Synthesis and characterization of biochar from waste biomass: An application for the removal of Arsenic from contaminated water

SUMMARY
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THESIS

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Summary

Water is the most necessary and basic requirement for the survival of all life forms, on the planet earth. Noticeably only 1 % of total water resources is usable and in that 1 % groundwater contributes about 96%. Over the last several decades, As contaminated groundwater posing several health-related issues. As poisoning can cause skin diseases, obstructive lung illness, arsenicosis, black foot disease, etc., and also lead to cancer in numerous body organs. The geogenic origin is the primary cause of arsenic pollution in groundwater. Several anthropogenic activities, such as mining, geothermal discharge, agricultural activities, feed additives, medicine etc. also pollute groundwater. As enters the human body primarily through the consumption of As contaminated drinking water.

Several physicochemical techniques have already been used for the treatment of As contaminated water. However, the high cost, sludge generation, less efficacy in removing pollutants, high energy cost, and specialized manpower requirement necessitate the development of a new and advanced treatment system for remediation of As from contaminated water. Besides these conventional techniques of As removal, adsorption has evolved as a simple, eco-friendly, cost-effective, time-saving and sustainable approach for water treatment including As removal without generating harmful secondary toxic by-products. Many studies have been conducted in this area and different types of adsorbents were investigated for their efficacy towards As removal. Biochar is found to be the most effective adsorbent and an emerging technique for the cost-efficient and sustainable removal of pollutants from contaminated water. The feedstock for biochar synthesis is available in bulk and synthesizing biochar from these waste biomasses not only helps to

solve the problem of waste disposal but also encourages the production of multifunctional adsorbents for the removal of As from contaminated water. According to the available literature, significant work has been done on the adsorption of As using biochar. However, the feedstock is still not been used for the development of biochar and has not been explored for their removal efficiency, mechanism and other multiple aspects. This is a major gap to be addressed in order to improve the applicability of biochar in the adsorption process. Based on these assumptions, this work has been performed in four different phases and key findings of the entire study are as follows:

Phase I: Characterization and application of pristine biochar for the removal of As(III) and As(V) synthesized using waste dry leaves of T*ectona sp.* and *Lagerstroemia speciosa* from an aqueous solution and groundwater.

- Firstly, four different biochar were synthesized without any modification using waste biomass of plant leave litter (*Tectona sp.* and *Lagerstroemia speciosa*) and vegetable waste (*Raphanus staivus* and *Artocarpus heterophyllus*).
- Only two biochar materials synthesized using dry leaves of *Tectona sp.* (TB 800) and *Lagerstroemia speciosa* (LB 800) showed high removal percentage of both the As species (As(III) and As(V)). Whereas, less than 10 % adsorption of both species of As was observed via biochar materials synthesized using vegetable waste. So, for further study TB 800 and LB 800 was used and in Phase III of the study, vegetable waste was modified and applied for As removal.

- The biochar was pyrolyzed at 800 °C and was characterized using different instrumental techniques such as SEM, EDX, BET, FTIR, XRD, zeta potential, pH_{ZPC}, PSA and XPS.
- The SEM and EDX results showed irregular and rough morphological surfaces and the elemental composition of both the adsorbents revealed that the TB 800 and LB 800 have 57.38 % and 55.51 % carbon by weight, respectively.
- About 94.6 % and 85.85 % of As(V) were adsorbed at pH 6 and pH 8 via TB 800 and LB 800, respectively. However, the highest (76.42 %) removal of As(III) was observed at pH 8 through TB 800 but in the case of LB 800, the removal of As(V) was found to be 61.67 %.
- Adsorption of As(III) and As(V) was probably due to electrostatic interaction and surface complexation mechanism. The presence of several oxygenated functional groups on the biochar surface, such as hydroxyl and carboxyl groups that play a very important role in the adsorption mechanism of As on biochar. The results were confirmed by the FTIR analysis of adsorbent before and after adsorption.
- Using TB 800, the maximum removal percentage of As(III) and As(V) was attained, with 77.9 % and 96.5 %, respectively. Noticeably, the highest removal of about 82% for As(V) and 72% for As(III) was observed by using LB 800 at the lowest initial concentration i.e. 0.5 mg/L.
- Findings of the batch adsorption investigation revealed that both the biochar materials were extremely effective in removing As(III) and As(V) from an aqueous solution as well as from groundwater, due to effective adsorption of As species from the solution. Both these materials can be successfully recycled up to four cycles.

- For the elimination of As(III), the adsorption capacity of TB 800 and LB 800 was 0.66 mg/g and 0.45 mg/g, respectively, while for As(V) the adsorption capacities of TB 800 and LB 800 were 1.25 mg/g and 0.71 mg/g, respectively.
- Experimental data followed the Langmuir model for As(V) removal using TB 800 and LB 800, Freundlich model for As(III) removal by LB 800 and Temkin model for As(III) removal by TB 800. Pseudo-second-order kinetics was observed and best fitted with the obtained As(III) and (V) removal data. Thermodynamic study revealed that the process of adsorption was endothermic for the removal of As(III) and exothermic for the adsorption of As(V) using TB 800 and LB 800
- In the next phase of the study, *Tectona sp.* and *Lagerstroemia speciosa* biomass were modified with the $FeCl_3$ to improve the adsorption capacity of biochar material and to minimize the dose requirement for As removal.

Phase II: Characterization of magnetic biochar synthesized using waste dry leaves and their application for the removal of As(III) and As(V) from an aqueous solution and groundwater.

- Waste dry leaves of *Tectona sp*. (MTB-800) and *Lagerstroemia speciosa* (MLB-800) were used to develop magnetic biochar materials. The ability of these synthesized biochars to adsorb As(III) and As(V) from an aqueous solution and groundwater was investigated.
- Both biochar materials were characterized by using SEM, EDX, FTIR, Raman spectroscopy, pH_{ZPC}, XRD, PSA and zeta potential.

- The SEM results elucidated that MTB-800 has an irregular shape and rough surface while MLB-800 has a smooth surface with an irregular shape. The results of EDX analysis showed that MTB-800 and MLB-800 have 42.79 % and 64.13 % carbon content, respectively. The presence of Fe in the EDX results indicates that the iron was successfully bound to the biomass materials. MTB-800 and MLB-800 consists 9.19 % and 5.01 % iron content, respectively, by weight percentage.
- Both the Fe-infused biochar were found to be effective in removing As(III) and As(V) from an aqueous solution and groundwater samples. MTB-800 and MLB-800 had a maximum As(III) adsorption of 92.1 % and 97.8 %, respectively. MTB-800 and MLB-800 on the other hand obtained the highest As(V) adsorption rate of 94.7 % and 96.7 %, respectively, at 0.5 mg/L As concentration.
- Results of the pH study reveal that the maximum 93.6 % adsorption of As(III) was achieved at pH 6 by MTB-800; while using MLB-800 the maximum adsorption was found to be 94.6 % at pH 8. However, adsorption of As(V) was found to be 92.85 % and 91.1 % at pH 5 by using MTB-800 and MLB-800, respectively.
- Adsorption capacity for the removal of As(III) was observed as 1.25 mg/g and 1.68 mg/g with MTB-800 and MLB-800, respectively. Whereas, the adsorption capacity of MTB-800 and MLB-800 was found to be 0.77 mg/g and 1.54 mg/g, respectively.
- Reusability test of the biochar revealed that it can be successfully reprocessed up to five cycles. Different models were explored to evaluate the breakthrough curve obtained in the column study.
- The adsorption process was well-fitted to the Langmuir model of isotherm and pseudo-second-order kinetic. The thermodynamics study revealed that the As(III) and As(V)

adsorption by MTB-800 and MLB-800 was exothermic which means the adsorption was reduced with increase in temperature.

- Batch and column studies showed that the dry leaves biomass can be successfully converted into biochar with magnetic properties and can be a good adsorbent for As(III) and As(V) removal. Both these biochar were able to adsorb significant levels of As from aqueous solution as well as from groundwater.

Phase III: Characterization and application of magnetic biochar synthesized using vegetable waste for As(III) and As(V) removal from an aqueous solution and groundwater.

- In this phase, fabrication of magnetic biochar was done by pyrolysis of waste leaves of *Raphanus sativus* (MRB) and *Artocarpus heterophyllus* (MJB) peel pretreated with $FeCl_3$ and was subsequently examined for As(III and V) adsorption from an aqueous solution.
- The characterization techniques such as SEM, EDX, FTIR, PSA, zeta potential, pH_{ZPC}, and VSM were used for biochar characterization.
- MRB-800 and MJB-exhibited irregular structure and rough surface. MRB-800 had high iron content by weight 44.40 % than MJB-800 (6.58 %), indicating that the *Raphanus sativus* and *Artocarpus heterophyllus* waste biomasses were successfully impregnated with iron, imparting magnetic properties to both adsorbents, as per the results obtained by EDX analysis.

- The highest As(III) adsorption was 81.85 % and 85.80 % for MRB-800 and MJB-800, respectively, whereas the highest As(V) removal was 60.7 % and 90.7 % for MRB-800 and MJB-800, respectively, at 0.5 mg/L initial As concentration.
- The highest removal of As(III) was 72.67 % and 88.4 % by MRB-800 and MJB-800, respectively, at pH 5 and 6. Whereas, the maximum adsorption of As(V) was found to be 72.35 % by MRB-800 and 92.65 % by MJB-800.
- MRB-800 showed greater efficiency towards the removal of both As species with q_{max} value 2.08 mg/g for As(III) and 2.03 mg/g for As(V). Whereas, the q_{max} value was 1.13 mg/g for As (III) and 1.26 mg/g for As (V) adsorption using MJB-800.
- Both adsorbents are stable, have lower particle size and are more efficient in removing both As species because they have more oxygen-containing surface functional groups. Two main important processes involved in As (III and V) adsorption were surface complexation and electrostatic attraction, which were better demonstrated by functional groups as well as the elemental composition of MRB-800 and MJB-800.
- Temkin and Freundlich isotherm was best fitted to the adsorption of As(III) and As(V) by MRB-800. Langmuir isotherm was best followed by the adsorption of As (III and V) by MJB-800. Pseudo-second-order kinetics was well simulated by the experimental data of As adsorption using both the adsorbents. Thermodynamic study showed that As (III) removal was exothermic while the As (V) adsorption was endothermic for MRB-800 and MJB-800, respectively.

Phase IV: Characterization and application of monometallic and bimetallic biochar prepared using *Tectona* dry waste leaves for the removal of As(III) from an aqueous solution and groundwater.

- In this study, the plant waste biomass was utilized for the synthesis of monometallic and bimetallic biochar. The biomass waste was pretreated with $FeSO_4$ for the synthesis of monometallic biochar whereas, it was pretreated with $FeSO_4$ and MnO_2 for synthesizing bimetallic biochar. These biochar materials were applied for As(III) removal from an aqueous solution as well as from groundwater samples.
- Fe-TB and Fe/Mn-TB both were characterized by using different analytical techniques such as SEM, EDX, FTIR, XRD, PSA, zeta potential and pH_{ZPC}
- The results of EDX showed the presence of Fe content in monometallic while Fe and Mn content in bimetallic biochar. Results of FTIR spectroscopy also confirm the impregnation of these metal salts with the plant biomass material.
- Enhanced removal of As(III) was observed with Fe/Mn-TB biochar which was greater than Fe-TB. The maximum adsorption was achieved about 90 % with Fe/Mn-TB, though ~84.85 % As was adsorbed using Fe-TB when the initial As concentration was 0.5 mg/L.
- The maximum adsorption of As(III) by Fe-TB was ~87.68 % at 4 pH. Whereas, the highest adsorption of As(III) was ~91.18 % achieved at 9 pH using Fe/Mn-TB.
- Adsorption capacity was 1.16 mg/g and 1.75 mg/g for As(III) removal using Fe-TB and Fe/Mn-TB, respectively, further the Fe-TB and Fe/Mn-TB were successfully recycled up to four cycles with optimum removal.

- The As adsorption was also assessed by kinetic study and the adsorption process has good compliance with pseudo-second-order kinetics. The As adsorption was followed freundlich isotherm model.
- The adsorption of As(III) by both the synthesized biosorbents i.e., Fe-TB and Fe/Mn-TB was endothermic, the adsorption was increased as the operating temperature was raised from 25 °C to 55 °C.
- Fe-TB and Fe/Mn-TB were also applied for the removal of As from groundwater. The removal of Arsenic by these biosorbents were controlled by different mechanisms like; electrostatic attraction, surface complexation and h-bond formation. Various functional groups were present on the biosorbents surface and hence many reactive surface binding sites were available on the biosorbent surface for the removal of As.