



As(III) removal using engineered biochar synthesized from waste biomass of a Timber plant refuse

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Abstract

The present study is dealing with the utilization of timber plant waste biomass for the synthesis of MnO₂-modified biochar (MnBC). The biochar was synthesized by the process of thermal pyrolysis of pretreated biomass with MnO₂ at a high temperature (800 °C). Modification of biomass with MnO₂ adds more oxygenated groups to the biochar that enhance adsorption capacity of adsorbent. The synthesized biochar material was characterized using different analytical techniques like; EDX (Energy Dispersive X-ray), SEM (Scanning Electron Microscopy), FTIR (Fourier Transform Infra-red Spectroscopy) and point of zero charge (pH_{ZPC}). The batch adsorption study was conducted for optimizing the process of As(III) adsorption via MnBC. The maximum adsorption capacity was 0.577 mg/g found at 2.5 mg/L initial concentration. The temperature study shows that the process of adsorption was endothermic.

Keywords: Arsenic; biochar; adsorption; kinetics; isotherms

1. Introduction

Biochar is a carbonaceous material produced through thermal conversion of waste biomass and was further utilized for various environmental applications. It is a stable carbon source and can be utilized as a carbon sink in the soil for several decades (Lehmann et al., 2021). It is also used as a soil conditioner to improve the fertility of soil, hovering crop productivity, enhance water holding capacity and soil nutrients, etc. when applied to the soil (Singh et al., 2021). In the last few years, biochar has been introduced as an adsorbing material for the treatment of contaminated water with various organic and inorganic contaminants including organic dye compounds, nutrients, heavy metals, etc. (Zhang et al., 2013). Various other commercially available biosorbents were also used for environmental remediation but are not eco-friendly and cost-effective and also generate secondary pollutants after absorbing the pollutants (Nguyen et al., 2022). Biochar is one of the advanced cost-effective biosorbent, it is utilized for the removal of water contaminants (Hammo et al., 2021).

Arsenic is one of the most toxic inorganic pollutants in groundwater released from naturally existing arsenic-bearing rocks or through anthropogenic activities. Consumption of As contaminated water causes various toxic effects on human beings such as; cardiovascular disease, cancer, skin lesions, etc. (Shaji et al., 2021). There are several methods reported for As removal from the water like co-precipitation, filtration, membrane technique, ion-exchange, oxidation, adsorption, etc. Amongst these removal techniques, adsorption is one of the simple, cost-effective method of As removal from contaminated water (Tiwari et al., 2021). Biochar in recent times is the growing technique and is highly used for the treatment of As from water.

In the present study, waste biomass of timber plant has been modified with MnO₂, and then it was used for the As

adsorption from an aqueous solution. A batch adsorption study was conducted for the process optimization of arsenic adsorption using biochar modified with Manganese (oxidative agent).

2. Materials and methods

2.1 Chemicals and reagents

Sodium arsenite (NaAsO₂) was used to prepare the stock solution of As(III) and the working solution was prepared by diluting the stock solution for conducting the study further. Hydrochloric acid (HCl), potassium phosphate (KH₂PO₄), potassium iodate (KIO₃), ascorbic acid (C₆H₆O₈), antimony potassium tartrate (C₄H₄O₆KSbO.1/2H₂O), ammonium molybdate ((NH₄)₆Mo₇O₂₄.4H₂O), sulphuric acid (H₂SO₄), etc. of analytical grade were used for the experiments.

2.2 Method of synthesis

Waste dry leaves of timber plant has been collected from the BBA University campus, Lucknow, India. Synthesis of modified biochar material was done by following the method discussed by Sahu et al., 2021. The collected leaves biomass were washed, dried, and grounded into fine particle size. A 30 g of powdered biomass was mixed with the 150 mL solution of MnO₂ (10 g MnO₂ dissolved in 150 mL distilled water). This mixture was agitated for 4 h and then filtered using a vacuum filter, the obtained material was kept overnight in a hot air oven. After that, the mixture was incorporated in a muffle furnace for 1 h at 800 °C. The final product was washed, dried, homogenized and stored for further environmental application.

2.3 Characterization

SEM and EDS analysis were used for the determination of morphological structure and elemental composition,

respectively, of synthesized biochar (JOEL JSM-6490 LV, Japan). Functional group analysis was done using FTIR (NICOLET 6700 Thermo Scientific, USA). The pH_{ZPC} of the material was identified by the method described by Verma and Singh (2019).

2.4 Batch adsorption

The batch adsorption study was accompanied by 250 mL of Erlenmeyer flask. A 50 mL arsenic solution was taken in the flask with a predefined dose of biochar. Effect of dose, temperature, pH of the solution, concentration and contact

time was studied by varying the dose, temperature, pH, initial As concentration and contact time, respectively. The mixture of adsorbate and adsorbent was agitated using an orbital shaker at a speed of 80 rpm. After that, the mixture was centrifuged and the supernatant was used for the determination of residual As(III) concentration in the solution after adsorption. Spectro molybdate colorimetric method (Verma et al., 2019) has been used for the As(III) determination using a spectrophotometer(117, Systronics, India) at wavelength 880 nm. The adsorption capacity of MnBC has been calculated by using the following equation:

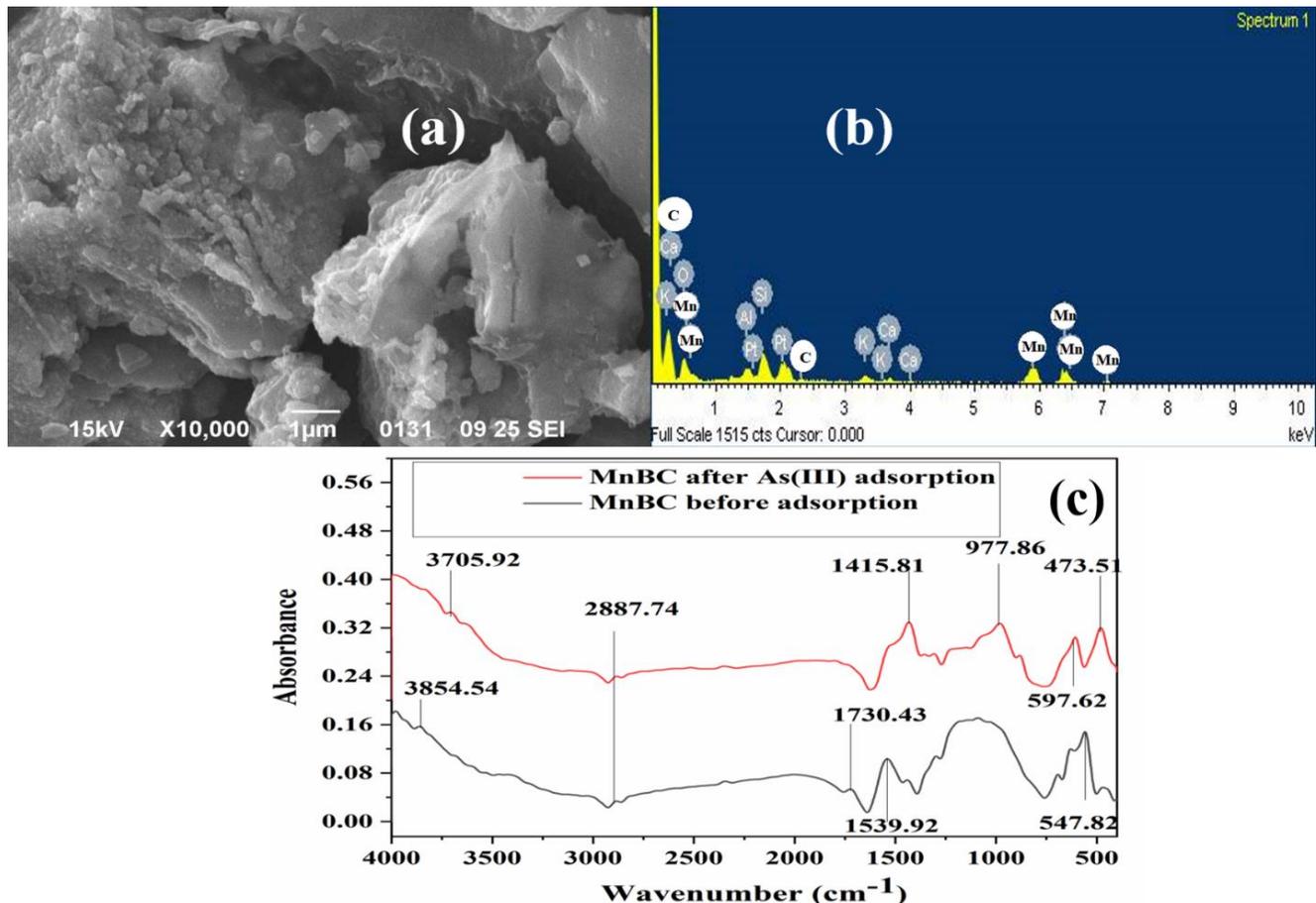


Fig. 1. a) SEM, b) EDS and c) FTIR of MnBC.

$$q_e = \frac{C_i - C_e}{m} \times V \tag{1}$$

Here, q_e and C_e is the adsorption capacity and final concentration of As, respectively, at an equilibrium point. V is the volume (liter) of As solution and m is the biochar mass.

3 Result and Discussion

3.2 Characterization

3.2.1 SEM and EDS

Fig. 1a. represents that the rough surface morphological structure of MnBC has a rectangular shape. The elemental composition of biochar shows the presence of carbon and

manganese which means the manganese has been successfully infused into the timber waste biomass (Fig. 1b).

3.2.2 FTIR

The FTIR spectrum of MnBC has been shown in Fig. 1c before and after adsorption of As(III). The peaks found near wavenumber 3854.54 and 3705.92 cm^{-1} are attributes to -OH (hydroxyl) group stretching. A small peak observed at 2887.74 cm^{-1} represents the bond of C-H and CH₂ or C=C groups that were attributed by 1730.43 cm^{-1} . The peaks found at 1539.92 and 1415.81 cm^{-1} correspond to the carboxylic acid group. The peaks at wavenumber 977.86 cm^{-1} show the

presence of asymmetrical stretching of OH vibration. The Mn-O group was represented by 597.62 and 473.51 cm^{-1} . The peak intensities and shifting were changed before and after As(III) adsorption which might be due to the involvement of some functional groups in the adsorption process.

3.2.3 pH_{ZPC}

The pH_{ZPC} of MnBC was found to be 9 which is basic. The biochar consists acidic nature below pH 9 and have more OH^- ion above pH 9.

3.3 Batch adsorption study

3.3.1 Effect of dose

The influence of biosorbent dose was studied at various doses (1 g/L – 6 g/L). The adsorption percentage for As(III) was increased by increasing the biochar dose from 1 g/L to 5 g/L but on further increasing the amount of dose no change in adsorption of As(III) was observed. The adsorption capacity of MnBC was reduced as the amount of dose increased. The maximum adsorption was achieved at 5 g/L of dose and the maximum capacity was 0.367 mg/g achieved at minimum dose i.e., 1 g/L (Fig. 2). This was might be due to the aggregation of biosorbent in the adsorbate solution that reduce the available surface area for As to get adsorbed by MnBC (Verma et al., 2021).

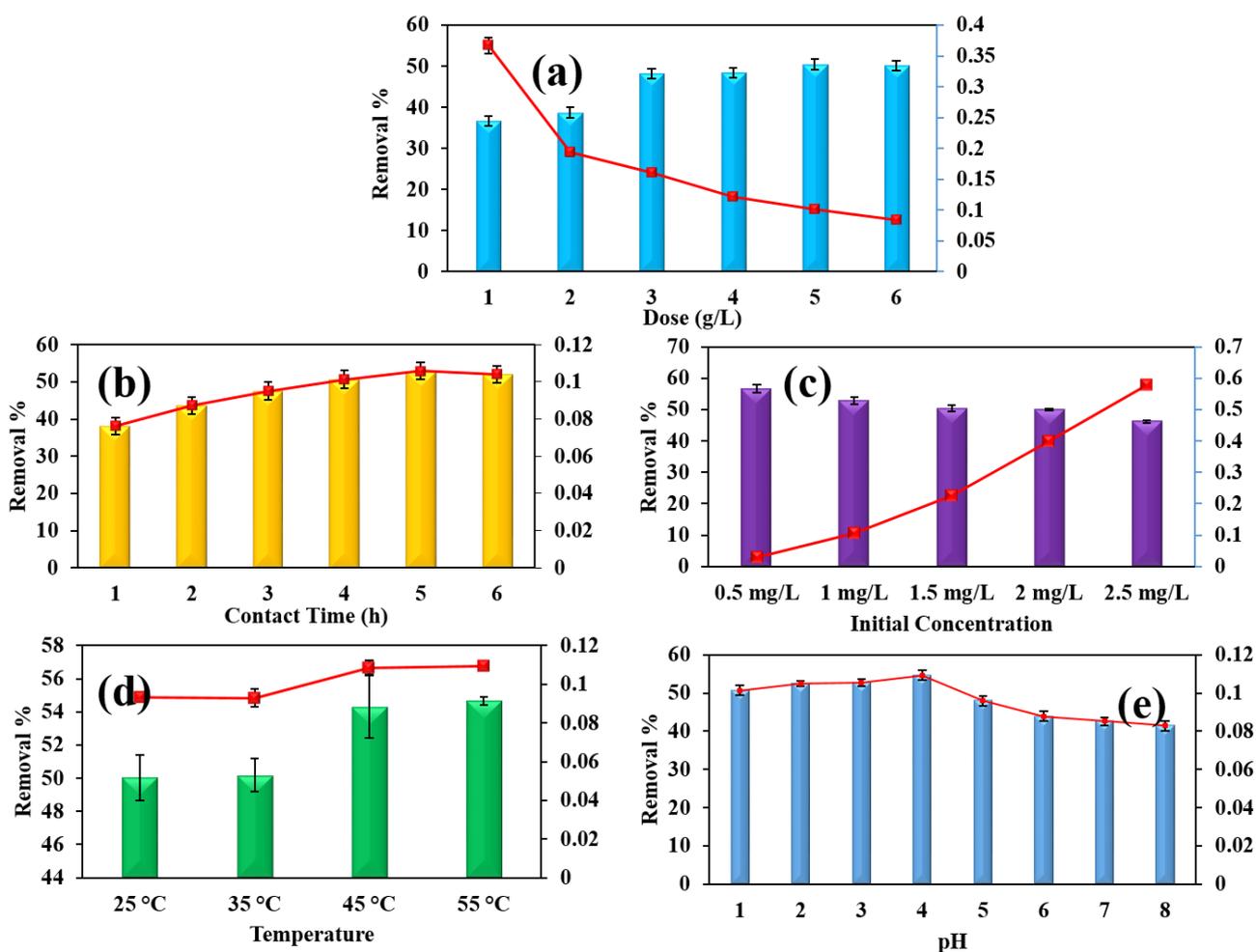


Fig. 2. Effect of a) biochar dose, b) contact time, c) Initial concentration of As(III), d) Operating temperature and e) pH of the solution.

3.3.2 Influence of initial concentration and contact time

Influence of concentration was done with varying initial concentration of As(III) (0.5 mg/L – 2.5 mg/L). The maximum adsorption was observed at lower initial concentration and on further increasing initial concentration, the adsorption was reduced. The adsorption capacity was 0.0283 mg/g at 0.5 mg/L initial As(III) concentration and 0.577 mg/g at 2.5 mg/g initial arsenic concentration (Fig. 2c). The obtained results

was might be due to the availability of active adsorbate binding sites on the biochar surface (Verma et al., 2021). It was observed in Fig. 2 b that As(III) adsorption was increased with increasing contact time and the highest adsorption was achieved at 5h. It was because of the saturation of reaction or binding sites present on the surface of biosorbent (Verma and Singh, 2022; Shukla et al., 2020).

3.3.3 Effect of temperature and pH

Four different temperatures were taken to check the influence of temperature on As(III) adsorption. As presented in Fig. 2d the adsorption of As(III) was increased with increasing operating temperature which means the method of adsorption was endothermic. The adsorption capacity of biochar was increased from 0.093 mg/g to 0.109 mg/g with an increasing operating temperature from 25 °C to 55 °C.

The pH of the solution is one of the most significant parameters to be studied in the adsorption process. The maximum adsorption was found at pH 4 with the highest adsorption capacity of 0.109 mg/g (Fig. 2e).

4. Conclusion

The successful synthesis of MnO₂ modified biochar was done and was applied for As(III) adsorption from an aqueous solution. The maximum adsorption capacity was 0.577 mg/g, attained with a higher initial concentration i.e., 2.5 mg/L. The higher temperature was favorable for the process of As(III) adsorption as the maximum adsorption was found at 55 °C temperature. Whereas the maximum adsorption capacity in pH study was 0.109 mg/g observed at pH 4 hence, it is concluded that the acidic pH is favorable to adsorb As(III) using MnBC. In the batch study, the adsorption percentage was not very high and it can be improved by further modification of biomass so that this material can be utilized not only for the treatment of As from aqueous solution but can also be used for the As contaminated groundwater.

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Author contribution

Lata Verma: Written-original draft, formal analysis, experimentation, methodology, conceptualization, methodology; Jiwan Singh: Supervision, reviewing and editing, validation.

Conflicts of Interest

There are no conflicts of interest declared by the authors.

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