Research Article

Received: 14 May 2018 Revised: 7 August 2018 Accepted article published: 18 August 2018 Published online in Wiley Online Library: 14 September 2018

(wileyonlinelibrary.com) DOI 10.1002/jctb.5801

Optimization of continuous arsenic biosorption present in natural contaminated groundwater

Bárbara E Pérez Mora,[a,b] Sebastián E Bellú,[a,b] María F Mangiameli,[a,b] Silvia I García[a,b] and Juan C González[a,b*]

Abstract

BACKGROUND: Arsenic (As) is a serious water pollution problem in the world. In Argentina, it is related to old volcanic activities; for example, the western region of Santa Fe State has concentrations higher than 0.1 mgAs L^{-1}. In this work, a green, sensitive method was used to determine As concentration, and its removal using chitosan in bed columns was studied. Mathematical models were used to explain sorption, and the process was optimized using statistical methods.

RESULTS: Arsenic quantification was realized with a bespoke modification of the As molybdenum blue method (detection limit = 0.0048 mg L^{-1}, quantification limit = 0.0145 mg L^{-1}). Chitosan molar mass, pH_{ZPC} and deacetylation degree were 350 ± 10 kDa, 6.3% and 76.2%, respectively. A maximum of 68.5% was obtained for As(V) removal at optimum conditions. Raising the bed column height produced an increment in breakthrough times, and the sorption process was favoured using low flow rates. Salinity, phosphate and nitrate concentration reductions were 60%, 50% and 70%, respectively.

CONCLUSIONS: Sorption studies have been carried out on groundwater, using columns packed with chitosan for arsenic removal. The process was optimized by a factorial design. Elution profiles were adjusted adequately with mathematical models. The modified analytical technique for arsenic quantification applied in groundwater, was successful.

Keywords: sorption; bioremediation; mathematical modelling; optimization; water

INTRODUCTION

At the present time, human exposure to naturally high concentrations of arsenic (As) in groundwater is one of the most widespread environmental problems in many countries.[1] This element is found as dissolved species, forming oxo-anions in natural waters. The predominant oxidation states are As(III), As(V) and, less frequently, As(0) and As(-III). The chemical speciation depends on the pH values of groundwater (pH 6.5–8.5).[2] It can be present in inorganic and organic forms, with the former, in general, being the most toxic for people.[3] The World Health Organization (WHO) recommends 0.01 mg L^{-1} as the maximum allowed As level for human and agriculture use, in order to reduce the negative impacts of this metalloid on human health. Although in Argentina the allowed value for drinking water[4] is 0.05 mgAs L^{-1}, elevated As concentrations are found in several states, such as Santa Fe, Córdoba and Chaco. The western region of Santa Fe State and Córdoba city, have concentrations that exceed 0.1 and 0.5 mgAs L^{-1}, respectively. Another relevant point to highlight is the variability of As concentrations reported in the groundwater as a consequence of several factors, such as the amount and frequency of rainfall. To take this issue into account, it is necessary to study a wide range of As concentrations. Additionally, the search of economic/effective methods for the determination and elimination of As in communities with few economic resources has resulted in the development of new As quantification/removal technologies. In recent years, a wide variety of As elimination systems have been applied to decrease the presence of As in drinking water, food and vegetables. Amongst these, sorption is considered one of the best alternatives for treatment of contaminated water because of its minimal sludge production, simplicity, low cost and high efficiency.[5] Conventional sorbents for As removal such as activated carbon and alumina are being displaced by new low-cost biosorbents such as plant biomass, algae, fungi, bacteria, and the biopolymers chitin and chitosan.[6–8] Chitosan is a natural cationic aminopolysaccharide obtained by deacetylation of chitin, and several studies have reported that this polymer has good efficiency as an As sorbent.[9,10] The presence of a large number of amino groups with affinity for arsenate ions, makes their favourable interaction possible. Its nontoxicity, abundance in nature and biodegradability are the main characteristics that make chitosan suitable for removing As from aqueous solutions.[11]

The major objective of the present work was to obtain the maximum sorption of As in groundwater onto chitosan using fixed-bed columns, by optimizing operational parameters of the columns (bed height and volumetric flow-rate). In order to describe the

* *Correspondence to: JC González, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, S2002LRK Rosario, Santa Fe, Argentina. E-mail: gonzalez@iquir-conicet.gov.ar*

a *Área Química General e Inorgánica, Departamento de Química-Física, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Rosario, Argentina*

b *Instituto de Química de Rosario-CONICET, Rosario, Argentina*

dynamics of the sorption process in a continuous treatment mode, experimental breakthrough curves were fitted with nonlinear equations deriving from Yoon–Nelson, Thomas and Modified Dose–Response models. The statistical method Response Surface Methodology (RSM) based on Central Composite Design (CCD) was developed.[12] and ANOVA, data regression and graphical analysis were performed to analyse the results.

MATERIALS AND METHODS

Groundwater samples were obtained from Piamonte Town, located in Santa Fe, Argentina. The characterization of groundwater is presented in Table 1.

Phosphate concentration was determined using Johnson's reducer and a colour reagent, prepared as follows:

Johnson's reducer: 14.0% sodium metabisulfite ($Na_2S_2O_5$), 1.4% sodium thiosulfate ($Na_2S_2O_3$) and 10.0% sulfuric acid (H_2SO_4), in a volume ratio of 2:2:1.

Colour reagent: 11.0% ascorbic acid ($C_6H_8O_6$), 3.0% ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), 1.1% antimony potassium tartrate ($C_4H_4K_2O_6Sb{\cdot}1/2H_2O$) and 14.0% sulfuric acid (H_2SO_4) in a volume ratio of 2:2:1:5.

Nitrate concentration was determined by a LAQUAtwin (Horiba Scientific, Japan) selective electrode, whereas a HANNA Conductivity Tester (DiST4, Romania) was used for conductivity/salinity measurement. The turbidity and colour of the samples were measured with a portable Habit 2100Q01 turbidimeter (Romania) and a HANNA water colour checker (HI 727, Romania), respectively.

In order to cover a possible range of As concentrations, water samples were supplemented by addition of sodium arsenate ($Na_2HAsO_4{\cdot}7H_2O$) solution until they attained 1.0 mg L^{-1} As(V). All of the reagents used for the current investigation were of analytical grade without any need for further purification.

Analytical methods

Arsenic concentrations in aqueous solutions were assessed by applying a bespoke modification of the As molybdenum blue method,[13] a simple and economical spectrophotometric procedure. In this the As(V) concentration was calculated from the absorbance difference between a reduced and a nonreduced sample. In the latter case, the absorbance would be given only by those interfering compounds which react with the colour reagent. Ten millilitre samples were divided in two parallel subsamples and acidified with 1.0% HCl (25 mL final volume). One of the subsamples was treated with 2.5 mL of reducing reagent (Johnson´s reducer), and the other was treated with 2.5 mL of Milli-Q water. After 30 min, 2.5 mL of colour reagent was added. Scheme 1 shows the steps followed in the determination of As(V).

After 30–40 min, absorbance at 890 nm was measured using a double beam spectrophotometer, with thermostatized cells and electronic temperature controller, Jasco V-550. Quartz cells of 10.0 cm optical path were used. As(V) concentration was calculated using the following equation [Eqn (1)]:

$$[\text{As (V)}] = \frac{\left(Abs_{\text{untreated}} - Abs_{\text{reduced}}\right)}{\varepsilon\, b} f \qquad (1)$$

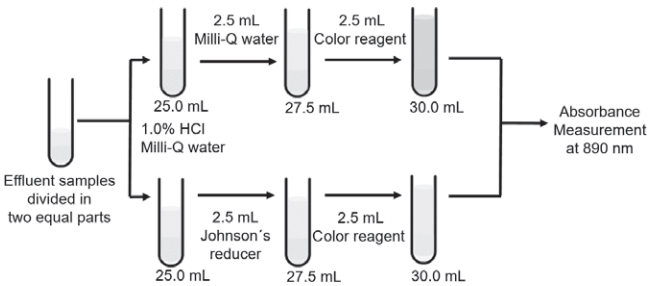
where *Abs* is the absorbance of the sample, untreated or reduced, at 890 nm, ε is the molar absorptivity (mol L^{-1} cm^{-1}), *b* is the optical path (cm) and *f* is the dilution factor.

It is pertinent to mention that this colorimetric method was used to determine the concentration of As present in groundwater of several Argentina cities as part of an interlaboratory program, and delivered comparable results to those obtained by more sophisticated and expensive methods [Atomic Absorption Spectrometry with Hydride Generation, graphite-furnace Atomic Absorption Spectrometry (SAA) and silver diethyldithiocarbamate].

Table 1. Characterization of groundwater (Piamonte Town)

Components	Pre-treatment values	Post-treatment values
As(V) (mg L^{-1})	0.035	<0.01
Turbidity (NTU)	0.01	0.01
Nitrate (mg L^{-1})	70	21
Conductivity (mS cm^{-1})	3.20	1.30
Phosphate (mg L^{-1})	0.02	0.01
Salinity (mg L^{-1})	2070	820

Initial groundwater pH = 8.45.



Scheme 1. Determination of As(V) concentration.

Limit of detection (LD) and limit of quantification (LQ) were 0.0048 and 0.014 mg L^{-1}, respectively. The LQ value was lower than the corresponding legislated number (0.050 mg L^{-1}). The molar absorptivity (ε) obtained in the experimental linear range (0.0050–0.50 mg L^{-1}) was 19 100 M^{-1} cm^{-1}. The use of a cuvette with an optical path of 10.0 cm allowed increase in the sensitivity of this method. In this spectrophotometric method, species such as phosphate and silicate do not interfere in the determination of As(V).

Chitosan characterization

pH zero-point charge determination

The Mular–Roberts method[14] was used to estimate the polymer pH zero-point charge (pH_{ZPC}). One gram of chitosan was suspended in 50.0 mL of 0.01 mol L^{-1} $NaNO_3$, at different initial pH_0 (5–8), and stirred 24 h (250 rpm) at room temperature. After the equilibrium time, the pH value (final pH) was measured. The difference between initial and final pH, ΔpH, was determined and plotted as a function of pH_0. The pH_{ZPC} value was indicated as the point where the resulting curve intersected the *x*-axis.

Chitosan molecular weight (M_η)

The molecular weight estimation of chitosan polymer was carried out applying the capillary viscosity method. The technique was statistically validated according to linearity and repeatability criteria. Diluted chitosan solutions (0.001–0.005 g mL^{-1}) were prepared dissolving chitosan in an aqueous mixture of 0.2 mol L^{-1} sodium chloride and 0.1 mol L^{-1} acetic acid. Relative viscosity (η_r) and specific viscosity (η_{sp}) were determined using a Cannon–Fenske

(modified Ostwal, 75 series, VAT) capillary viscometer at 25 °C and calculated according to Eqns (2) and (3), respectively:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0} \tag{2}$$

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} \tag{3}$$

where t and t_0 are the draining time and, η and η_0 are the viscosity, of diluted chitosan solutions and solvent, respectively. Huggins and Kramer demonstrated the empirical relationship between viscosity and concentration,[15,16] which can be described by Eqns (4) and (5):

$$\eta_{red} = \frac{\eta_{sp}}{C} = [\eta] + k_H\ [\eta]^2\ C \tag{4}$$

$$\frac{\ln\ \eta_r}{C} \approx [\eta] + k_K\ [\eta]^2\ C \tag{5}$$

where k_H and k_K are the Huggins and Kramer constants, respectively and C is the solution concentration (g mL^{-1}). The term η_{sp}/C represents the reduced viscosity, η_{red}. The graphical representation of equations 4 and 5, allows to obtain, by extrapolation at zero concentration, the intrinsic viscosity value, $[\eta]$ (mL g^{-1}). With this data, the viscosity average molecular weight (M_η) of chitosan samples, can be calculated, applying the Mark–Houwink–Sakurada expression [Eqn (6)]:

$$[\eta] = K\ \left(M_\eta\right)^a \tag{6}$$

where $K = 1.81 \times 10^{-3}$ mL g^{-1} and $a = 0.93$.[17]

Deacetylation degree percentage (DDA)

Chitosan deacetylation degree (DDA) was performed by ^{1}H nuclear magnetic resonance (NMR) based method.[18] ^{1}H NMR spectrum was collected in a Bruker Advance 300 MHz Digital, with parameters NS = 64, SW = 12.98, O1P = 5.5 and T = 70 °C. A 5.0 mm NMR test tube was filled with 5.0 mg of chitosan and vacuum dried for 3.0 h at 50 °C. To dissolve the polymer, 0.5 mL of 2.0% DCl/D_2O solution was added and the tube was kept at 70 °C.

Hirai and Lavertu reported a peak around 4.9 ppm, assigned to the C1 proton of the glucosamine unit in chitosan, and peaks at 3–4 ppm assigned to C2–C6 protons of glucosamine and *N*-acetylglucosamine units.[19,20] The C1 proton of the *N*-acetylglucosamine unit appeared around 5.2 ppm, obtained from chitosan solution. The DDA% was determined with Eqn (7), from the Hirai method.[19]

$$\text{DDA}\% = \left(1 - \frac{\frac{1}{3}\ ICH_3}{\frac{1}{6}\ IH_{2-6}}\right) \times 100 \tag{7}$$

where ICH_3 is the integral intensity of resonance band due to CH_3 residue of N-acetylglucosamine and $IH_{2\text{-}6}$ is the sum of integral intensities of H_2, H_3, H_4, H_5 and H_6, protons. Replacing the experimental values of these terms in Eqn (7), resulted in Eqn (8).

$$\text{DDA}\% = \left(1 - \frac{\frac{1}{3} \times 3}{\frac{1}{6}\ \text{x}\ (22.1 + 3.1)}\right) \times 100 \tag{8}$$

Continuous up-flow fixed-bed column sorption experiments

Borosilicate glass columns of 10.0 cm length and 2.0 cm internal diameter were filled with different known amounts of commercial chitosan. Chitosan was previously hydrated in 250 mL of Milli-Q water at pH 4.5 by addition of 1.7 mol L^{-1} H_2SO_4 solution with constant agitation. The polymer, preserved between two polyurethane filters, was packed inside the column reaching the desired height and packing density. A solvent flow (H_2SO_4, pH 4.5) was applied in order to reach a flow rate and internal pressure constant to ensure complete hydration of chitosan, prevent appearance of air bubbles inside the column and keep the effluent pH constant over time.

Groundwater containing 1.0 mg L^{-1} of As(V) was pumped through the bed column at desired flow rates, with a peristaltic pump (Gilson Minipuls 3) in an up-flow mode, at pH 4.5 and room temperature (25 °C). Samples were collected at different times to determinate the As(V) effluent concentration. The sorption process was continued until arsenic concentration in the samples reached the inlet concentration.

The As(V) sorption icapacity (q_t) was determined from Eqn (9):

$$q_t = \frac{m_{in} - m_{out}}{m_s} = \frac{C_0\ V_{ef} - Q \int_0^t C_{eff}\ (t)\ \text{dt}}{m_s} \tag{9}$$

In Eqn (9), q_t represent the amount of As(V) uptake per unit mass of chitosan (sorption capacity) in mg g^{-1}, m_{in} and m_{out} are the total mass of As(V) input and output from the fixed-bed column (mg), m_s is the dry mass of chitosan (g), C_0 and C_{eff} are the initial and effluent contaminant concentrations (mg L^{-1}), V_{ef} is the total volume of treated contaminated water (L), Q is the volumetric flow-rate (L min^{-1}) and $\int_0^t C_{eff}\ (t)$ dt represents the elution profile area (mg). Integration limits, 0 and t, are the times associated to 0 and 0.95 C:C_0 ratios, respectively.

The As(V) mass not retained (m_{out}) was calculated by integrating the column elusion profile and multiplying by the volumetric flow rate. The amount of arsenic ions entering through the column (m_{in}) can be calculated with Eqn (10):

$$m_{in} = \frac{C_0\ Q\ t_e}{1000} \tag{10}$$

where t_e (min) is the column saturation time when C:C_0 = 0.95. Finally, As(V) removal percentage (%R) can be obtained from m_{in} and m_{out}, through Eqn (11):

$$\%R = \frac{m_{in} - m_{out}}{m_{in}} \times 100 \tag{11}$$

Experimental column data modelling

Several mathematical models describe the dynamics of the sorption process using fixed-bed columns. They help to analyse and explain the experimental data and predict changes due to different operational conditions.

Thomas model

The Thomas equation is one of the most frequently applied models to represent the sorption process performance in continuous systems.[21] Column data might be used to calculate: the solid phase concentration of sorbate per sorbent unit (q_{TH}) and the minimum height of the bed (L_{min}) necessary to acquire a measurable breakthrough time, t_b (when the C:C_0 ratio is 0.05).

This model assumes that: (i) radial and axial dispersions in the fixed-bed column are absent; (ii) sorption is described by a pseudo-second-order kinetics, reduced to a Langmuir isotherm at equilibrium; (iii) dead volume is not significant; (iv) the sorption process is carried out under isobaric and isothermal conditions; and (v) properties of the solid and liquid phases remain constant. A mathematical expression of this model is presented in Eqn (12):

$$\frac{C}{C_0} = \frac{1}{1 + e^{\frac{k_{TH}\, q_{TH} \rho_p\, A\, L}{Q} - k_{TH}\, C_0\, t}} \tag{12}$$

where k_{TH} is the Thomas rate constant ($m^3\ mol^{-1}\ min^{-1}$), A is the cross-sectional area of the column (m^2), L is the height of the column bed (m), t is the sample acquisition time (min) and ρ_p is the packing density ($kg\ m^{-3}$).

Yoon–Nelson model

Yoon and Nelson developed a simple model aimed at gas or vapour adsorption on activated carbon.[22] This model does not require data regarding the physical properties and characteristics of sorbate, being less complex than other models. The probability of sorbate breakthrough on a sorbent is specified in Eqn (13).

$$\frac{C_0}{C} = \frac{1}{1 + e^{k_{YN}\,(\tau - t)}} \tag{13}$$

In Eqn (13), K_{YN} is Yoon-Nelson's proportionality constant (min^{-1}) and τ is the time when output concentration equals to half of the input concentration. It is possible to calculate q_{YN} ($mg\ g^{-1}$) if the next equation [Eqn (14)] is applied:

$$q_{YN} = \frac{0.5\, C_0 Q\, 2\, \tau}{m_s} \tag{14}$$

Modified Dose–Response model

This model was developed for describing different types of pharmacology processes but is now also used to analyse column sorption processes.[23] The Modified Dose–Response model can be defined by Eqn (15):

$$\frac{C}{C_0} = 1 - \frac{1}{1 + \left(\frac{C_0 Q\, t}{q_{DR}\, m_s}\right)^a} \tag{15}$$

where a is the model constant.

The fitting error resulting from use of the Thomas model is minimized when Modified Dose–Response is applied, especially for elusion profiles with short and long breakthrough times. In Eqns (12)–(15) the terms Q, C, C_0 and m_s have the same meaning as previously defined in Eqns (9)–(11). Additionally, q_{TH}, q_{YN} and q_{DR} are the maximum concentrations of solute sorbed on the solid phase ($mg\ g^{-1}$) for Thomas, Yoon–Nelson and Modified Dose–Response models, respectively.

Optimization of As(V) adsorption on chitosan

The response surface methodology (RSM) is well-defined as a set of mathematical techniques and advantageous statistics, used to model and analyse the response of interest, which is influenced by numerous variables.

For As(V) removal optimization, a rotable central composite design (CCD) was selected after preliminary tests. A 13 experiments CCD came from the compositional arrangement $2^k + 2k + n$, with two factors ($k = 2$) and five central points ($n = 5$). Design Expert (v7.0, USA) was used for data analysis. Table 2 presents the range and levels of independent variables (column bed height and volumetric flow rate).

Table 2. Coded levels for independent factors used in the experimental design

		Coded levels				
Factors	Symbol	$-\alpha$	−1	0	1	$+\alpha$
Flow rate (Q, mL min^{-1})	X_1	3.0	3.5	4.8	6.0	6.6
Column height (h, cm)	X_2	5.0	7.0	10.0	13.0	15.0

In order to study the As(V) percentage removal and recognize the most relevant terms of the model, a second-order polynomial equation [Eqn (16)], was applied:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i,j=1\ (i \neq j)}^{k} \beta_{ij}\, X_i\, X_j + \varepsilon \tag{16}$$

where Y is the response, β_0 is the constant coefficient, β_i and β_{ii} are the linear and quadratic coefficients (respectively) of the independent factor X_i, β_{ij} is the coefficient of interaction between the independent factors X_i and X_j and, finally, ε represents the model error.

For the RSM, experimental conditions were pH = 4.5, packing density = 270 $kg\ m^{-3}$ and $[As(V)]_0 = 1.0\ mg\ L^{-1}$, and evaluated factors were bed height, h (3.0–6.6 cm) and volumetric flow rate, Q (5.0–15.0 mL min^{-1}).

In order to fit the response function to the experimental data, regression analysis was performed. The probability P-value, standard error of coefficient (SE coefficient) and T-value were applied to determine the significance of the regression coefficients for each parameter. The value P is the smallest level of significance to reject the null hypothesis and determine which variables are statistically significant, SE is a measure of the variation in estimating the coefficient and T is the ratio of the coefficients to the standard error. These effects are significant when their probability level is 5% ($P < 0.05$). Usually, the higher and lower values of T and P, respectively, the more significant are the corresponding coefficient terms.[24] A positive value of the regression coefficient means an enhancing effect, whereas a negative sign indicates an opposed effect of the factor in the response.

ANOVA is the most reliable way to evaluate the quality of the adjusted model and it was used to verify the statistical significance of the ratio of mean square due to regression and mean square due to residual error (F-value). The variation in the response can be explained by the regression model equation when a large F is acquired. To decide whether F is large enough to indicate statistical significance, an associated P is used. If P for a large F is lower than 0.05, it means 95% confidence, and the model is statistically significant.[25] To probe the relationship between three and two variables, 3D Surface and Contour graphs can be applied.[26] Both kinds of graph can be helpful to identify: (i) optimum settings and (ii) the best settings for each response.

RESULTS AND DISCUSSION

Chitosan characterization

For chitosan pH_{ZPC} determination, it is important to know the pH value at which the polymer surface does not present charge. In

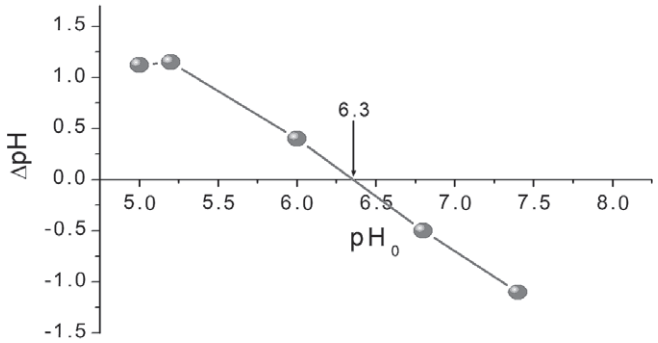


Figure 1. The pH of zero-point charge of chitosan polymer. Sorbent dose 20 g L^{-1}, $NaNO_3$ 0.01 mol L^{-1}, $T = 25\,°C$, 24 h equilibrium time.

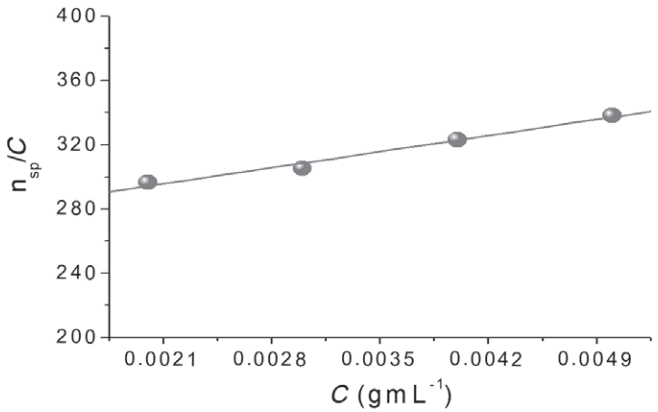


Figure 2. Graphical representation of experimental data fitting with the Huggins' function.

this study, the chitosan pH_{ZPC} obtained was 6.3, a value similar to data in the literature (Fig. 1).[27] At pH lower than 6.3 the amino groups are protonated, and therefore the polymer surface area is positively charged, showing a great tendency to adsorb anions.[28] Arsenic acid predominates only at extremely low pH, a rare situation in groundwater. At pH 3.0–6.9, As(V) is found as $H_2AsO_4^-$. This means there is a favourable interaction between NH_3^+ groups in chitosan and $H_2AsO_4^-$ species under pH 6.3.

In order to determine the chitosan molar mass, a viscosimetry technique was used. A decrease in the reduced viscosity could be observed as the polymer concentration decreased (Fig. 2). This result indicated that, under our experimental conditions, it was appropriated to use the Huggins expression. The graph derived from the Kramer equation is presented in Fig. 3. According to these functions, the intrinsic viscosity, $[\eta]$, was 265 mL g^{-1} and the chitosan average viscous molecular mass was 350 ± 10 kDa.

According to the literature,[18] H^1 NMR has been found to be the most reliable method for determining DDA%. The result thus obtained was 76.2%.

Bed height and volumetric flow-rate effects: experimental column data modelling

The breakthrough curves for As(V) sorption on chitosan, using bed height columns of 3.0 and 6.6 cm (2.30 and 5.10 g, respectively), at 10.0 mL min^{-1} constant volumetric flow-rate, are presented in Fig. 4. It is evident that the breakthrough time (t_b) and the saturation time (t_e) showed an increment with a higher bed height. Saturation time of the column was high due to the increment in the

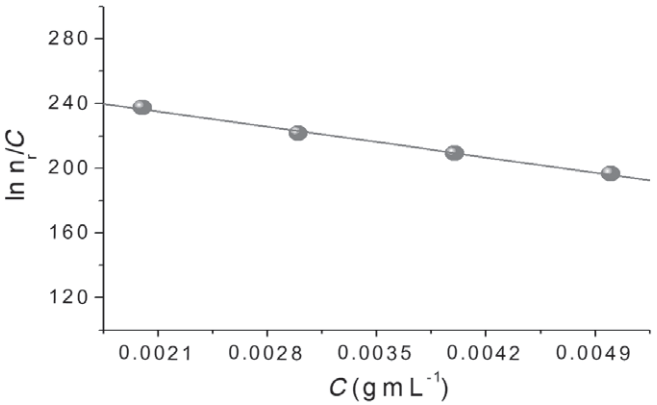


Figure 3. Graphical representation of experimental data fitting of Kramer's function.

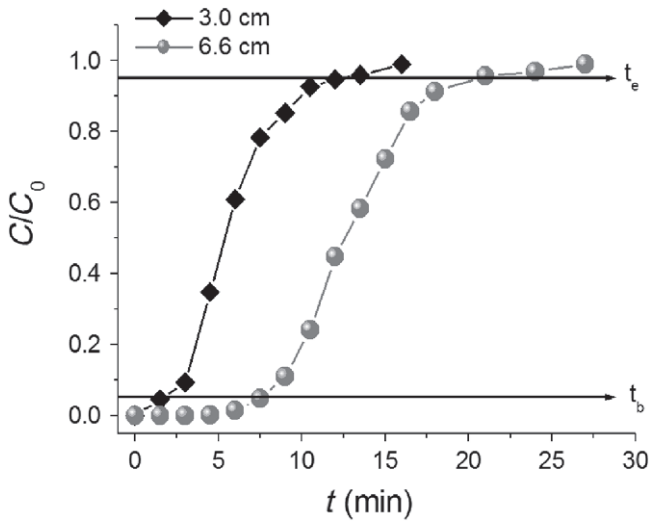


Figure 4. Breakthrough curves for different bed heights. Experimental parameters: $[As(V)]_0 = 1.0$ mg L^{-1}, $Q = 10.0$ mL min^{-1}, pH = 4.5, $\rho = 270$ kg m^{-3}, $T = 25\,°C$.

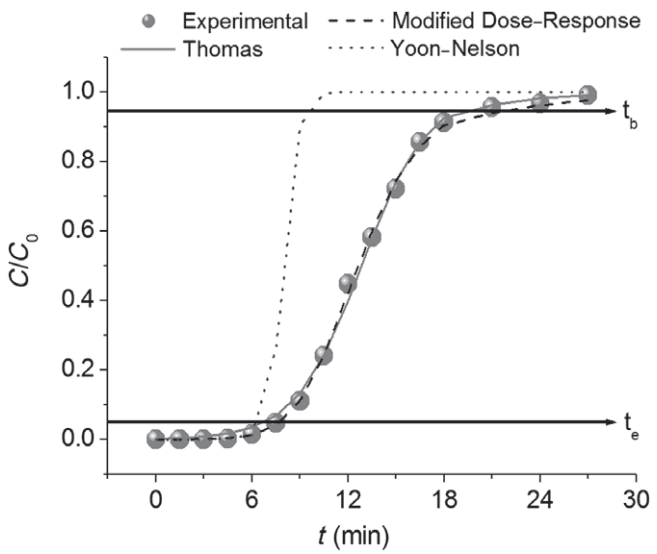


Figure 5. Elution profiles described by Thomas, Modified Dose–Response and Yoon–Nelson models. Experimental parameters: [As(V)] = 1.0 mg L^{-1}, $h = 6.6$ cm, $Q = 10$ mL min^{-1}, pH = 4.5, $\rho = 270$ kg m^{-3}, $T = 25\,°C$.

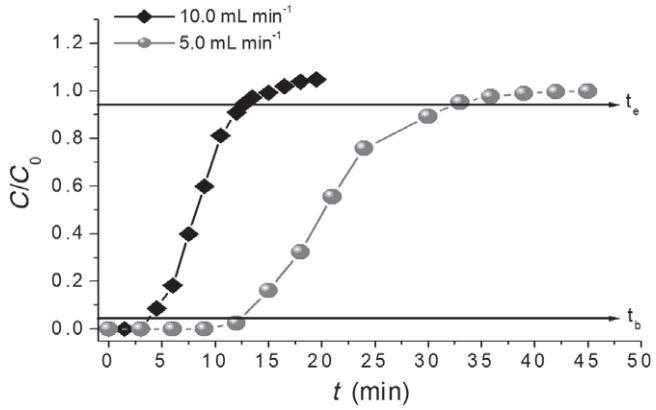


Figure 6. Breakthrough curves for different flow rates. Experimental parameters: [As(V)] = 1.0 mg L^{-1}, h = 4.8 cm, pH = 4.5, ρ = 270 kg m^{-3}, T = 25 °C.

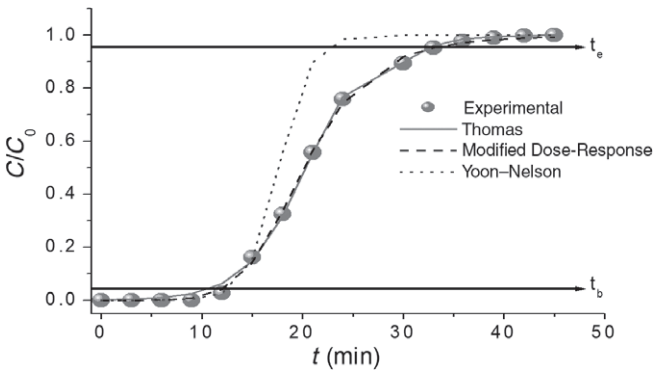


Figure 7. Elution profiles described by Thomas, Modified Dose–Response and Yoon Nelson models. Experimental parameters: [As(V)] = 1.0 mg L^{-1}, h = 4.80 cm, Q = 5.0 mL min^{-1}, pH = 4.5, ρ = 270 kg m^{-3}, T = 25 °C.

quantity of active binding sites present in the biopolymer, allowing a greater retention and, therefore, a low effluent concentration of the pollutant. This behaviour also was observed by other authors.[29]

Experimental data were best described by Modified Dose–Response and Thomas models. The R^2 values of both models exhibited a good fit to the experimental data (Fig. 5), whereas the Yoon–Nelson model could not be used to fit these data.

Breakthrough curves at two values of volumetric flow (5.0 and 10.0 mL min^{-1}) with a constant sorbent bed height of 4.8 cm (3.70 g) are shown in Fig. 6. A lower flow rate causes a longer residence time of the sorbate inside the column, favouring the sorption process and breakthrough occurs at longer times. This result is in agreement with an increase in treated water volume with a C:C_o ratio < 0.05. Modelling of one experimental elution curve with the suggested models is shown in Fig. 7. It can be concluded that, as was observed previously, Modified Dose–Response and Thomas models represent the experimental results better than the Yoon–Nelson model. Table 3 exhibits the parameters of the different mathematical models.

Table 4. Full factorial design for the independent variables with responses for As(V) removal

Run order	X_1: flow rate (mL min^{-1})	X_2: bed height (cm)	Response (% removal) Experimental	Predicted
1	10.0	6.6	64.11	64.28
2	15.0	4.8	50.02	48.11
3	10.0	4.8	60.50	63.90
4	5.0	4.8	55.12	57.18
5	10.0	3.0	43.99	42.91
6	13.0	6.0	55.87	56.86
7	13.0	3.5	45.98	47.08
8	10.0	4.8	63.25	63.90
9	7.0	6.0	70.01	67.92
10	10.0	4.8	64.22	63.90
11	7.0	3.5	48.10	46.43
12	10.0	4.8	65.05	63.90
13	10.0	4.8	67.13	63.90

Optimization for As(V) biosorption process

A CCD method was applied in this study to find out the optimal conditions to remove As(V) from contaminated groundwater. A total of 13 experimental runs were performed to examine the combined effect of two different independent parameters (bed height and volumetric flow rate) on As(V) percentage removal. Table 4 presents the experimental design and results obtained. Interpretation of ANOVA was performed to evaluate the quality of the adjusted model. To investigate the factor effects, 3D Response Surface and Contour plots were employed.

The second-order model expression for the parameters studied in the optimization of the chitosan-As(V) sorption, can be

Table 3. Parameters for Thomas and Modified Dose–Response models

Factor	Thomas model				Modified Dose–Response model			
h[a] (cm)	k_{TH} (m^3 mol^{-1} min^{-1})	q_{TH} (µg g^{-1})	R^2	χ^2	a	q_{DR} (µg g^{-1})	R^2	χ^2
3.0	61.7	37.3	0.9981	0.0004	6.9	41.0	0.9990	0.0001
6.6	56.2	14.4	0.9974	0.0004	5.5	18.5	0.9984	0.0002
Q[b] (mL min^{-1})								
5.0	81.7	9.5	0.9991	0.0002	7.6	10.1	0.9992	0.0002
10.0	65.0	16.7	0.9992	0.0002	5.4	21.8	0.9998	0.0006

[As(V)] = 1.0 mg L^{-1}, pH = 4.5, ρ = 270 kg m^{-3}, T = 25 °C.
[a] h = 4.8 cm.
[b] Q = 10.0 mL min^{-1}.

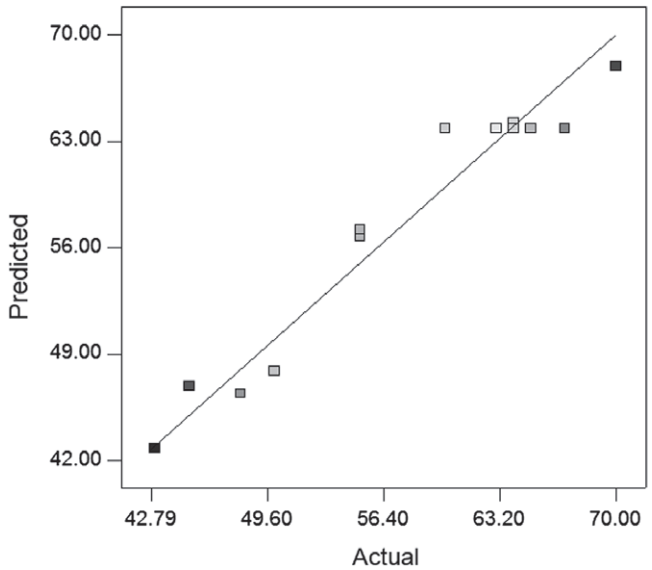


Figure 8. Comparison between actual and predicted values of RSM for As(V) biosorption.

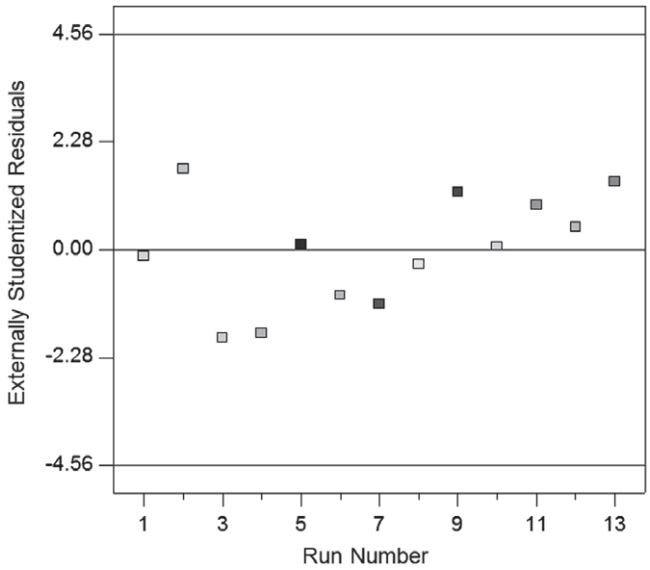


Figure 9. Plot of studentized residuals *versus* experimental run number.

expressed in coded units by Eqn (17):

$$\%R = 63.50 - 3.17\,X_1 + 7.76\,X_2 - 5.64\,X_1^2 - 4.87\,X_2^2 - 3.42\,X_1X_2 \quad (17)$$

The regression model obtained for As(V) removal was appropriated ($R^2 = 0.9477$): this means the model explains 94.77% of the response variability.[30] The predicted R^2 (0.7506) is in reasonable agreement with the adjusted R^2 (0.9104), which rules out the presence of outliers. Figure 8, shows the relationship between actual and predicted values, and the relative goodness-of-fit of the model. Besides, adequate precision resulted equal to 13.90, which implies the entire response surface can be navigated. No outliers were observed for a significance level of 0.05 and residuals were scattered randomly around ±4.56 (Fig. 9).

Table 5 presents ANOVA results. The observed *F*-value was 25.38, suggesting that the model was significant, with $P < 0.05$. Therefore, the null hypothesis, which indicates that none of the independent variables (bed height and volumetric flow rate) explains the variation of the dependent variable (% removal of As), was rejected. The nonsignificant lack-of-fit value ($F = 1.14$) showed that the developed model was valid.[31] However, the linear effect of selected factors *h* and *Q* was statistically significant ($P < 0.05$). The bed height showed a stronger influence than the flow rate ($P < 0.0001$ and $T = 8.43$), which also could be deduced from the coefficient factors in Eqn (17). The percentage

Table 5. Estimated regression coefficients (using coded units) of ANOVA for experimental response (%*R*) for As sorption in continuous mode

Term	Coefficients	Standard error	*T*-value	*P*-value
Intercept	63.50	1.18	53.81	<0.0001
X_1	−3.17	1.02	−3.11	0.0169
X_2	7.76	0.92	8.43	<0.0001
X_1X_2	−3.42	1.55	−2.21	0.0437
X_1^2	−5.64	1.07	−5.27	0.0012
X_2^2	−4.87	0.97	−5.02	0.0016

ANOVA

Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	*P*-value
Model	899.46	5	179.89	25.38	0.0002
Residual	49.62	7	7.09		
Lack-of-fit	22.82	3	7.61	1.14	0.4355
Pure Error	26.80	4	6.70		
Cor Total	949.08	12			

Standard deviation	2.66	R^2	0.9477
Mean	57.62	Adj R^2	0.9104
CV (%)	4.62	Pred R^2	0.7506
PRESS	236.74	Adeq Precision	13.897

P <0.05 indicates that the model terms are significant, whereas the values >0.100 are not significant.

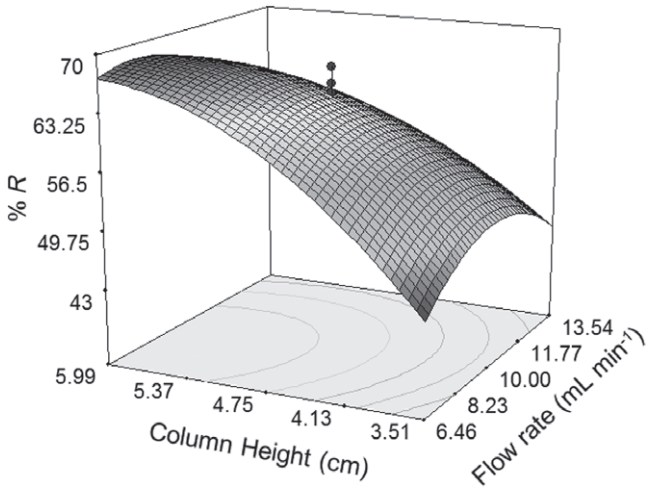


Figure 10. 3D Response Surface plot for % As(V) removal for combined effect of bed height and flow rate.

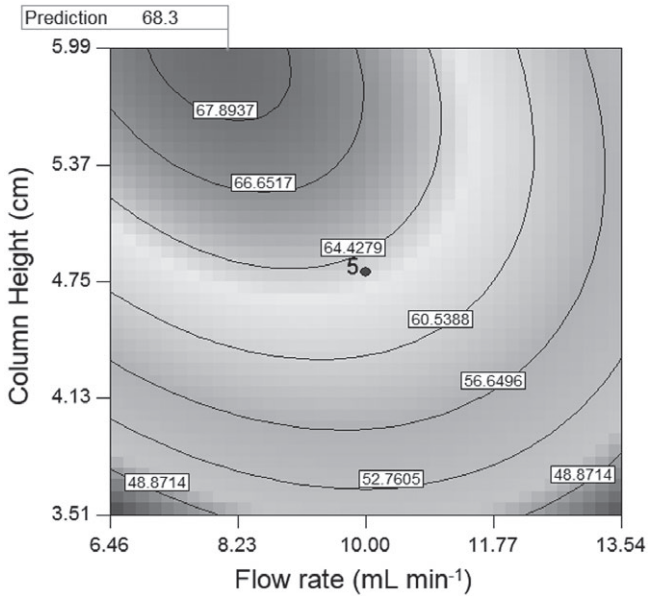


Figure 11. Contour plot of %As removal efficiency representing volumetric flow rate and column bed height.

removal of As increased with a bed height increment in the range studied.

Quadratic effect and two-factor interactions were significant, indicating that there was a curve relationship between factors and response.

Quantitative effects of the factors

The combined effects of flow rate and bed column height on As(V) removal efficiency at constant As(V) concentration (1.0 mg L^{-1}), pH (4.5) and packing density (270 kg m^{-3}), is depicted in 3D view and Contour Response Surface plots. Figure 10 visualizes the clear increase in As(V) removal resulting from increasing the bed height and decreasing the flow rate. In this way, the capability to maximize the arsenic removal applying a continuous sorption process, within the factor levels studied in this work, was clearly demonstrated. The curved contour lines in Fig. 11 show that there was a strong interaction between bed height and flow rate, reflected by the corresponding *P*-value. The optimal conditions for As adsorption from groundwater using chitosan as sorbent were: 5.9 cm bed column height and 7.8 mL min^{-1} volumetric flow-rate, being 68.3% the theoretical maximum As(V) removal. Under these conditions, three independent experiments for As sorption in up-flow fixed-bed column mode were conducted. The experimental value reached (68.5 ± 0.5%) was in agreement with the maximum predicted by the experimental design.

Chitosan at pH 4.5 works like a cation exchanger because its protonated NH_2 groups can interact with arsenate ions; additionally, there could be retention of other anions present in groundwater. The reduction in nitrate and phosphate concentrations, and in conductivity/salinity in the effluent samples after short sorption treatment times were 70%, 50% and 60% respectively, supporting this ionic interaction. At long sorption treatment times, no reduction of these compounds was evident, and therefore it could be assumed that the polymer binding sites are saturated with these ions.

Recovery of As from columns was performed with 0.05 mol L^{-1} H_2SO_4 solution at 0.1 mL min^{-1} flow rate. It was observed that the percentage of As(V) desorption was 92% in agreement with a weakly bonded As(V)/chitosan active sites. The As(V) removal percentage during the second cycle sorption was 88%, indicating no strong changes in the interaction biopolymer/As(V). Therefore, the polymer maintained its structural stability after the first cycle of regeneration.

CONCLUSIONS

This study was focused on: (i) As(V) detection and quantification by means of an optimized, green, cheap and accessible spectrophotometric method with a suitable sensitivity for use in groundwater (a complex matrix); and (ii) optimization of As(V) sorption present in groundwater onto chitosan, a natural, biodegradable biopolymer, in a continuous column mode by the Response Surface Methodology. It was found that As(V) uptake increased with increased bed height, but decreased with the flow rate. It was found that As(V) uptake increased with an increment of the bed height, but decreased with a flow rate increment. These results demonstrate the possibility of employing chitosan as a sorbent for As(V) removal in a continuous process and the usefulness of statistical models. There was an additional finding that (iii) nitrate, phosphate and salinity/conductivity reduced in the effluent under short sorption treatment times. Consequently, the effluent water quality suggests that the treated groundwater could be used not only for household purposes, but also as irrigation water without affecting sensitive agricultural crops.

ACKNOWLEDGEMENTS

We thank the National Research Council of Argentina (CONICET) PIP 0037, National Agency of Scientific and Technological Promotion (ANPCyT) PICT 2016-1611, Santa Fe Province Agency of Science, Technology and Innovation ASACTEI N° AC 2015-0005, N° resol 118-16 project number 2010-174-16 and National University of Rosario (UNR) BIO425 for financial support.

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