Synthesis and Application of Egg Shell Biochar for As(V) Removal from Aqueous Solutions

Asma Akram, Shazma Muzammal, Muhammad Bilal Shakoor, Sajid Rashid Ahmad, Asim Jilani, Javed Iqbal, Abdullah G. Al-Sehemi, Aboul Kalam and Samia Faisal O. Aboushoushah

1 College of Earth and Environmental Sciences, University of the Punjab, Lahore 54000, Pakistan; asmakhanasmakhan230@gmail.com (A.A.); shazmamuzamil@gmail.com (S.M.); sajidpu@yahoo.com (S.R.A.)
2 Center of Nanotechnology, King Abdul Aziz University, Jeddah 21589, Saudi Arabia; iqbaljavedch@gmail.com
3 Research Center for Advanced Materials Science (RCAMS), King Khalid University, Abha 61413, Saudi Arabia; agmasq@gmail.com (A.G.A.-S.); abul_k33@yahoo.com (A.K.)
4 Department of Chemistry, College of Science, King Khalid University, Abha 61413, Saudi Arabia
5 Department of Physics, King Abdul Aziz University, Jeddah 21589, Saudi Arabia; saboushoushah@kau.edu.sa

Abstract: Arsenic in water bodies has increased to toxic levels and become a major issue worldwide. Among various treatment methods, the removal of As from polluted water with low-cost and environmental-friendly sorbents such as biochar is considered a promising technique nowadays. In a recent experiment, the treatment of As-contaminated water using egg shell biochar was studied. Various parameters affecting the sorption, such as pH, contact time, sorbent dose, As(V) concentration and the effects of anions, were also examined. The results revealed that at a pH of 4.5, a maximum sorption of 6.3 mg g⁻¹ was observed, and the As(V) removal was 96% with an As concentration of 0.6 mg L⁻¹ and a sorbent dose of 0.9 g L⁻¹. At a contact time of 2 h (120 min), a maximum sorption of 6.3 mg g⁻¹ was noted with a removal percentage of 96%. The sorption of As(V) was obtained at an optimal sorbent dose of 0.9 g L⁻¹. The SEM-EDS data illustrated that biochar consisted of a large number of active sites for As(V) adsorption, and As appeared on the biochar surface after the sorption experiments. Moreover, XPS analyses also confirmed the presence of As(V) on the biochar surface after treatment with As-contaminated water. In a nutshell, the results of this study demonstrate that egg shell biochar has notable efficiency in the removal of As(V) from aqueous solution and that egg shell biochar could be a cost-effective and environmental-friendly sorbent for the treatment of As(V)-contaminated water, specifically in developing countries.

Keywords: arsenate; biosorption; biochar; egg shell; wastewater

1. Introduction

The contamination of surface as well as groundwater due to certain natural and anthropogenic activities such as volcanic eruption, flooding, tornadoes, windstorms, smelting, mining, industrial manufacturing, etc. has become an emerging problem of global concern [1,2]. Different pollutants contribute to the increasing water pollution and, out of all of these pollutants, carcinogenic heavy metalloid(s) including lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) rank the highest in terms of deteriorating the water quality worldwide [3].

Due to the excellent persistency and mobility of As, it can attach to the particles present in the air and can move long distances [4]. Moreover, based upon its carcinogenic nature, it is also known to be life-threatening. Yellow, black and grey As are the three most common allotropic forms of arsenic. It exists in both inorganic forms, such as arsenite and arsenate, as well as organic forms, e.g., dimethylarsinate (DMA) and monomethylarsonate (MMA) [5,6]. Arsenic is also present in the earth’s crust and comprises four oxidation states,
namely elemental (0), arsine (−3), arsenite (+3) and arsenate (+5) [4]. Arsenate, which is a pentavalent form of As, is considered less toxic than its trivalent form, i.e., arsenite.

According to the USEPA, inorganic As is classified as a Class 1 toxin due to its predominance and wide distribution in the environment. According to some researchers, due to the intake of arsenic-contaminated drinking water, people of Asian countries such as Pakistan, India and Bangladesh are at life-threatening risk [7].

Due to the rising concern of As in drinking water, the WHO recommended a safe limit of As in drinking water, i.e., 50 µg L\(^{-1}\), which, after noting adverse health effects, was reduced to 10 µg L\(^{-1}\) [8].

Arsenic removal from water is the need of the hour in terms of ensuring the supply of clean water to our communities and for future generations. Arsenite and As(V) can both be abstracted from the water using conventional techniques such as oxidation, coagulation, filtration, ion exchange and chemical precipitation [9]).

Oxidation involves the usage of different oxidants for the transformation of arsenite into arsenate. These oxidants include oxygen, ozone, chlorine, chlorine dioxide, monochloramine and hydrogen peroxide [10]. This technique is not very viable due to increased sludge production and disposal problems. The coagulation process uses different coagulants such as alum or lime but the hindrance is that the generation of toxic sludge and the pre-treatment is also essential to this process. Alumina and different ion-exchange resins are used in the ion-exchange technique, which also has several drawbacks such as insufficient removal of arsenic as well as high running costs and sludge disposal problems. On the other hand, biological methods are also being used, such as phytoremediation, bioremediation and phytofiltration. The major downside of these processes is that they are not very efficient in temperate regions and are considered to be highly expensive techniques. Thus, the above-mentioned techniques are not very efficient due to their greater running costs, higher sludge production and final disposal issues [11,12].

Above all of these techniques, biosorption has turned up as a cost-effective and feasible method for the removal of aqueous As from water. This method uses diverse biosorbents, combining As and other heavy metals. Among all the biosorbents that are prepared using agricultural waste or other sources, biochar has been proven to be highly sustainable and efficient in the removal of heavy metals [13,14].

As a biosorbent, biochar possesses numerous functional groups such as carbonyl (C=O), amino groups (-NH\(_2\)) and hydroxyl (-OH). These groups occur on biochar surface and help in eliminating heavy metals such as mercury (Hg), chromium (Cr) and As. A large number of organic materials can be used for the production of biochar; these may include sawdust, forage, plant biomass, rice husks, paper mill waste, poultry manure, walnut shells and egg shells [15].

Biochar is formed as a result of thermo-chemical transformations such as pyrolysis, gasification and torrefaction. The removal of specific contaminants using biochar occurs due to its diverse characteristics such as porosity, acid–base behavior and elemental composition, which totally rely on the pyrolysis temperature. However, the sorption mechanism differs according to the characteristics of both the contaminant and the biochar [16].

Biochar is produced using a range of materials such as husk, straw, sludge, sawdust, tea waste and peanut shell, which are applied with minimal requirements of cost and energy [17]. Various studies have provided evidence of the successful application of biochar in elimination of toxic heavy metals from contaminated water. Moreover, biochars have been proven to be superior to activated carbons. Based on type of biochar, heavy metal is reported to be removed following different mechanisms; for example, physical sorption, complexation, precipitation and electrostatic reactions. Furthermore, different sorption models could be applied to enhance our understanding about the potential of biochar for the removal of heavy metals, and it is necessary to improve this technology for wastewater remediation.

Since egg shells chemically contain 94% calcium carbonate, 1% magnesium carbonate and 4% organic matter [18], egg shells can be used to make biochar and can be applied to
water contaminated with arsenic. Different studies have been carried out on the practicability of using egg shells for diverse purposes such as biodiesel production and dimethyl carbonate synthesis, and as biosorbents, in water-treatment processes [19]. Thus, in this study, we used egg shell biochar with the objectives of (a) examining the removal efficiency of egg shell biochar for As(V) in drinking water, (b) analyzing the performance of egg shell biochar in aqueous environments as a function of the initial As concentration, biosorbent dose, pH, contact time and effect of various anions and (c) delineating the mechanism responsible for As(V) adsorption on biochar by applying SEM-EDS and XPS techniques as well as kinetic modeling.

2. Materials and Methods

2.1. Reagents, Chemicals and Analysis

By dissolving suitable amount of sodium arsenate (Na₂HAsO₄) salt in distilled water, stock solution of As (1000 mg L⁻¹) was prepared. By diluting the stock solution, various sub-stock solutions, of diverse concentrations, were prepared. The main theme in preparing the sub-stock solution was conducting the batch experiments. Chemicals such as sodium nitrate (NaNO₃), sodium sulfate (Na₂SO₄) and potassium hydrogen phosphate (K₂HPO₄) were used for studying the effects of anions. To set the pH of the solutions in the experiment, 0.01 M HCl and 0.01 M NaOH solutions were prepared. All the chemicals and reagents used in experiment were of analytical grade [20]. A spectrophotometer was used to determine the As(V) in the sorption experiment sample.

2.2. Biochar Preparation

Egg shells in this experiment were collected from different areas of Lahore. After their collection, the debris of the egg shells were washed off with clean water and, to avoid any kind of noxious odor, they were dried in sunlight for 6–7 h. They were then put in an oven after passing from a shredder, and allowed to dry in the oven at 70 °C for 24 h to remove all moisture. After that, the material was placed in a preheated muffle furnace at 450 °C for 2 h. This step was conducted to convert the egg shells into biochar and followed the method of Qayyum et al. [21]. After two hours, the materials were cooled down at room temperature without catching any moisture. Then, the prepared biochar was ground with the help of a mortar and pestle or a grinder until it attained the shape of a fine powder, which was then sieved to reach the size of 250 μm. The moisture content and total solids were 2 and 90%, respectively.

2.3. Experimental Procedure

To test the sorption efficiency of egg shell biochar for As(V), the batch sorption method was used. Experiments, with all parameters, were performed in 50 mL plastic tubes by adding up the egg shell biochar in 25 mL of sorption working solution of the required pH, temperature and As ion concentration. NaOH and HCl solutions of 0.01 M were utilized for adjusting the pH of the solutions. An orbital shaker was used to shake the solutions for contact time of 2 h. The following equation (Equation (1)) was used to determine the As removal (%) [22]:

\[
\text{%age removal} = \frac{C_o - C_e}{C_o} \times 100
\]

where \(C_o\) in mg L⁻¹ shows initial concentration of As and \(C_e\) in mg L⁻¹ represents equilibrium As concentration.

The adsorbed per-unit biomass of egg shell biochar (\(q_e\)) was measured using Equation (2):

\[
q_e = \frac{(C_o - C_e)V}{m}
\]

where \(q_e\) (mg g⁻¹) = equilibrium sorption capacity, \(V\) (L) = quantity of solution, \(m\) (g) = mass of biosorbent.
2.4. pH

The effects of pH values ranging from 3 to 8 on As(V) sorption were examined using 25 mL of solution with a preliminary As(V) concentration of 6 mg L\(^{-1}\), a sorbent dose of 0.9 g L\(^{-1}\) and a contact time of 2 h.

2.5. Contact Time and Kinetic Modeling

This experiment was performed with the contact time varying from 1 to 240 min (1, 10, 30, 60, 90, 120, 180 and 240) with initial an As concentration of 6 mg L\(^{-1}\) and a biosorbent dose of 0.9 g L\(^{-1}\) at a pH of 4.5. The As(V) removal mechanism was analyzed through kinetic modeling (Supplementary Material).

2.6. Initial Concentration of As

This effect was studied with various As(V) concentrations ranging from 0.01 to 10 mg L\(^{-1}\) (0.01, 0.1, 0.5, 0.7, 1, 3, 6, 8 and 10) while other parameters were kept constant, such as the biosorbent dose of 0.9 g L\(^{-1}\) and the contact time of 2 h at a pH of 4.5. The mechanism of adsorption by biochar was analyzed using isotherm modeling (Supplementary Material).

2.7. Biochar Dose

This effect was considered at different biosorbent doses of egg shell biochar (0.1, 0.5, 0.7, 0.8, 0.9 and 1 g L\(^{-1}\)) at an initial As concentration of 6 mg L\(^{-1}\) and a contact time of 2 h at a pH of 4.5 in all solutions.

2.8. Effect of Anions

The effects of anions such as sulfate, nitrate and phosphate on As(V) removal were also examined with a sorbent dose of 0.9 g L\(^{-1}\), an As concentration of 6 mg L\(^{-1}\) and a contact time of 2 h at a pH of 4.5.

2.9. Molybdenum Blue Method for As Analysis

For applying this method, antimonial-arsenomolybdate complex was formed to analyze the concentrations of As(V) in the samples. In brief, reagent A was prepared using ammonium molybdate tetrahydrate, potassium antimony tartrate and 9 M sulfuric acid. Reagent A (0.4 mL) and 0.2 mL of freshly prepared ascorbic acid was added up to 9.4 mL of the sample volume using a 15 mL test tube. According to same method, a blank solution was also prepared to test the solutions in a spectrophotometer. Standards of different concentrations (0, 1, 2, 5, 7 and 10 ppm) were prepared. Quantities of 50 mL of solution for each concentration were made in distilled water using sodium arsenate solution. Then, 0.2 mL ascorbic acid and 0.4 mL reagent A, as well as 9.4 mL from a 50 mL solution of each concentration, were used to fill the test tube up to 10 mL. The solutions were kept at a room temperature of 20 °C for 1 h. After the given time, when the complex (antimonial-arsenomolybdate) was formed, all the mixtures turned blue. When the blue color appeared, the mixtures were subjected to analyses using a spectrophotometer at wavelength of 870 nm [23].

2.10. Analyses of Surface Properties

The FTIR spectroscopy was used to identify functional groups of biochar. The surface morphological features and elemental configuration were examined using a field emission scanning electron microscope (FESEM) (JEOL- JSM7600-F, Tokyo, Japan) equipped with an energy-dispersive X-ray (EDX-Oxford, UK). Similarly, surface features of the egg shell biochar with and without As(V) were attained by employing X-ray photoelectron spectroscopy (XPS) (model ESCALAB 250-@Al-Ka-1486.6 eV, Thermo Fisher Scientific, Waltham, MA, USA).
3. Results and Discussion

3.1. Solution pH

The pH plays a vital role in determining and changing certain physiochemical properties of metal ions [24]. A slight or harsh change in the solution’s pH can result in the alteration and modification of biosorbents. Knowing the status of the pH, different values were considered to determine its effect on As(V) sorption. However, As(V) sorption for egg shell biochar was noticed to be very fast, when the pH initially increased from 3 to 5. The maximum sorption of As(V) was obtained at a pH value of 4.5. At this pH, the amount of As(V) adsorbed was 6.3 mg g\(^{-1}\) (Figure 1a,b). On the other hand (Figure 1a,b), the removal percentage of As(V) with respect to pH is given, i.e., around 94% removal was obtained at a pH of 4.5. Moreover, the pH greatly influences the adsorption capacity; for instance, the significant removal of As(V) was due to the neutralization of positively and negatively charged ions when the pH was acidic. On the contrary, as the pH was increased from 5 to 8, a substantial decrease in sorption capacity was seen. Not only this, acidic pH also influences the protonation of such carbon-based sorbents, which ultimately results in providing positively active sites and developing a strong electrostatic relationship of negative As(V) species with positive sorbent surface sites [24,25]. It has, therefore, been established by many researchers that the adsorption of As(V) is at its maximum when the pH is acidic, mostly because when it is increased from 7, a competition between As and OH\(^{-}\) ions usually starts, which affects the adsorption process [26]. Our data are also in agreement with other researchers such as Sattar et al., [3], who reported the use of peanut shell biochar (PSB) for efficient adsorption of As from polluted water. The comparison between peanut shell (PS) and PSB demonstrated that the removal efficiency of PSB was far higher than that of PS. Approximately 95%, As(III) and 99%, As(V) were removed from As-polluted water at pH 7.2 and 6.2, respectively. Other factors such as the initial As concentration, contact time and sorbent dose also influenced the sorption capacity of PSB. The highest arsenic removal was recorded at a 0.6 g L\(^{-1}\) sorbent dose, a contact time of 2 h and 5 mg L\(^{-1}\) initial arsenic concentration.

![Figure 1](image_url)

**Figure 1.** Adsorption of As(V) as a function of pH (a,b) and contact time (c,d) in water.

This decrease in arsenate removal as the pH value increased clearly demonstrated that basic pH is less effective in the sorption of arsenate as compared to acidic pH. Moreover, optimal pH, i.e., acidic pH, also contributes to the subsiding of competition between hydroxyl/carboxyl species and arsenate species. Alkaline pH, on the other hand, can become the reason for the onset of this kind of competition and cause disturbances in the sorption process [27].
3.2. Contact Time and Kinetic Modelling

Figure 1c,d represents the ability of egg shell biochar with respect to the variation of the contact time for the removal of As(V). Moreover, two phases of sorption kinetics are considered very important to attain the stability stage, i.e., the slower stage and the rapid stage [26].

At the start, the egg shell biochar showed rapid removal of As(V), and when the contact time was extended to about 1 h, the removal efficiency was increased even more. However, the maximum removal of As(V) was observed at 2 h, just when the system stabilized itself. The concentration at which the maximum amount of As(V) was removed was 6.3 mg g⁻¹. The percent removal of arsenate at 2 h was noted to be 96%, which can be seen in Figure 1d.

After the maximum removal was reached, further increases in contact time did not show any promising rise or fall in the removal of arsenate. Rather, the removal rate remained almost constant with the increasing time. The main reason why the contact time of two hours was recorded as the most suitable time for maximum As(V) removal was that, at that time, the biosorbent, i.e., egg shell biochar, showed great attraction of As(V) uptake from water; thus, during the early phases of this process, excess sorption often occurred more conveniently [28]. Moreover, at this contact time (2 h), a great number of sorption sites were accessible, which eventually increased the binding ability of metalloids, and this further helped in the distribution of metal ions into the pores of the biosorbent [28].

Kinetic data of As(V) adsorption on egg shell was further elaborated using famous kinetic models such as the pseudo first-order (PFO) and pseudo second-order (PSO) models (Figure 2a,b), while the values obtained from kinetic modelling are given in Table 1. The $R^2$ calculated for PSO (0.99) showed that PSO was the best-fitted model to explain the As(V) adsorption on biochar as compared to PFO (Table 1). Furthermore, the $q_e$ value computed in PSO (6.53 mg g⁻¹) was higher than the $q_e$ value of PFO (3.89 mg g⁻¹). Thus, sorption sites on egg shell biochar might have influenced the As(V) adsorption rate, while chemisorption was the dominant phenomenon for the adsorption of As(V) by biochar, since the PSO model provided the best fit to the kinetic data [29].

![Figure 2](image_url)

**Figure 2.** Kinetic modeling data of As(V) adsorption using peanut shell biochar: (a) PFO; (b) PSO.
Table 1. Kinetic model parameter data for egg shell biochar.

|       | PFO       |       | PFO       |       |
|-------|-----------|-------|-----------|-------|
|       | $q_e$ (mg g$^{-1}$) | $k_1$ (min$^{-1}$) | $R^2$    | $q_e$ (mg g$^{-1}$) | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $R^2$    |
| 3.89  | 0.01      | 0.97  | 6.53      | 0.15   | 0.99               |

3.3. Initial As(V) Concentration

An insignificant decline or enhancement in the initial As(V) concentration can cause obvious effects on the removal and sorption capabilities. Figure 3a contains a graph showing the relationship between the equilibrium As(V) concentration and the sorption. The effect of the As(V) concentration on the sorption capability of the eggshell biochar was explored by applying diverse As(V) ion concentrations (0.01–10 mg L$^{-1}$), at a sorbent dose of 0.9 g L$^{-1}$, a pH of 4.5 and 2 h of contact time. Figure 2b gives a clear idea that with the increasing of the As(V) concentration, the sorption also increased. At an initial concentration of 0.01 mg L$^{-1}$, the sorption of As(V) was much less but a progressive rise in sorption occurred right after the initial concentration of 1 mg L$^{-1}$. After 1 mg L$^{-1}$, the sorption remained sufficient and showed a sharp rise because the sorption of As(V) had not reached the equilibrium phase.

Figure 3b shows that with the enhancement in the As(V) concentration from 0.01 to 10 mg L$^{-1}$, the egg shell biochar sorption capacity was amplified. This clearly proved that with the increasing of the initial concentration, the removal efficiency of As(V) increased efficiently. However, right after equilibrium was obtained at 6 mg L$^{-1}$, the sorption of As(V) remained nearly constant, showing that at lower sorbate concentrations, the maximum active sites that were occupied were present. Isotherm models such as the Langmuir and Freundlich models were applied and data are given in Table 2. The Freundlich model described that the value of $n$ was <1, indicating that As(V) adsorption was considered a
favorable process (Table 2). Moreover, the $R^2$ value calculated in the Freundlich model was also greater (0.97) than that of the Langmuir model (0.89). It could be inferred that the As(V) adsorption was a multi-layer adsorption process or that adsorption occurred on heterogeneous surfaces.

Table 2. Equilibrium isotherm modeling data of As(V) adsorption on egg shell biochar.

| Isotherm Models | Parameters |
|----------------|------------|
| Langmuir       | $Q_L$ 0.89 (mg g$^{-1}$) |
|                | $R^2$ 0.89 |
|                | $K_L$ 5.55 (L g$^{-1}$) |
| Freundlich     | $Q_F$ 1.83 (mg$^{1-n}$ g$^{-1}$ L$^n$) |
|                | $R^2$ 0.97 |
|                | $N$ 0.41 |

3.4. Sorbent Dose

The sorbent dose is a critical parameter that affects the removal efficiency of various sorbents. A minor change in sorbent dose can cause considerable changes in the removal and sorption of As(V). For this As(V) experiment, Figure 3b, shows a graph of the relationship between the sorbent dose and the As(V) sorption. Primarily, the removal effectiveness of As(V) was low. As the amount of sorbent dose increased up to 0.7 g L$^{-1}$, the removal efficiency was enhanced progressively up to 88% (Figure 3b). The rising sorbent dose and the consequent increases in the extent of the active sorption sites were the reasons for the ongoing enhancement in the As(V) removal efficacy [30].

It was observed that there was an increase in As(V) sorption from 64.58% to 95.50% with the escalating of the sorbent dose from 0.1 to 0.9 g L$^{-1}$. This was probably because of the accessibility to a huge amount of surface sites and the improved number of exchangeable sites for As(V) sorption that occurred with the rising sorbent dose [31]. On the other hand, a further increase in the sorbent dose (0.9–1 g L$^{-1}$) resulted in a decrease in As(V) sorption from 95.5% to 88.33%, which could have been due to the overlaying of sorption sites [32].

3.5. Effects of Anions

Many anions including sulfate, phosphate and nitrates are also present in wastewater, which might influence the As sorption capacity of biochars. Figure 3c illustrates the influence of anions on As(V) sorption. The data showed that As(V) removal was largely affected by the presence of these anions in the solution. The lowest removal of As(V) was observed when phosphate was present—about 39% As(V) removal was attained; the presence of nitrate and sulfate caused 55 and 60% As(V) removal, respectively. The occurrence of phosphate considerably influenced the As(V) sorption potential of biochar as compared to nitrate and sulfate since phosphate is analogous to As(V), and thus, could replace As(V) on the sorption sites of biochar [33].

3.6. FTIR

The surface functional groups of egg shell biochar before and after As(V) adsorption are presented in Figure 4. It was observed that, in natural egg shell biochar, the band at around 3320 cm$^{-1}$ showed hydroxyl—OH group stretching vibrations [3]. At approximately 1390 cm$^{-1}$, the peak demonstrated the C=O vibrations present in ketones quinones and carboxylates [34]. Moreover, the band at 869 cm$^{-1}$ might have been a result of the C–H stretching in aromatic groups. After As(V) adsorption, the peaks changed to 3310, 1400 and 866 cm$^{-1}$, respectively, indicating As(V) adsorption on egg shell biochar. At the end, the FTIR data pointed to the presence of important surface functional moieties, which provided high As(V) adsorption capacity for the egg shell biochar.
3.7. SEM-EDS

The surface porosity and morphology of biochar was estimated using the SEM technique. Figure 5 elaborates that the structure of the egg shell biochar seemed to be irregular, rough and uneven, with a lot of pores of various sizes and shapes providing enough sorption places and pores. The EDS analyses of biochar with and without As(V) showed that the weight % values of elements such as C, O and Ca were 15.80, 50.99 and 33.21%, respectively, in raw biochar (Figure 6a,b). After As adsorption, the elemental weight % of C, O and Ca was changed to 15.88, 44.99 and 31.23%, respectively, while As also appeared (6.80%) on the biochar. The presence of egg shell biochar indicated that this biochar has significant potential to remove As(V) from water. Moreover, after As(V) loading, the O/C ratio also improved from 0.31 to 0.35, demonstrating an increase in the O-containing functional groups, which was helpful in As(V) removal [35].
Figure 6. EDS data of As(V) sorption on egg shell biochar: (a) raw biochar; (b) As(V)-loaded biochar.

3.8. XPS

Figure 7 demonstrates the XPS data of egg shell biochar before and after the addition of As. Discrete bands of C (1s), Ca (2s), O (1s) and N (1s) were recorded on the biochar, and As (3d) also appeared on the biochar after As adsorption.

Figure 7. XPS survey scan of As(V) adsorption on egg shell biochar.
The results also confirmed that the C, Ca, O and N percentages were 54.2, 8.1, 36.8 and 0.9%, respectively, on the raw biochar. After As(V) adsorption, the percentages of C, Ca, O and N were changed to 53.3, 8.3, 35.2 and 1.7%, respectively, while As was also noted to be present at a level of 1.5% on the biochar. Hence, the presence of As on egg shell biochar indicated the suitability of egg shell biochar for As abatement in water.

4. Conclusions

In this study, an eco-friendly and reliable method was used to treat As, particularly its pentavalent form, i.e., As(V), using biochar prepared from egg shell. Various parameters such as contact time, pH, As concentration, sorbent dose and anion presence were evaluated in order to check the efficiency of As(V) removal using egg shell biochar. The results were very interesting as, at pH 4.2, 96% As(V) removal was observed. Likewise, at a sorbent dose of 0.9 mg L\(^{-1}\), 95.5% of As(V) was removed; a contact time of 2 h was noted to be perfect for maximal As(V) removal. The SEM results confirmed that the biochar had an uneven and irregular structure with sufficient pores, while the EDS data positively indicated the presence of As on the biochar. Moreover, XPS scans also showed the occurrence of O-rich functional groups and the adsorption of As on the biochar. Thus, instead of using other highly expensive and pollution-causing biological or physiochemical techniques, this method is preferred for reducing or completely removing As(V) from aqueous media owing to the great economic and environmental benefits of converting egg shell into biochar.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal12040431/s1, File S1: Equilibrium modeling.

Author Contributions: Conceptualization, A.J. and M.B.S.; methodology, A.A. and S.M.; software, A.J. and M.B.S.; validation, M.B.S. and S.R.A.; formal analysis, A.J. and M.B.S.; investigation, S.M. and A.A.; resources, S.R.A. and J.I.; writing—original draft preparation, A.A., S.M. and M.B.S.; writing—review and editing, M.B.S. and A.J.; visualization, A.G.A.-S., A.K. and S.F.O.A.; supervision, M.B.S.; project administration A.G.A.-S., J.I., A.K. and S.F.O.A.; funding acquisition, A.J., J.I., A.K. and S.R.A. All authors have read and agreed to the published version of the manuscript.

Funding: We are thankful to the University of the Punjab for providing support. The authors acknowledge the support and funding of King Khalid University through the Research Center for Advanced Materials Science (RCAMS) under grant no: RCAMS/KKU/0010/21.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors are thankful to the University of the Punjab and King Khalid University for supporting this work.

Conflicts of Interest: The authors have no conflict of interest.

References

1. Muthusaravanan, S.; Sivarajasekar, N.; Vivek, J.S.; Paramasivam, T.; Naushad, M.; Prakashmaran, J.; Gayathri, V.; Al-Duaij, O.K. Phytoremediation of Heavy Metals: Mechanisms, Methods and Enhancements. Environ. Chem. Lett. 2018, 16, 1339–1359. [CrossRef]
2. Nadeem, N.; Zahid, M.; Tabasum, A.; Mansha, A.; Jilani, A.; Bhatti, I.A.; Bhatti, H.N. Degradation of reactive dye using heterogeneous photo-Fenton catalysts: ZnFe\(_2\)O\(_4\) and GO-ZnFe\(_2\)O\(_4\) composite. Mater. Res. Express 2020, 7, 015519. [CrossRef]
3. Sattar, M.S.; Shakoor, M.B.; Ali, S.; Rizwan, M.; Niazi, N.K.; Jilani, A. Comparative Efficiency of Peanut Shell and Peanut Shell Biochar for Removal of Arsenic from Water. Environ. Sci. Pollut. Res. 2019, 26, 18624–18635. [CrossRef] [PubMed]
4. Garelick, H.; Jones, H.; Dybowska, A.; Valsami-Jones, E. Arsenic Pollution Sources. Rev. Environ. Contam. Vol. 2009, 197, 17–60. [CrossRef]
5. Welch, A.H.; Westjhon, D.B.; Heisel, D.R.; Wanty, R.B. Arsenic in Ground Water of the United States: Occurrence and Geochemistry. Groundwater 2000, 38, 589–604. [CrossRef]
6. Rai, A.; Tripathi, P.; Dwivedi, S.; Dubey, S.; Shri, M.; Kumar, S.; Tripathi, P.K.; Dave, R.; Kumar, A.; Singh, R. Arsenic Tolerances in Rice (Oryza Sativa) Have a Predominant Role in Transcriptional Regulation of Set of Genes Including Sulphur Assimilation Pathway and Antioxidant System. Chemosphere 2011, 82, 986–995. [CrossRef]
7. Chakraborti, D.; Rahman, M.M.; Das, B.; Murrill, M.; Dey, S.; Mukherjee, S.C.; Dhar, R.K.; Biswas, B.K.; Chowdhury, U.K.; Roy, S.; et al. Status of Groundwater Arsenic Contamination in Bangladesh: A 14-Year Study Report. *Water Res.* **2010**, *44*, 5789–5802. [CrossRef]

8. WHO. *Guidelines for Drinking-Water Quality,* World Health Organization: Geneva, Switzerland, 2011; Volume 4.

9. Siddiqui, S.I.; Naushad, M.; Chaudhry, S.A. Promising Prospects of Nanomaterials for Arsenic Water Remediation: A Comprehensive Review. *Process Saf. Environ. Prot.* **2017**, *126*, 60–97. [CrossRef]

10. Nicomel, N.R.; Leus, K.; Folens, K.; Van Der Voort, P.; Du Laing, G. Technologies for arsenic removal from water: Current status and future perspectives. *Int. J. Environ. Res. Public Health* **2016**, *13*, 62. [CrossRef]

11. Jilani, A.; Olhman, M.H.D.; Ansari, M.O.; Hussain, S.Z.; Ismail, A.F.; Khan, I.U. Graphene and its derivatives: Synthesis, modifications, and applications in wastewater treatment. *Environ. Chem. Lett.* **2018**, *16*, 1301–1323. [CrossRef]

12. Al-Othman, Z.A.; Ali, R.; Naushad, M. Hexavalent Chromium Removal from Aqueous Medium by Activated Carbon Prepared from Peanut Shell: Adsorption Kinetics, Equilibrium and Thermodynamic Studies. *Chem. Eng. J.* **2012**, *184*, 238–247. [CrossRef]

13. Mathew, B.B.; Jaishankar, M.; Biju, V.G.; Beeregowda, K.N. Role of Biosorbents in Reducing Toxic Metals. *J. Toxicol.* **2016**, *2016*, 4369604. [CrossRef] [PubMed]

14. Shakoor, M.B.; Niazi, N.K.; Bibi, I.; Shahid, M.; Saqib, Z.A.; Nawaz, M.F.; Shaheem, S.M.; Wang, H.; Tsang, D.C.W.; Bundschuh, J.; et al. Exploring the Arsenic Removal Potential of Various Biosorbents from Water. *Environ. Int.* **2019**, *123*, 567–579. [CrossRef] [PubMed]

15. Shakoor, M.B.; Niazi, N.K.; Bibi, I.; Shahid, M.; Saqib, Z.A.; Nawaz, M.F.; Farooqi, A.; Naidu, R.; Rahman, M.M.; Murtaza, G.; Luttge, A.; et al. Effective Removal of Cr(VI) from Wastewater Using Biochar Derived from Walnut Shell. *Int. J. Environ. Res. Public Health* **2021**, *18*, 9670. [CrossRef]

16. Gurwick, N.P.; Moore, L.A.; Kelly, C.; Elias, P. A Systematic Review of Biochar Research, with a Focus on Its Stability in situ and Its Promise as a Climate Mitigation Strategy. *PLoS ONE* **2013**, *8*, e79392. [CrossRef]

17. Makuchowska-Fryc, J. Use of the Eggshells in Removing Heavy Metals from Waste Water—The Process Kinetics and Efficiency. *Ecol. Chem. Eng.* **2019**, *26*, 165–174. [CrossRef]

18. Wang, X.; Guo, Z.; Hu, Z.; Zhang, J. Recent Advances in Biochar Application for Water and Wastewater Treatment: A Review. *PeerJ* **2020**, *8*, e9164. [CrossRef] [PubMed]

19. Al-Saadi, H.S.; Shakoor, M.B.; Jilani, A.; Ahmad, S.; Raza, M.; Al-Qaied, A.; Al-Qwaiea, D.A.H.; et al. The Evaluation of Arsenic Contamination Potential, Speciation and Hydrogeochemical Behaviour in Aquifers of Punjab, Pakistan. *Chemosphere* **2018**, *199*, 737–746. [CrossRef] [PubMed]

20. Qayyum, M.F.; Abid, M.; Danish, S.; Saeed, M.K.; Ali, M.A. Effects of Various Biochars on Seed Germination and Carbon Mineralization in an Alkaline Soil. *Pak. J. Agric. Sci.* **2015**, *51*, 977–982.

21. Prasad, K.S.; Ramanathan, A.L.; Paul, J.; Subramanian, V.; Prasad, R. Biosorption of Arsenate (As$^{+5}$) and Arsenate (As$^{+3}$) from Aqueous Solution by *Arthrobacter* sp. *Biomass. Environ. Technol.* **2013**, *34*, 2701–2708. [CrossRef]

22. Lenoble, V.; Deluchat, V.; Serpaud, B.; Bollinger, J.C. Arsenite Oxidation and Arsenate Determination by the Molybdene Blue Method. *Talanta* **2003**, *61*, 267–276. [CrossRef]

23. Shakoor, M.B.; Nawaz, R.; Hussain, F.; Raza, M.; Ali, S.; Rizwan, M.; Oh, S.-E.; Ahmad, S. Human Health Implications, Risk Assessment and Remediation of As-Contaminated Water: A Critical Review. *Sci. Total Environ.* **2017**, *601*, 756–769. [CrossRef] [PubMed]

24. Zhou, L.; Liu, Y.; Liu, S.; Yin, Y.; Zeng, G.; Tan, X.; Hu, X.; Hu, X.; Jiang, L.; Ding, Y.; et al. Investigation of the Adsorption-Reduction Mechanism of Hexavalent Chromium by Ramie Biochars of Different Pyrolytic Temperatures. *Bioresour. Technol.* **2016**, *218*, 351–359. [CrossRef]

25. Shakoor, M.B.; Niazi, N.K.; Bibi, I.; Murtaza, G.; KunhiKrishnan, A.; Seshadri, B.; Shahid, M.; Ali, S.; Bolan, N.S.; Ok, Y.S.; et al. Remediation of Arsenic-Contaminated Agricultural Waste Using Biosolids. *Crit. Rev. Environ. Sci. Technol.* **2016**, *46*, 467–499. [CrossRef]

26. Marín-Rangel, V.M.; Cortés-Martínez, R.; Cuevas Villanueva, R.A.; García-Romó, M.G.; Martínez-Flores, H.E. As (V) Biosorption in an Aqueous Solution Using Chemically Treated Lemon (*Citrus Aurantifoliaswingle*) Residues. *J. Food Sci.* **2012**, *77*, 10–14. [CrossRef] [PubMed]

27. Khalil, U.; Shakoor, M.B.; Ali, S.; Rizwan, M. Tea Waste as a Potential Biowaste for Removal of Hexavalent Chromium from Wastewater: Equilibrium and Kinetics Studies. *Arab. J. Geosci.* **2018**, *11*, 1–9. [CrossRef]

28. Ali, S.; Rizwan, M.; Shakoor, M.B.; Jilani, A.; Anjum, R. High sorption efficiency for As (III) and As (V) from aqueous solutions using novel almond shell biochar. *Chemosphere* **2020**, *243*, 125330. [CrossRef] [PubMed]

29. Das, S.; Jain, J.S.; Kar, S. Bioaccessibility and Health Risk Assessment of Arsenic in Arsenic-Enriched Soils, Central India. *Ecotoxicol. Environ. Saf.* **2013**, *92*, 252–257. [CrossRef]

30. Feng, N.; Guo, X.; Liang, S.; Zhu, Y.; Liu, J. Biosorption of Heavy Metals from Aqueous Solutions by Chemically Modified Orange Peel. *J. Hazard. Mater.* **2011**, *185*, 49–54. [CrossRef]

31. Sahmoun, M.N.; Louhab, K.; Boukhari, A. Advanced Biosorbents Materials for Removal of Chromium from Water and Wastewaters. *Environ. Prog. Sustain. Energy* **2011**, *30*, 284–293. [CrossRef]
33. Pehlivan, E.; Tran, H.T.; Ouédraogo, W.K.I.; Schmidt, C.; Zachmann, D.; Bahadir, M. Sugarcane Bagasse Treated with Hydrous Ferric Oxide as a Potential Adsorbent for the Removal of As (V) From Aqueous Solutions. *Food Chem.* 2013, 138, 133–138. [CrossRef] [PubMed]

34. Kahraman, H.T.; Pehlivan, E. Cr6+ removal using oleaster (Elaeagnus) seed and cherry (Prunus avium) stone biochar. *Powder Technol.* 2017, 306, 61–67. [CrossRef]

35. Chen, Y.; An, D.; Sun, S.; Gao, J.; Qian, L. Reduction and removal of chromium VI in water by powdered activated carbon. *Materials* 2018, 11, 269. [CrossRef]