Application of Agro-Industrial Waste for Arsenic Removal from Contaminated Water

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**Abstract**

Adsorption is a promising method for treating water contaminated with arsenic. Biosorption involves the use of a sustainably produced bioadsorbent, based on the principles of circular economy. However, the selectivity of the adsorbent in the presence of other common anions in water, such as sulfate and phosphate, represents a significant challenge. This study aimed to evaluate the potential of a new adsorption technology developed from sugarcane bagasse for purifying water contaminated with arsenic. The bioadsorbent was synthesized and tested for its ability to remove arsenic in laboratory conditions (spiked aqueous solution) and in a relevant environment (arsenic-contaminated groundwater). The results revealed that the ability of the bioadsorbent to remove As(V) was significantly reduced in the presence of sulfate anions due to an antagonistic effect. However, it still showed the ability to remove arsenic even in the presence of strong competitors. The performance of the bioadsorbent was evaluated through continuous adsorption mode using arsenic-contaminated groundwater. This study demonstrated the occurrence of an overshooting phenomenon, which is probably due to the presence of sulfate anions in water.

*Keywords:* Competitive Adsorption; Sulfate; Phosphate; Arsenate; Water Treatment.

# 1. Introduction

Arsenic can be found in surface and groundwater in concentrations varying from 12.1 to 723.1 µg L−1 [1]. As discussed by Abdolali et al. [2], conventional water treatment methods are ineffective to remove toxic elements in concentrations lower than 100 mg L−1.

Adsorption can be an effective water treatment method for arsenic removal, offering effectiveness, low cost, and operational flexibility [3]. To effectively remove highly environmentally harmful anions such as arsenic, the adsorbent needs to have the ability to selectively remove arsenic even when other competing anions are present in the water.

Anions such as sulfate and phosphate are usually present in water in concentrations from 10 to 100 times higher than arsenic [4]. These anions compete with arsenic for the active sites of the adsorbent, reducing its efficiency in removing arsenic. In addition to selectivity, a sustainable adsorbent must be produced from low-cost and renewable materials widely available worldwide.

This study aimed to assess a novel adsorption technology, developed through the chemical modification of sugarcane bagasse (SB), for treating water contaminated with arsenic.

# 2. Material and methods

# *2.1. Material*

Epichlorohydrin (EPI) was purchased from Sigma-Aldrich. Triethylamine (TEA), *N*,*N*-dimethylformamide (DMF), ethanol (EtOH), and diethyl ether were purchased from ACS (Brazil). Sodium arsenate heptahydrate, hydrochloric acid (37 wt.% in H2O), and sodium hydroxide microbeads (NaOH) were purchased from Neon (Brazil). Monobasic sodium phosphate and sodium sulfate were purchased from Synth (Brazil).

SB was ground and sieved to separate the 100-mesh fraction. This fraction was washed with distilled water at 70 ºC for 60 min. Then, the SB was extracted in a Soxhlet apparatus for 240 min using cyclohexane and ethanol (1:1, v/v) to obtain pretreated SB.

# *2.2. Adsorption technology*

The adsorption technology was prepared from the chemical modification of SB with EPI and TEA in presence of DMF, as illustrated in Figure 1.

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**Fig. 1**. Synthesis route for production of the arsenic adsorption technology.

# *2.3. Batch adsorption of arsenic in the presence of other anions*

The performance of the bioadsorbent was assessed in multicomponent systems using a design for constrained surfaces for mixtures containing arsenate, sulfate, and phosphate anions in different molar proportions.

An evaluation of different proportions of these anions was carried out to obtain a ternary mixture at all experimental points whose concentrations were equal to 1.0 mmol L−1. The mixtures predominantly contained the sulfate anion, found in relevant environments where water in contaminated with arsenic.

The pH of the solutions was adjusted to 8.00 ± 0.01 to ensure the prevalence of the species of interest in the solution (anions in their divalent form). The experiments were performed using an equilibrium time of 30 min and a bioadsorbent dose of 0.2 g L−1.

# *2.4. Adsorption performance of continuous arsenic water treatment technology*

The performance of the bioadsorbent was assessed in a prototype consisting of a fixed-bed adsorption column operated continuously for 10 h to treat groundwater contaminated with arsenic (68 ± 8 µg L−1). The continuous adsorption was carried out as described by Xavier et al. [5]. For this, 0.50 g of bioadsorbent was packed into a 10 mm jacketed glass column, with a flow rate of 10 mL min−1. The operation mode used was an upward flow to prevent

the formation of preferential channels during

operation of the column.

# 3. Results and discussion

# *3.1. Batch adsorption of arsenic in the presence of other anions*

The performance of the bioadsorbent in removing As(V) was assessed in both mono- and multicomponent systems to account for the influence of coexisting anions in the water.

In the mixture design, the highest removal of As(V) was observed in experiment 8C1 (Table 1). In this experiment, the initial concentration of S(VI) was five times higher than that of As(V), and the concentration of P(V) was 2.4 times lower than that of As(V). As a result, sulfate removal was one of the lowest, showing a decrease in the total adsorption capacity of the bioadsorbent and indicating a mutual effect on adsorption.

It was observed that the difference in performance obtained for each of the three anions was not very significant in terms of efficiency (*E*). This indicates that although there is an antagonistic effect, the bioadsorbent is still capable of removing arsenic even in the presence of other anionic species.

The adsorption capacity of the bioadsorbent was evaluated in a monocomponent systems using initial concentrations defined by the overall centroid (C2) (Table 1). The results showed that the bioadsorbent had a higher affinity for sulfate anions, with a *Q*max value in the monocomponent system closest to the *Q*total values in the multi-component system (Table 2).

Table 1. Experimental matrix for mixture design for the adsorption of sulfate, phosphate, and arsenate (pH 8.00, 25.0 ± 0.1 ºC, 200 rpm, 30 min, 0.2 g L−1).

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Run** | **Concentration /**  **mmol L−1** | | | ***Q*máx / mmol g−1** (d) | | | | **Efficiency (*E*) / %** | | |
| ***C*i, S(VI)** | ***C*i, P(V)** | ***C*i, As(V)** | ***Q*max,S(VI)** | ***Q*max,P(V)** | ***Q*max,As(V)** | ***Q*total** | **S(VI)** | **P(V)** | **As(V)** |
| **1V** (a) | 0.977 | 0.010 | 0.013 | 0.724 | 0.002 | 0.005 | 0.731 | 13.8 | 4.4 | 74 |
| 0.693 | 0.002 | 0.004 | 0.699 | 13.2 | 4.1 | 6,1 |
| **2V** (a) | 0.715 | 0.125 | 0.160 | 0.436 | 0.016 | 0.043 | 0.495 | 11.2 | 3.0 | 5,0 |
| 0.411 | 0.016 | 0.045 | 0.472 | 10.6 | 3.0 | 5.2 |
| **3V** (a) | 0.862 | 0.125 | 0.013 | 0.593 | 0.022 | 0.003 | 0.618 | 12.8 | 4.0 | 4.8 |
| 0.557 | 0.019 | 0.003 | 0.579 | 12.0 | 3.5 | 3.9 |
| **4V** (a) | 0.830 | 0.010 | 0.160 | 0.489 | 0.001 | 0.039 | 0.529 | 11.0 | 3.0 | 4.6 |
| 0.482 | 0.0004 | 0.038 | 0.521 | 10.7 | 0.9 | 4.5 |
| **5C1** (b) | 0.904 | 0.010 | 0.087 | 0.646 | 0.002 | 0.027 | 0.675 | 13.2 | 5.8 | 5.9 |
| **6C1** (b) | 0.789 | 0.125 | 0.087 | 0.512 | 0.024 | 0.022 | 0.558 | 12.2 | 4.5 | 4.9 |
| **7C1** (b) | 0.920 | 0.068 | 0.013 | 0.690 | 0.014 | 0.004 | 0.707 | 14.0 | 4.7 | 6.0 |
| **8C1** (b) | 0.773 | 0.068 | 0.160 | 0.439 | 0.028 | 0.083 | 0.551 | 10.6 | 9.4 | 9.9 |
| **9C2** (c) | 0.846 | 0.068 | 0.087 | 0.545 | 0.014 | 0.028 | 0.587 | 12.0 | 5.0 | 6.1 |
| (a) Extreme vertices of mixture design. | | | | | | | | | | |
| (b) Centroid of mixture design. | | | | | | | | | | |
| (c) Overall centroid of mixture design. | | | | | | | | | | |
| (d) Dependent variables used to construct the special cubic models. | | | | | | | | | | |

The adsorption capacity of sulfate was 2.2 and 1.7 times higher than that of phosphate and arsenate, respectively. This indicates that the bioadsorbent demonstrated considerable As(V) adsorption capability, as evidenced by the high removal efficiency (*E* = 80.8 ± 0.3%) achieved under these experimental conditions, even when equilibrium conditions were less favorable.

**Table 2**. Adsorption capacity for sulfate, phosphate, and arsenate anions in monocomponent systems (pH 8.00, 25.0 ± 0.1 ºC, 200 rpm, 30 min, 0.2 g L−1).

|  |  |  |  |
| --- | --- | --- | --- |
| **Anions** | ***C*i / mmol L−1** | ***Q*max / mmol g−1** | ***E* / %** |
| Sulfate | 0.846 | 0.59 ± 0.02 | 13 ± 1 |
| Phosphate | 0.068 | 0.27 ± 0.01 | 87 ± 2 |
| Arsenate | 0.086 | 0.35 ± 0.01 | 80.8 ± 0.3 |

The highest sulfate adsorption capacities were achieved in the regions with the highest concentrations of S(VI) and lowest concentrations of As(V) (see Fig. 2(a)). This can be explained by the antagonistic effect caused by the inhibition of adsorption of one species over another. A greater influence of the As(V) concentration was observed in the response surface plotted for the variable *Q*total (see Fig. 2(b)), which was favored by higher concentrations of S(VI), whose chemical equilibrium was purposely favored.

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(b)

(a)

**Fig. 2**. Synthesis route for production of the arsenic adsorption technology.

# *3.2. Adsorption performance of continuous arsenic water treatment technology*

The competition for the active sites of the bioadsorbent can impact the performance of the biomaterial in continuous mode (adsorption columns). This can lead to a phenomenon known as overshooting, which would cause an increase in the output concentration of the initially adsorbed element (arsenic) due to its release into the solution.

The arsenic concentration in the column effluent indicates the occurrence of the “overshooting” phenomenon at 180 min (Fig. 3). This confirms that was observed in batch adsorption studies in multicomponent system, which showed that the bioadsorbent had a greater affinity for sulfate, an anion found in the water samples in a concentration 18 times greater than the arsenate concentration.



**Fig. 3**. Arsenic concentration profile in a water sample as a function of the operating time of the column ([As] = 68 ± 8 µg L−1, pH 6.94 ± 0.01, *V̇* = 10 mL min−1, *Z* = 3.0 cm, 25.0 ± 0.1 ºC).

Even under unfavorable thermodynamic conditions, the bioadsorbent retained most of the arsenic that was fed into the column. This result is in compliance with the Brazilian potability standard for the majority of the time. After 300 min of operation, the phenomenon of overshooting was no longer observed, and complete removal of all fed arsenic occurred after this period.

# 4. Conclusions

The ability of the bioadsorbent to remove arsenic is affected by the antagonistic effect of sulfate anions in the system. However, the biomaterial can still remove arsenic even when sulfate anion is present. The concentration of arsenic in water samples is in the order of micrograms per liter, so the biomaterial is effective at removing it even in the presence of other anions such as sulfate. However, more in-depth studies of adsorption in continuous mode need to be carried out to understand how the presence of common anions in water, such as sulfate, can result in the overshooting phenomenon. The adsorption technology developed in this study reached a technology readiness levels (TRL) 5, with the validation of the technology components and the prototype in the laboratory and relevant environment.

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