REMOVAL ARSENIC IN DRINKING WATER BY CAPACITIVE DEIONIZATION

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ABSTRACT

Concentrations of arsenic that reach values of 2.35 mg L-1 have been identified in potable water sources in Mexico. Such concentration is above to the maximum permissible limit of 0.025 mg L-1 set by the Mexican Standard. It has been estimated that nearly 500,000 people living in rural areas are exposed, through their water intake, to concentrations of arsenic in excess of 0.05 mg L-1. The objective of this study was to evaluate the removal of arsenic present in the water for human consumption in the town of Huautla, Morelos, Mexico using electrochemical technology. This technology was developed in Canada and it is based in the principle of capacitive deionization, as an electrostatic charging system formed by carbon electrodes. The electrodes are supplied with direct current (~1V, 0-375A), which produces surfaces with positive and negative charge. The ionic compounds that contain arsenic are thus electrostatically adsorbed onto the electrodes, and the water obtained reached concentrations below 0.005 mg L-1 as total arsenic. The average percentage of arsenic removal was 98.51% and the volume of reject water was 3%. The results of this study indicate that this technology is more efficient and potentially more economical than conventional technologies.

Key words: Potabilization, rain water, multiples filtration

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ABSTRACT

Concentrations of arsenic that reach values of 2.35 mg L-1 have been identified in potable water sources in Mexico. Such concentration is above to the maximum permissible limit of 0.025 mg L-1 set by the Mexican Standard. It has been estimated that nearly 500,000 people living in rural areas are exposed, through their water intake, to concentrations of arsenic in excess of 0.05 mg L-1. The objective of this study was to evaluate the removal of arsenic present in the water for human consumption in the town of Huautla, Morelos, Mexico using electrochemical technology. This technology was developed in Canada and it is based in the principle of capacitive deionization, as an electrostatic charging system formed by carbon electrodes. The electrodes are supplied with direct current (~1V, 0-375A), which produces surfaces with positive and negative charge. The ionic compounds that contain arsenic are thus electrostatically adsorbed onto the electrodes, and the water obtained reached concentrations below 0.005 mg L-1 as total arsenic. The average percentage of arsenic removal was 98.51% and the volume of reject water was 3%. The results of this study indicate that this technology is more efficient and potentially more economical than conventional technologies.

PALABRAS CLAVE

Potabilización, captación de agua de lluvia, filtración en múltiples etapas

INTRODUCTION

Arsenic toxicity is widely known from poisoning cases and medical uses. Recent epidemiological reports of cancer and health problems such as "black foot" and non-cancerous skin diseases associated with arsenic in Taiwan even a concentration of 0.020 mg L^{-1} (Tseng, 1977; EPA, 2001).

The presence of arsenic in groundwater has been found to exceed the international standards in countries like India, Taiwan, United States, Argentina, as well as in Mexico states, Baja California

Sur, Chihuahua, Coahuila, Durango, Guanajuato, Guerrero, Hidalgo, and Morelos, (Armienta *et al*., 1997; Cebrian *et al*., 1994; Cole *et al*., 2004; Rodríguez *et al*., 2004).

Conventional technologies are used to remove more effective As(V) than in removing As(III) like as: coagulation, followed by filtration, Lime softening, activated alumina, ion exchange, adsorption using zeolite (Rivera and Piña, 2000), reverse osmosis, etc. These technologies are effective in removing arsenic from water supplies. However, they present some problems. For example, most of them produce waste sludge contaminated with arsenic, which requires proper disposal. Some are expensive given that they require sophisticated equipment. While others presents difficulties when used in areas with low economical resources.

The objective of this study was to evaluate the removal of arsenic present in the water for human consumption in the town of Huautla, Mexico using electrochemical technology.

The objective of this study vas obtained from de community of Huautla, within tha municipality of Tlaquiltenango in the southern region of the state of Morelos (Figure 1). This community has 1,200 inhabitants and its water sources are the Cruz Pintada dam and the mine shute Pájaro Verde. It has a water distribution network and a storage tank with capacity of 60 m^3 (INEGI, 2000, CEAMA, 2001).

GROUNDWATER SOURCE AREA

The groundwater used for this study was obtained from the community of Huautla, within the municipality of Tlalquiltenango in the southern region of the state of Morelos (Figure 2). This community has 1,200 inhabitants and its water sources are the Cruz Pintada dam and the mine shute Pajaro Verde. It has a water distribution network and a storage tank with a capacity of 60 m^3 (INEGI, 2000, CEAMA, 2001).
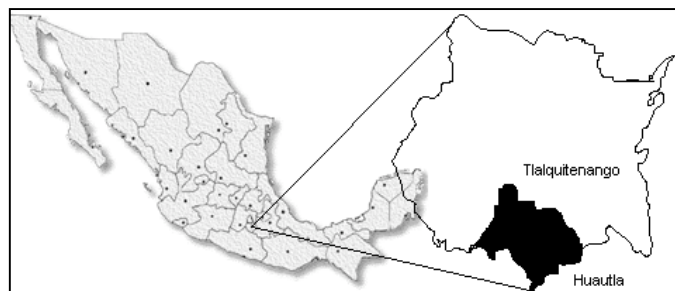

Figure 1. Location map of Morelos State, study case.

METHODOLOGY

Water quality at the source

A disinfected water sample was obtained directly from the Pajaro Verde mine shute and its physico-chemical characteristics were analyzed according to Mexican Standards and Standards Methods (1998). Total arsenic and soluble arsenic were determined using an atomic absorption spectrophotometer (AAS) Perkin Elmer Model 2380, equipped with a hydride generator Perkin Elmer Model MHF-10.

Treatability tests

The treatability tests were performed using a capacitive deionization plant Model DesEL-4k (Figure 2) at the Potable Water Systems laboratory of Instituto Mexicano de Tecnología del Agua (IMTA). This plant has a nominal treatment capacity of 3.3 L min^{-1} for an initial TDS concentration of 1000 mg L-1, it operates at a pressure of 1.0 kg cm^{-2}, and its electrical supply is rated for 127 Vac, single phase, 15 A, 50/60 Hz. The two capacitive deionization cells of this plant are connected electrically in series and hydraulically in parallel. Each cell is supplied with a peak voltage of 1.2 Vdc and a

maximum peak current of 375 A. The energy consumption of the DesEL plant was measured during the course of some experiments using a watthour meter Soar Model 2700.

Design of experiments

The experimental design involved 3 different configurations of the DesEL process, in which all parameters were kept constant except for the adsorption time (Table 1). In addition, raw waters with three different concentrations of As and Pb were used at the process inlet. The experiments No.1 to 3, and 8 to 10 were performed with the raw water sample exactly as taken from the storage tank located in Huautla (Table 2). The same water was spiked with salts of As and Pb for all other experiments. Experiment No. 4 involved water with an As concentration of 0.8201 mg L^{-1}, while experiments No. 5 to 7 involved water with concentrations of As and Pb of 0.8201 mg L^{-1} and 0.0267 mg L^{-1}, respectively.

Figure 2. Front view (left) and rear view (right) of DesEL-4k plant showing pure and reject water outlets, deionization cells, and solenoid valves.

The salts used to spike the raw water samples were sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), J.T. Baker and lead chloride ($PbCl_2$), CTR Scientific.

Table 1. DesEL process configurations used in experiments.

Parameter	Units	DesEL configuration		
		A	B	C
Adsorption time	s	300	360	480
Desorption time	s	120	120	120
Purge time	s	20	20	20
Pure water upper EC limit	mS cm^{-1}	0.15	0.15	0.15
Reject water lower EC limit	mS cm^{-1}	3.00	3.00	3.00

To distinguish between the energy consumed by the various parts of the DesEL process, incremental energy consumption measurements were performed with configuration C. In this way the energy consumed for controls, pump, and adsorption and desorption processes were determined during a particular experiments.

RESULTS and DISCUSSION

Water quality

The average water quality results of the raw water sample taken from the Pajaro Verde mine shute and the samples of water treated with capacitive deionization are shown in Table 2. The working temperature of these measurements varied between 20.1 and 23.3 ºC.

Table 2. Average characteristics of the raw water and the water treated with capacitive deionization.

Parameter	Raw water from Pajaro Verde mine shute	Water treated with capacitive deionization	Permissible limits (NOM 127-SSA1-1994)
Physical			
True Color, UPt-Co	10	-	20
EC, μS cm^{-1}	492	25.21	-
Total suspended solids, mg L^{-1}	0.13	-	-
Total dissolved solids, mg L^{-1}	339.4	-	1000
Turbidity, UTN	0.1	0.02	5
Chemical			
pH	7.79	7.3	6.5 - 8.5
Arsenic $_{Total}$, mg L^{-1}	0.2098	< 0.005	0.025
Arsénico $_{Dissolved}$, mg L^{-1}	0.2005	0.0048	
Lead, mg L^{-1}	0.0267	< 0.01	0.01
Residual chlorine, mg L^{-1}	0.56	0.02	0.2 - 1.5
Total organic carbon, mg L^{-1}	2.99	-	-
Hardness$_{Total}$, mg L^{-1}	164	49.89	500

The raw water from Pajaro Verde meets all the physico-chemical parameters and metal concentration limits of the Mexican Standard, NOM-127-SSA1-1994, except for total arsenic, which is 8 times higher than the permissible limit. In Table 2 it may be seen that 95.57% of the total arsenic is in soluble form.

The removal of arsenic from water using conventional technologies depends on its oxidation state, being As(V) removal more effective than As(III) removal. Arsenic can be pre-oxidized using oxidizers like chlorine, ferric chloride and permanganate. However, pre-oxidation with chlorine can generate undesirable chlorinated organic by-products in the presence of dissolved organic matter. Therefore, it is preferable to use ozone or hydrogen peroxide (EPA, 1998).

Treatability tests

The treatability results of each experiment are presented in Table 3. The process configuration during the experiments No. 9 and 10 was changed after a few cycles to reach earlier a steady state of the bulk EC value of the treated water.

As result of CO_2 solvation into the demineralized water, the pH of the treated water decreased by approximately 2 units with respect to the pH of 7.79 observed in the raw water. Aeration of the treated water increased the pH value back to 7.3. On average, the treated water showed reductions in EC of 94.88% and in hardness of 69.58%.

The change in total As concentration in the raw water from 0.2098 mg L^{-1} to 0.8201 mg L^{-1} through the addition of sodium arsenate as described in the methodology did not have a major impact on the As removal efficiencies of the respective experiments, which were 97.62% and 99.39%. In all the experiments, the total As concentration in the treated water resulted in less than 0.005 mg L^{-1}, which is at least 5 times lower than the maximum permissible limit defined by NOM-127-SSA1-1994 and at most equal to the Maximum Contaminant Level (MCL) proposed by EPA, 2001. The detection limit of the atomic absorption method used in the analysis of arsenic is 0.005 mg L^{-1}, which is appropriate considering the maximum permissible limit of 0.025 mg L^{-1} set by Mexican Standard. Moreover, the final concentration of As in the treated water produced from the various experiments did not exhibit any correlation with the various durations of the ion adsorption stage of the process.

This would be expected given that the concentration of arsenic in the raw water was very low with respect to the concentration of TDS, which has a strong correlation too with the EC value used to control the process. Therefore, the removal efficiency of arsenic with the DesEL process is expected

to remain high regardless of the duration of the ion adsorption stage for As and TDS concentrations typically found in groundwater.

The adsorption rate of total As during the experiments No. 4 to 7 can be estimated as follows:

As adsorption rate = Inlet - Oulet
As adsorption rate = C_i Q – C_0 Q
As adsorption rate = Q (C_i – C_0)
As adsorption rate = 4.375 L min^{-1} (0.8201 – 0.005) mg L^{-1}
As adsorption rate = 3.57 mg min^{-1}

Tabla 3. Summary of treatability results

Exp. No.	Config.	Raw water		Treated water					
		As$_{Total}$ mg L^{-1}	Pb mg L^{-1}	Volume L	pH	EC µS cm^{-1}	Hardness$_{Total}$ mg L^{-1}	As$_{Total}$ mg L^{-1}	Pb mg L^{-1}
1	A	0.2098	-	26.0	6.01	38.7	74	<0.005	-
2	B	0.2098	-	26.9	5.74	20.4	38	<0.005	-
3	C	0.2098	-	33.3	5.76	25.3	-	<0.005	-
4	C	0.8201	-	34.9	5.71	20.8	44	<0.005	-
5	C	0.8201	0.0267	35.0	5.46	17.4	59	<0.005	<0.01
6	C	0.8201	0.0267	35.0	5.55	12.5	54	<0.005	<0.01
7	C	0.8201	0.0267	35.0	5.75	18.7	54	<0.005	<0.01
8	C	0.2098	-	35.0	5.75	30.5	54		-
9	C: 6 cycles, A: 12 cycles	0.2098	-	415	6.14	33.1	27	<0.005	-
10	A: 4 cycles, B: 16 cycles	0.2098	-	412	6.33	34.7	45	<0.005	-

The reject water from the various experiments presented total As concentrations that varied between 1.786 and 7.031 mg L^{-1} (Table 4). Moreover, the As adsorption rate was calculated for each experiment and multiplied by the respective adsorption times per cycle. The result is an estimate of the total milligrams of As adsorbed per cycle which, as illustrated in Figure 4, correlates (R^2 = 0.9877) to the concentrations of As found in the reject waters. Such correlation appears to indicate that the As ions are adsorbed onto the electrodes only for as long as the electrical field promotes ionic adsorption and that they are not otherwise stored in the system.

An appropriate method for dispoising the As contained in the reject water will be subject of a future study.

Tabla 4. Summary of reject water results

Exp. No.	Volume %	pH	EC µS cm^{-1}	Arsenic $_{Total}$ mg L^{-1}	Pb mg L^{-1}
1	3.3	7.48	7310	1.80	-
2	3.4	7.53	7890	1.80	-
3	3.1	7.49	9320	2.77	-
4	2.9	7.55	9040	-	-
6	2.3	7.49	7850	7.03	-
7	2.9	7.96	7960	6.01	<0.01
8	2.9	7.09	8110	-	-
9	4.8	7.24	5600	-	-
10	4.1	7.39	5220	1.95	-
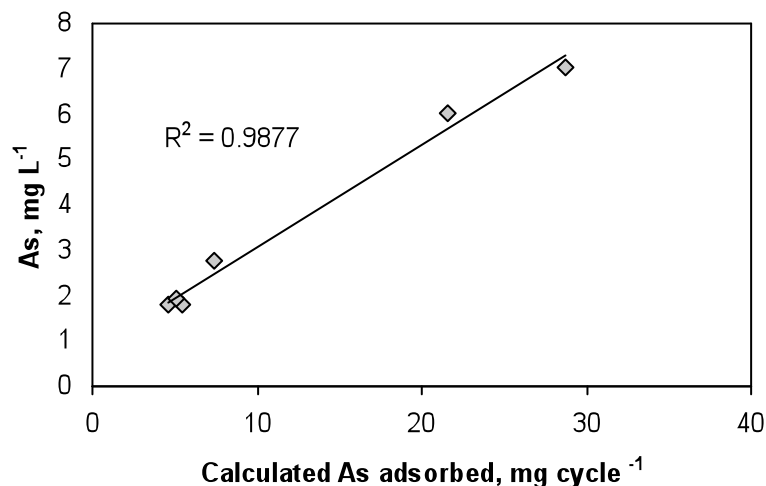
Figure 4. Concentration of As in reject water vs. calculated As adsorbed per cycle.

With respect to the final Pb concentrations in the treated water of experiments No. 5, 6 and 7, they all were below 0.010 mg L^{-1}, which meets the maximum permissible limit of NOM-127-SSA1-1994.

As result of CO_2 solvation into the demineralized water, the pH of the treated water decreased by approximately 2 units with respect to the pH of 7.79 observed in the raw water. Aeration of the treated water increased the pH value back to 7.3. On average, the treated water showed reductions in EC of 94.88%, in total dissolved solids of 95.05% and in hardness of 69.58%.

The change in total As concentration in the raw water from 0.2098 mg L^{-1} to 0.8201 mg L^{-1} through the addition of sodium arsenate as described in the methodology did not have a major impact on the As removal efficiencies of the respective experiments, which were 97.62% and 99.39%. In all the experiments, the total As concentration in the treated water resulted in less than 0.005 mg L^{-1}, which is at least 5 times lower than the maximum permissible limit defined by NOM-127-SSA1-1994.

The reject water volume from the various experiments was 3.0% of the total volume treated, and presented total As concentrations that varied between 1.786 and 7.031 mg L-1 and 3.0% r An appropriate method for disposing of the As contained in the reject water will be subject of a future study.
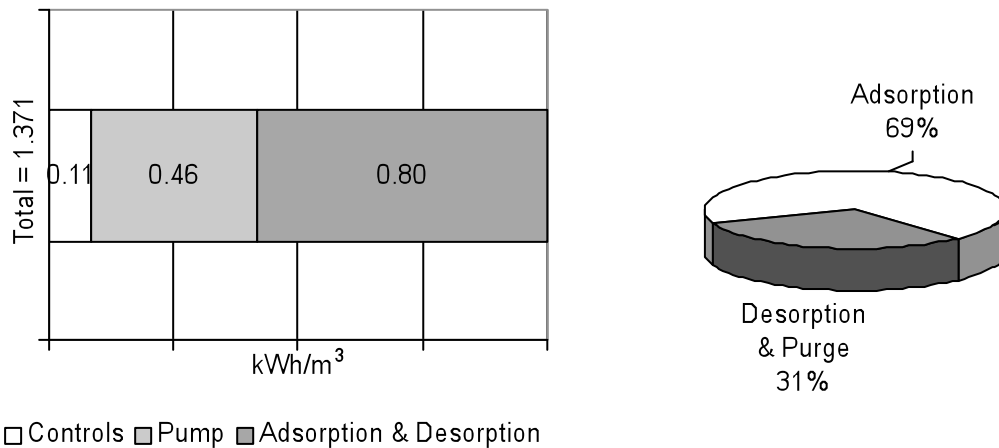

Energy consumption

The specific energy consumption of the DesEL-4k plant was determined for experiments No. 6, 9 and 10. For each of these experiments, the average adsorption time was different, while the average desorption time was kept equal. As indicated by Figure 5, a correlation exists ($R^2 = 0.9711$) between the specific energy consumption and the ratio of desorption time to adsorption time. The values of specific energy consumption ranged from 1.371 to 1.67 kWh m^{-3}, the lowest being for experiment No. 6, which had the longest adsorption time. Thus, each particular application of a DesEL plant requires finding optimum configuration values to attain a better economy for the process.

The specific energy consumption of 1.371 kWh m^{-3} observed during experiment No. 6, was broken down into the energy consumed by the controls, the pump and the adsorption and desorption parts of the process. As presented in Figure 6a, the energy consumed by the controls and the pump is significant for the plant DesEL-4k, adding up to 0.57 kWh m^{-3}. Typically, this amount is less significant in larger DesEL plants given that more water is treated with the same controls and with more efficient pumping. The specific energy dedicated by the DesEL-4k plant to the adsorption and desorption parts of the process was 0.8 kWh m^{-3}, approximating the overall specific energy consumed by bigger DesEL plants.
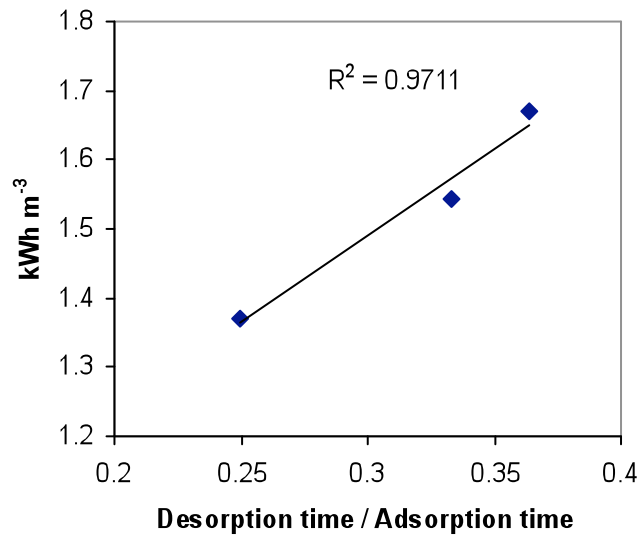
Figure 5. Specific energy consumption of plant DesEL-4k expressed in kWh per volume of treated water vs. the ratio of desorption time over adsorption time.

a)   b)

Figure 6. 6a) Specific energy consumption breakdown of controls, pump, and the adsorption & desorption parts of the capacitive deionization process using a DesEL-4k plant. 6b) Percentage energy consumed during the desorption and purge stages compared to the adsorption stage. Both charts correspond to configuration C (Table 1).

CONCLUSIONS

The arsenic removal capability of the DesEL-4k plant proved to be sufficient in all the experiments, resulting in treated water with a total As concentration at least 5 times below the maximum permissible limit defined by NOM-127-SSA1-1994 and at least 2 times below the Maximum Contaminant Level (MCL) proposed by EPA.

The efficiency of As removal can be expected to be unaffected by changes in the duration of the ion adsorption stage for concentrations of As that occur naturally in groundwaters.

Arsenic does not remain in the capacitive deionization cells, as indicated by the correlation between the concentration of As in the reject water and the calculated amount of As adsorbed onto the electrodes per cycle.

The Pb removal capability of the DesEL-4k was sufficient to meet the Mexican Standard NOM-127-SSA1-1994.

The low values of specific energy consumption obtained are an attractive feature of the DesEL system considering that energy represents the sole input of the DesEL system. Along with very low maintenance requirements, low operational costs and free of chemical additives, the DesEL system appears to offer a manageable and, potentially, economically viable technology for the removal or arsenic from groundwater, in comparison to the another techniques like as reverse osmosis, electrodialysis reversal, nanofiltration,, coagulation/flocculation, activated alumina.

The operating and maintenance cost is U$ 0.087 m^{-3} for drinking water.

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