Optimisation of arsenate removal from water by an integrated ion-exchange membrane process coupled with Fe co-precipitation

Mafalda Pessoa Lopes, Claudia F. Galinha, João G. Crespo, Svetlozar Velizarov*

LAQV-REQUIMTE, Chemistry Department, FCT, Universidade Nova de Lisboa, 2829-516
Caparica, Portugal

Abstract

The present work investigates the performance of an ion-exchange membrane process for arsenate removal, consisting in integrating Donnan dialytic transport of arsenic with its simultaneous precipitation in a separate receiver compartment. The process performance was improved by adding a bicarbonate-carbonate buffer in the receiver solution, where iron (III) chloride was used to precipitate the arsenic. This system allowed to maintain the treated water pH within the acceptable drinking water range of 6-9, without further control. A Response Surface Methodology (RSM) was used to infer about the effect of the supply water characteristics (initial arsenic concentration and pH) and operating conditions (mass ratio of iron to arsenic) on the degree of arsenic removal. It was found that the initial pH of the receiver solution was also a required input to predict accurately the arsenic concentration in the treated water (for a predefined treatment time). The model developed has a fitting R^2 value of 0.99 and a prediction error of 6.6 µg/L of As. The methodology presented permits to develop a simple decision tool (either through the use of equations or visual plots) to determine the effective amount of iron to be used in the treatment of As contaminated water.

Keywords: Arsenate removal; Drinking water; Donnan dialysis; Response Surface Methodology (RSM); Ion-exchange membrane reactor

1. Introduction

The removal of arsenic (As) from drinking water has been an extremely important research topic during the last few decades [1,2]. Arsenic is one of the most toxic naturally occurring elements present in different locations of the world and its efficient removal from drinking water supplies is still challenging [3,4]. Ravenscroft et al. 2009, reported at least 70 countries worldwide with contaminated waters, affecting more than 140 million people [5]. Countries, such as Bangladesh and India (West Bengal), are the most affected regions, with reports documenting As concentrations ranging between 100-5000 µg/L [6–8].

Despite the World Health Organization (WHO), US Environmental Protection Agency and European Commission actual recommendations for As concentration permissible limit of 10 µg/L (0.01 mg/L) for drinking water [8,9], several countries, like China, Bangladesh, Pakistan, Thailand, Vietnam, Nepal, Ghana and most South American countries, still apply a maximum arsenic permissible limit of 50 μg/L [10,11]. These are countries, in which the As contaminated water problems are more severe, due to higher contamination levels and/or water scarcity.

Various methods have been proposed for As removal from drinking water, such as precipitation and coagulation/flocculation, electrocoagulation, adsorption by iron oxides and activated alumina, ion exchange processes and pressure-driven membrane processes, each of them with specific advantages and disadvantages [12–22].

In this work, an integrated process is studied, schematically represented in Figure 1, using an anion-exchange membrane, for transport of arsenate from contaminated water to a receiver compartment, in which it is precipitated through ferric chloride addition. This integrated ion-exchange membrane / co-precipitation process concept is based on Donnan dialysis principles [23–25]), requiring the presence of so-called “driving” counter-ion(s) in the receiving compartment, with which the target counter-ion(s) in the feed (water) compartment are inter-exchanged via an appropriate membrane transport occurring in opposite directions. If adequate hydrodynamic conditions are provided, minimising possible concentration polarisation effects in the liquid boundary layers on the two sides of the membrane (which were assured in our study) the process is under target counterion (arsenate in the present case) membrane mass transfer control. When entering the receiver compartment, arsenate is co-precipitated through $FeCl_3$, added in excess to this compartment, thus keeping the arsenate concentration difference between the two compartments high (i.e., high process driving force). Co-precipitation of As occurs mainly through adsorption (association of the dissolved contaminant with the surface of the precipitate), but also by occlusion (entrapment of As, in the interior of growing precipitating particles) [26,27]. In the receiver compartment (Figure 1), X^- represents the “driving” counter-ions selected and added (i.e., Cl^- and HCO_3^-/CO_3^{2-}), while Fe^{3+} is used to precipitate As. The surface reactions leading to co-precipitation of arsenate in the present system are the following [26,27]:

$$\equiv \mathrm{Fe}^{w,s}\mathrm{OH} + \mathrm{H}^+ \rightleftharpoons \equiv \mathrm{Fe}^{w,s}\mathrm{OH}_2^+$$

$$\equiv \mathrm{Fe}^{w,s}\mathrm{OH} \rightleftharpoons \equiv \mathrm{Fe}^{w,s}\mathrm{O}^- + \mathrm{H}^+$$

$$\equiv \mathrm{Fe}^{w,s}\mathrm{OH} + \mathrm{AsO}_4^{3-} + 3\mathrm{H}^+ \rightleftharpoons \equiv \mathrm{Fe}^{w,s}\mathrm{H}_2\mathrm{AsO}_4 + \mathrm{H}_2\mathrm{O}$$

$$\equiv \mathrm{Fe}^{w,s}\mathrm{OH} + \mathrm{AsO}_4^{3-} + 2\mathrm{H}^+ \rightleftharpoons \equiv \mathrm{Fe}^{w,s}\mathrm{HAsO}_4^- + \mathrm{H}_2\mathrm{O}$$

$$\equiv \mathrm{Fe}^{w,s}\mathrm{OH} + \mathrm{AsO}_4^{3-} + \mathrm{H}^+ \rightleftharpoons \equiv \mathrm{Fe}^{w,s}\mathrm{AsO}_4^{2-} + \mathrm{H}_2\mathrm{O}$$

$$\equiv \mathrm{Fe}^{w,s}\mathrm{OH} + \mathrm{AsO}_4^{3-} \rightleftharpoons \equiv \mathrm{Fe}^{w,s}\mathrm{OHAsO}_4^{3-}$$

where the superscripts *w* and *s* stand for water and solid, respectively.

The precipitation of arsenate in the receiving compartment facilitates its removal, as a slurry (precipitate with a much lower volume), instead of a liquid stream.

However, while the excess of FeCl_3 in the receiver compartment must be sufficient to guarantee the desired level of arsenate removal (i.e., below the maximum allowed level (MCL) of arsenic in the treated water) depending on local legislations, the Fe dosage should be optimized in order to avoid possible Fe permeation through the membrane (“leakage”) from the receiving compartment to the treated water and its associated acidification below acceptable limits, a problem which was identified in preliminary tests.

Therefore, the objective of this study is to develop and validate a mathematical model using the most relevant process parameters for prediction of arsenic concentration in the treated water.

Four input parameters were considered: the initial As concentration in the water, the water pH, the ratio of Fe/As used in the receiver and the initial pH of the receiver solution. The As removal process performance was investigated in order to optimise the ratio of [Fe]/[As] employed for reducing the As content in the contaminated water below the maximum contaminant level (MCL), imposed by a given country´s legislation.

The model is developed following the Response Surface Methodology (RSM), which is a multivariate regression tool, based on statistical analysis, that allows to find correlations between factors (explanatory variables) and response variables through regression models, optimised for each response studied [28]. To define the experiments required for the development of such regression models, a design of experiments (DoE) is required. Such mathematical methods are applied to reveal the relationships between the factors (*e.g.*, characteristics of the water to be treated and operation parameters of the process) and responses (e.g., performance variables), within specific operating ranges, and thus, allowing process optimisation.

2. Materials and Methods

2.1. Experimental Set-up

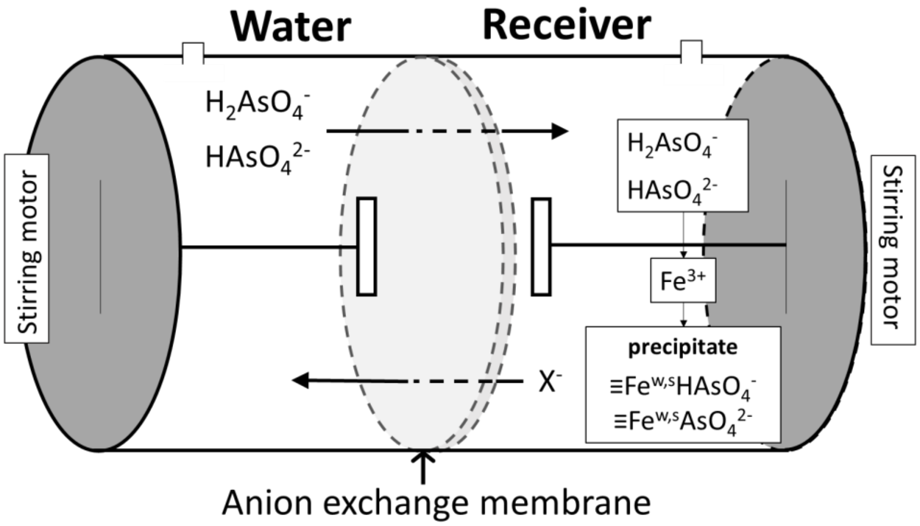

Figure 1. Schematic representation of the Donnan dialysis experiments performed.

The experimental set-up (Figure 1) consisted in two compartments of 136 ml each, one for the receiver solution and the other for the contaminated water separated by an anion-exchange membrane, with a surface area of 11.3 cm^2. Both receiver and water compartments were stirred at 700 rpm to minimise possible concentration polarisation effects. All experiments were performed in batch operation mode at a room temperature of 24ºC. Samples of 2 ml each were taken periodically (pre-defined time intervals ≈ 2 hours) from the water and the receiver solution compartments for measurement of pH, conductivity and subsequent chemical analyses.

The membrane used was an anion-exchange membrane (AEM) Neosepta AXE 01 from ASTOM, Japan. The membrane is made of cross-linked polystyrene, containing quaternary ammonium groups, in a poly(vinyl chloride) reinforcing net, with an electrical resistance of 1.5 Ω cm^2, 26.5% water content, ion exchange capacity between 1.6 and 2 meq per g of dry membrane, and thickness of 0.15 mm, as reported in a previous work [25].

2.2. Reagents and solutions

All solutions were prepared freshly for each assay, using deionised water with electrical conductivity equal or lower than 1 μS/cm, and analytical grade reagents: $Na_2HAsO_4.7H_2O$, $FeCl_3.6H_2O$, Na_2CO_3, $NaHCO_3$, NaOH and HCl. Solutions mimicking arsenate contaminated water were prepared with deionised water and sodium arsenate ($Na_2HAsO_4.7H_2O$) to the desired concentrations. The receiving solutions were prepared with a sodium bicarbonate-carbonate buffer ($NaHCO_3 + Na_2CO_3$) and ferric chloride ($FeCl_3.6H_2O$). The buffer (0.1 M or 0.2 M, depending on the experiments) was prepared for an ambient temperature of 20°C according to the supplier (Sigma – Aldrich, biological buffers [29]) instructions for a pH ~9.2.

2.3. Analytical techniques

ICP (Inductively Coupled Plasma - Atomic Emission Spectrometry) was used to assess the content of As, Fe and Na elements in water and receiver solution samples. All samples were previously filtered using disposable filters (cellulose acetate) with 0.22 µm of pore size. The equipment used was from Horiba Jobin-Yvon, France, Ultima, equipped with a 40.68 MHz RF generator, a Czerny-Tner type monochromator with 1.00 m (sequential) and a Hydride Generator with concomitant metals analyser (CMA) (the detection limit for As was 0.5 µg/L). The pH of the samples was assessed using a pH probe from ORION, Model 720 A.

2.4. Response surface methodology

For the experimental design, three independent factors were considered: the Fe/As ratio (in mass units) to be used, the initial concentration of arsenic in the water and the pH of the water to be treated (designated respectively as [Fe]/[As] ratio, $[As]_{water(i)}$ and $pH_{water(i)}$). A DoE methodology was applied using a central composite face centred (CCF) design with three replicas of the central point. This experimental design allowed to infer about the correlation of the 3 factors, at 3 levels (minimums, maximums and middle values) with 17 experiments. The [Fe]/[As] ratio, pH and As concentrations to be used in each of the 17 experiments accordingly with the DoE are shown in Appendix A - Supporting information (Table S1).

For the response surface methodology (RSM), a multi-linear regression (MLR) model, integrating quadratic and interaction factors, was chosen. The DoE and data analysis were performed using a MODDE 12 software. The statistical parameters (R^2, Q2, Model validity and Reproducibility) associated to model quality were calculated with this software, as described in the User Guide to MODDE [30].

3. Results and Discussion

3.1. Optimisation of the As removal process

In order to maintain the water pH within an acceptable drinking water range (between 6 and 9) [1] during the treatment process, a pH control is required. Although this could be done through the use of precise pH reagents dosing pumps and pH control systems, this increases the monitoring/control requirements, and thus, the complexity of the process. Therefore, an initial experiment was performed using a bicarbonate-carbonate buffer in the receiver compartment (Figure 2). In this experiment, an initial arsenic concentration of 4 mg/L and a [Fe]/[As] mass ratio of 200 were applied (corresponding to 800 mg/L of Fe). The results show that, after 7 hours, the arsenic content in water compartment dropped to 36 µg/L, and after 26 hours of operation the concentration decreased further to 20 µg/L of As, which is below the maximum contaminant level of 50 µg/L, acceptable in most countries, where the As contamination poses a higher concern. Moreover, it is perceptible that arsenic precipitation occurred in the receiver compartment, remaining only 87 µg/L of soluble As-containing species in the receiver solution (Figure 2A). Furthermore, a visual inspection of the membrane showed no deposits at the membrane surface. These results support the working process concept proposed; however, to treat water with a higher initial As content and/or to achieve lower As concentration in the treated water, there may be a need for using a higher [Fe]/[As] ratio.

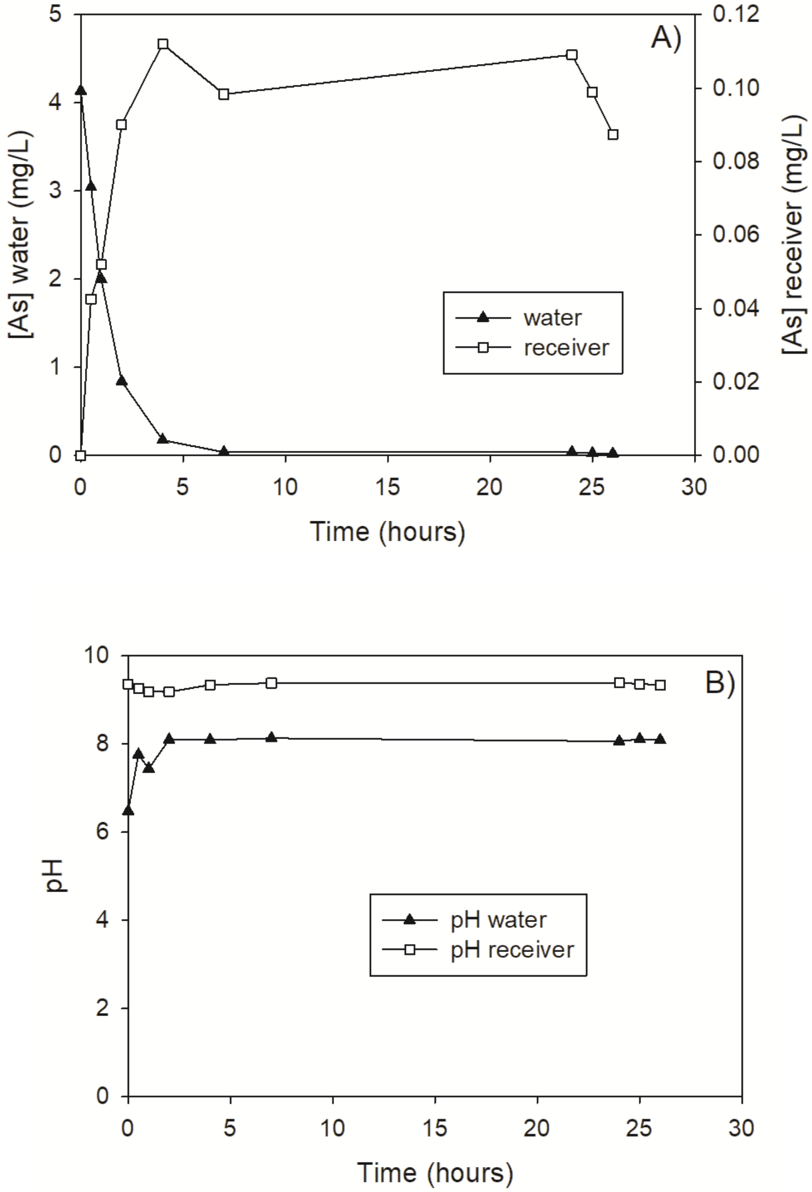

Figure 2. Experimental data obtained: A) Arsenic concentration profiles in the water and receiver solutions and B) pH in the water and receiver solutions, when using the initial conditions [As]= 4 mg/L; pH= 6.48; ratio Fe/As= 200 and 0.1 M of bicarbonate - carbonate buffer in the receiver).

In Figure 2B, it is also noticeable that the use of the buffer in the receiver maintained the water pH within acceptable values for drinking water. It is also noticeable that the water pH tends to approach the pH of the receiver (the pH of the water after 26 hours of operation was 8.09). Therefore, if a higher iron (III) chloride concentration is used, the buffer capacity might not be sufficient. Consequently, all the subsequent experiments performed for optimisation of the [Fe]/[As] ratio were performed with a 0.2 M bicarbonate – carbonate buffer, independently of the amount of Fe used. This buffer concentration was chosen to maintain the water compartment within the pH range acceptable for drinking water, while avoiding excessive consumption of chemicals.

To further optimise the removal process (in terms of the $FeCl_3$ content required for As removal) and study the effect of As concentration and water pH on the process performance, a Response Surface Methodology (RSM) methodology was used. The study was performed for [Fe]/[As] ratios between 100 and 400, and assuming As contamination levels between 0.5 and 5 mg/L, in water with pH varying between 6 and 9. The range of As concentration chosen for this study was based on the high concentrations found in countries such as Bangladesh, India and Thailand [31,32]. The concentration of Fe added to the receiver ranged between 50 mg/L and 2000 mg/L, corresponding respectively to the lowest [Fe]/[As] ratio for the lowest As concentration, and highest [Fe]/[As] ratio for the highest As concentration tested.

The response studied was the concentration of As in the treated water (the variable to be predicted/minimised). However, since the performance of the process under batch operating conditions evolves along time, the As concentration in the treated water was assessed at 4, 6, 8 and 22 hours of operation. Actually, a scenario of 8 hours of operation seems to be a judicious choice when aiming to treat a batch volume of water under real conditions (possibly overnight, for both, practicality and process simplicity reasons).

The 17 experiments resulting from the DoE (Table S1) were applied in practice with slightly different values, mainly due to differences between the amount of As added to water and that measured analytically (the analytical values were used). The [Fe]/[As] ratio was calculated from the amount of Fe added and As measured (as it would be done by an operator of the system in the field). The conditions actually used in the 17 experiments and the As concentration in the water compartment after the 8 hours of treatment, $[As]_{water(8h)}$, (the response) are displayed in Table 1.

Table 1. Experimental operating conditions used in each batch and experimental results of pH in the receiver (at the beginning of the experiment) and arsenic concentration in the treated water after 8h of working process

Experimental conditions				**Parameters assessed**	
Exp. Name	$[As]_{water(i)}$ (mg/L)	$pH_{water(i)}$	[Fe]/[As] ratio	$pH_{receiver(i)}$	$[As]_{water(8h)}$ (mg/L)
N1	0.54	6.00	92.6	8.63	0.007
N2	6.00	6.00	83.3	7.92	0.122
N3	0.60	9.00	83.3	9.01	0.262
N4	6.23	9.10	80.2	8.30	0.063
N5	0.53	6.00	377.3	8.53	0.006

N6	6.12	6.00	326.8	7.24	0.224
N7	0.58	9.05	344.8	8.37	0.007
N8	6.04	9.00	331.1	6.66	0.000
N9	0.46	7.25	271.7	8.70	0.005
N10	5.36	7.25	233.2	7.38	0.061
N11	3.08	6.00	223.2	7.86	0.094
N12	2.58	8.10	266.5	8.05	0.003
N13	3.02	7.25	91.0	8.94	0.000
N14	2.95	7.50	372.9	7.30	0.000
N15	3.13	7.25	219.9	8.07	0.000
N16	2.97	7.25	231.5	8.25	0.000
N17	3.24	7.25	212.2	8.04	0.000

The RSM was applied to this experimental data in order to identify a mathematical model able to correlate the operating conditions (factors) with the performance response after 8h of working process. However, the first model obtained using the three selected factors ($[As]_{water(i)}$; $pH_{water(i)}$ and [Fe]/[As] ratio) fitted poorly the experimental values, even after model optimisation by input selection and by addition of quadratic and interactions terms (best model achieved with a R^2 of 0.6). Therefore, the inclusion of other variables assessed during the experiments (pH, electrical conductivity and iron concentration, in both compartments) was also tested. This approach aimed at adding more information about the process to the model and, thus, achieving better fitting of the experimental data. It was found that, besides the three independent factors initially considered, the initial pH in the receiver (shown in Table 1 – $pH_{receiver(i)}$) shows a strong effect on the process performance and therefore should be also included as a model input. Despite the bicarbonate-carbonate buffer present in the receiver compartment, which was the same in all experiments, when iron is added in high concentrations it causes a decrease of pH in the receiver solution. Therefore, this parameter has to be also considered as a dependent variable, depending on the Fe concentration in the receiver solution.

The best model obtained, after optimisation, included four inputs, the three independent factors and the initial pH in the receiver. The prediction of the response ($[As]_{water(8h)}$) was obtained by considering quadratic and interaction terms, as shown in Equation (1):

$$\mathbf{[As]_{water(8h)}} = 3.419 + 0.1042 \times [As]_{water(i)} - 0.2203 \times pH_{water(i)} + 0.002679 \times [Fe]/[As] - 0.6383 \times pH_{receiver(i)} + 0.003114 \times [As]_{water(i)}^{2} + 0.02361 \times pH_{water(i)}^{2} - 8.90\text{x}10^{-07} \times ([Fe]/[As])^{2} - 0.03409 \times pH_{receiver(i)}^{2} - 0.01878 \times [As]_{water(i)} \times pH_{water(i)} - 0.0003761 \times pH_{water(i)} \times [Fe]/[As] \qquad \mathbf{(1)}$$

The arsenic concentration in the water after 8 hours of process operation can be predicted using the mathematical model defined by Equation (1) and compared with the experimental values obtained and presented in Table 1, $[As]_{water(8h)}$. The plot of the observed *versus* predicted values for $[As]_{water(8h)}$ (Figure 3) shows the agreement between the predicted values and the values measured experimentally.

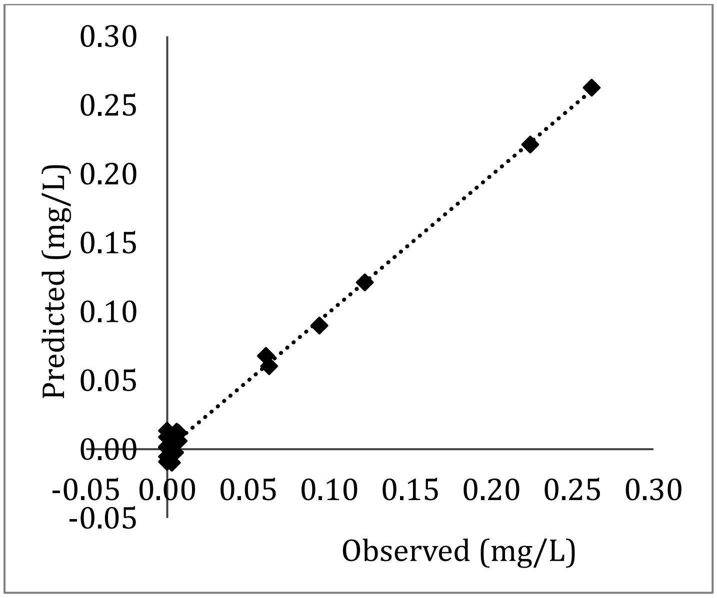

Figure 3. Observed (measured) versus predicted values of As concentration in water after 8 hours of operation.

As it can be seen in Figure 3, the predicted and observed values of As in the treated water (after 8h) are extremely close, indicating a good model fitting and agreement between experimental and predicted values (with a regression coefficient R^2 of 0.993). Additional model statistical parameters (Q2, Model validity and Reproducibility), confirmed the quality of model fitting and validity. By definition, Q2 estimates the future prediction precision and should be greater than 0.1 for a significant model and greater than 0.5 for a good model [30]. The value of Q2 obtained for the present model was 0.926, assuring that a good model prediction was obtained. Regarding model validity, which was 0.62 for the present model, it should be higher than 0.25, to exclude statistically significant problems, such as the presence of outliers, an incorrect model or a transformation problem [30]. Furthermore, when the replicates are almost identical, or in models with Q2>0.9, the model validity can be low even though the model is good. For the present model, despite the high value of Q2, the model validity is considerably higher than 0.25, meaning that the model is statistically valid. Reproducibility, defined as the variation of the replicated compared to overall variability should be greater than 0.5 [30], which was confirmed by its value of 0.998.

Nevertheless, in Figure 3, some dispersion can be seen at values below 10 μg/L, which is the range where the experimental error and detection limit most impact the accuracy of the values (measured and predicted). Indeed, the error of the model (calculated as root mean square error, RMSE) is 6.6 μg/L, which is within the range of the detection limit of As by ICP (5 μg/L). However, since the target values of As concentration in the treated water are near zero, assuming an error similar to the detection limit is acceptable. Furthermore, the model was developed based on experimental data (arsenic concentration in the initial and treated water, pH measurements in water and receiver compartments and amount of iron added to the receiver), which have associated experimental and analytical errors. Actually, arsenic measurements had an average error of 10% calculated for the entire range of As used in this work, resulting both from the intrinsic ICP instrumental precision limits and sampling collection. Therefore, models' accuracy is, in the best case, as good as the accuracy of the experimental data used, meaning that the best prediction error that can be achieved will not be lower than 10%.

3.2. Model Validation

Aiming at validating the model developed and in order to ensure that its predictions are accurate, two case studies where performed: one at high arsenic contamination (5 mg/L), and the other at a medium arsenic contamination (1 mg/L).

After preparing the synthetic contaminated water samples, through addition of Na_2HAsO_4 and pH adjustment, they were analysed in terms of arsenic content by ICP. The arsenic concentration and pH of the two samples are shown in Table 2. To treat these samples, 1312 mg/L and 258 mg/L of Fe were used, respectively for each case study, aiming at maintaining similar [Fe]/[As] ratio in both experiments. However, despite the similar [Fe]/[As] ratios used, the amount of iron in the two receiver solutions is different, thus resulting in different receiver pH values.

Table 2. Conditions of the experiments and model predictions of [As] after 8h of operation

		Case study 1	Case study 2
inputs	[As]water(i) (mg/L)	4.8	1.0
	pHwater(i)	8.1	7.1
	[Fe]/[As] (w/w)	273	258

	(Fe (mg/L))	(1312)	(258)
	$pH_{receiver}(i)$	7.10	8.54
model prediction	$[As]_{water(8h)}$ (mg/L)	0.046	below detection limit (< 0.005)

Table 2 shows, for each case study, the conditions of the validation experiments and the model prediction of the final arsenic concentration in the treated water after 8h of operation (using Equation (1)). According with the model, in case study 1, the As is removed below the limit of 50 µg/L, while in case study 2 the Fe concentration used is optimal for complete removal of As.

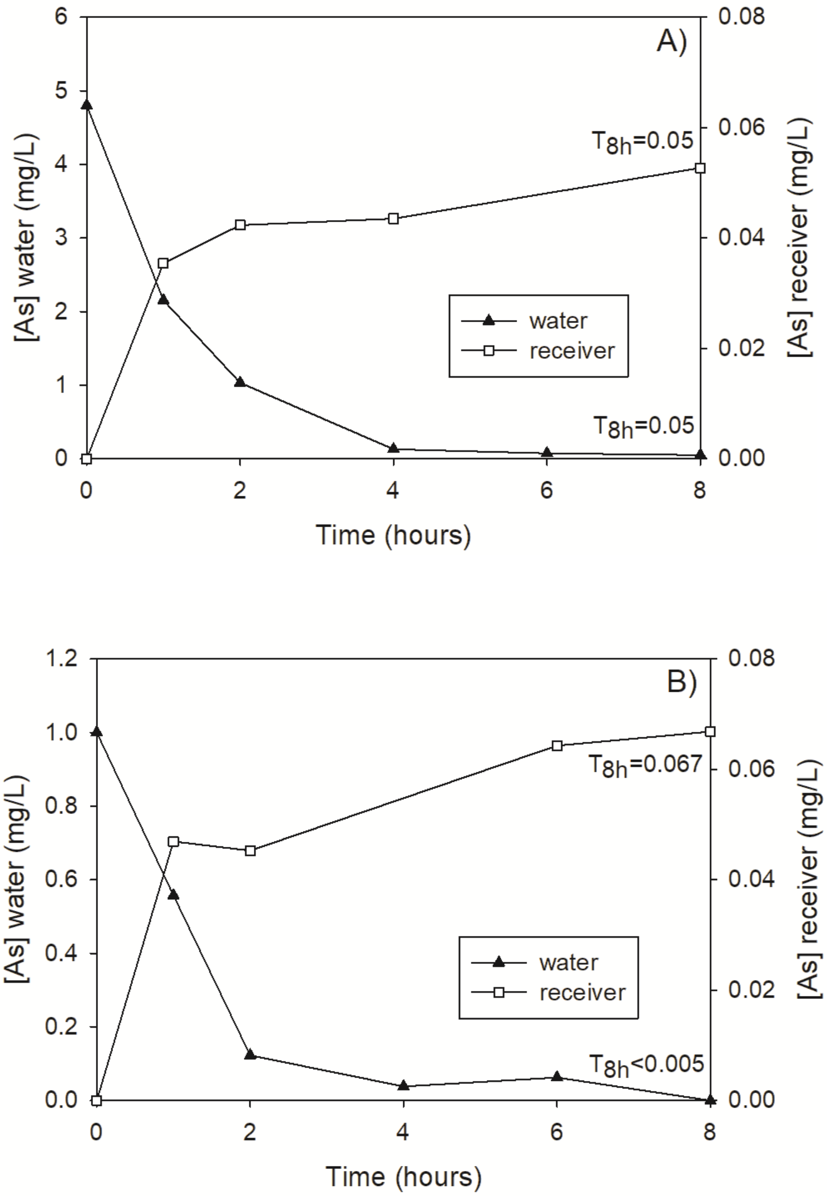

Figure 4. Experimental data of arsenic concentration in water and receiver compartments obtained during 8 hours of water treatment for A) case study 1 and for B) case study 2.

As it can be seen in Figure 4A, in case study 1 the As concentration measured in the treated water was 0.050 mg/L after 8 hours of operation, which is in agreement with the model prediction of 0.046 mg/L (within the ±6.6 µg/L error), with an error below 10%.

The experiment presented a slight iron leakage to the water compartment, <0.021 mg/L during the 8 hours duration of the experiment, which however remained well below its drinking water MCL of 0.5 mg/L. Additionally, the water pH was maintained within the acceptable drinking water pH range (between 7-9), due to the buffer used in the receiver compartment.

In case study 2 (Figure 4B) the As concentration after 4 hours was already below the MCL of 50 µg/L. Furthermore, the actual experimental value was 0 µg/L of As (not detected) after 8 hours. The iron leakage observed during the 8 hours of operation was minimal (below 0.010 mg/L) and the water pH was also maintained within the acceptable drinking water pH range (between 7-8.5).

Overall, these results prove the accuracy of the model and suggest that the approach followed in this work can be successfully used to develop a practical mathematical tool able to be used for deciding the amount of iron required to treat As-contaminated water supplies.

3.3. Mathematical decision tool

To estimate the concentration of iron, in the receiver compartment, required to treat a specific feed water (characterised by pH and As concentration) Equation (1) can be used (*e.g.*, by assuming $[As]_{water(8h)}=0$). However, the pH of the receiver is not known *a priori*, before preparing the receiver solution (it depends on the composition of the receiver solution). Therefore, a linear correlation between the pH and iron present in the receiver was established for the 17 experiments performed with a R^2 of 0.86 (Figure S2).

Therefore, for prediction purposes, the correlation between initial pH of the receiver and the initial iron concentration was used by inclusion of the following equation:

$$pH_{receiver(i)} = -0.000987[Fe] + 8.756 \qquad \textbf{(2)}$$

in which the *[Fe]* is the initial iron concentration in the receiver (calculated from [As] water(i) x ratio [Fe]/[As]) and the $pH_{receiver(i)}$ is the initial pH in the receiver.

A useful equation (for decision purposes) is then achieved through the replacement of the $pH_{receiver(i)}$ by this equation (Equation (2)) in the initial model (Equation (1)):

$$[As]_{water(8h)} = 3.419 + 0.1042 \times [As]_{water(i)} - 0.2203 \times pH_{water(i)} + 0.002679 \times [Fe]/[As] - 0.6383 \times (-0.000987[Fe] + 8.756) + 0.003114 \times [As]_{water(i)}^2 + 0.02361 \times pH_{water(i)}^2 - 8.90\text{x}10^{-07} \times ([Fe]/[As])^2 - 0.03409 \times (-0.000987[Fe] + 8.756)^2 - 0.01878 \times [As]_{water(i)} \times pH_{water(i)} - 0.0003761 \times pH_{water(i)} \times [Fe]/[As] \qquad \textbf{(3)}$$

Using Equation (3), it is possible to estimate the Fe concentration required in the receiver (*e.g.*, using the Solver Function in Excel) in order to reach a defined concentration of As in the treated water ($[As]_{water(8h)}$), based only on the initial concentration of As in the water, $[As]_{water(i)}$, and the water pH, $pH_{water(i)}$. This mathematic decision tool is valid in the range of concentrations tested with the design of experiments.

Equation (3) can be also used to assess visually the effect of water pH and As concentration, and [Fe]/[As] ratio, in the As removal. Therefore, in Figure 5, Equation (3) is plotted as contour plots for different initial As concentrations in contaminated water. The shapes of the contour plots show the extent of the interactions between the input parameters and arsenic removal.

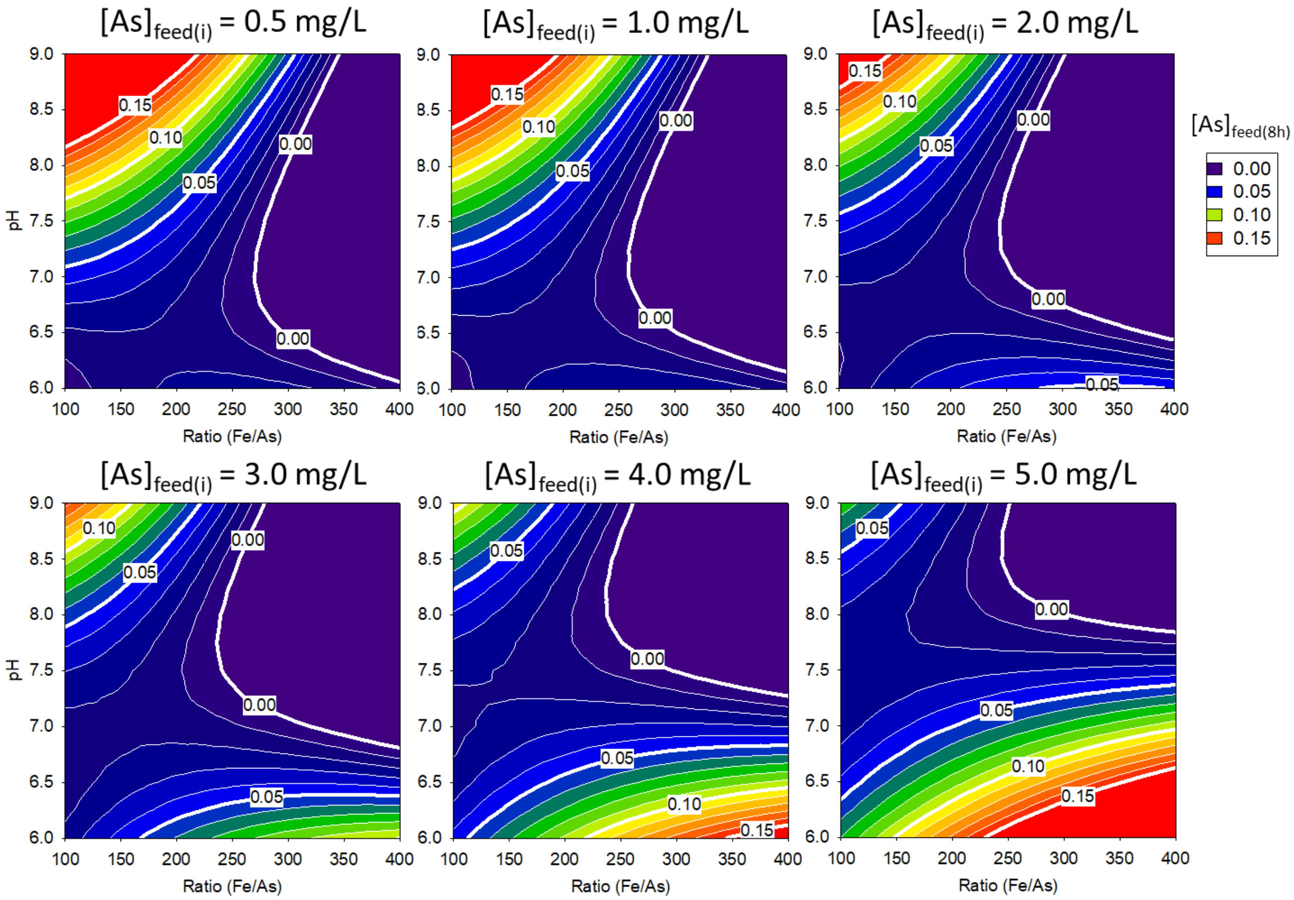

Figure 5. Response contour plots of the Model for different As water contamination levels (in the range 0.5 to 5 mg/L).

The contour plots show the efficiency of As removal, when varying the pH in the water (Y axes) and the [Fe]/[As] ratio (X axes), accordingly with the arsenic concentration in the contaminated water to be treated (indicated in the top of each plot). In case of a relatively low As contamination (0.5 mg/L), it can be noted that, according to the model, a [Fe]/[As] ratio between approx. 350 and 400 can be used successfully for water treatment, independently of the initial pH of water (for the entire pH range in study 6-9). However, to minimise the use of iron (and thus avoid iron leakage to the treated water), a smaller ratio (<300) can be used, when the water pH is between 6.5 and 7.5.

For a high As contamination (5 mg/L) in drinking water, it can be observed that, for acidic water, it is not possible to reach values below the MCL of 10 µg/L, under the operating conditions used. However, it is interesting to note that better results are obtained at the lowest ratio of 100. Furthermore, when analyzing the experiment N6 (Table 2) (Figure S3), where the water used had 6.12 mg/L of As and pH of 6, although the removal of As was not complete after 8 hours of operation, after 22 hours, the concentration of As in the water was below the detection limit (<5 µg/L). This result indicates that the removal of As in these conditions may be slower, but achievable, meaning that the degree of As removal achieved after 8 hours of operation could be increased with the extension of operating time.

Based on the model developed, it can be concluded that for As concentrations between 0.5 and 2 mg/L, it is always possible to have an almost complete removal (near to 0 µg/L) of As. This result is important because reducing the arsenic concentration to values below 10 µg/L has been reported to be highly challenging by using other arsenic removal techniques [1,2].

According with the model obtained, a possible option for an efficient removal of As (within 8 hours), when its initial concentration is very high, can be the addition of an alkali to the water to increase its pH. Although the addition of chemicals to drinking water may sometimes not be feasible and/or desirable, a simple correction of pH can be a possible way to ensure efficient As removal in this system.

From a practical and process engineering perspective, the mathematic tool, either in the form of an equation (Equation (3)) or contour plots, can be used when the operator first knows the actual amount of arsenic and pH of the water to be treated, in order to estimate the amount of Fe required to remove the As present in the drinking water source.

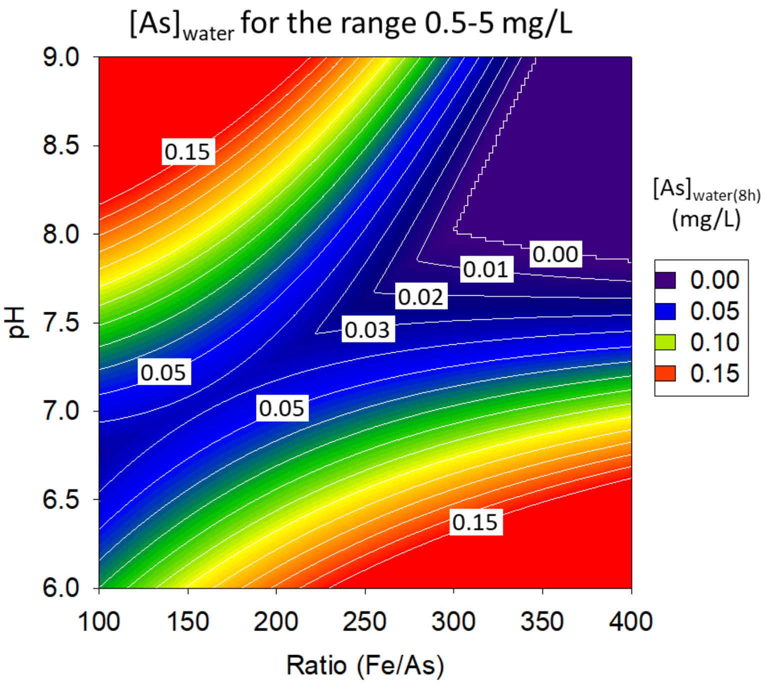

Figure 6. Overlapping (showing the maximums) of the 6 response contour plots from Figure 5.

In Figure 6, showing the overlapping of the contour plots in Figure 5 (maximum of $[As]_{water(8h)}$ for each pair of [Fe]/[As] ratio and pH values), the area where the As concentration is zero corresponds to complete As removal for all the ranges studied (pH, [Fe]/[As] ratio and initial As water content). From the overlapping of the contour plots, it can be concluded that for [Fe]/[As] ratios above 300 and initial water pH in the range 7.5-9, the treatment process will always reduce the arsenic contamination to levels below the MCL of 50 µg/L, independently of the initial arsenic concentration (within the As range studied of 0.5 to 5 mg/L). Furthermore, it can be confirmed visually that As removal below the MCL of 50 µg/L is always possible when the water pH is higher than 6.5, by adjusting the ratio Fe/As.

Despite the increased difficulty to treat acidic water with high As concentration, revealed by the model obtained, it is important to note that the study was limited to a [Fe]/[As] ratio between 100 and 400, and only 8 hours of operation, meaning that other performances may be achieved by changing the [Fe]/[As] ratio and operation time extension.

It is noteworthy that the experimental conditions used to develop this contour plot (8 hours of contact time and a ratio between volume of water treated and membrane area of 120 L/m^2), correspond to 15 L of water treated per square meter of membrane, per hour (L/(m^2.h)), which is a rather competitive value if we consider that no periodical cleaning or regeneration is required, representing a competitive advantage when comparing with some other methods proposed.

3.4. Application considerations

The major cost in membrane processes are due to the cost of membranes and due to the need of their replacement. Therefore, a rough estimation of the price of the membranes per volume of treated water was made. Using the laboratory conditions, aiming at performing two batches of 8h per day and using the system every day of the year, assuming that the cost of membranes can be of 50 euro/m^2 (which is a realistic value) and that they can be used during 5 years before replacement, the price of the membranes will be of 0.11 euro/m^3 of treated water. Although this is only a preliminary estimation based on laboratory data, it is a promising value, taking in account the savings expected in the chemicals (when compared with direct chemical precipitation of arsenate) and the highly improved water quality. Therefore, the cost of ion-exchange membranes, does not seem to limit their application for As removal from drinking water through the proposed process.

For practical use of this process, a special care must be taken when selecting the composition of the receiver. Furthermore, since the receiver solution is kept in a closed compartment and is not drained during the process, it can be reused for consecutive water batches, allowing minimal use of reagents, even when high concentrations of reagents are required. This feature is extremely important because, at first sight, one may think that a high [Fe]/[As] mass ratio involves a high expenditure of chemicals, which is not true at all. Thus, only the amount of reagents that precipitate require replacement.

Regarding the development of the mathematical model, the experimental conditions used during the calibration period (including not only As concentration, but also physicochemical properties and ionic composition of both receiver and water solutions) should be similar to the ones used in place, to avoid extrapolation and ensure optimal prediction.

4. Conclusions

In the present work, an integrated ion-exchange membrane process coupled with a co-precipitation strategy for removal of arsenate from aqueous solutions was mathematically modelled and experimentally validated.

- A mathematical model for the prediction of arsenic concentration in the treated water was developed using four input parameters (the initial As concentration in the water, the pH of the water, ratio of Fe/As used in the receiver and the initial pH of the receiver) with a fitting R^2 value of 0.99 and a prediction error of 6.6 µg/L of As.
- A correlation between the iron concentration and pH in the receiver was developed, which permits to optimise (minimise) the amount of iron to be used based only on the pH and As concentration of the water to be treated.

- Despite the complex mechanisms involved in the process studied, the mathematical methodology developed reveals the complex behaviour (non-linear) of the process performance when key parameters (pH of water and Fe added in the receiver) are changed.
- It was shown the potential of using mathematical data analysis, such as used in RSM, not only to understand the effect of key parameters in process performance, but also as a practical tool to be used in the implementation of the process.
- In model validation experiments, it was found that a [Fe]/[As] mass ratio range between 100 and 400 can be used to optimise the arsenic removal degree, without any significant iron leakage to the treated water.
- The treated water pH was maintained within the recommended drinking water range of 6-9, without necessity of any external pH regulation and/or control.

The use of the proposed mathematical decision tool (after model calibration according to the presented methodology) can highly simplify the decision about the optimal process operating conditions for the specific characteristics of an incoming water, thus enhancing the applicability of the process. This decision is additionally facilitated by the possibility of using contour plots in a simple visual way.

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Appendix A. Supporting Information

Table S1: Design of experiments (DoE) – Central Composite Face (CCF) design matrix.

Exp Name	$[As]_{water(i)}$ (mg/L)	$pH_{water(i)}$	Fe/As ratio
N1	0.50	6.00	100
N2	5.00	6.00	100
N3	0.50	8.50	100
N4	5.00	8.50	100
N5	0.50	6.00	400
N6	5.00	6.00	400
N7	0.50	8.50	400
N8	5.00	8.50	400
N9	0.50	7.25	250
N10	5.00	7.25	250
N11	2.75	6.00	250
N12	2.75	8.50	250
N13	2.75	7.25	100
N14	2.75	7.25	400
N15	2.75	7.25	250
N16	2.75	7.25	250
N17	2.75	7.25	250

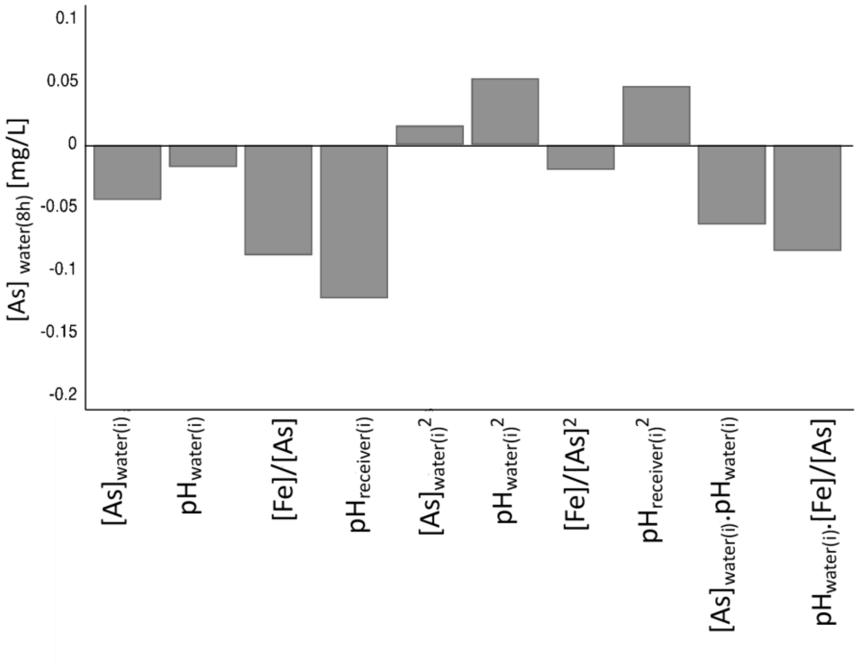

Figure S1. Normalised regression coefficients (scaled and centered) of the model obtained for $[As]_{water(8h)}$ prediction (normalised coefficients allow for comparison between input weights).

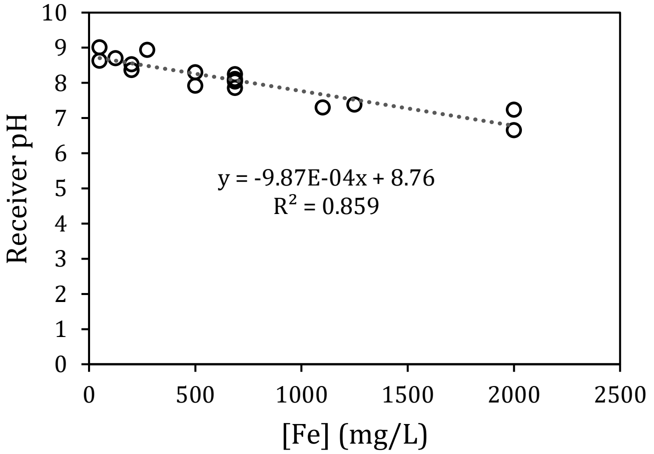

Figure S2. Correlation between initial pH and iron concentration in the receiver.

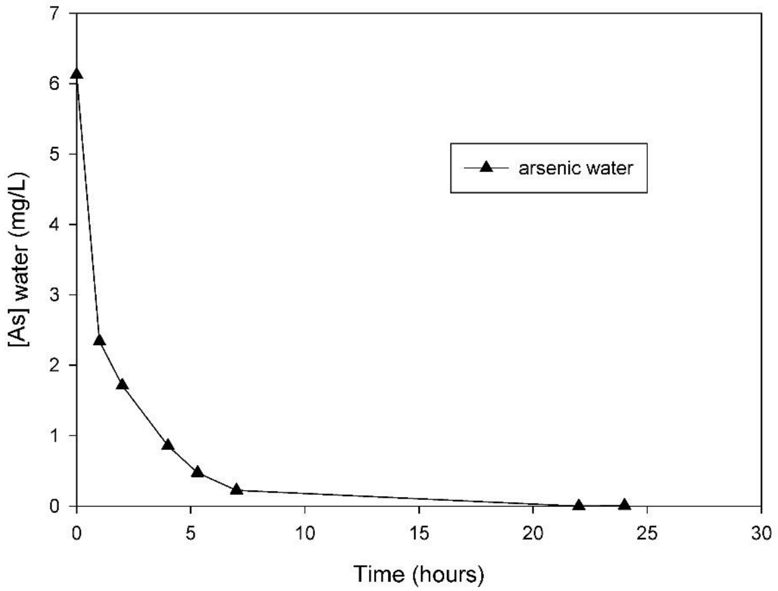

Figure S3. Arsenic concentration profile in the treated water of experiment N6 from the Design of Experiments (with the initial conditions: [As]water(i)=6.12 mg/L; pHwater(i)=6.00 and [Fe]/[As] ratio= 326.8).

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