

## A promising stable chitosan-Fe (III) adsorbent for arsenate removal from drinking water

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**ABSTRACT:** Chitosan-Fe (III) beads have been reported as good adsorbents for arsenic. NaOH is normally reported as iron hydroxide precipitating agent and high amounts of washing water is needed to stabilize the pH. In this study, NH<sub>4</sub>OH was used, as it evaporates easily, a quick rinsing was enough to get neutral pH. Batch kinetic and isotherms tests with 1 mg/L As (V) solutions were carried out. The adsorption process was slow (5d for 80% removal) and followed a pseudo-second order kinetic model, meaning that chemical sorption was the rate-limiting step. However, the adsorption in the kinetic study and the Langmuir adsorption capacity were 8.69 mg/g and 16.22 mg/g respectively. Furthermore, the calculation of adsorption capacity in equilibrium with 10 µg/L (q<sub>10</sub>) using Freundlich parameters gave 3.15 mg/g. This means that the material has a similar As (V) adsorption capacity (mg/g) to the ones reported for iron-chitosan beads and others adsorbents. Therefore, the material is promising, and further fixed bed studies are recommended.

### 1 INTRODUCTION

Removal of arsenic from water by adsorption is widely applied. Among the adsorbents, chitosan-iron (oxyhydr)oxide beads have been reported as effective due to the formation of a very stable Fe:As complex (De Marques Neto *et al.*, 2013). Normally, beads are produced by dropping a chitosan-iron solution into aqueous sodium hydroxide (He *et al.*, 2016). However, the beads produced need high amounts of washing water to remove the residual alkaline reagent to obtain the beads with neutral pH. Besides, depending on the procedure, swollen and unstable beads can be obtained. In this study, chitosan-Fe(III) material, stable and with neutral pH, were obtained by using NH<sub>4</sub>OH as precipitating solution. Besides the improvement in the method, the aim of the study was to evaluate the adsorption capacity of the material by batch adsorption and kinetic experiments.

### 2 MATERIALS AND METHODS

#### 2.1 Chitosan-Fe(III) beads synthesis

Chitosan powder (2.5% w/v) was dissolved in acetic acid (0.5%) and commercial FeCl<sub>3</sub> was added (0.12 M). The spherical shape beads were

obtained by dropping the solution into NH<sub>4</sub>OH (1.75% v/v) under continuous stirring using a magnetic stirrer. After 3 h, the beads were collected, and rinsed with a small amount of water since the evaporation of the ammonia result in beads with almost neutral pH. Finally, the beads were oven dried at 45°C overnight.

#### 2.2 Kinetic adsorption experiments

Duplicate adsorption experiments were conducted in an orbital shaker at 20°C and 130 rpm. Tap water was spiked with 1 mg/L As(V) and placed in contact with 0.1 g/L of the chitosan-Fe(III) beads for 8 days. The pH was adjusted to 7.0 using HCl or NaOH. Samples were taken after 4 h and every 24 h thereafter. The data was fitted using the pseudo first and pseudo second order models (Ngah *et al.*, 2005), respectively (Equations 1 and 2).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where  $q_e$  and  $q_t$  are the amount of As(V) adsorbed on adsorbent (mg/g) at equilibrium and at time  $t$ , respectively.  $k_1$  and  $k_2$  are the rate constants for

pseudo-first order adsorption (/min) and pseudo-second order adsorption (g/mg/min) respectively.

### 2.3 Batch adsorption studies

Adsorption experiments were carried out by shaking 0.5 L of 1 mg/L As(V) and pH 7.0 solutions in an orbital shaker at 130 rpm and 25°C for 7 days. The dose of adsorbent was varied from 0.02 g/L up to 0.1 g/L. All adsorption experiments were conducted in duplicate. The data were fitted using the linearized Freundlich and Langmuir isotherm models according to equations (4) and (5), respectively.

$$\log(q_e) = \log(K_F) + \left(\frac{1}{n}\right)\log(C_e) \quad (4)$$

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

where  $q_e$  (mg/g) and  $C_e$  (mg/L) are the adsorption capacity and the concentration of As(V) in the equilibrium.  $K_F$  and  $1/n$  are the Freundlich parameters related to adsorption capacity and adsorption intensity, respectively. The parameter  $b$  is the Langmuir sorption equilibrium constant (L/mg) and  $Q_m$  is the maximum adsorption capacity (mg/g), which corresponds to the monolayer adsorption capacity.

### 2.4 Analytical methods

The arsenic measurement was performed following the 3113A method (APHA, AWWA, & WEF, 2005) with a Perkin Elmer AAnalyst 800 (DL: 2.5 µg/L and QL: 5 µg/L).

## 3 RESULTS AND DISCUSSION

### 3.1 Synthesis of the chitosan-Fe(III) beads

In contrast to others beads procedures (Gupta *et al.*, 2009; He *et al.*, 2016; Padilla-Rodríguez *et al.*, 2014), in this case,  $\text{NH}_4\text{OH}$  quickly evaporates, therefore, excess base is removed easily. Although the formulated material swelled around 85% in contact with water, it maintained an appropriate mechanical strength for use in filtration systems.

The formulated beads also presented a uniform rounded shape with a mean grain size of 1.2 mm, making them suitable for column packaging.

### 3.2 Adsorption kinetics

The arsenic adsorption by the beads was relatively slow (Figure 1), only around 10% was adsorbed in the first 4h of the experiment. Moreover, the equilibrium and maximum adsorption capacity

were reached after around 120 h (5 d) with 80% removal. Contrary, Marques Neto *et al.* (2013) and He *et al.* (2016) reported similar chitosan iron materials, with and without glutaraldehyde, more than 90% removal in 2h and 24h, respectively. Even though the differences are significant, it is important to consider that both were performed at higher temperature (25°C instead of 20°C) and using higher initial concentration, 75 mgAs/L and 4.9 mgAs/L versus 1 mgAs/L.

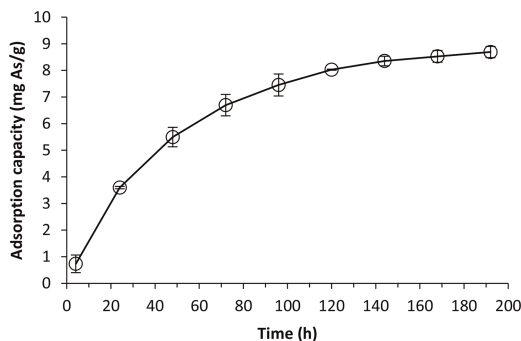


Figure 1. Kinetics of As(V) removal (initial As(V) concentration 1 mg/L, adsorbent dose 0.1 g/L, shaking for 8 days at 20°C).

Regarding the kinetic modelling the data adjusted better to the pseudo second order ( $R^2$  0.997) than the pseudo first ( $R^2$  0.922) suggesting that the rate-limiting step may be chemical adsorption (Ngah *et al.*, 2005). The experimental adsorption capacity ( $q_e = 8.69$  mg/g) was close to the calculated one ( $q_e = 11.25$  mg/g), confirming the pseudo second order model. The capacity obtained was higher than 2.05 mg/g and lower than 13.24 mg/g reported by He *et al.* (2016) and Marques Neto *et al.* (2013) respectively. The rate constant ( $k_2 = 2.86 \times 10^{-5}$  g/(mg·min), which was two orders of magnitude lower than the studies of Marques Neto *et al.* (2013) and He *et al.* (2016),  $7.09 \times 10^{-3}$  g/(mg·min) and  $5.84 \times 10^{-3}$  g/(mg·min), respectively, confirms that the adsorption process is slower. However, the high adsorption capacity of this experiment and the isotherms (below) confirms that this material has potential and column studies are suggested.

### 3.3 Equilibrium isotherms

The data fitted well both Langmuir ( $R^2$  0.962) and Freundlich ( $R^2$  0.966) models (Figure 2). The Langmuir monolayer maximum capacity,  $Q_m$  of 16.22 mg/g, was about eight times higher than previous studies for similar iron chitosan granular materials. Gupta *et al.* (2009) and Padilla-Rodríguez *et al.* (2014) reported 2.24 mg/g and 2.72 mg/g, respectively.

The Freundlich isotherm, with  $K_F$  of 15.38 (mg/g)(L/mg) $^{1/n}$  and  $1/n$  of 0.345, indicates good

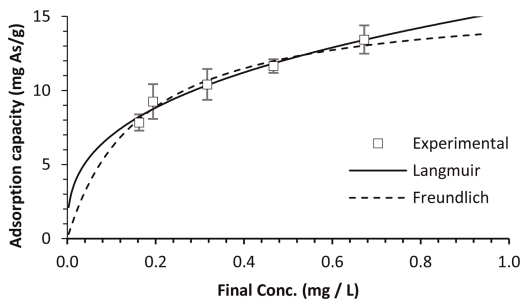


Figure 2. Adsorption isotherms (initial As (V) concentration 1 mg/L, adsorbent dose 0.02–0.1 g/L, 130 rpm, 7 day, 20°C).

adsorption strength and relatively high adsorbent loading at low concentrations, showing favorable isotherms (Worch 2012). Besides, using the Freundlich parameter, a  $q_{10}$  adsorption capacity in equilibrium with 10  $\mu\text{gAs/L}$  was calculated. The  $q_{10}$  of 3.15 mg/g obtained is higher to 0.42 mg/g calculated by using the data of Padilla *et al.* (2014) for iron chitosan beads. Accordingly, with Sinha *et al.* (2011) the high capacity obtained in the present study is comparable to magnetic ion exchange resins MIEX and granular ferric hydroxide GFH with 3.16 mg/g and 2.51 mg/g at pH 5.5 and 7.5 respectively.

#### 4 CONCLUSIONS AND RECOMMENDATIONS

The synthesized beads were stable, and a small amount of washing water was needed to have a constant pH. The adsorption process was rather slow needing up to 5 days for 80% removal. However, both the pseudo second order kinetic model, and the Langmuir and Freundlich isotherms results showed very high adsorption capacity, superior or similar to previous chitosan beads and other types of arsenic adsorbents. Therefore,

the results indicate a promising material and fixed bed filtration evaluation is recommended.

#### ACKNOWLEDGEMENTS

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