Arsenic adsorption from aqueous solution and groundwater using monometallic (Fe) and bimetallic (Fe/Mn) Tectona biochar synthesized from plant refuse: mechanism, isotherm, and kinetic study

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ABSTRACT

The present study deals with the utilization of waste biomass of Tectona plant refuse to synthesize the monometallic and bimetallic biochar and to examine their performance for As(III) removal from aqueous solution as well as from groundwater. The biochar materials were characterized using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Particle Size Analysis (PSA), zeta potential and pHZPC. The enhanced removal of As(III) was observed with Fe/Mn-TB (bimetallic) which was greater than Fe-TB (monometallic) biochar. The highest adsorption was 90.35 % and 84.85 % achieved with Fe/Mn-TB and Fe-TB, respectively, at 0.5 mg/L. As initial concentration 0.5 mg/L. The adsorption capacity was found to be 0.91 mg/g and 1.89 mg/g, respectively, by Fe-TB and Fe/Mn-TB. The adsorption process of As(III) has good compliance with pseudo-second order kinetics as well as Freundlich isotherm model. As(III) was adsorbed by the Fe-TB and Fe/Mn-TB possibly by electrostatic attraction, H-bond formation and complexation mechanism. Both these materials successfully removed As(III) from aqueous solution as well as from groundwater thus it can be used for the eradication of As(III) from the affected areas by utilizing them as an adsorbent in continuous flow system.

Keywords: Arsenic adsorption, Biochar, Bimetallic biochar, Groundwater treatment

Graphical Abstract
1. Introduction

The damaging influence of Arsenic contamination on the groundwater has led to a devastating impact on the human population worldwide. Arsenic contamination in drinking water is a major issue nowadays, especially in the economically weak regions of India, China, Chile, Argentina, United States, Bangladesh, etc. [1]. In India, the main affected states are West Bengal, Jharkhand, Bihar and Uttar Pradesh. Ganga river flood plain, in Assam the Brahmaputra river flood plain, and Manipur have been severely exposed to arsenic contamination in drinking water above the threshold limits [2, 3]. Northern Indian states are densely populated areas and the drinking water demands are dependent mostly on deep wells which are highly affected by Arsenic toxicity. According to recent studies, it has been reported that due to high Arsenic concentration in Assam, West Bengal the habitants of this area are suffering with a number of fatal diseases. Consumption of As contaminated water above its permissible limits (10 μg/L) can cause various serious diseases like skin, lungs, bladder cancer, hypertension, gastrointestinal infections, diabetes, mitochondrial damage, etc. [4].

Groundwater Arsenic contamination is not only associated with the arsenic-containing rocks or minerals but it is also related to the solubility of host minerals, pH, and redox condition. The contamination of arsenic arises because of the reductive dissolution of minerals containing Arsenic into it [5, 6]. Enhancement of several natural biogeochemical activities notably escalates the discharge of extremely toxic As from the arsenic-bearing mineral rocks [7]. Additionally, several anthropogenic activities such as arsenical pesticide application onto the crops, mining and pharmaceutical mistreatment are responsible for the direct addition of different forms of As to the water [8]. Arsenic is generally called as the invisible killer because of its imperceptibility in water. World Health Organization sets the arsenic permitted limit of 10 μg/L in drinking water [9]. It was reported that the As concentration in drinking water and wastewater was found typically in the range of 0.1-230 mg/L, which is much higher than the permitted threshold limits [10]. Therefore, it is very necessary and significantly prodigious to develop efficient methods for arsenic decontamination from water.

Various techniques have already been used for the As treatment from water such as coagulation, membrane filtration, ion exchange, reverse osmosis, chemical precipitation, electrocoagulation, advanced oxidation, lime softening, ultrafiltration, adsorption, etc. [11, 12, 13, 14]. Among these techniques, adsorption appeared as a promising method because of its easy application cost-effectiveness, and greater efficiency in the removal of pollutants from water [15, 16]. Recently, carbon-based nanomaterials have been also used for the remediation of multiple environmental toxic compounds via the process of adsorption [17, 18, 19]. The process of adsorption is also found to be effective in removing sulfur from liquid hydrocarbon fuels [20]. Various feedstocks were used for the preparation of adsorbents such as agricultural residue waste (wood, rice husk, maize cob, maize stalk), garden grass and plants residual waste, food waste, sludge, eggshell [21], tires waste [22] etc. and were applied for the removal of different organic and inorganic pollutants from water [23, 24].

Biochar is a cost-effective, porous, carbon enriched compound prepared by thermal decomposition of organic biomass under oxygen-limited environment and it consists of high potential as an efficient adsorbent because of its high surface area, porosity, and complex structure [25]. Biochar is recognized as the most efficient biosorbent for the removal of As from contaminated water. Biochar is easier to synthesis and more eco-friendly, to improve the textural properties of biochar variant methods has been opted in multiple studies, which includes chemical treatment (acid and base), microwave treatment, impregnation of metal, etc. [26, 27].

As per the available literature, no single study yet performed on synthesis of biochar derived from Tectona sp. using these metal salts. These synthesized biochar modified with (Fe/Mn) were first time utilized for the treatment of groundwater contaminated with As. Various lignocellulosic waste yet not discovered for their efficacy in removing metal contaminate water. Thus, this research work urged upgrading and making use of available lignocellulosic waste biomass from the BBA University campus, Lucknow. The present study intended at assessing the Arsenic removal efficiency of biochar, synthesized by utilizing waste biomass of Tectona was modified with Fe and Fe/Mn. The impact of various operational factors like pH of the solution, dose of biochar, initial concentration of adsorbate and temperature were also conducted to optimize the adsorption process. To understand the mechanism of the adsorption; isotherm models, adsorption kinetics, thermodynamics studies along with the structural and surface properties of the biosorbent were also investigated.

2. Materials and Methods

2.1. Chemical and Reagents

Analytical grade reagents and chemicals were used in the study. Sodium arsenate and sodium arsenite were castoff for preparation of stock solution (1000 mg/L) of adsorbate and the experimental adsorbate solution was formulated by water down the stock solution using DI water. Hydrochloric acid (HCl), potassium phosphate (KH₂PO₄), potassium iodate (KIO₃), ammonium molybdate ([NH₄]₆Mo₇O₂₄·4H₂O), antimony potassium tartrate (CsH₃O₂ KSbO₄·1/2H₂O), L-ascorbic acid (C₆H₈O₆), sulphuric acid (H₂SO₄), manganese oxide (MnO₂), iron sulphate (FeSO₄) etc. were supplied by fisher scientific, India.

2.2. Synthesis of Biochar

Waste biomass of Tectona sp. was collected from the campus of BBA University, Lucknow, India. Collected waste was firstly washed with distilled water at least three times and oven-dried at 105 °C temperature. The dried biomass was chopped into small pieces of almost equal size. The material was then grounded and sieved to obtain a homogenized powder. Two different biochar materials were synthesized in the present study. A 30 g powdered biomass was added to the 150 mL solution of FeSO₄ (10 g FeSO₄ dissolved in 150 mL distilled water) to synthesize the monometallic magnetic biochar. However, Fe/Mn-TB (bimetallic) biochar was synthesized by mixing 30 g of powdered biomass in 150 mL of FeSO₄ and
using pH meter (Water Analyser, 371 Systronics). Using 0.1 M solutions of NaOH and HCl and the pH was measured to be 4 h. In case of pH study, the working solution pH was maintained with different initial concentration of As(III) and contact time (30 min-360 min). Contact time study shows that the equilibrium was found to be 4 h. For the pH study, the working solution pH was maintained using 0.1 M solutions of NaOH and HCl and the pH was measured using pH meter (Water Analyser, 371 Systronics).

The adsorption capacity of biosorbents for As(III) removal was calculated using equation given below:

$$\text{Adsorption capacity} (q_e) = \frac{V(C_i - C_f)}{m}$$ (1)

2.5. Adsorption Kinetics

The kinetics experiment was conducted using three renowned models of kinetics comprising the pseudo-first-order, pseudo-second-order kinetics and intraparticle diffusion model. The rate of As(III) adsorption was analyzed using pseudo-first-order kinetics reaction [31]:

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t$$ (2)

where the quantity of adsorbate adsorbed by adsorbent is signified by $q_e$ at an equilibrium point and $q_t$ at time $t$. $k_1$ is the rate constant for pseudo-first-order kinetics and its value was evaluated from log $(q_e-q_t)$ against $t$ slope.

Pseudo-second-order kinetics model was also applied for analyzing the rate of As(III) adsorption via Fe-TB and Fe/Mn-TB using following equation:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t$$ (3)

where adsorbed amount of As(III) by biosorbent was denoted by $q_t$ (mg/g). The constant for pseudo-second order kinetics is implied by $k_2$ and its value was evaluated from $t/q_t$ versus $t$ plot slope.

The equation for intraparticle diffusion model has been written as follows:

$$q_t = k_i t^{1/2} + C$$ (4)

Here, intraparticle diffusion constant was associated with $k_i$ and $C$ is the constant linked with the boundary layer of biosorbent. The constants values were evaluated by the slope of $q_t$ against $t$ plot.

2.6. Adsorption Isotherms

The batch experimental data was also described through an adsorption isotherm. The experiment was conducted with different initial As(III) concentrations, a fixed amount of biosorbent dose and pH etc. The isotherm models of adsorption are generally used to define the design of process of adsorption. The isotherm constraints can be used to comprehend the surface properties of biochar and removal mechanism optimization. Three different isotherm models Langmuir (Eq. 5 and 6), Freundlich (Eq. 7) and Temkin (Eq. 8) were used to evaluating the experimental data [32];

$$\frac{C_e}{q_e} = \frac{1}{Q_b b} + \left(\frac{1}{Q_b b}\right) C_e$$ (5)

$$R_t = \frac{1}{1 + bC_e}$$ (6)
where equilibrium concentration of As(III) in the aqueous solution is symbolized by $C_e$ (mg/L), $q_e$ and $Q_0$ denotes the equilibrium adsorption capacity and maximum amount of adsorbate adsorb by biosorbents, respectively (mg/g). A dimensionless factor of Langmuir isotherm is denoted by $R_L$ and it describes the favorability of the adsorption process. $b$ (L/g) is the Langmuir constant which is related to the binding site affinity. $b$ (J/mol) epitomizes the constant of the heat of adsorption and the binding constant is denoted by $K_T$. $K_T$ (mg/g (L/mg$^{1/n}$)) and $n$ are the Freundlich constant which represents adsorption capacity and favorability of As(III) adsorption. A higher value of $K_T$ indicates the higher capacity of adsorption and the heterogeneity of the biosorbent surface is demonstrated by a value of $1/n$ in the range of 0 to 1, the lower its value more heterogeneous the surface [33].

### 2.7. Thermodynamics

Thermodynamic studies help to investigate the impact of various temperatures on the adsorption of As(III) via Mn-TB and Fe/Mn-TB. The parameters of thermodynamics were calculated using the following equations:

\[
K_c = \frac{q_e}{C_e} \quad (9)
\]

\[
\ln C_e = \frac{\Delta H^0}{R} - \frac{\Delta S^0}{RT} \quad (10)
\]

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (11)
\]

where $q_e$ (mg/g) and $C_e$ (mg/L) are the amount of As(III) adsorbed by Fe-TB and Fe/Mn-TB and As(III) concentration at equilibrium, respectively. Gibb’s free energy, enthalpy and entropy are denoted by $\Delta G$ (kJ/mol), $\Delta H$ (kJ/mol) and $\Delta S$ (kJ/mol), correspondingly. $R$ is the ideal gas constant (8.302 kJ/mol k) and $K$ is temperature.

### 3. Result and Discussions

#### 3.1. Characterization

**3.1.1. SEM and EDS**

An SEM image of the sample was generated using an electron beam. The interaction of these electrons (primary electron beam) with the surface of biochar illustrates the topography and composition of the biochar materials [34, 35]. The surface morphology of Fe-TB and Fe/Mn-TB was determined using SEM and Fig. 1a-h presented the SEM and EDS images of Fe-TB and Fe/Mn-TB before and after As(III) adsorption. The scanning electron micrographs indicated that both the biochar materials were irregular in shape with a rough surface. There was no change in morphological structure observed in the case of Fe-TB before and after As(III) adsorption (Fig. 1a and b) but in the case of Fe/Mn-TB there were spherical large clumps was found on the biosorbents surface (Fig. 1c and d), that might indicate the presence of Mn on to the surface of the material.

EDS is an analytical technique for determining the elemental composition of the sample and also reveals the quantity of the elements present in the sample. Core level vacancies are created as a result of secondary electron emission. When upper-level electrons fall on the vacant ones, then the x-rays are emitted that are corresponding to the energy difference generated between both these levels, which can be used to diagnose that element [34]. Fig. 1e-h, represent the elemental composition of both biosorbent which reveals that the Fe-TB has 39.76 % and Fe/Mn-TB has 23.19 % of carbon by weight %. The presence of Fe and Mn shows the successful infusion of these elements into the waste biomass. The EDS spectrum shows distinct peaks of oxygen (O), carbon (C), iron (Fe) and manganese (Mn), with suitable weight and atomic percentage (Fig. e-h and Table S1).

![Fig. 1. SEM images](image-url)

Fig. 1. SEM images (a) and (b) before and after As(III) adsorption using Fe-TB, respectively, (c) and (d) before and after As(III) adsorption using Fe/Mn-TB, respectively, EDX images (e) and (f) before and after As(III) adsorption using Fe-TB, respectively, (g) and (h) before and after As(III) adsorption using Fe-TB, respectively.
3.1.2. FTIR
The surface functional group of Fe-TB and Fe/Mn-TB before and after loading of As(III) was analyzed using FTIR and the spectrum was shown in Fig. 2a and b. The FTIR spectra of Fe-TB and Fe/Mn-TB show a distinct number of peaks and also the variations in peaks before and after As(III) adsorption. In the spectrum of FTIR, the peaks identified at wavenumber 3855.54-3002.73 cm\(^{-1}\) were attributed to –OH (hydroxyl) bonds. Asymmetric C-H stretching vibration produces a peak with low intensity at 2889.46 and 2332.14 cm\(^{-1}\) \([35, 36]\). The peaks 1730.50 and 1799.45 cm\(^{-1}\) in the IR spectrum are consigned to carbonyl groups in ester. Whereas, the peaks with 1528.59, 1518.74 cm\(^{-1}\) wavenumber ascribes to the presence of carboxyl group (-COOH) or C=C bond \([9]\). The peaks at wavenumbers 1435.02 and 1430.09 cm\(^{-1}\) are assigned to C-H asymmetric vibration whereas, 1311.90 characterize C-O bonds \([34]\). A peak of 1287.27 cm\(^{-1}\) ascribed to the stretching of C=O vibration and bending vibration of C-H in the plane. The peaks near 690.56-552.66 cm\(^{-1}\) indicated the occurrence of Fe-O iron stretching \([37]\). Some small peaks appeared near wavenumber 739.80 and 483.72 corresponding to the Mn-O stretching \([38]\). An almost similar pattern of the spectrum was found for Fe-TB before and after As(III) removal but the change in the peaks intensity might be due to the adsorption of As onto the biosorbent surface. In the case of Fe/Mn-TB FTIR spectra before and after adsorption, the peak 1430.09 cm\(^{-1}\) intensity was increased. A shift in peaks and change in peak intensities might be due to the adsorption of As and this could be described by some of the adsorbate and adsorbents (functional groups) interaction.

3.1.3. XRD
The crystallographic and amorphous properties of biosorbents were evaluated through X-ray diffraction analysis. Fig. 2c and d shows the XRD pattern of Fe-TB and Fe/Mn-TB, having narrower and distinct peaks indicating the crystalline nature of both the biochar materials. The formation of iron oxide ensued in crystalline biosorbents nature. In Fig. 2c the sharp and narrower diffraction peaks at 2\(\theta\) = ~26°, ~30°, ~35°, ~41°, ~43°, ~53°, ~57° and ~62°, corresponded to miller indices (012), (104), (110), (113), (026), (116), (018) and (214), respectively for Fe-TB indicates that Fe-TB consists single Fe compound in the e\(\alpha\)Fe\(_2\)O\(_3\) crystal structure. This validates the formation of biochar having magnetic properties. Similar peaks have been also identified by Ibrahim et al. \([39]\); Yang et al. \([40]\).

The XRD pattern for FeMn-TB before and after As(III) adsorption was shown in Fig. 2d. The diffraction peaks of Fe/Mn-TB at 2\(\theta\) = ~26°, ~29°, ~35° and ~56° corresponds to the miller indices (012), (104), (110), and (018), respectively, for the plane of hematite i.e., \(\alpha\)-Fe\(_2\)O\(_3\). Whereas the diffraction peaks at 2\(\theta\) = ~43° and ~47° resemble the miller indices (420) and (411), correspondingly, a plane of manganese oxide (\(\beta\)-MnO\(_2\)). The diffraction peak found at 2\(\theta\) = ~62° (Miller indices (531) represents the plane of MnO\(_2\)). The change in the pattern and intensities of diffraction peaks was might be due to some interaction taking place between the adsorbate and biosorbents surface. Similar diffraction peaks were also reported in the study conducted by Tan et al. \([41]\); Yang et al. \([40]\).

3.1.4. Particle size analysis
Particle size analysis of Fe-TB and Fe/Mn-TB was performed to

![Fig. 2. (a) and (b) FTIR analysis of Fe-TB and Fe/Mn-TB, respectively, (c) and (d) XRD analysis of Fe-TB and Fe/Mn-TB, respectively, (e) PSA analysis of Fe-TB and Fe/Mn-TB, and (f) Zeta potential of Fe-TB and Fe/Mn-TB.](image-url)
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examine the size of the biosorbent. For particle size analysis the biochar was initially homogenized and ultra-sonicated after being added to ethanol i.e., the dispersal medium. As presented in Fig. 2e, the hydrodynamic diameter of Fe-TB and Fe/Mn-TB in dispersal medium ranges from 100-200 nm and 350-750 nm, respectively.

3.1.5. Zeta potential

The values of the zeta potential are associated with the particle surface charge. Surface functional groups of biosorbents after protonation and deprotonation can generate a net charge on the surface of the solid biochar particles, which forms an electrical double layer near the surface in solution [42]. The magnitude of zeta potential illustrates the degree of stability and incipient stability of biosorbent in dispersion media, which undertake the electrostatic repulsion amongst dispersed medium and biosorbent. Fig. 2f shows that the zeta potential value was <±30, hence both the materials were not highly stable. The zeta potential value for Fe-TB and Fe/Mn-TB was found in a range of -0.209 mV-1.43 mV and -17.3 mV-1.36 mV, respectively. So, both these materials show incipient stability.

3.1.6. pHZPC

The point of zero charge is one of the very essential parameters of biosorbent to be determined. The point of zero charge describing the pH-dependent net surface charge on biosorbent is zero. The pHZPC of both the biosorbent was determined after its synthesis and the values of the point of zero charge for Fe-TB were 2.9 and 8.2 for Fe/Mn-TB.

3.2. Adsorption Experiment

3.2.1. Effect of biochar dose on As(III) adsorption

The biochar concentration in As(III) solution is one of the most essential factors in the adsorption process. The process of adsorption is highly influenced by the increasing or decreasing amount of biochar concentration in an aqueous solution of As(III). The influence of biochar (Fe-TB and Fe/Mn-TB) dosage on As(III) adsorption was assessed by varying biochar quantity in the range of 0.5 g/L-4 g/L. Fig. 3a represents the outcomes of dose study and it was found that the adsorption of As(III) was maximum with 2 g/L (~83.8 %) and 2 g/L (~90 %) using Mn-TB, Fe-TB and Fe/Mn-TB, respectively. At certain limits increasing the amount of biosorbent increases the accessible active sites for As adsorption which favors greater adsorption. Though raising the concentration of biosorbent beyond a certain point may cause agglomeration or formation of biochar clumps, which enhance the particle size and decrease the surface area [43, 44, 45], resulting in decreased adsorption of As(III) increasing dosage of Fe-TB and Fe/Mn-TB. A similar description for adsorption of As using biochar materials was conducted by Verma and Singh, [46] and also by Li et al. [24] reported that adsorption of As was decreased with an increased adsorbent dose.

3.2.2. Effect of pH on adsorption of As(III)

The solution pH is one of the very vital parameters defining surface charge, speciation of adsorbate, and degree of ionization, etc. The pH effect on As(III) adsorption was examined by varying the pH...
of the solution in the range of 3-10 while keeping other constraints remains constant like initial As concentration (1.0 mg/L), temperature (25 °C), pH (7) and contact time (240 min). The As adsorption occurred at acidic and alkaline conditions, respectively, by Fe-TB and Fe/Mn-TB. Fig. 3b presented the obtained results that illustrate that the maximum adsorption of As(III) by Fe-TB was ~87.68 % at 4 pH and slightly decreased with increment in pH of a solution. Whereas, the highest adsorption of As(III) was ~91.18 % achieved at 9 pH by using Fe/Mn-TB. Below pH 9.2 As(III) is present as H₃AsO₃ in an aqueous medium and beyond pH 9.3 this neutral form of As dissociated into negatively charged arsenite ions (H₃AsO₃⁻) [47]. As the pHZPC of Fe-TB and Fe/Mn-TB was 2.9 and 8.2, respectively, below this pH value both these materials were positively charged and above this pH, the biosorbent surface has a net negative charge [4] and the neutral charged As (H₃AsO₃) species was adsorbed onto negatively charged biosorbent surface and effective adsorption was found at pH 4 and 9. The removal of As(III) was not much affected by the pH of the solution, only a slight reduction in adsorption was observed with varying solution pH. Sahu et al. [48] have also reported similar findings in their study on the effect of pH on adsorption of As by magnetic biosorbent. Removal of As is very much dependent on As species to be adsorbed and pH of the solution [49].

3.2.3. Effect of initial As concentration and contact time on adsorption

The impact of initial adsorbate concentration on adsorption of As(III) was investigated for Fe-TB and Fe/Mn-TB by varying initial adsorbate from 0.5 mg/L to 2.5 mg/L, pH 7 with different time intervals at ambient operating temperature i.e. 25 °C. As illustrated in Fig. 3c and d that adsorption of As(III) by both biosorbents decreased with increasing concentration from 0.5 mg/L to 2.5 mg/L. The highest adsorption was found to be 84.85 % by Fe-TB and 90.35 % by Fe/Mn-TB, at 0.5 mg/L initial concentration. A gradual decrease in adsorption of As(III) was observed on an increasing initial concentration from 0.5 mg/L to 2.5 mg/L because of the saturation of biosorbent surface that limits the active adsorption sites [50]. Initially, the biosorbents offer a large surface area for adsorption of As, conversely, as the initial adsorbate concentration increases, most of the surface-active binding sites become saturated, which reduces the surface area for adsorption of As molecules by Fe-TB and Fe/Mn-TB, thus the removal of As also get reduced. The adsorption capacities of biosorbent increased with an increase in As(III) initial concentration. The maximum adsorption capacity for As(III) removal by Fe-TB was 0.83 mg/g and 1.00 mg/g by Fe/Mn-TB at 2.5 mg/L initial adsorbate concentration (Fig 4a and b).

The whole study was performed for 6 h, using both the biosorbents (Fe-TB and Fe/Mn-TB). A similar adsorption pattern was achieved with both the biosorbent i.e., with an increasing contact time of adsorbate and adsorbent, the removal of As was also improved, and the time of equilibrium was attained in 240 min for both the biosorbents but there was no significant increase in As(III) adsorption was observed on further increasing contact time (Fig. 3c and d). Primarily, the number of vacant binding active sites was available abundantly but after a certain time period these vacant sites were occupied by the As ions and a decrease in available active binding sites resulted in decreased As adsorption [51, 52].
3.2.4. Effect of temperature on adsorption of As(III)
The impact of temperature on adsorption of adsorbate i.e. was studied using different temperatures (25 °C to 55 °C), pH 7, initial As concentration (1.0 mg/L) and 2 g/L of biosorbents (Fe-TB and Fe/Mn-TB) dose. The obtained experimental results show that with increasing operating temperature from 25 °C to 55 °C, adsorption of As(III) was also increased (Fig. 3e and f). The maximum adsorption of As was found to be ~89.42 % and ~90.42 % at 55 °C using Fe-TB and Fe/Mn-TB, correspondingly. The process of As(III) adsorption via Fe-TB and Fe/Mn-TB was found to be endothermic. The adsorption capacity was also increased with an increased temperature (Fig. 4c and d). An increase in removal percentage with temperature elevation was might be due to the high temperature helping to incapacitate the high activation barrier, resulting in an increase in adsorption. As reported by Kazi et al. [53] sometimes biosorbents need high temperature or sometimes need low temperature for the activation of surface-active binding sites. Almost similar results were also reported in a study done by Sahu et al. [48] in which the highest removal was observed at 55 °C operating temperature using a magnetic biosorbent.

3.3. Regeneration Study
Regeneration of spent or used biochar is a very essential step and a very significant characteristic of any biosorbents. An alkaline solution of 0.1 M NaOH solution was utilized as an eluent as a desorbing solution to investigate the possibility of regenerating the biosorbents employed in desorption for reuse [44]. This study is one of the most essential criteria for measuring the efficacy of biosorbents that have been synthesized. For recycling of Fe-TB and Fe/Mn-TB, the used biochar was separated out physically from As(III) solution after adsorption using a magnet then kept in desorbing solution (0.1 M NaOH) for 24 h and after that washed with deionized water until its pH reaches to neutral. The biochar materials were then dried and used for the next adsorption cycle. The results

<table>
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<tr>
<th>Isotherm model</th>
<th>Parameters</th>
<th>Fe-TB</th>
<th>Fe/Mn-TB</th>
</tr>
</thead>
<tbody>
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<td>Langmuir isotherm</td>
<td>$Q_0$ (mg/g)</td>
<td>1.166±0.170</td>
<td>1.749±0.132</td>
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<td></td>
<td>$b$ (L/mg)</td>
<td>2.653±0.741</td>
<td>2.598±0.602</td>
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<td></td>
<td>$R_L$</td>
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<td>0.133±0.026</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.978</td>
<td>0.953</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>$K_F$ (mg/gL/mg)$^{1/n}$</td>
<td>0.935±0.017</td>
<td>1.634±0.005</td>
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<tr>
<td></td>
<td>$n$</td>
<td>1.789±0.100</td>
<td>1.510±0.094</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.993</td>
<td>0.996</td>
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<tr>
<td>Temkin isotherm</td>
<td>$K_T$ (L/g)</td>
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<td>32.750±6.855</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.976</td>
<td>0.953</td>
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Table 1. Values of Isotherm Parameters for As(III) Adsorption Using Fe-TB and Fe/Mn-TB.

Fig. 5. Plot for (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Temkin isotherm and (d) Thermodynamics study for Fe-TB and Fe/Mn-TB, (e) and (f) Plots of pseudo-second-order kinetics for As(III) adsorption by Fe-TB and Fe/Mn-TB, respectively. (experimental conditions: dose 2 g/L (Fe-TB and Fe/Mn-TB), 25 °C temperature, 1.0 mg/L initial As concentration, pH 7, 80 rpm and contact time 360 min).
show that the removal percentage was decreased with a number of cycles. The pattern of decreased adsorption percentage per cycle for both biosorbent was almost similar. Fig. 4e presented that the adsorption of As(III) was dropped from 80.3 % to 46.4 % for Fe-TB and 87.8 % to 48.8 % from the initial first to fourth regeneration cycle.

3.4. Removal of As from groundwater

The groundwater contaminated with As was collected from Kaisarganj (KG) (27.2515 °N, 81.5473 °E) and Jarwal (J) (27.1634° N, 81.5391°E) which are situated in district Bahraich (Uttar Pradesh), India near Nepal border. The collected samples were firstly analyzed for evaluating As concentration present in each sample and the concentration of As was found to be 0.10 mg/L and 0.092 mg/L in the KG and J samples, respectively. The detected concentration in these samples was higher than the permissible limits set by WHO i.e., 10 μg/L. Then the samples were treated using 2 g/L doses of Fe-TB and Fe/Mn-TB and the shaking speed was 80 RPM. Adsorption of As(III) was ~80.5 % (KG) and ~85.38 % (J), respectively, for Fe-TB whereas, ~83.63 % and ~86.13 %, respectively, for KG, J by Fe/Mn-TB (Fig. 4f).

3.5. Isotherm Study

The experimental design of the adsorption process was described by using the adsorption isotherms. The obtained results revealed that the adsorption of As(III) on Fe-TB ($R^2=0.993$) and Fe/Mn-TB ($R^2=0.996$) shows more conformity with the Freundlich isotherm model with a greater value of $R^2$ than that of Temkin and Langmuir isotherm (Fig. 5 a-c). The compliance of the adsorption process with the Freundlich model of isotherm explained the physisorption and multilayer sorption mechanism [34]. The process of As(III) adsorption is said to be a favorable physical process when the value of the Freundlich constant ($1/n$) is less than 1 and close to 0 [37]. All the values were given in Table 1.

3.6. Kinetics Study

To determine the best operating conditions, sorption mechanism and rate-controlling step, the kinetics of As removal was investigated using kinetic models. This information is very important for biosorbent efficiency in the process of adsorption. To optimize the design parameters, it is essential to understand the rate of adsorption removal of pollutants from contaminated water. The kinetic study was performed with different initial As(III) concentrations and contact time. Based on obtained results it was illustrated that the experimental data shows better compliance with the Pseudo-second order kinetics than pseudo-first-order kinetics. The results show the instant enhancement in uptake of As(III) with increasing contact time and obeyed slow adsorption rate to attain the equilibrium. Moreover, about 80 % of As was adsorbed through Fe/Mn-TB within 1 h, while ~70 % of As was adsorbed after 1-2 h using Fe-TB and did not show any rapid change. This happened might be due to the elaboration of adequate Arsenic binding sites on the Fe/Mn-TB surface. The data were fitted well to the pseudo-second-order kinetics with a value of regression coefficient ($R^2$) above 0.9986 (Fig. 5e and f) (Table S2). The pseudo-first-order kinetics were presented in Fig. S1a and b. In the present study, two different biochar materials i.e., monometallic (Fe-TB) and bimetallic (Fe/Mn-TB) were used and both these materials were having different surface morphology and structure as well as different elemental compositions as revealed in the SEM and EDX result. They also possess different surface functional groups as well as, the removal efficiency also varies. The values obtained from kinetics study showed that adsorption capacity ($q_e$ (mg/g)) of Fe/Mn-TB (1.0350 mg/g) was quite higher than that of Fe-TB (0.8497 mg/g). This was might be due to the changes in the biosorbents structure as the biomass was infused with different metal salts and possessed different properties.

The intraparticle diffusion model was also examined to assess the rate-controlling step and uptake mechanism for As(III) adsorption by synthesized Fe-TB and Fe/Mn-TB. Fig. S1c and d, show that the regression of intraparticle diffusion was not a straight line and does not pass through the origin which might be due to the varying contact time and distinctive mass transfer rate. Thus, intraparticle diffusion was not the only rate-limiting factor involved in As(III) adsorption process.

3.7. Thermodynamics

The results of thermodynamic study revealed that the values of entropy and enthalpy was found to be positive. 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 (Fig. 5 d). The results were verified by the negative value of $\Delta G^\circ$ for As(III) adsorption by Fe-TB and Fe/Mn-TB. The value of $\Delta S$ was 0.0662 kJ/mol for Fe-TB and 0.0484 kJ/mol for Fe/Mn-TB, respectively. Whereas, the value of $\Delta H^\circ$ was 0.0182 kJ/mol and 0.0117 for As(III) adsorption using Fe-TB and Fe/Mn-TB, correspondingly. The process of adsorption is spontaneous and feasible represented by negative $\Delta G^\circ$ values i.e., found in a range of -19.720 to -21.707 kJ/mol and -14.409 to -15.861 kJ/mol using Fe-TB and FeMn-TB, respectively, as biosorbent for As(III) removal (Table S3). The positive $AS^\circ$ values designate increases randomness between the interface of solid biosorbent surface and liquid adsorbate whereas, the positive value of $\Delta H^\circ$ represents the endothermic process of adsorption [55, 56].

4. Proposed mechanism of As adsorption on to Fe-TB and Fe/Mn-TB

Fig. 6 shows the proposed mechanism of As adsorption onto the synthesized monometallic and bimetallic biochar. Monometallic and bimetallic biochar comprise abundant functional groups, that can provide enough adsorptive interaction sites on the biosorbent surface for the As adsorption [57]. For example, FTIR spectra of Fe-TB and FeMn-TB contain various oxygenated surface functional groups because of the oxidative modification or oxidative treatment of biomass. The oxidative modification substantiates the presence of oxygen-containing functional groups on biosorbents surface like; -OH, COOH, etc. A minor alteration of the spectral pattern was observed after As loading to Fe-TB. A peak near wavenumber 3116.00 cm$^{-1}$ disappeared and the peak found at 1139.58 cm$^{-1}$ was shifted to 1080.43 cm$^{-1}$ which were allocated to -OH and C-O bond stretching [4]. An increase in the 567.44 cm$^{-1}$ peaks intensity
was also observed which was assigned to the Fe-O group and that shows the involvement of iron in the adsorption of As in the case of Fe-TB. Whereas in the case of Fe/Mn-TB, the peak at wavenumber 3732.42 cm⁻¹ appeared and the intensity of peaks at 1430.09, 1475.15 and 552.66 and 483.72 cm⁻¹ was increased, which corresponds to C=O, C-H, Fe-O and Mn-O stretching, respectively, after loading of As on to the biosorbent. The change in the intensities of the peaks might be due to the involvement of these functional groups in the As adsorption [38] or these changes was might be due to the formation of new complexes due to the interaction of biosorbent with the As and was supported by the complexation mechanism [58].

The electrostatic attraction was also a possible mechanism that favors the adsorption of As onto the biosorbent surface. As(III) was adsorbed by the Fe-TB and Fe/Mn-TB at pH 4 and pH 9, correspondingly, as the pHZPC of Fe-TB was 2.3 and Fe/Mn-TB was 8.2, that means the biosorbent contains more OH- ions above this pH and below, this pH these biosorbents consists H+ or positive surface charge. Below pH 9.2 As(III) is present in its neutral form i.e., H₃AsO₅ and was get adsorbed by the negatively charged biosorbents through electrostatic attraction [59]. Removal of As can also be accelerated by the formation of H-bonds between the aromatic groups present on the biochar surface and molecules of arsenite. A similar adsorption mechanism was also reported by Jing et al. [60].

Fig. 6 shows the oxidation of As(III) to As(V), followed by precipitation and adsorption of As(V). As(III) was oxidized to As(V) at the same time Mn(IV) was reduced to Mn(III) and Mn(II). On the surface of the biochar, As(V) and Mn(II) are produced by oxidation of As(III) and the reduction of Mn(IV) can precipitate as MnHAsO₄·H₂O. Furthermore, surface complexation with the Mn-OH group on MnO₂ can be used to eliminate the produced As(V). By the mechanism of surface complexation, functional groups present on the surface of biochar substrate like (-OH and -COOH) can adsorb As(III) directly [4, 61].

5. Conclusions

Two different biochar materials were synthesized by infusion of Fe (monometallic) and Fe/Mn (bimetallic) with Tectona waste biomass. Both of these biochar materials were made in an identical way, except the metal salts used to synthesize them. These biosorbents were applied to inspect their applicability for As(III) removal from aqueous solution as well as from groundwater. Fe-TB and Fe/Mn-TB were found to be very effective in removing As(III) with maximum adsorption of 84.85 % and 90.35 %, respectively, at the lowest initial As concentration. The maximum adsorption capacity (qmax) was 1.16 mg/g and 1.75 mg/g for the removal of As(III) by Fe-TB and Fe/Mn-TB, respectively. The biochar materials can be reutilized up to four cycles with maximum removal of As(III) in the first cycle i.e., 80.3 % for Fe-TB and 87.8 % for Fe/Mn-TB that reduced to 46.4 % (Fe-TB) and 48.8 % (Fe/Mn-TB) in forth cycle. Adsorption of As(III) from groundwater shows 80.5 % (KG) and 85.38 % (J) removal, respectively, for Fe-TB whereas, 83.63 % (KG) and 86.13 % (J) removal, respectively, by Fe/Mn-TB. Isotherm and kinetics study revealed that the experimental data were best fitted to Freundlich isotherm model and pseudo-second-order kinetics, correspondingly and endothermic nature of adsorption was showed by thermodynamic study. The results of EDX, XRD and FTIR sows successful infusion of Fe and Mn in the biomass. These biosorbents were found very effective in the As(III) adsorption from synthetically formulated As solution as well as from groundwater. As these biochar materials shows effective removal of As(III) from aqueous solution as well as from groundwater, thus can be further used as in filter development. The development of these biosorbents in large scale will not only help to eliminate As(III) from contaminated water but also helps to manage the lignocellulosic waste that is present in the environment in large amount.

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Author contributions

L.V. (Ph.D student) conducted all the experiments and prepared original manuscript and J.S. (Assistant professor) reviewed and did all the possible corrections and supervised the work.

Conflict of interest

The authors declare that there is no conflict of interest.

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