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Removal of Arsenic from Wastewater Using Hydrochar Prepared from Red Macroalgae: Investigating Its Adsorption Efficiency and Mechanism

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Abstract: Arsenic (As) is a prominent carcinogen component produced via both geogenic and anthropogenic processes, posing serious risks to human health. This study aimed to investigate the potential of hydrochar prepared from red macroalgae for removing As from synthetic wastewater. The hydrochar was produced through 5 h hydrothermal carbonization (HTC) treatment at 200 °C, and then, chemically activated with ferric chloride hexahydrate (FeCl₃·6H₂O). SEM analysis revealed a permeable structure of hydrochar, while FTIR analysis detected the occurrence of several functional groups at the hydrochar interface. EDS analysis showed an increase in carbon concentration after FeCl₃·6H₂O activation. Hydrochar was then tested in batch experiments to investigate its As removal efficiency, with ICP-MS used to determine the levels of As after the adsorption process. The results showed that As removal efficiency increased with increasing initial As concentration from 50 to 250 mg/L, and the highest As removal efficiency was 84.75% at a pH of 6, initial concentration of 0.25 mg/L, and adsorbent dose of 1000 mg at 120 min. The Langmuir isotherm model supported the occurrence of homogeneous adsorption over the surface of hydrochar, while the pseudo-second-order model confirmed the chemisorptive nature of the process.

Keywords: hydrothermal carbonization; macroalgae; arsenic removal; activated hydrochar; Langmuir and pseudo models; wastewater treatment

1. Introduction

Achieving optimal wastewater treatment for reuse depends on several factors, including the initial wastewater quality, the intended use of the treated water, local regulations, and available resources [1–4]. Despite these variables, there are standard steps and technologies commonly used in wastewater reuse. These methods encompass biological treatments, such as conventional and anammox-based systems, as well as advanced oxidation techniques like ozonation or UV/H₂O₂ [5–8]. Furthermore, advanced membrane processes, including reverse osmosis, nanofiltration, and ultrafiltration, are also widely utilized.

Arsenic (As) is a highly toxic element that occurs in more than 200 mineral varieties [9]. Natural events, such as volcanic eruptions, flooding, and soil erosion, and human activities, such as irrigation, mining, and pesticide usage, contribute to its presence in the environment [10,11]. As exists in two forms: organic and inorganic. The dominant forms of organic As are arseno-sugars, dimethyl-arsenic acid, and monomethyl-arsenic acid, and they can be found in shellfish as a product of biological processes in surface water. Inorganic arsenic
forms, such as arsenate As (V) and arsenite As (III), can commonly be found in natural water sources [12]. The intake of arsenic-contaminated water can have severe health consequences, including cancer, cardiovascular disease, and reproductive effects. To mitigate these effects, the World Health Organization recommends a limit of 10 µg/L of As in drinking water [13]. Pfeiffer et al. recorded that five out of 54 drinking water samples had arsenic levels exceeding the World Health Organization (WHO)’s maximum permissible limit, with a maximum recorded concentration of 300 µg L\(^{-1}\) of arsenic in the drinking water samples [14]. Shahid et al.’s study documented that the mean groundwater arsenic (As) content reported in 43 studies was 120 µg/L, with a range from 0.1 µg/L to 2090 µg/L. It also noted that about 73% of the mean As content values in these studies exceeded the World Health Organization (WHO)’s permissible limit of 10 µg/L for drinking water, while 41% exceeded the permissible limit of 50 µg/L for arsenic in Pakistan [15]. Research has shown a link between the risk of congenital heart disease and maternal exposure to arsenic in drinking water, even when the exposure levels are low [16,17].

Conventional methods for removing As from drinking and wastewater include adsorption, coagulation/precipitation, membrane methods, ion exchange, and lime softening, with adsorption being the most effective [18]. However, cost remains a significant challenge in the widespread implementation of adsorption methods [12]. To overcome this challenge, natural materials, such as olive core, peat, and algae, have been used as low-cost adsorbents to remove heavy metal ions from wastewater [19]. In addition, thermochemical processes can transform biomass into high-carbon-content products, such as charcoal, which can also be used as adsorbents [20].

Hydrothermal carbonization (HTC) is a promising technology that transforms low-calorie biomass into carbon-based solids known as hydrochar [21]. The process is carried out at specific retention times (0.5–24 h) and pressures (2–10 MPa) and relatively low temperatures (180–350 °C) [22,23]. Unlike other processes, HTC can transform biomass into hydrochar without an energy-intensive drying phase. In addition, underwater biomass is a valuable source as it requires less agricultural land and yields higher biomass production. This carbon product can be transformed into various biofuels through microbial activity or thermochemical processes [24].

Biochar, especially hydrochar, has emerged as a favored adsorbent in environmental cleanup efforts [25]. Biochar can be divided into two categories: pyrochar and hydrochar. Pyrochar is produced through the pyrolysis of dried biomass under specific conditions such as optimal temperatures, heating rates, and retention times [26]. Activation techniques can improve the physical and chemical properties of pyrochar, including its specific surface area, surface functional groups, and pore structures, making it more effective for applications such as As (V) adsorption [27,28]. For instance, magnetic MnFe\(_2\)O\(_4\)-engineered pyrochar has an As (V) adsorption capacity of 90 mg/g [29], and zirconium-iron-modified pyrochar can remove As (V) with a capacity of 62.5 mg/g [30]. On the other hand, hydrochar is synthesized through the HTC of wet biomass and has specific functional groups, such as carboxyl and hydroxyl [31]. However, its limited surface area and dispersed porous structures can reduce its effectiveness. Therefore, activations, such as sulfonation, magnetization, oxidation, and ammoniation, are essential to improving the comprehensive functionalities of hydrochar [32]. Although hydrochar has successfully been used in various organic or inorganic contaminant treatment processes, research on its ability to remove As contamination has been limited [31]. Further studies are necessary to fully evaluate the renewability of hydrochar-based adsorbent materials. Ref. [33] evaluated the ability of hydrochars derived from olive pomace oil to adsorb As. The effect of FeCl\(_3\) activation and additional hydrothermal treatment was assessed at various pH values, and the impact of solution pH on the stability and production of hydrochar was analyzed. The results showed that while alkaline HTC decreased the stability of the adsorbent, it improved As (V) adsorption to 4.1 mg/g, and the iron coating of the adsorbent [34].

The purpose of this research is to determine the ability of macroalgae-based hydrochar as a sustainable resource to eliminate As from wastewater. Macroalgae, distinct from
microalgae, possess plant-like attributes with higher protein content and a composition rich in cellulose, lignin, and hemicellulose. Several studies have explored the potential of hydrothermal carbonization (HTC) as an environmentally friendly and versatile technique for sustainable biomass processing. Biller and Ross (2012) investigated the application of HTC for producing biochar, biocrude, and syngas from algal biomass, showcasing its versatility in converting various biomass sources [35]. Patel et al. (2021) addressed ecological issues caused by waste seaweed through HTC, emphasizing the circular green solution of producing hydrochar and nutrient-rich liquid slurry from the seaweed [36]. Rasam et al. (2021) examined the impact of different parameters on the HTC process for Sargassum horneri macroalgae and used machine learning techniques to estimate key process parameters [37]. Spagnuolo et al. (2023) furthered the exploration of HTC by investigating hydrochar recovery from Sargassum muticum macroalgae and assessing its potential in adsorbing organic water pollutants for environmental remediation [38]. Spagnuolo, Bressi et al. (2023) explored the practical applications of HTC solutions by investigating the reuse of discarded liquid phases as seed-priming treatments for Phaseolus vulgaris L., highlighting the benefits of HTC in agriculture and resource management [39]. The utilization of macroalgae offers a sustainable and renewable resource, and has promising applications in hydrochar, biofuels, and bioproducts, potentially transforming the sustainable landscape [20]. In this study, we explored the novel application of macroalgae-based hydrochar for arsenic removal, a previously unexplored avenue. Our findings reveal macroalgae-based hydrochar’s promising potential as an effective method for mitigating arsenic contamination in wastewater. The hydrochar was produced through biosynthesis and was thoroughly characterized before being chemically activated with FeCl$_3$·6H$_2$O. FeCl$_3$·6H$_2$O is a well-known chemical activator for hydrochar due to its iron content, and can introduce functional groups and surface modifications to the hydrochar, making it more effective in adsorbing contaminants like arsenic (As). Zhang et al.’s study focuses on creating an arsenic (As) adsorption material called iron-modified hydrochar using hydrothermal carbonization (HTC) with different iron species: FeCl$_3$·6H$_2$O, FeSO$_4$·7H$_2$O, and Fe(NO$_3$)$_3$·9H$_2$O. It investigates their physicochemical properties, iron retention stability, and As adsorption capabilities [40]. Ghanizadeh et al. used iron chloride as a chemical activator to impregnate activated carbon with iron because iron impregnation is a well-known and effective method for enhancing the adsorption properties of activated carbon [41]. Iron impregnation can significantly improve activated carbon’s ability to remove various contaminants, including arsenic, from water. The presence of iron on activated carbon’s surface introduces active sites that can chemically bind with the target contaminants. These active sites enhance the adsorption capacity and efficiency of the activated carbon [42]. To evaluate its proficiency in extracting arsenic (As) from a liquid solution and to explore the impact of variables like pH, temperature, and initial As concentration, we carried out comprehensive kinetic and equilibrium studies. These investigations delved into the adsorption process, examining its control through both chemical and physical adsorption mechanisms. The results of this study have important implications for the potential use of macroalgae-based hydrochar as a sustainable resource for removing As from contaminated water sources.

2. Materials and Methods

2.1. Chemicals

This study employed several materials, including Reagecon MT chemical, which are standard for ICP and ICP-MS, at a concentration of 1000 µg/mL (1000 ppm) in 2–5% nitric acid (HNO$_3$). Other materials used were extra-pure ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), citric acid monohydrate, and sodium hydroxide (NaOH), as well as additional HNO$_3$.

2.2. Preparation of Hydrochar (HC)

The complete process of hydrochar preparation and activation is illustrated in Figure S1 in the Supplementary Materials file. Red macroalgae was collected from the beach near
Katti Kund, Gharo, in Krachi, Sidnh, Pakistan. The samples were thoroughly cleaned using tap water and distilled water, and then, dried at room temperature for 48 h. The dried samples were then ground and sieved to obtain particles greater than 600 μm in size [43].

To produce hydrochar, a Teflon-lined stainless-steel reactor with a 100 mL capacity was used. The hydrochar was produced through the HTC process. A catalytic solution of 40 mg of citric acid (monohydrate) was mixed with 50 mL of distilled water, and 10 g of dried algal sample was added to the solution. The mixture was then added to an autoclave and placed in a preheated oven for 5 h at 200 °C. After 5 h, the carbon product was washed, filtered, and dried for an additional 5 h at 120 °C. The final hydrochar product was weighed.

2.3. Activation of Hydrochar

The hydrochar was activated using iron (III) chloride hexahydrate (FeCl\textsubscript{3}·6H\textsubscript{2}O). To prepare a solution, 4.98 g of FeCl\textsubscript{3}·6H\textsubscript{2}O was dissolved in 30 mL of distilled water and mixed thoroughly. Hydrochar (3 g) was then added to the solution, and the pH was maintained between 7 and 7.5. The mixture was placed in an electronic shaker and agitated at 200 rpm for 24 h to provide sufficient time for activation. After 24 h, the solution was centrifuged for 30 min, the supernatant was discarded, and the activated hydrochar was filtered. The activated hydrochar was then washed 3 to 4 times with distilled water, and the pH was measured after the final wash to ensure it was free of impurities. Finally, the activated hydrochar was dried at 120 °C to obtain the final sample. Inductively coupled plasma mass spectrometry (ICP-MS) was used to identify the As level in water after treatment.

2.4. Surface Morphology and Characterization of Hydrochar (HC) and Activated Hydrochar (AHC) Samples

Scanning Electron Microscope (SEM) imaging and Energy-Dispersive X-ray Spectroscopy (EDS) analysis were performed using a Hitachi S-4800 Field Emission SEM build with an EDS analysis feature on the hydrochar sample to observe its surface and identify its elemental composition, respectively. In SEM, an electron beam is focused on the sample surface to generate an image of the sample, while EDS helps in determining the elemental composition by analyzing the X-ray signals produced by the sample. FTIR spectroscopy was also performed using a Nicolet™ i520 FTIR Spectrometer to identify the functional groups present in the sample. Infrared radiation in the range of approximately 10,000 to 100 cm\textsuperscript{-1} was directed towards the sample, and the adsorbed energy was transformed into vibrational energy. This was then detected as a spectrum between 4000 cm\textsuperscript{-1} and 400 cm\textsuperscript{-1}, providing a molecular fingerprint of the sample and offering insights into its functional groups.

2.5. Batch Adsorption

A batch test was used to evaluate As removal efficiency using hydrochar as an adsorbent. The batch test was carried out in 15 mL falcon tubes at a temperature of 25 °C. The solutions of 0.1 M nitric acid and 0.1 M sodium hydroxide were used to maintain the pH of the test solution at 2, 4, 6, 8 and 10. A 0.25 mg/L concentration of As with a fixed amount of adsorbent (magnetized hydrochar) dose of 0.01 g was used in all experiments. The study employed a range of time intervals (30, 60, 90, 120, and 150 min) to observe the kinetics of the adsorption process. Varied arsenic concentrations (0.05, 0.1, 0.15, 0.2, and 0.25 mg/L) were introduced to assess the impact of initial concentration on removal efficiency. Additionally, different dosages of the adsorbent (200 mg, 400 mg, 600 mg, 800 mg, and 1000 mg) were employed in separate experiments to examine their influence.

In a batch test, the adsorption process is allowed to reach equilibrium, and the amount of contaminant adsorbed onto the surface of the adsorbent is measured. This information can then be used to evaluate the adsorption capacity and kinetics of the adsorbent and to determine the optimal conditions for removing the contaminant from the solution.
2.6. Calculations

The amount of As adsorbed, $q_t$, was calculated using Equation (1).

$$q_t = (C_0 - C_t) \times \frac{V}{m} \quad (1)$$

where $q_t$ is the amount of As adsorbed at time $t$ (mg/g), $C_0$ is the initial As concentration (mg/L), $C_t$ is the As concentration at time $t$ (mg/L), $V$ is the As solution volume (mL), and $m$ is the adsorbent mass (mg).

The As removal efficiency, $\eta_{As}$, was calculated using Equation (2) as follows:

$$\eta_{As} = \left( \frac{C_0 - C_i}{C_0} \right) \times 100 \quad (2)$$

where $C_0$ is the initial As concentration (mg/L), and $C_i$ is the As concentration remaining at the end of reaction (mg/L).

2.6.1. Isotherm Models

To study the equilibrium adsorption of As, the Langmuir and Freundlich isotherm models were used. Equation (3) for the Langmuir isotherm model is given below:

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_{max}} \cdot \frac{1}{C_e} + \frac{1}{q_{max}} \quad (3)$$

where $q_e$ is the quantity of heavy metal adsorbed per unit weight of adsorbent (mg/g), $C_e$ is the equilibrium concentration (mg/L), $K_L$ is the Langmuir adsorption parameter/constant (L/mg), and $q_{max}$ is the maximum adsorption capacity (mg/g). Equation (4) for the Freundlich adsorption isotherm model is as follows:

$$\log q_e = \log K_f + \frac{1}{n \cdot \log C_e} \quad (4)$$

where $q_e$ is the quantity of heavy metal adsorbed per unit weight of adsorbent (mg/g), $C_e$ is the equilibrium concentration (mg/L), $K_f$ is the Freundlich constant (adsorbent’s relative adsorption capacity (mg/g), and $1/n$ is the adsorption intensity.

2.6.2. Kinetic Models

The pseudo-first- and pseudo-second-order models were applied to describe the kinetics of As removal and explain the differences in the kinetic rates. According to [44], Equation (5) for the pseudo-first-order model can be written as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 \times t \quad (5)$$

where $q_e$ is the amount of heavy metal adsorbed at equilibrium (mg/g), $q_t$ is the amount of heavy metal adsorbed at time $t$ (mg/g), and $K_1$ is the pseudo-first-order rate constant.

Equation (6) for the pseudo-second-order model is presented as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \quad (6)$$

where $K_2$ is the pseudo-second-order rate constant.

Equation (7) for the intra-particle diffusion model is presented as follows:

$$q_t = K_{diff} \frac{1}{2} + C \quad (7)$$

$q_t$ is the amount of arsenic adsorbed at time $t$;
$K_{diff}$ is the intra-particle diffusion rate constant;
$C$ is the intercept.
3. Results
3.1. SEM Analysis of Hydrochar

SEM photographs of the hydrochar and activated hydrochar samples with a magnification of ×1000 are shown in Figure 1a,b, respectively. The images highlight that a variety of pores appeared on the surface of the hydrochar due to the evaporation of the chemical activator. A similar porous structure and rough topography of carbon samples after chemical activation was reported by [45]. Likewise, Petrović et al. [46] also found similar disorganized cracks on their samples. In contrast, the surface morphology of activated hydrochar is heterogeneous, with pores of varied diameters. Because of the pores and cracks on the surface of activated hydrochar, molecules can effortlessly clog and flow into the voids. The SEM image of activated hydrochar demonstrates that the surface is substantially smoother after the chemical activation of the sample.

![SEM photographs of hydrochar and activated hydrochar samples with a magnification of ×1000](image)

Figure 1. SEM image of adsorbent: (a) topography of hydrochar sample before activation; (b) topography of hydrochar.

3.2. Elemental Composition and Changes during Activation of Hydrochar

The EDS analysis showed that carbon and oxygen were the most abundant elements in non-activated hydrochar, constituting 34.4% and 50.6%, respectively (Figure S2a). After activation, the dominant elements in the hydrochar samples changed, and carbon, oxygen, magnesium, aluminum, silicon, nitrogen, chlorine, sulfur, phosphorus, iron, and sodium were the most abundant components, as shown in Figure S2b in the Supplementary Materials file.

Table S1 in the Supplementary Materials file shows the weight percentage and atomic weight percentage of various elements present in both the activated and non-activated samples of hydrochar. Moreover, the activation process (heating of AHC for 5 h at 120 °C) led to the appearance of chloride and iron in the hydrochar sample. The activation also increased the carbon percentage and decreased the oxygen percentage. The percentages of silicon, sulfur, and phosphorous also decreased after activation. Yan et al. [47] found that the bamboo sample they studied contained 2.0%, 23.3%, and 74. % of Mn, O, and C, respectively. The presence of silicon and other elements in hydrochar samples has also been reported in other studies [48]. Ma et al. [49], produced hydrochar from lignin and reported the availability of 57.6% carbon and 8.9% oxygen in their sample.

3.3. Identification and Impact of Surface Functional Groups of HC, AHC during As Adsorption, and AHC after As Adsorption

The functional groups on the surface of hydrochar (HC), activated hydrochar (AHC), and activated hydrochar after As adsorption (AHC+As) were identified using the FTIR approach, and the results are presented in Figure 2. The spectra of HC, AHC, and AHC+As were found to be similar. C-H stretching vibrations were present between 2755 cm⁻¹ and
2990 cm$^{-1}$, and C-H bending was observed at a peak of 1970 cm$^{-1}$. The peak level at and C-O stretching vibration bands at 1124 cm$^{-1}$ and 1455 cm$^{-1}$ were detected. These findings are consistent with previous studies, such as Lei et al. [50], who identified similar functional groups in hydrochar derived from Salix biomass. Figure 2 also highlights that after activation, the Fe-O group was also present as a peak at 570 cm$^{-1}$.

Figure 2. FTIR adsorption spectra: hydrochar sample before activation, FTIR spectra of hydrochar sample after activation, and activated hydrochar spectra after As adsorption.

The functional groups present on the surface of hydrochar after the chemical activation are shown in Figure 2. The peak 3261 cm$^{-1}$ indicated the occurrence of O-H stretches, and the peak at 1390 cm$^{-1}$ was attributed to the tensile bonding of OH, which is likely due to the adsorption of water on the surface of nanoparticles [51,52]. The C=O and COO stretching peaks were likely linked to carboxyl groups, which can enhance resistance to alkaline conditions [53]. The curves at 1501–1510, 3390, and 2140 cm$^{-1}$, respectively, indicated N=O stretching, N-H bending, and N-C-S stretching, respectively. Correspondingly, C=O stretching and C=C stretching were observed as peaks at 1395, 1660, and 2232 cm$^{-1}$, respectively.
The presence of functional groups, including hydroxyl, carboxyl, and amide, enhances As adsorption [54]. The availability of certain organic acid functional groups, such as OH or COO\(^-\), may contribute to the variation in As adsorption trends [55]. Kumar and Jiang [56] provided evidence that the availability of amine, hydroxyl, and carboxyl functional groups increased after the activation of their sample, which contributed to As adsorption. Similarly, in this study, the presence of amine, hydroxyl, and carboxyl functional groups increased after activation, significantly improving As adsorption.

3.4. Factors Affecting As Removal

3.4.1. Effect of pH

The availability of binding sites on the adsorbent surface is dependent on the pH of the solution, with hydrogen ions having a strong affinity for heavy metal ions, which can affect their binding to the adsorbent [57,58]. In this study, the effects of pH on the As adsorption capacity of activated hydrochar was investigated. As removal efficiency was measured at pH levels ranging from 2 to 10, and the findings are presented in Figure 3a. The results show that the neutral pH was most effective in removing As, at 150 min of equilibrium time, 200 rpm shaking speed, a pH of 6.5, an As concentration of 0.25 mg/L, and a hydrochar dosage of 1000 mg/L. The pH graph reveals that as the pH increased from 2 to 6, the removal efficiency and adsorption capacity rose significantly by 49% and 77%, respectively. However, at a pH of 10, the efficiency and adsorption capacity decreased.

Previous studies have reported similar optimal pH ranges for As removal. Kamala et al. [59] found that the efficacy of As removal by fresh biomass was dependent on a pH range of 6 to 8, with the optimal adsorption taking place at a pH of 6. Likewise, Abtahi et al. [60] found that maximum As (IV) adsorption was achieved at a pH of 6. However, it is important to note that the optimal pH range may vary depending on the adsorbent material and the experimental conditions.

3.4.2. Effect of Adsorbent Dosage

The following experiment aimed to determine the effect of adsorbent dosage, ranging from 200 to 1000 mg, on the efficiency of As removal and the adsorption capacity of As by activated hydrochar. According to the results presented in Figure 3b, the efficiency was increased from 52.5% to 82% with an increase in adsorbent dosage, while the adsorption rate of As (adsorption capacity) shows an inverse relationship with the adsorbent dosage. The graph shows that the maximum adsorption capacity occurred at 1g. This trend in the experiment shows that an increased amount of adsorbent provides more binding sites, which enhances the sorption mechanism and improves the efficiency of As removal [61]. Rahmani et al. [62] suggested a suitable dosage of 1 g/L for As adsorption experiments.

3.4.3. Effect of Initial As Concentration

Figure 3. Factors affecting the As removal efficiency of AHC: (a) effect of pH, (b) effect of AHC (adsorbent) dosage, (c) effect of As concentration, (d) effect of contact time.
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3.4.3. Effect of Initial As Concentration

The purpose of this experiment was to investigate the adsorption behavior of an adsorbent at different As concentrations, ranging from 0.5 mg/L to 0.25 mg/L, under a constant adsorbent dosage of 1000 mg. As shown in Figure 3c, the As removal efficiency and removal capacity of the adsorbent increased as the As concentration increased. It was predicted that the low initial concentration of As limited the possibility of collision between the adsorption sites of the adsorbent and As, resulting in a lower As removal efficiency. However, with increasing initial As concentrations, the difference in concentration became greater, which led to a higher adsorption capacity and a faster rate of As removal [63]. A similar pattern was investigated in Christobel’s batch study [64].

3.4.4. Effect of Contact Time

The purpose of this experiment was to investigate the effect of contact time on the As removal efficiency and adsorption capacity of activated hydrochar. The results are presented in Figure 3d, which shows that the As removal efficiency increased from 67% to 85.05%, while the adsorption capacity improved to 0.1701 mg/g. The maximum adsorption was achieved at 120 min. Mandal et al. also found that 120 min was the optimal time for removing As [65]. In contrast, Q. Li et al. [66] examined the efficiency of two different adsorbents, magnesia-loaded fly ash cenospheres (MGLC) and manganese-loaded fly ash cenospheres (MNLC), for As removal. The equilibrium point for MNLC adsorption was reached after 120 min. As removal typically occurs in stages, with the initial stage being quick. As the contact time passes, the rate of removal slows until equilibrium is reached. The monolayer and fast adsorption are probably caused by ion exchange or physical adsorption on the surface of the adsorbent. However, as time passes, fewer active sites become available, and competition from existing metal ions slows down the adsorption rate due to fewer binding sites [67].

The findings of this research are consistent with the study of Dudek and Koodyska [68], who concluded that 120 min is an appropriate duration to achieve As removal equilibrium [68]. Attinti et al. [69] also used silicon nanoparticles covered with goethite and achieved equilibrium at 120 min.

3.5. Equilibrium Investigation

Adsorption is a process that involves interactions between adsorbate and adsorbent molecules, as well as between these molecules and the solvent. Of the five types of processes that can occur during adsorption, the adsorbent–adsorbate interaction is particularly important, as it must be maximized in order for the adsorption operation to take place [70].
The equilibrium properties of heavy metal adsorption on the adsorbent surface can be determined using the Langmuir and Freundlich isotherm models [71]. Figure 4a shows a graph of 1/qe vs. 1/Ce, which was used to derive the Langmuir isotherm model, determine the value of qmax, and obtain the experimental data. The Freundlich isotherm was used to determine whether surface adsorption was heterogeneous or multilayer [72]. The value of Kf was estimated using experimental data from the Freundlich isotherm model and a graph of log Qe vs. log Ce, as shown in Figure 4b. Table 1 provides the calculated values for the constants in both models. In this study, the Langmuir model was followed because the R^2 value of the Langmuir model was 0.981 and qmax was 3.8314 mg/g, whereas the R^2 of the Freundlich model was 0.9173, which is less than the R^2 value of Langmuir model, indicating that surface adsorption was not multilayer or heterogeneous.

In a study by Altundoğan et al. [73], red mud was used as an adsorbent for As removal from an aqueous solution. The results showed that the Langmuir isotherm could successfully model the adsorption behavior of As on the red mud. The Langmuir isotherm assumes that adsorption occurs on a homogeneous surface with a finite number of identical sites, and that there is no interaction between adsorbed molecules. In another study by Goswami et al. [74], the Langmuir isotherm was used to model the adsorption of cadmium ions on modified rice husk. The Langmuir model provided a good fit to the experimental data, indicating that the adsorption process was monolayer and homogeneous. Likewise, in a research study by Goldberg and Johnston [75], the Langmuir isotherm was used to model the adsorption of gold complexes on activated carbon. The Langmuir model provided a good fit to the experimental data and was used to determine the maximum adsorption capacity of the activated carbon.

In this study, R^2 values indicate that the Langmuir isotherm model and the metal ion elimination method strongly correlate, and suggest that biosorption had continuous adsorption energy. If the adsorbate–adsorbent interaction is stronger than the other interactions, a monolayer is formed. The first adsorbed molecule acts as a starter for the second molecule, which is tightly bound to the first molecule in a binding site. The homogenous increase in binding sites on the biomass surface is mainly attributed to the strong correlation between the Langmuir isotherm and the findings of [76].

According to Yu et al. [77]’s study, the adsorption process of As onto adsorbents (based on multi-amino-functionalized cellulose) is best described by the Langmuir model, which suggests that it is a monolayer adsorption process. The Langmuir model also provides the maximum adsorption capacities (Qmax) for As (III) and As (V), which are 5.71 mg/g and
75.13 mg g\(^{-1}\), respectively. Chaudhry et al. [78] demonstrated that when the temperature of the solution was increased from 27 to 45 °C, the Langmuir adsorption capacity of IZBOCS for As (V) showed a significant increase from 45.05 to 84.75 mg g\(^{-1}\). The feasibility of the adsorption process was indicated by the separation factor values, which were 0.435, 0.489, and 0.508 at 27 °C, 35 °C, and 45 °C, respectively. Moreover, Cheng et al. [79] used iron oxide nanoparticles for As removal and highlighted that the sorption isotherms were found to be well described by the Langmuir equation, which yielded a maximum sorption capability of 83 mg g\(^{-1}\) for As (V) at a pH of 3 and 42 mg g\(^{-1}\) for As (III) at a pH of 7. The adsorption process on FG2 was found to follow a pseudo-second-order kinetic model and was well fitted in the Langmuir isotherm, with a maximum adsorption capacity of 69.44 mg g\(^{-1}\) at a pH of 3 [80]. Correspondingly, other studies that used different materials for As adsorption and for which adsorption fitted the Langmuir isotherm are mentioned in Table 1.

Table 1. Summary of kinetic constant values of Langmuir isotherm model and Freundlich isotherm model.

<table>
<thead>
<tr>
<th>Material</th>
<th>As Species</th>
<th>Langmuir Isotherm Model Parameters</th>
<th>Freundlich Isotherm Model Parameters</th>
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<td></td>
<td>KL (L/mg)</td>
<td>Q max (mg/g)</td>
<td>R(^2)</td>
</tr>
<tr>
<td>Activated hydrochar</td>
<td>As (III/V)</td>
<td>0.0123</td>
<td>3.8314</td>
<td>0.981</td>
</tr>
<tr>
<td>Multi-amino-functionalized cellulose</td>
<td>As (III)</td>
<td>0.21</td>
<td>5.71</td>
<td>0.970</td>
</tr>
<tr>
<td></td>
<td>As (V)</td>
<td>0.078</td>
<td>75.13</td>
<td>0.992</td>
</tr>
<tr>
<td>Iron–zirconium binary oxide-coated sand (27, 35 and 45 °C)</td>
<td>As (V)</td>
<td>0.0104</td>
<td>45.05</td>
<td>0.957</td>
</tr>
<tr>
<td></td>
<td>As (V)</td>
<td>0.0083</td>
<td>66.22</td>
<td>0.856</td>
</tr>
<tr>
<td></td>
<td>As (V)</td>
<td>0.0077</td>
<td>84.75</td>
<td>0.955</td>
</tr>
<tr>
<td>Iron oxide nanoparticles</td>
<td>As (III)</td>
<td>0.4</td>
<td>42</td>
<td>0.978</td>
</tr>
<tr>
<td>Iron oxide nanoparticles</td>
<td>As (V)</td>
<td>0.8</td>
<td>83</td>
<td>0.998</td>
</tr>
<tr>
<td>Magnetic graphene oxide nanocomposites</td>
<td>As (V)</td>
<td>0.385</td>
<td>69.44</td>
<td>0.905</td>
</tr>
<tr>
<td>Iron oxide nanoparticles</td>
<td>As (V)</td>
<td>0.11</td>
<td>28.57</td>
<td>_</td>
</tr>
<tr>
<td>Magnetic gelatin-modified biochar</td>
<td>As (V)</td>
<td>0.81</td>
<td>43.15</td>
<td>0.89</td>
</tr>
<tr>
<td>Phosphorus (P)-modified biochar (PLBC) (Taraxacum mongolicum Hand-Mazz)</td>
<td>As (III)</td>
<td>0.08</td>
<td>30.76</td>
<td>0.843</td>
</tr>
<tr>
<td>Ultisol</td>
<td>As (V)</td>
<td>137.3</td>
<td>24.27</td>
<td>0.995</td>
</tr>
<tr>
<td>Ultisol + biochar</td>
<td>As (V)</td>
<td>66.4</td>
<td>21.51</td>
<td>0.996</td>
</tr>
<tr>
<td>Ultisol + biochar derived from aluminum-treated rice straw</td>
<td>As (V)</td>
<td>77.0</td>
<td>25.97</td>
<td>0.994</td>
</tr>
<tr>
<td>Ultisol + aluminum-treated biochar form rice straw</td>
<td>As (V)</td>
<td>185.5</td>
<td>26.95</td>
<td>0.996</td>
</tr>
<tr>
<td>Rice-husk biochar-stabilized iron and copper oxide nanoparticles</td>
<td>As (III/V)</td>
<td>0.19</td>
<td>20.32</td>
<td>0.555</td>
</tr>
</tbody>
</table>

3.6. Kinetic Study

Three different kinetic models, the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, were examined in this study. Table 2 provides the kinetic constant values obtained from the first- and second-order and intra-particle diffusion models. These models are commonly used in solid–liquid systems [85]. In the past, numerous studies have been conducted that investigate hydrochar performance based on kinetic models using
first- and second-order and intra-particle diffusion models for the removal of different heavy metals and other contaminants [86–88]. As shown in Figure 5a, plotting ln(qe-qt) against time (t) yielded the experimental data for the pseudo-second-order model and K1 values. Figure 5b demonstrates a relationship between t/qe and time (t) to compute pseudo-second-order experimental data and the value of k2 (Table 2). The intra-particle diffusion model is often employed to gain insights into the adsorption process and to determine if it is controlled by intra-particle diffusion. This model is the primary rate-limiting step. The qt versus \(\sqrt{t}\) plot should exhibit a linear relationship, starting from the origin with a small C value. Figure 5c investigates an intra-particle diffusion model within the studied medium, from which we derived critical parameters to assess the process. The R2 yielded a value of 0.61899, indicating the model’s ability to explain approximately 61.899% of the variance in the adsorption data. The diffusion rate constant (k diff) was measured at 0.00322, representing the rate at which adsorption occurs, with an associated uncertainty of \(\pm 0.00146\). ‘C’, serving as the intercept in our adsorption equation, was determined to be 0.17051, with an uncertainty of \(\pm 0.01383\). These findings provide fundamental insights into the adsorption process within the medium and highlight the role of the intercept ‘C’ in our adsorption equation, despite this not being a modest fit of the model to the data. Further investigation and potential model refinement may be required to improve the goodness of fit. The determination coefficient (R2) value was 0.9567, while the R2 value for the pseudo-second-order model was 0.9913, indicating that the pseudo-second-order model was more suitable for this study than the pseudo-first-order model. The higher R2 values suggest that the pseudo-second-order model more accurately predicted the experimental data obtained during the investigation of the kinetics of As adsorption on macroalgae-based hydrochar than the pseudo-first-order model. This suggests that the As (III) elimination process in the studied system is chemical rather than physical. In addition, Goldberg and Johnston [75] observed that their results also followed the second-order model.

### Table 2. Summary of kinetic constant values of pseudo-first-order model and pseudo-second-order model.

<table>
<thead>
<tr>
<th>Materials</th>
<th>As Species</th>
<th>Pseudo-First-Order Model Parameters</th>
<th>Pseudo-Second-Order Model Parameters</th>
<th>Intra-Particle Diffusion Model Parameters</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K1 ((\text{min}^{-1}))</td>
<td>qe. Cal. ((\text{mg/g}))</td>
<td>R2</td>
<td></td>
</tr>
<tr>
<td>Activated hydrochar</td>
<td>As (III/V)</td>
<td>-0.0053</td>
<td>0.078</td>
<td>0.9567</td>
<td></td>
</tr>
<tr>
<td>Untreated red-mud biochar</td>
<td>As (V)</td>
<td>1.195</td>
<td>451.4</td>
<td>0.983</td>
<td></td>
</tr>
<tr>
<td>Red-mud-modified biochar</td>
<td>As (V)</td>
<td>1.446</td>
<td>1656.5</td>
<td>0.900</td>
<td></td>
</tr>
<tr>
<td>Untreated red-mud biochar</td>
<td>As (III)</td>
<td>0.805</td>
<td>296.0</td>
<td>0.948</td>
<td></td>
</tr>
<tr>
<td>Red-mud-modified biochar</td>
<td>As (III)</td>
<td>0.686</td>
<td>377.9</td>
<td>0.911</td>
<td></td>
</tr>
<tr>
<td>Iron oxide nanoparticles</td>
<td>As (V)</td>
<td>0.50</td>
<td>0.66</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>Phosphorus (P)-modified biochar</td>
<td>As (III)</td>
<td>0.23 ± 0.028</td>
<td>16.3 ± 0.4</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>(PLBC)/Taraxacum mongolicum</td>
<td></td>
<td>0.020 ± 0.002</td>
<td>17.1 ± 0.4</td>
<td>0.997</td>
<td></td>
</tr>
<tr>
<td>Hand-Mazz</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[83]</td>
</tr>
<tr>
<td>Magnetic gelatin-modified biochar</td>
<td>As (V)</td>
<td>0.03</td>
<td>26.64</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.00142</td>
<td>28.389</td>
<td>0.92</td>
<td></td>
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</table>
Table 2. Cont.

<table>
<thead>
<tr>
<th>Materials As Species</th>
<th>Pseudo-First-Order Model Parameters</th>
<th>Pseudo-Second-Order Model Parameters</th>
<th>Intra-Particle Diffusion Model Parameters</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K1 (min⁻¹)</td>
<td>qe. Cal. (mg/g)</td>
<td>R²</td>
<td>K2 (mg g⁻¹ min⁻¹)</td>
</tr>
<tr>
<td>Magnetic Fe₃O₄/Douglas fir biochar composites As (III)</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0.337</td>
</tr>
<tr>
<td>Magnetic Fe₃O₄/Douglas fir biochar composites As (III)</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0.319</td>
</tr>
<tr>
<td>Magnetic Fe₃O₄/Douglas fir biochar composites As (III)</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0.049</td>
</tr>
<tr>
<td>Rice-husk biochar-stabilized iron and copper oxide nanoparticles As (III/V)</td>
<td>0.17</td>
<td>1.75</td>
<td>0.839</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Note: N.A. = Non-available.

Wu et al. [86] investigated the correlation coefficients of different kinetic models for different materials. The results show that the pseudo-first-order kinetics had low correlation...
coefficients ($R^2 < 0.9$), which was considered unfavorable. On the other hand, the pseudo-second-order model had very high correlation coefficients ($R^2 \geq 0.99$) for all the data examined. In another study based on the fit coefficient ($R^2 = 0.913$), it was determined that the pseudo-second-order model was a good fit for the adsorption process. This indicated that the rate-limiting step in the process was the chemisorption of As (V), which involved a chemical interaction between As (V) ions and polar functional groups on the adsorbent, such as ion exchange and the chelating reaction [81]. Also, Navarathna et al. [87] made composites of Magnetic $\text{Fe}_3\text{O}_4$ and Douglas fir biochar (MBC), and showed that the adsorption kinetics data were most accurately represented by the pseudo-second-order model, with an $R^2$ value greater than 0.99.

The use of both biochar@Fe and biochar@Cu in combination effectively removes As and can be accurately represented by the pseudo-second-order kinetic model. This model assumes that each As ion is associated with two M-OH centers during the chemical adsorption reaction. Because the concentration of As ions is lower than the number of available metal hydroxyl active sites (M-OH), the overall reaction rate can be approximated by a pseudo-second-order reaction [85]. Ahmed et al. [83] investigated phosphorus (P)-modified biochar (PLBC) for As adsorption. The pseudo-first-order kinetic model appeared to fit well (with $R^2 = 0.97$), but it underestimated the adsorption rate in the first 20 min. On the other hand, the pseudo-second-order kinetic model provided a slightly better fit to the experimental data, with an $R^2$ value of 0.99. These results suggest that the overall adsorption process may be influenced by electron exchange or sharing between the sorbent and sorbate, indicating that chemisorption could be the rate-limiting step. Similarly, other studies that used different materials for As adsorption that fitted the pseudo-second-order model are mentioned in Table 2.

4. As Removal Mechanisms

Figure 6 shows the mechanism of As adsorption in hydrochar, which is believed to be primarily through surface complexation [88]. The activated hydrochar has a high surface area and a porous structure, which provides numerous active sites for chemical interactions. The active sites are primarily located on the surface of the hydrochar, where they can interact with contaminants in the surrounding environment. Wang et al. [89] synthesized two types of biochar composites using pinewood biochar and Ni/Mn oxides or Ni/Mn-layered double hydroxides. The first type was produced via the pyrolysis of pinewood biochar (NMMF) with Ni/Mn oxides, while the second type was produced via the precipitation of Ni/Mn-layered double hydroxides onto the pinewood biochar (NMMB) using $\text{MnCl}_2\cdot4\text{H}_2\text{O}$ and $\text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$. The As (V) removal efficiency of NMMB and NMMF was tested using a 12 mg/L As (V) solution, and the results showed that NMMB had higher efficiency at 98% compared to NMMF, which had 10.6% removal efficiency. Both modified biochars showed an improved maximum As (V) sorption capacity compared to the unmodified biochar, with NMMB having a capacity of 6.520 g/kg and NMMF having a capacity of 0.549 g/kg [89]. Figure 6 illustrates the potential mechanisms responsible for the immobilization of As on the activated hydrochar surfaces. In contrast, Alkurdi et al. [88] observed that the point of zero charge for activated hydrochar was a solution pH of higher than 8, which resulted in a positively charged surface of the hydrochar. This positively charged surface facilitated strong electrostatic forces between As (V) and the surface.

When As comes into contact with the hydrochar surface, it can form strong chemical bonds with functional groups, such as carboxyl (HCOO), hydroxyl (-OH), and amino (-NH$_2$) groups [90]. These functional groups can act as electron donors and can form a complex with the As through a process known as ligand exchange (Figure 6). The complex formed by hydrochar and As is believed to be stable and can remain in place for a long time. As can interact with these electrons, forming a stable complex. The understanding of these mechanisms has been applied to the development of activated biochar materials for water remediation. For instance, the incorporation of nano-zero-valent iron (Fe$_0$) into biochar can improve the immobilization of As (V) in water by creating strong chemisorption
interactions through an oxidation and reduction reaction on the surface of the biochar [88]. To investigate the binding mechanism between As and AHC, we conducted a comparison of FTIR spectra before and after adsorption, as illustrated in Figure 2. In Figure 2, we also compared the FTIR spectra of AHC and HC prior to the adsorption of arsenic ions. All three materials displayed broad adsorption bands at 1395 and 1660 cm\(^{-1}\), which can be attributed to the vibrations of C=O bonds [91]. Notably, this adsorption bands exhibited minimal changes following arsenic adsorption, suggesting that the O-H and the C=O bond were not significant contributors to the adsorption process.

Simultaneously, we observed the appearance of a prominent and well-defined peak at 820 cm\(^{-1}\), mainly associated with As-O. These symmetric and asymmetric As-O vibrations within the Fe structure imply the formation of iron arsenate precipitation on the material’s surface [92,93].

Figure 6. Schematic of potential mechanisms for the adsorption of As on activated hydrochar surface [52,88,90].

Simultaneously, we observed the appearance of a prominent and well-defined peak at 820 cm\(^{-1}\), mainly associated with As-O. These symmetric and asymmetric As-O vibrations within the Fe structure imply the formation of iron arsenate precipitation on the material’s surface [92,93].

5. Future Outlook and Perspectives Trends

1. The removal of As from wastewater using activated hydrochar extracted from macroalgae has been shown to be a highly effective method. The increasing demand for sustainable and cost-effective methods for treating As-contaminated wastewater is driving the growth of this technology. Macro-algae are abundant and could be
harvested in large quantities, making them an attractive option for the production of hydrochar. In addition, the production process is low-cost and energy-efficient, making it an attractive option for small-scale operations.

2. Another research direction should be the development of advanced techniques for the activation of hydrochar, such as chemical, thermal, and microwave activation. These techniques could improve the adsorption capacity and efficiency of hydrochar, making it an even more practical solution for As removal from wastewater.

3. It is expected that the use of activated hydrochar extracted from macro-algae will continue to grow as the demand for sustainable and effective methods for treating As-contaminated wastewater increases. In addition, the development of new and improved methods for the activation of hydrochar and the use of other sustainable materials for the production of hydrochar is expected to drive the growth of this technology in the future.

Overall, the future outlook and trends of As removal from wastewater by activated hydrochar extracted from macro-algae are very positive. This technology is expected to play an increasingly important role in addressing the challenge of As contamination in wastewater.

6. Conclusions

Hydrochar extracted from red macroalgae is a suitable adsorbent for As adsorption after activation with FeCl$_3$·6H$_2$O. Our SEM results revealed a smoother surface and an increase in porous areas after hydrochar activation, providing As with a larger surface area to adsorb. FTIR analysis showed the presence of amines, hydroxyl, and carboxyl functional groups, which played an essential role in improving As adsorption. Our EDS results indicated the presence of carbon and oxygen due to the burning process and the presence of Fe and Cl after activation. The batch experiments showed that the optimum pH level for As removal was 6.0, and increasing the adsorbent dosage enhanced the As removal efficiency from 52.5% to 82%, but the rate of As adsorption (adsorption capacity) was not improved. Furthermore, the variation in initial As concentration affected the adsorption process. This study best followed the Langmuir isotherm model, indicating the formation of a monolayer over the adsorbent’s surface. The kinetic study showed that the pseudo-second-order model best fit the experimental data, suggesting that chemical bonding took place between the contaminant and the functional group present on the surface of the activated hydrochar.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15213866/s1, Figure S1. Systematic diagram to prepare hydrochar and activate hydrochar with FeCl$_3$·6H$_2$O; Figure S2. Elemental spectra of the hydrochar sample before activation (a) and after activation (b). Note: S (sulfur), C (carbon), N (nitrogen), O (oxygen), Fe (iron), Na (sodium), Mg (magnesium), Al (aluminum), Si (silicon), P (phosphorus), Cl (chlorine); Table S1. Element compound weight and atomic weight percentage of hydrochar and activated hydrochar sample.

Author Contributions: All authors contributed to the study conception and design. Material preparation and data collection and analysis were performed by A.K.K. and H.E.A.-H. The first draft of the manuscript was written by A.K.K., H.E.A.-H., J.M. (Joanna Majtacz) and T.A.K. The final manuscript was written and revised by M.R. and J.M. (Jacek Mąkinia). All authors commented on previous versions of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data and materials are available upon request.

Conflicts of Interest: This study was conducted in line with the Helsinki Declaration. All authors participated the work, and read and approved the final manuscript. All the authors agree to publish it. The authors have no relevant financial or non-financial conflict of interest to disclose.
References


11. Khatoon, J.; Intekhab, A.; Dhak, D. Effect of Uncontrolled Fertilization and Heavy Metal Toxicity Associated with Arsenic(As), Lead(Pb) and Cadmium (Cd), and Possible Remediation. *Toxicolology* 2022, 477, 153274. [CrossRef]


13. Hashmi, M.Z.; Ahmed, Z.; Rehan, S.U.; Reka, A.A. A Review on Arsenic Status in Environmental Compartments from Pakistan. *Arab. J. Geosci* 2023, 16, 130. [CrossRef]


30. Patel, N.; Acharya, B.; Basu, P. Hydrothermal Carbonization (HTC) of Seaweed (Macroalgae) for Producing Hydrochar. *Biofuels* 2021, 14, 1805. [CrossRef]


36. Patel, N.; Acharya, B.; Basu, P. Hydrothermal Carbonization (HTC) of Seaweed (Macroalgae) for Producing Hydrochar. *Energies* 2021, 14, 1805. [CrossRef]


44. Yuh-Shan, H. Citation Review of Lagergren Kinetic Rate Equation on Adsorption Reactions. *Sciencesmetrics* 2004, 59, 171–177. [CrossRef]


61. Abtahi, M.; Mesdaghinia, A.; Saeedi, R.; Nazmara, S. Biosorption of As(III) and As(V) from Aqueous Solutions by Brown Macroalga *Colpomenia Sinusosa* Biomass: Kinetic and Equilibrium Studies. *Desalination Water Treat.* 2013, 51, 3224–3232. [CrossRef]


93. Huang, Y.; Gao, M.; Deng, Y.; Khan, Z.H.; Liu, X.; Song, Z.; Qiu, W. Efficient Oxidation and Adsorption of As(III) and As(V) in Water Using a Fenton-like Reagent, (Ferrihydrite)-Loaded Biochar. *Sci. Total Environ.* 2020, 715, 136957. [CrossRef]

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