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# Characteristics of arsenic adsorption to sorghum biomass

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**Abstract**

The development of efficient and economic new adsorbent materials for the removal of arsenic from groundwater is a priority in regions where human health is directly affected by elevated arsenic concentrations. Adsorption of arsenic on sorghum biomass (SB) was investigated for the removal of arsenic from aqueous solutions. Potentiometric titrations and FTIR analysis evidenced two potential binding sites associated with carboxyl and hydroxyl groups. Batch experiments were carried out to determine the equilibrium time for arsenic adsorption to SB. The effect of pH on arsenic adsorption to SB was investigated for a pH range of 2.0–10.0. A strong influence of pH was demonstrated with a maximum removal of arsenic at pH 5.0. Freundlich and Langmuir isotherms were applied to equilibrium data. The Freundlich model fitted the equilibrium data and provided evidence for site heterogeneity at the binding surface. Column experiments were performed to obtain the breakthrough curves for both non-immobilized sorghum biomass and immobilized sorghum biomass.


*Keywords:* Sorghum biomass; Adsorption; Binding sites; pH; Equilibrium isotherms

## 1. Introduction

High levels of arsenic in drinking water is a major concern in several developing regions [1–5]. The elevated levels are directly related to anthropogenic activities such as agriculture, manufacturing, mining, and smelting [6]. Inorganic arsenic is well recognized as a human poison and chronic exposure to elevated arsenic concentrations in drinking water has caused vascular disorders, such as dermal pigments (black foot disease) and skin and lung cancer [7,8].

A range of technologies, such as precipitation, ion exchange, solvent extraction, adsorption on activated carbon, and iron materials [9–12] have been used for the removal of arsenic from aqueous solutions. Many of these methods have high maintenance cost and require relatively expensive mineral adsorbents which offset performance and efficiency advantages.

A promising approach is sorption technology, where biomaterials are used to remove heavy metals from aqueous solution. Significant research has been conducted on biomaterials for their metal sorption capacity [13,14], because of their low cost and high efficiency for metal removal. Sorption is the cheapest available technology when the biomass is a waste material.

Sorption mechanisms can be metabolism dependent (a function of the microbial cell activity) or independent [15], although the most common mechanisms are adsorption, ion exchange, complexation, and/or microprecipitation. Cell walls, consisting mainly of polysaccharides, proteins, and lipids, offer many functional groups which can bind ions, and these include carboxylate, hydroxyl, sulfate, phosphate, amide and amino groups. Metal sorption performance depends on external factors such as pH, other ions in solution which may be in competition, organic material such as complexing agents, cell metabolic products which may cause metal precipitation, and temperature [15].

This study presents a detailed investigation of arsenic adsorption on sorghum biomass (SB). SB is an important staple food crop in Africa, South Asia, and Central America, and is the fifth major cereal crop in the world after wheat, rice, maize and barley. It is also grown in the United States, Australia, and other developed nations for animal feed [16]. SB is therefore a plentiful waste product which could be used for metal sorption.

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In this study, the functional groups on SB for arsenic adsorption were identified and batch experiments were carried out to determine the influence of pH on arsenic adsorption. Equilibrium models were applied to describe the adsorption isotherm. Finally, maximum adsorption capacities were calculated from column experiments operated under different flow regimes.

## 2. Materials and methods

### 2.1. Standards and reagents

All chemicals were of analytical grade and were obtained from Merck (Barmstadt, Germany) and Perkin-Elmer (Boston, MA, USA). All solutions were prepared with deionized water. All utensils and bottles utilized in the experiments were washed with 5% nitric acid solution and rinsed with deionized water. The arsenic stock solution, $1000 \pm 5\,\mathrm{mg\,l^{-1}}$, was obtained from Merck. Standards for calibration as well as arsenic solutions ($0.1–20\,\mathrm{mg\,l^{-1}}$) for batch and column experiments were prepared from the stock solution.

### 2.2. Preparation of biomass

Farm waste SB from the Guanajuato, Mexico region was washed several times with deionized water to remove any particles, or soluble materials. Biomass was dried at 60 °C, ground in a bladed mixer to particles less than 0.1 mm in diameter, and sieved through stainless steel sieves, ASTM–AASHO standards. Sieved particles were washed with 0.01 M HCl until the supernatant was clear. The biomass was separated from the supernatant then dried in an oven (Heraeus UT6060, Ettenleur, The Netharlands) at 100 °C for 12 h. This biomass was called non-immobilized sorghum biomass (NISB) and used for all experiments unless otherwise stated.

### 2.3. Potentiometric titration and chemical modeling

Potentiometric titration [17] was carried out for a biomass concentration of $5\,\mathrm{mg\,ml^{-1}}$. Ten 50-ml flasks were used for this experiment. The weighed biomass was mixed with 20 ml deionized water ($CO_2$ free). An aliquot of 0.1 M NaOH was added to each flask containing the biomass suspension. Flasks were agitated using a shaker (200 rpm) at room temperature to equilibrium, which was found to be 12 h from preliminary adsorption equilibrium tests. Equilibrium pH was measured using a pH meter.To evaluate the nature and concentration of functional groups, experimental data were analyzed in an adsorption chemical model (Eq. (1)):

$$C_{\mathrm{Na}} = \sum_{i=1}^{N} \frac{B_i X}{1 + [\mathrm{H^+}]/K_i} + \frac{K_{\mathrm{W}}}{[\mathrm{H^+}]} - [\mathrm{H^+}] \quad (1)$$

where $C_{\mathrm{Na}}$ is the Na concentration in the suspension for each addition of 0.1 M NaOH solution, $B_i$ and $X$ are the quantity of the specific functional groups per unit mass of biomass ($\mathrm{mmol\,g^{-1}}$) and the biomass concentration, respectively, and $K_i$ and $K_{\mathrm{W}}$ are the acidic equilibrium constant and the water dissociation constant, respectively.

In Eq. (1), two parameters are obtained for each functional group: $K_i$ and $B_i$. The titration model (Eq. (1)) was simultaneously fitted to all the points on the titration curve through a nonlinear regression method.

To confirm the main functional groups on the cell membrane of the protonated and arsenic bound biomass, IR studies were carried out through Fourier transform infrared analysis (FTIR) on a Perkin-Elmer 1620.

### 2.4. pH profile experiments

Batch laboratory experiments, as previously reported [18], were used for the pH profile studies. A biomass suspension of $10\,\mathrm{mg\,ml^{-1}}$ was prepared in 0.01 M HCl. The pH of the suspension was adjusted to 2.0, allowed to equilibrate and 2 ml aliquots of the suspension were transferred in triplicate into six 8 ml tubes. Subsequently, 2 ml of $1\,\mathrm{mg\,l^{-1}}$ arsenic solution (pH 2.0) was added to each tube. Controls were also prepared. All the tubes were equilibrated in a shaker for 12 h. The initial pH of each tube was kept constant through a specific buffer solution [19]. The samples were then centrifuged (Sargent-Welch, Buffalo Grove, IL, USA) at 3000 rpm for 5 min. The final pH of the respective supernatants was recorded and analyzed for arsenic concentration. This experiment was carried out for a pH range of 2.0–10.0 to determine the optimal pH value for maximum arsenic adsorption.

### 2.5. Kinetic experiments

To determine the contact time required for the adsorption equilibrium experiments, kinetic experiments were examined first. The prepared biomass sample was resuspended in deionized water with a concentration of $10\,\mathrm{mg\,ml^{-1}}$. The solution was then adjusted to pH 5.0 and 2 ml of $1\,\mathrm{mg\,l^{-1}}$ arsenic solution (pH 5.0) was added to each tube. All tubes were equilibrated in a shaker. The pH of the solution was maintained at the desired value (pH 5.0) by the addition of buffer [19]. Samples were regularly removed and analyzed for arsenic concentration.

### 2.6. Equilibrium adsorption isotherms

Equilibrium adsorption isotherms were determined by shaking 2 ml of biomass ($10\,\mathrm{mg\,ml^{-1}}$) with 2 ml of arsenic solution at concentrations ranging from 0.1 to $100\,\mathrm{mg\,l^{-1}}$ (pH 5.0) for a set equilibrium time (12 h). After centrifugation, the samples were analyzed for arsenic content. The equilibrium data were analyzed in accordance with Freundlich and/or Langmuir isotherms, Eqs. (2) and (3), respectively [20,21]:

$$\text{Freundlich}: \quad q = K_{\mathrm{F}} C^{\beta} \quad (2)$$

$$\text{Langmuir}: \quad q = \frac{K_{\mathrm{L}} C q_{\mathrm{m}}}{1 + K_{\mathrm{L}} C} \quad (3)$$

where $q$ is the amount adsorbed at equilibrium ($\mathrm{mg\,kg^{-1}}$), $C$ the equilibrium concentration of the adsorbate ($\mathrm{mg\,l^{-1}}$), $q_{\mathrm{m}}$ the

Table 1
Running conditions for the non-immobilized sorghum biomass (NISB), and immobilized sorghum biomass (ISB) columns

| Column | Active bed (cm) | Empty bed volume (ml) | Pore volume (ml) | Amount of biomass (g) | Size of biomass (mm) | Influent arsenic concentration ($mg\,l^{-1}$) | Flow rate ($ml\,min^{-1}$) |
|---|---|---|---|---|---|---|---|
| NISB | 40 | 1155 | 535 | 150 | 0.18–1.4 | 5 | 10 |
| ISB | 40 | 865 | 530 | 140 | 0.25–0.5 | 5 | 10 |

maximum adsorption capacity ($mg\,kg^{-1}$), $K_F$ and $K_L$ are constants, and $\beta$ is an empirical parameter which varies with the degree of heterogeneity ($0<\beta<1$) of adsorbing sites.

### 2.7. Column experiments

A cylindrical column of 5.4 cm inner diameter and 50 cm height was used for adsorption experiments. The column was packed with the prepared biomass. To promote compaction, the column was filled continuously with the biomass and deionized water while the sides of the column were lightly vibrated. The bottom of the column was filled with sand (0.25–0.5 mm) to prevent clogging. The pH of the column was maintained at 5.0 and the effluent pH was checked to ensure that the column was at the optimal binding pH. The column was equipped with a pump and a tank (for gravity flow) and operated until a steady-state effluent concentration was reached. To obtain the hydraulic detention time of the column, pore volume was divided by the flow rate. Running conditions for the column experiments are shown in Table 1. Immobilization of biomass was as previously reported [22].

### 2.8. Analytical methods

Total arsenic content in all experiments was determined by Hydride Generation-Atomic Absorption Spectrometry (HG-AAS, Perkin-Elmer MHS 15, Perkin-Elmer AAnalyst 100, Boston, MA, USA). All the samples were pre-reduced from As(V) to As(III) by adding 10% KI according to a pre-determined dilution factor (DF). This prevents interferences between the two oxidation states of arsenic. Samples were stored at least 30 min in the dark and were analyzed within 3 h of sampling. A 1 ml sample was pipetted into a 50 ml volumetric flask where 10 ml of 1.5% HCl was added as diluent. Subsequent inline hydride generation (Perkin-Elmer MHS 15) with argon and sodium borohydride reductants (3% $NaBH_4$ in 1% NaOH solution) and AAS detection allowed determination of total arsenic species down to $10\,\mu g\,l^{-1}$ at a wavelength of 193.7 nm. The signals for each sample were read to provide a mean and relative standard deviation. Calibrations were performed for the removal range of analysis (0.1 to $5\,mg\,l^{-1}$). The instrument response (50 μl of the $1000\,mg\,l^{-1}$ arsenic stock solution records an absorbance of close to 0.2) was periodically checked with known arsenic standards.

### 2.9. Error analyses

The adsorption experiments were run in triplicate in order to evaluate the experimental reproducibility. The confidence of data generated in the present investigations has been analyzed by standard statistical methods to determine the mean values and standard deviation. Each data set was calculated at the 95% confidence level ($P<0.05$) to determine the error margin [23]. The correlation coefficient for the calibration curve of 0.986 or greater was obtained and computed as required to confirm the linear range for a minimum of 12 data points.

## 3. Results and discussion

### 3.1. Titration curve and chemical modeling

A potentiometric titration experiment was carried out to determine functional groups present in the biomass (Fig. 1). Neither one nor two functional sites were sufficient to describe the titration curve (Fig. 1). However, a three-site model was able to describe the entire titration curve (Fig. 1) using Eq. (1). The first site was established as the most abundant ($1.98\pm0.16\,mmol\,g^{-1}$) having the equilibrium constant ($pK_H$) for proton binding at $4.9\pm0.1$. Carboxyl groups in biological polymers have $pK_H$ values ranging from 3.5 to 5.0 [24] and the FTIR spectrum (figure not shown) provided absorbance peaks at 1735, 1655, 1605, 1429, 1374, 1247, 1163, and $1107\,cm^{-1}$ all being stretching of carboxyl groups [25–27]. SB is in the cellulose group [28], which has many binding sites including carboxyl. So, there is significant evidence that the first functional group was carboxyl.

The final functional group ($1.45\pm0.19\,mmol\,g^{-1}$) was observed at a $pK_H$ value at $9.9\pm0.2$ and hydroxyl groups generally show $pK_H$ values between 9.5 and 10.5 [21]. The FTIR absorbance peak at $3352\,cm^{-1}$ [29] is further evidence for a hydroxyl group. The second group ($pK_H=5.5\pm0.5$) could not be definitely identified as there are a range of functional groups (i.e. phosphoryl, amino, and imidazole) of biological polymers that have $pK_H$ values in the range 5.0–6.0 [24].

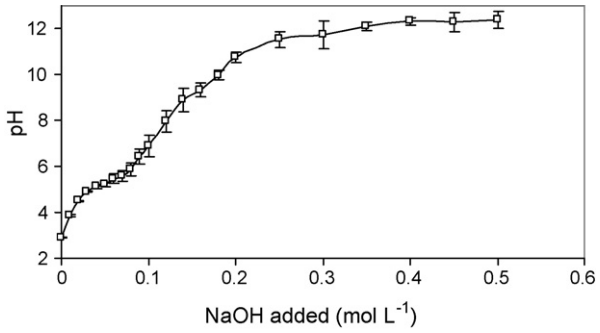


Fig. 1. Biomass potentiometric titration curve. The biomass concentration was $5\,mg\,ml^{-1}$.

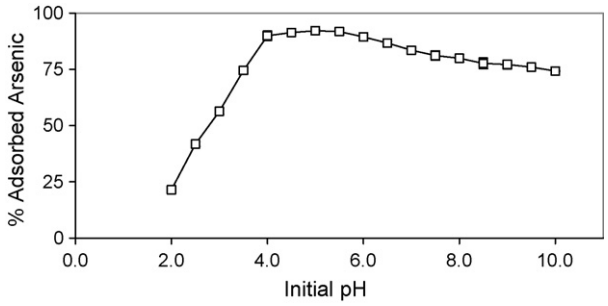


Fig. 2. Arsenic adsorption to SB as a function of initial solution pH at a biomass concentration of 10 mg ml$^{-1}$. Arsenic concentration was 1 mg l$^{-1}$ and the contact time was 12 h. The initial pH of the solutions was kept constant by using specific buffer solutions.

### 3.2. Influence of pH on arsenic adsorption

Experiments were performed to determine the effects of pH on arsenic binding to SB as this is an important parameter influencing adsorption. The adsorption of arsenic to SB is presented in Fig. 2 as a function of pH. Most of the arsenic is bound to SB at an initial pH range of 4.0–6.0, $H_2AsO_4^-$ being the dominant equilibrium species in the pH range 2.0–7.0. The adsorption of the arsenate is expected to be favored at a pH less than $pH_{zpc}$ (zpc: zero proton charge) of the adsorbents [25]. From the titration analyses, a carboxyl group has been found at a pH value of 5.0 and it is likely that this is the main adsorption site for arsenate. Although the adsorption site and the dominant arsenic species ($H_2AsO_4^-$) are negatively charged, yet they can be bonded together because of the geometric configuration of each atom [30]. Arsenic is positively charged which is the central atom in the dominant arsenic species ($H_2AsO_4^-$). As it is positively charged, therefore, it might have some kind of attraction toward the carboxyl group through the geometric configuration [30]. Physical force might be another possible explanation behind this negatively charged bonding. However, further experiments (chemical modification, electro microscopic study, etc.) are needed.

The relatively small adsorption capacity in the extreme acidic region might be attributed to the dissolution of the substrate [31] and a consequent decrease in the number of active sites. At a low pH, the complex formed via the interaction between arsenic ions and acidic functional groups would be expected to be destabilized since the values of conditional stability constants decrease with pH. It has also been suggested that the complexation of $H^+$ on active surface sites is responsible for minimal or negligible arsenic ion uptake at a low pH [32].

### 3.3. Kinetic studies

This experiment was conducted in order to determine the optimal time for arsenic binding to SB at the optimal pH. Since all soluble materials were eliminated during prior washings, arsenic binding should be dominated by the SB material itself. Fig. 3 demonstrates that more than 80% of arsenic adsorbs to SB within one hour. The rapid binding of the metal ions by SB could indicate that metals are being adsorbed onto the surface of the biomass. It has been found elsewhere that metal adsorption to biomass is within 5 min and only the surface of the sorbent is highly active during this time period [33]. Equilibrium is slowly approached within the next 12 h. Equilibrium conditions can be influenced both by the metal concentration and by the liquid/solid (L/S) ratio [34]. However, in our study low L/S and initial arsenic concentrations were used to avoid these effects.

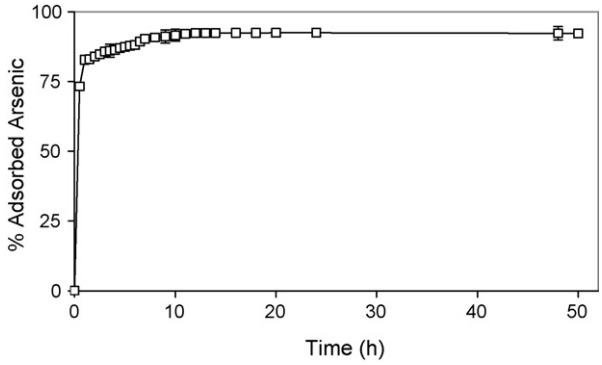


Fig. 3. Kinetic studies for arsenic binding to SB. The solution pH was 5.0, the biomass concentration was 10 mg ml$^{-1}$ and the arsenic concentration was 1 mg l$^{-1}$.

### 3.4. Adsorption isotherms

Equilibrium adsorption studies were performed to provide the maximum arsenic adsorption capacities of SB. Two equilibrium adsorption isotherms, Freundlich and Langmuir, were tested. Fig. 4 shows the adsorption equilibrium isotherm, which is then transformed to the linear forms of the Freundlich and Langmuir isotherms (Eqs. (2) and (3)) to determine the Freundlich and Langmuir parameters that are listed in Table 2. The best fit for the equilibrium data are provided by the Freundlich isotherm, probably due to the heterogeneous nature of the surface sites involved in the arsenic uptake [35]. Freundlich assumes neither homogeneous site energies nor limited levels of sorption and is the result of overlapping patterns of several Langmuir-type adsorption curves occurring at different sites on the complex SB surface. Fig. 4 together with the values of the parameters

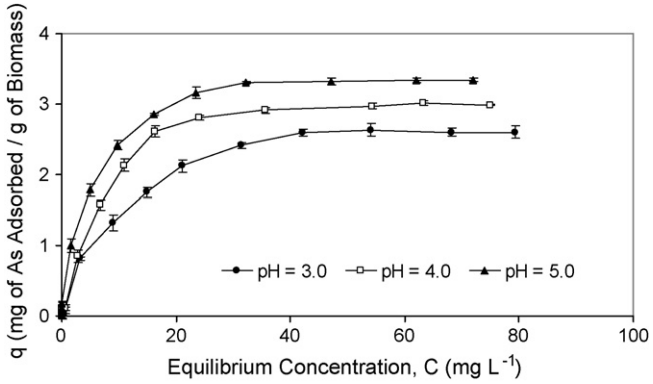


Fig. 4. Equilibrium adsorption isotherms of arsenic at pH values of 3.0, 4.0, and 5.0. The biomass concentration was 10 mg ml$^{-1}$ and the contact time was 12 h.

Table 2
Isothermal parameters obtained from linearization of experimental data

| pH | Freundlich | | | Langmuir | | |
|---|---|---|---|---|---|---|
| | $K_F$ | $\beta$ | $R^2$ | $K_L$ | $q_{max}$ | $R^2$ |
| 3.0 | 0.73 | 0.71 | 0.993 | 0.55 | 2.9 | 0.989 |
| 4.0 | 0.94 | 0.72 | 0.995 | 0.38 | 3.1 | 0.990 |
| 5.0 | 1.02 | 0.72 | 0.991 | 0.26 | 3.6 | 0.980 |

presented in Table 2 show that the binding of arsenic on SB is pH dependent. An increase in the sorption intensity ($\beta$) and sorption capacity ($K_F$) of SB was found for pH values up to 5 of the aqueous metal solutions. The increase in the arsenic uptake per unit weight of SB was also found from the Langmuir model and the maximum capacity ($q_{max} = 3.6\,mg\,kg^{-1}$) of the biomass was obtained at a pH value of 5.0.

### 3.5. Column experiments

The batch laboratory procedure showed that SB has the ability to bind arsenic ions and remove them from solution, but a batch system would not be practical for removing arsenic from tapped groundwater. Therefore, column experiments were performed to study the binding of arsenic to SB under different flow conditions (pump and gravity flow). This experiment was conducted separately for NISB and ISB to compare the capacity between non-immobilized and immobilized biomass as well as to avoid the clogging problems found for non-immobilized biomass.

Effluent arsenic concentrations for the NISB and ISB column are shown in Fig. 5. Arsenic removal below the guideline value ($50\,\mu g\,l^{-1}$), provided by World Health Organization (WHO), was observed for up to 31 and 27 pore volumes for the NISB and ISB columns, respectively for an influent arsenic concentration of $5\,mg\,l^{-1}$. Breakthrough (>60 and >65 $\mu g\,l^{-1}$ for NISB and ISB, respectively) occurred after 33 and 27 h for NISB and ISB, respectively. Then the columns slowly decreased in their ability to remove arsenic from solution, with the NISB column saturated at 150 h and the ISB column at 120 h. The maximum adsorption capacity and the supply of fresh water (below the guideline value provided by WHO) for the NISB column were 2.765 mg of As/g of NISB and 16.2 l in 27 h and for the ISB column were 2.437 mg of As/g of ISB and 14.4 l in 24 h, respectively.

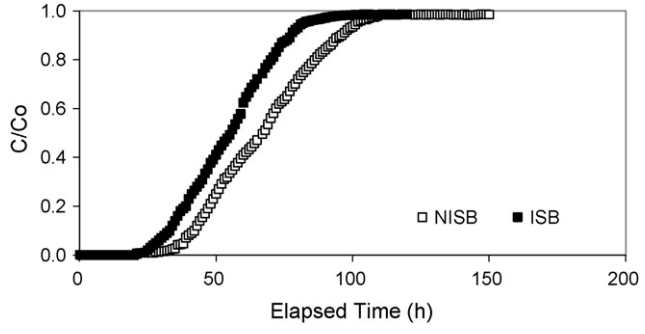


Fig. 5. Effluent arsenic concentration© from the NISB and ISB column for an influent arsenic concentration ($C_0$) of $5\,mg\,l^{-1}$. The column was operated at a flow rate of $10\,ml\,min^{-1}$ and had a mean hydraulic detention time of 53.5 and 53 min for the NISB and ISB columns, respectively.

## 4. Conclusions

This work demonstrates the effectiveness of SB in adsorbing arsenic from aqueous solutions. Potentiometric titration and FTIR analysis evidenced two potential binding sites associated with carboxyl and hydroxyl groups. The equilibrium time for arsenic adsorption on SB was 12 h. The effects of pH on arsenic adsorption to SB were investigated for a pH range of 2.0–10.0 and the maximum removal of arsenic was found at an initial pH value of 5.0. The Freundlich isotherm fitted the equilibrium data and provided evidence of site heterogeneity at the binding surface. Column experiments were performed for NISB, and ISB with different flow conditions. The maximum adsorption capacity for the NISB and ISB columns were 2.765 mg of As/g of NISB and 2.437 mg of As/g of ISB, respectively. This sorption capacity was found very efficient compare with other commonly used sorbents (2.16 mg/g of As(V) with *Moringa oleifera* Lamarck seed powder [36]; 28.57 μg/g of As(III) with iron oxide-coated sand [37].

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