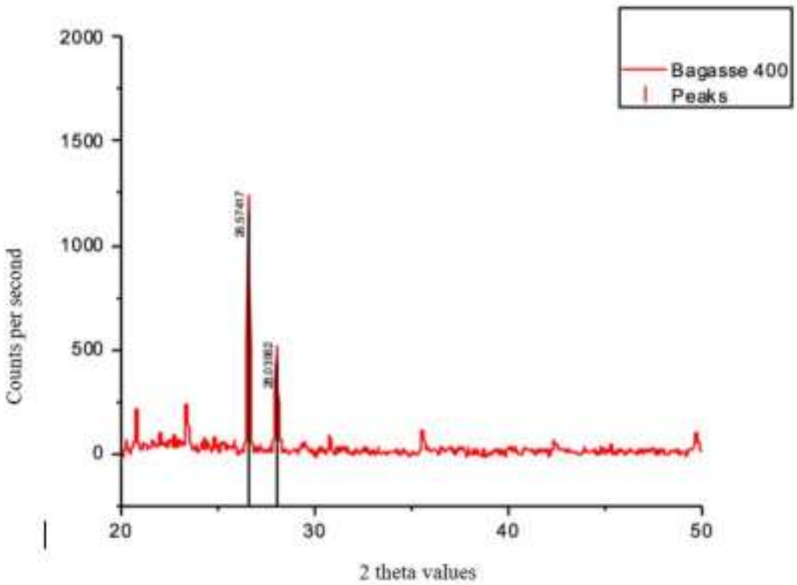

Fig. 4. Bagasse synthesized at 400℃ XRD

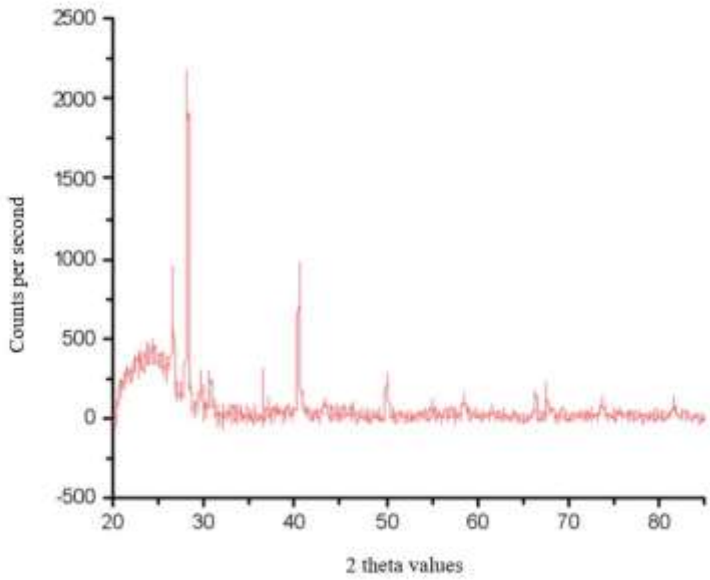

Fig. 5. Wheat straw synthesized at 300℃ XRD

3.3 Atomic Adsorption Spectroscopy

Findings. Each type of biochar removed a certain quantity of cadmium. From the graph (fig 6.) it is evident that wheat straw and bagasse had the highest removal efficacy at each quantity of biochar used.

Effect of biochar dosage. As the quantity of biochar used increases, the amount of cadmium removed also increases. This could mean that more than 0.1 gm of biochar per 10 ml of contaminated water could potentially remove all cadmium heavy metal ions in an 81ppm solution.

Effect of pyrolysis temperature. Two types of biochar were synthesized from the same feeder material but at different temperatures. It is evident from fig 6. that as the temperature of synthesis for rice husk increases from 300° to 400°, the amount of cadmium removed also increases.

Effect of feeder material. From the literature review it was found that wheat straw has an increased aromaticity and carbon content as the temperature of pyrolysis increases from 300° to 400°. Bagasse has the presence of several minerals, it is possible that cadmium was precipitated out of the solution or is bound on the surface of the char.

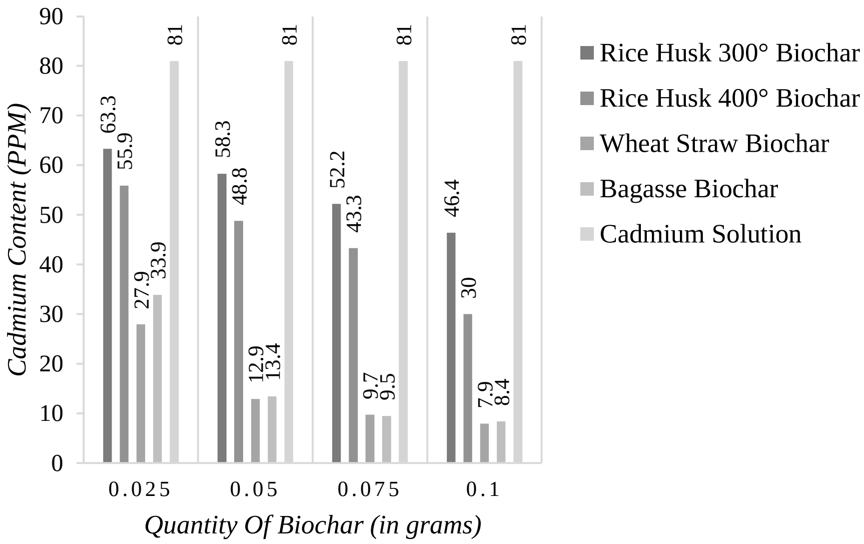

Fig. 6. Amount of cadmium removed across different char quantity and types

4 Conclusion

It is evident from the analysis that an increase in the amount of biochar applied to cadmium contaminated water results in a higher removal capacity. While an increase in the temperature could also play a role in the removal efficiency, only rice husk was analysed at two different temperatures hence, the data set is too small to support this. Bagasse and wheat straw biochar removed the highest amount of cadmium and as the ration of biochar to contaminant was increased the removal of heavy metal increased.

There is a further need to test the efficiency of a mixed ratio of biochar and the efficiency of removal of a mixed ratio of contaminants by a fixed ratio of char. A SEM analysis could further help in ascertaining the mechanism by which the heavy metal ion was removed by bagasse and wheat straw biochar.

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