

Arsenic removal from drinking water using Reverse Osmosis

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Abstract

Arsenic is an element that naturally occurs in rocks and sediments. In some areas, arsenic is released to ground water and can contaminate drinking water sources. Since arsenic is toxic in high doses and a carcinogen, the World Health Organisation (WHO) recommends arsenic levels lower than 10 µg/L in drinking water.

This thesis describes the removal of arsenic in a reverse osmosis system. Arsenic is usually present in water in two oxidation states, as arsenite (As(III)) or arsenate (As(V)). Arsenate is usually easier to remove than arsenite, and the experiments have emphasized the removal of arsenite in double filtration process and compared to the removal of arsenate.

Previous studies at UMB have found reverse osmosis as an efficient way to remove arsenite when the water is filtrated twice .

The treatment from arsenates gave a removal efficiency of 97-99 % after one filtration and it is evident that removal of As(V) is close to 100 % efficient.

The removal of arsenite in the first filtration was in the range 55 - 65 % and in the second filtration between 40 % and 55 %. The total arsenic removal after two filtrations was found to be between 75-92 %.

For test water consisting both with arsenite and arsenate, the RO system gave a total arsenite removal between 81 - 92 %.

One of the theories for the removal efficiency of As(III) through double filtration RO was oxidation. Tests of the reject water were tested and showed oxidation rates 0 - 38 % in the first filtration and between 0 - 35 % in the second. Many samples had zero content of pentavalent arsenic, so generally difficult to judge by what principle arsenic is oxidized in the system.

Keywords: Arsenic, reverse osmosis, water treatment, removal rate, oxidation, double filtration.

Background

Elemental arsenic and arsenic compounds are classified as "toxic" and "dangerous for the environment" in the European Union under directive 67/548/EEC. The International Agency for Research on Cancer (IARC) recognizes arsenic and arsenic compounds as group 1 carcinogens. Arsenic is known to cause arsenicosis owing to its manifestation in drinking water, "the most common species being arsenate [HAsO_2^- ; As(V)] and arsenite [H_3AsO_3 ; As(III)]". Trace amounts of arsenic are often found in the groundwater, open fresh water sources, seas and oceans.

Chemists have found that arsenic in natural waters can be in various forms, which is important in choosing analysis, methods of migration, as well as varying toxicity of these compounds. Trivalent arsenic is in 25-60 times more toxic than pentavalent. Compounds of As (III) in water are normally present in the form of arsenous acid H_3AsO_3 , which is weak ($\text{pK}_a = 9.22$), and compound As (V) are present in the form of significantly stronger arsenic acid H_3AsO_4 ($\text{pK}_a = 2.20$) and its anions H_2AsO_4^- and HAsO_4^{2-} .

World Health Organization and the world community paid attention to the problem of pollution the drinking water by arsenic in 2006, reducing the maximum permissible concentration of 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$. Before the adoption of this decision there were serious researches in various regions of the planet, as well as drinking water crisis in South Asian countries (Bangladesh, etc.), which led to several fatal.

Today the problem of purifying water from arsenic to the norms of the new standard rather acute for developed countries, as well as for Africans countries and South Asia. Not many municipal treatment plant today can solve this task. In developed countries, people have an active interest in the quality of drinking water and, if necessary, use special filters and pets, removing arsenic compounds. In developing countries (Bangladesh, Nepal, Taiwan, Burkina Faso, etc.) The World Health Organization conducts installation of special treatment systems for municipal wells.

It should be noted that the materials traditionally used in water filters and filtering systems are not able to remove arsenic from drinking water. In the world today, there are several commercially available special sorbents, as well as there are studies and searches constantly working to develop new, cheaper materials.

Analytical Methods for Determining Arsenic

Plasmic Spectrometric Methods

The plasmic spectrometric methods are based on the emission of electromagnetic radiation by elements excited e.g. in high temperature. Each element emits radiation of characteristic wavelengths (allowing qualitative analysis) and intensity proportional (at a given temperature) to the concentration of this element (allowing quantitative analysis). Emission of radiation by an atom of a given element is related to changes in the energy states of electrons from the outer electronic shell. An appropriately high quantum of energy (thermal, electric) provided to the atom makes one or more electrons jump to a higher energy level, causing the atom's excitation. The higher the energy of excitation, the greater the richness of the electronic transitions and the complexity of the emission spectrum.

Using mass spectroscopy (MS) the detection limit was 0.08 $\mu\text{g/L}$, after hydride generation and reduction. The determinations with hydride generation can be performed in the continuous flow of the analyte and in the batch system, getting comparable results at the detection limit of 4 $\mu\text{g/L}$, or with injection supply of the analyte (FIA). Introduction of the analyte and hydride generation can be used irrespective of the method of detection: AES, or MS. Mass spectrometry ensures the detection limit of 0.006 $\mu\text{g/L}$ without preliminary concentration of the analyte.

The Standard Methods recommend Hydride Generation Atomic Adsorption Spectrometry (HGAAS), the spectrophotometric method with silver diethyldithiocarbamate and Inductively Coupled Plasma method (ICP) for determination of arsenic, and the ways of sample preparation for analyzes.

Experimental Design

All experiments were done in IMT (Mathematical science and technology) and IPM (Plant science) department laboratories, Norwegian University of Life Science (NMBU). Reverse osmosis system installed by Malthe Winje Company, Norway. Water samples were tested at the laboratory at IPM using inductively coupled plasma mass spectrometry (ICP-MS).

Materials and methods

The arsenic solutions used were mixed at IPM laboratory to a concentration of 4 g/L. Arsenic(V) sample was prepared by $\text{Na}_2\text{HAsO}_4 \times 7\text{H}_2\text{O}$ (Sodium Hydrogen arsenat hepta hydrate, 98%) Case number is 10048-95-0, formula weight – 310 g/mole. Arsenic (III) sample was prepared by Na_2AsO_2 (Sodium arsenite solution contain Arsenic trioxide, 100%) (VWR international, Germany).

Arsenic (III) and Arsenic (V) were mixed with tap water and prepare arsenic contaminated water with different concentrations. The pH was adjusted by Nitric acid (HNO_3) and Sodium hydroxide (NaOH).

The analysis in a mass spectrometer can give us the concentrations of total arsenic, as well as separated concentrations of As (III) and As (V). But separated analyzes are much more expensive. So for separation As (III) and As (V) was used ion exchange method. A samples (300-500 ml) passed through an ion exchange (IE) resin, As (V) was adsorbed on resin, and As (III) remained in the water. Samples were taken and analyzed before and after the IE, so we had concentrations of total As and As (III), the difference between them – As (V).

The ion exchange resin used was Dowex 21K XLT Resin from Dow, a high efficiency, uniform particle size, strong base anion exchange resin. The matrix is of styrene-DVB gel and charged with chloride (Dow n.d.-a).

The RO-unit was used to test the removal of As(V), As(III) and a combination of As(III) and As(V).

Arsenic (III) and Arsenic (V) sample prepared separately for each experiment, total experiment was divided into three steps. In first step experiment was design for As (V), As (III) and mixture As (V) with As (III). In this experiment 500 liters arsenic contaminated water was prepared with different concentration levels of Arsenic: from $50\mu\text{g/L}$ to $200\mu\text{g/L}$, without pH correction. The flow rate in system was applied 100 L/h.

Results

Firstly was made a little check of IE separation to get sure that it works as we expect. As (V) has to be adsorbed by IE resin and As (III) should pass through it.

Table 1 Check of IE separation

Exp. №	As (III), $\mu\text{g/L}$	As (V), $\mu\text{g/L}$	Inlet (As (Tot)), $\mu\text{g/L}$	Outlet (As (III)), $\mu\text{g/L}$
1	50	0	53.0	0.6
2	0	50	51.0	49.0
3	50	50	110.0	44.0

This check shows that this method is effective for separation As (III) and As (V). The error is less than 5 %.

In this work I performed three sets of experiments for arsenic removal from drinking water. First step experiment was for As (V), As (III) and mixture As (V) + As (III). The removal efficiency of double filtration process is shown in Table 2.

The removal efficiency of As (V) is very high. It's absolutely enough one step filtration to remove almost 100 %. So efficiency of this process was proved and in farther research we don't explore As (V) removal.

Table 2 First step of research. The removal efficiency of double filtration process.

Exp. №	As (III), $\mu\text{g/L}$	As (V), $\mu\text{g/L}$	Inlet			1 filtration		2 filtration			Removal rate As (Tot), %
			As (III), $\mu\text{g/L}$	As (V), $\mu\text{g/L}$	As (Tot)	Removal rate As (III), %	Removal rate As (V), %	As (Tot)	Removal rate As (III), %	Removal rate As (V), %	
1	50	-	49	7	19	61.22	-	8.6	54.74	-	84.64
2	100	-	110	-	39	64.55	-	18	53.85	-	83.64
3	150	-	170	-	77	54.71	-	43	44.16	-	74.71
4	200	-	230	-	97	57.83	-	59	39.18	-	74.35
5	-	50	0.3	45.7	1.2	-	97.37	0.6	-	51.67	98.74
6	-	100	2.9	107.1	1.3	-	98.79	0.7	-	48.46	99.39
7	-	150	-	170	1.2	-	99.29	0.4	-	68.33	99.78
8	-	200	-	230	1.4	-	99.39	0.4	-	69.29	99.81
9	25	75	24	86	9.4	65.42	98.72	8.3	32.52	76.67	92.45
10	50	50	45	55	20	64.44	92.73	9.8	45.00	80.44	90.20
11	75	25	85	45	36	62.35	91.11	14	62.50	85.88	89.23
12	50	100	43	127	27	41.86	98.43	24	28.00	58.14	85.88
13	100	50	84	76	52	44.05	93.42	30	36.17	64.29	81.25
14	100	100	84	126	81	8.33	96.83	29	68.83	71.43	86.19

The As (III) removal is less effective than As (V). At first filtration removal rates varied between 50-65 %, and at second filtration – 40-55 %. Total removal rates after 2 filtrations are 75-85 %. This are not enough for higher initial concentrations to reach requirements.

Figure 1 shows efficiency of each step of filtration process.

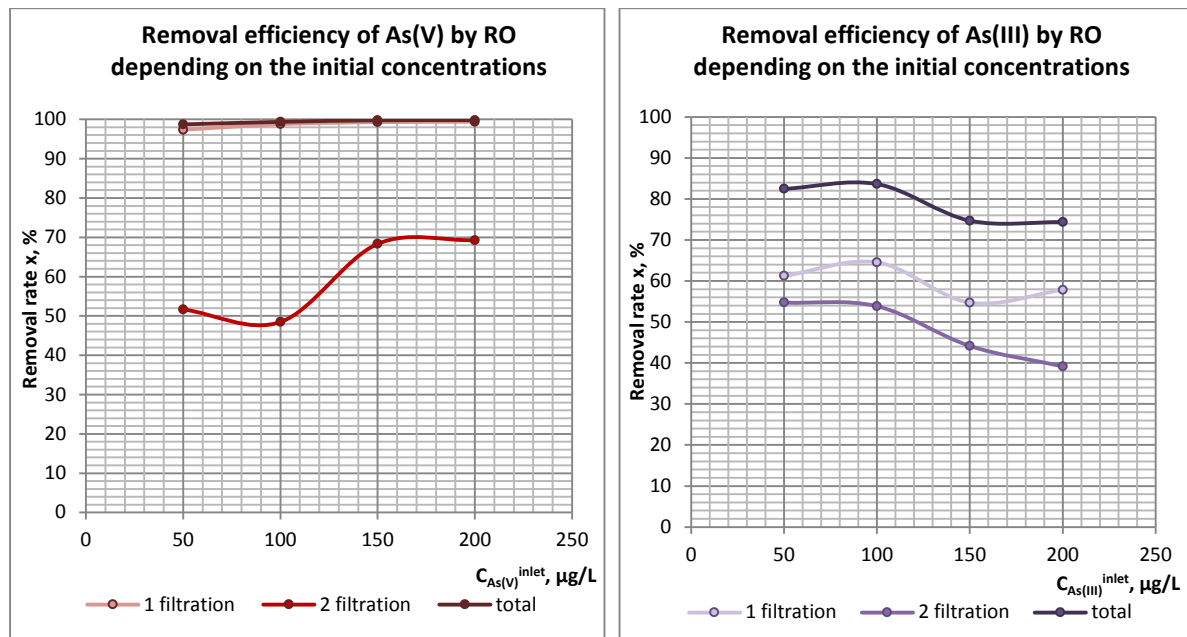


Figure 1 Removal efficiency of As (III) and As (V) depending on initial concentrations according to filtration step.

Figure 2 illustrate the impact of ratio As (V)/As (III) on treatment process from mixture of Arsenic.

Removal efficiency of second step of RO filtration doesn't suppose to be. That molecules of As that goes through the membrane on first step should pass through it on second step as well. But results show that there are 40-55 % of removal. One of the possible reason is oxidation As

(III) to As (V) during filtration process. Then removal efficiency could increase because of As (V) presence. This reason we tried to explore on the farther steps.

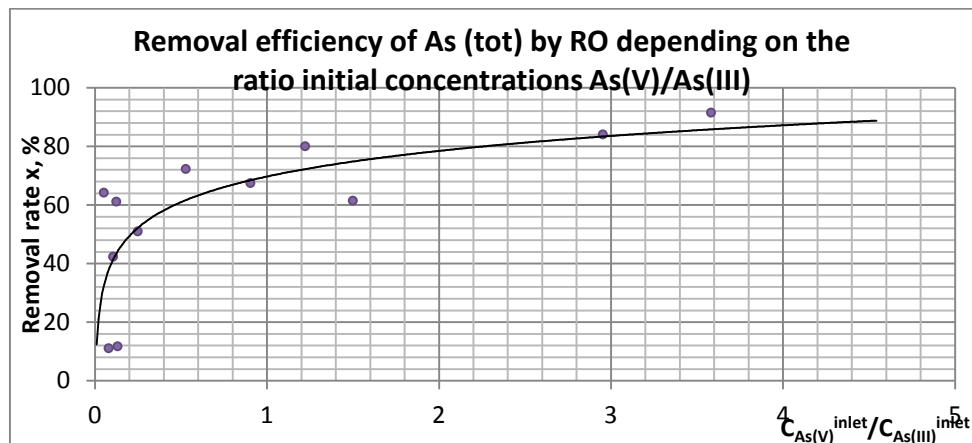


Figure 2 Removal efficiency of As (tot) by RO depending on the ratio initial concentrations As(V)/As(III).

Another two steps of research were for arsenic (III). Were used two different flow rates: 50 and 100 L/hour. Also was done IE separation on each step of treatment process and were measured concentrations of As (III) and As (V) as well for checking if there are any oxidation processes in the system.

Table 3 Second step of research. The removal efficiency of double filtration process for As (III).

Exp. №	As (III), µg/L	As (V), µg/L	Inlet		1 filtration		2 filtration		Removal rate As (Tot), %
			As (III), µg/L	As (V), µg/L	Removal rate As (III), %	Removal rate As (V), %	Removal rate As (III), %	Removal rate As (V), %	
Flow rate 100 L/h									
1	50	-	48.5	7.0	46.39	71.43	36.54	65.98	67.37
2	200	-	185	25	40.54	100.00	38.14	63.24	64.76
Flow rate 50 L/h									
3	50	-	45	11	48.89	63.64	39.13	68.89	73.21
4	100	-	86	14	45.35	57.14	44.68	69.77	70.00
5	200	-	160	50	43.75	80.00	31.11	63.24	64.76

From the Figure 3 we can say that removal efficiency is decreasing with increasing of initial concentrations. As well as on second filtration step efficiency is low than on first step. RO process with flow rate 100 L/hour is more effective than with 50 L/hour.

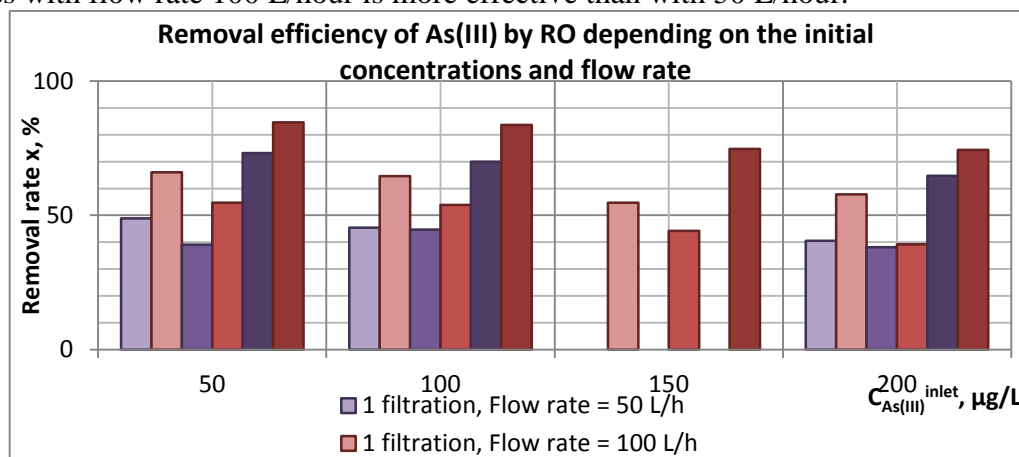


Figure 3 Removal efficiency of double filtration process depending on the initial concentrations according to different flow rates.

Oxidation rates in system during the process are shown in the Table 4 and on the diagram 4.

Table 4 Oxidation processes during RO filtration.

Exp. №	As (III), µg/L	As (V), µg/L	Inlet			1 filtration			2 filtration		
			As (III), µg/L	As (V), µg/L	Ox. rate, %	As (III), µg/L	As (V), µg/L	Ox. rate, %	As (III), µg/L	As (V), µg/L	Ox. rate, %
Flow rate 100 L/h											
1	50	-	48.5	7.0	12.6	26	2	7.1	16.5	0.5	2.9
2	200	-	185	25	11.9	110	0	0	68.0	6.0	8.1
Flow rate 50 L/h											
3	50	-	45	11	19.6	23	4	14.8	14	1	6.7
4	100	-	86	14	14.0	47	6	11.3	26	4	13.3
5	200	-	160	50	23.8	90	10	10	62	7	10.1

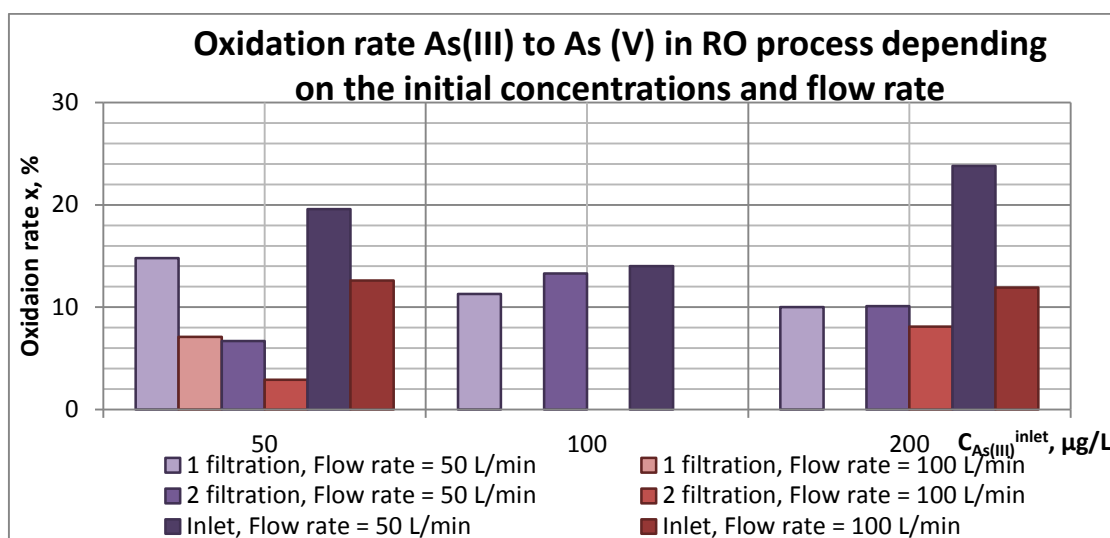


Figure 4 Oxidation processes on the second step of research

The results of oxidation in system show that in the inlet water we already have 10-25 % of As (V). That means that in the solutions of As (III) prepared in IPM laboratory As (V) is present. Also As (V) is present in water after first and second filtration. That prove our hypothesis of oxidation processes in system cause of almost 100 % removal rate of As (V). The concentrations of As (V) are higher after second filtration step.

According to some mistakes on preparation step was done checking of analytical errors of ICP-MS analyze. Set of experiments with two inlet concentrations was done. On each step of process we took two same samples and analyzed them. Results of this check are shown in the Table 5. Errors are almost absent, only a couple of samples had errors in 1-2 µg/L.

Table 5 Check of ICP-MS analyzing

	As (III), µg/L			Error, %	As (V), µg/L			Error, %
	1	2	Meen		1	2	Meen	
As (III) = 50 µg/L								
Inlet	48	49	48.5	1.03	7	7	7	0
1 filtration	26	26	26	0	2	2	2	0
2 filtration	16	17	16.5	3.03	1	0	0.5	50
As (III) = 200 µg/L								
Inlet	190	180	185	2.7	20	30	25	20
1 filtration	110	110	110	0	0	0	0	0
2 filtration	69	67	68	1.47	5	7	6	16.67

The third step of experiments was done as Full Factor Experiment (FFE). In this set three factors were varied in all combinations: pH, Flow rate and initial concentrations. The results are shown in the Table 6 – removal efficiency and in Figure 5 – the oxidation rates.

Table 6 Third step of research. Full Factor Experiment (FFE)

№	pH, Z ₁	Flow rate, Z ₂ , L/h	Initial concentration, Z ₃ , µg/L	Removal rate, %		
				1 filtration	2 filtration	Total
1	8	200	100	64.00	27.78	74.00
2	6	200	100	73.64	62.07	90.00
3	8	100	100	67.00	57.58	86.00
4	6	100	100	64.00	44.44	80.00
5	8	200	50	75.44	64.29	91.23
6	6	200	50	74.14	59.33	89.48
7	8	100	50	64.29	40.00	78.57
8	6	100	50	62.50	38.10	76.79

It should be noted several consistent patterns: in the experiments with bigger flow rates the degree of removal increase, the effect of pH is not clear, no regularities, the impact of the initial concentration also remains unclear, we again have the scatter points.

During FFE has also been analyzed the oxidation rates in raw water and after each filtration step. Somehow, when applying 200 L/hr observed greater oxidation. The reason is unclear. Many samples had zero content of pentavalent arsenic, so generally difficult to judge by what principle arsenic is oxidized in the system.

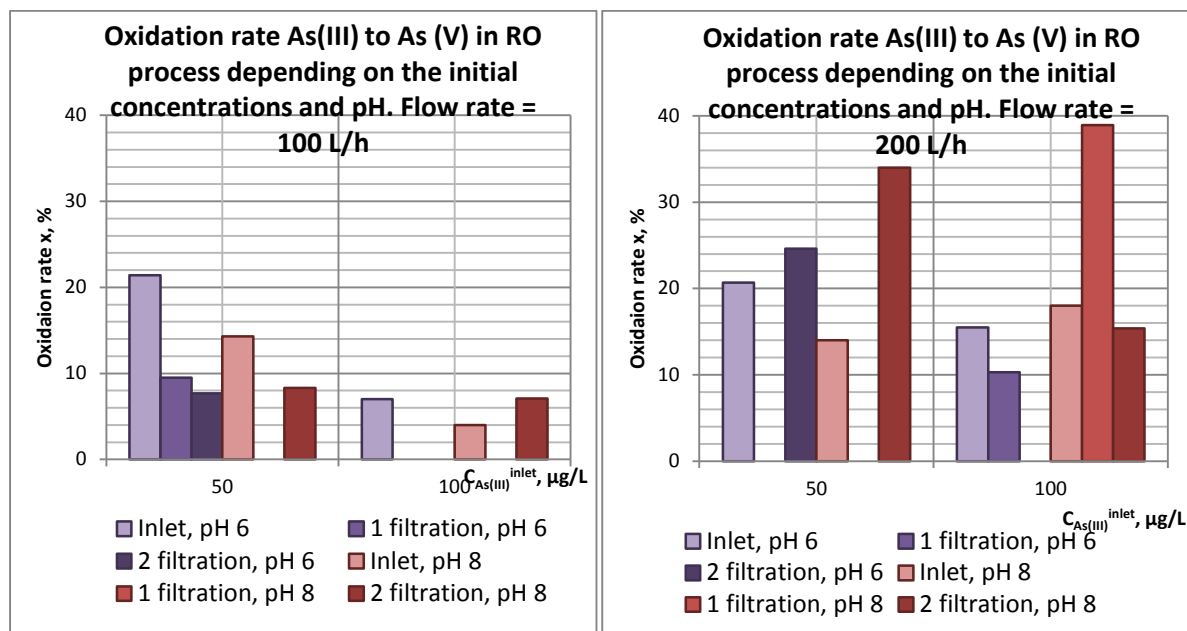


Figure 5 Oxidation processes in FFE.

After all steps was done summarizes of influence of the initial concentrations and flow rates. This results are shown in Figures 6 and 7.

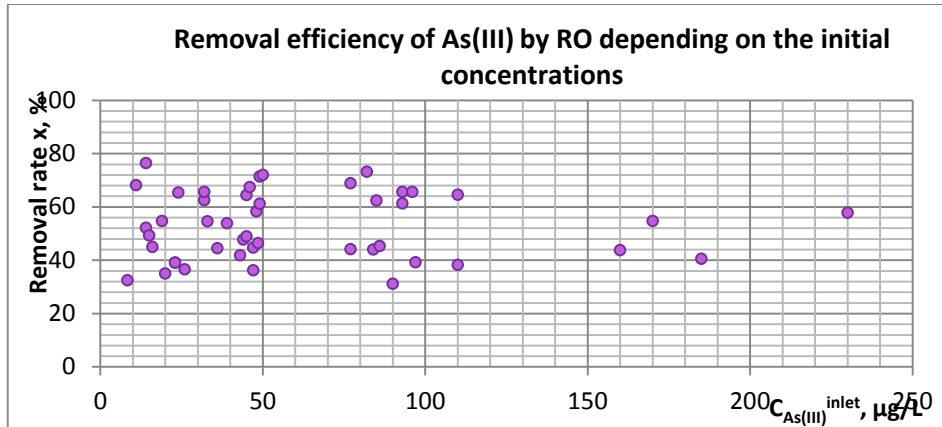


Figure 6 The influence of the initial concentrations on the removal efficiency of RO process.

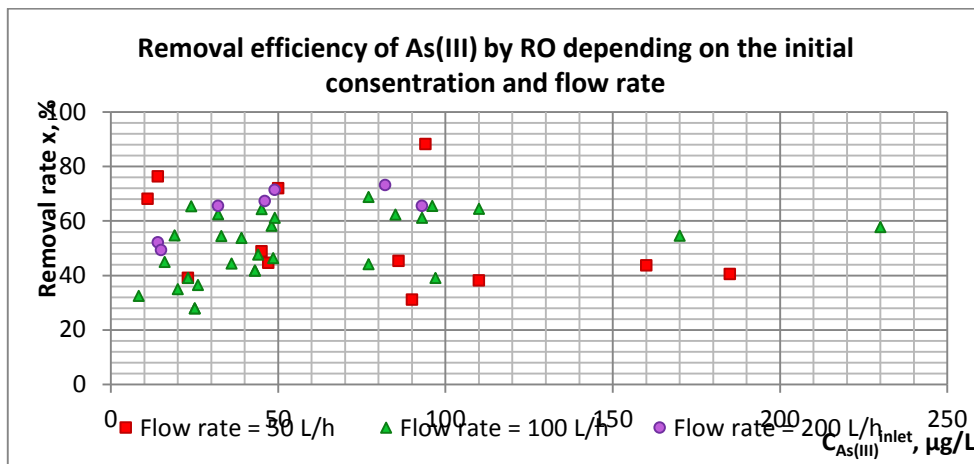


Figure 7 The influence of the flow rates on the removal efficiency of RO process.

In Figure 6 we see the big scatter of points. Removal rates are changed from 30 to 80 %. It's very difficult to say anything according to this figure. There is quite low reproducibility of results.

The graph on the Figure 7 shows the dependence of the initial concentration on removal rate at different flow rates: 50, 100, 200 L/hr. Most of the points with the flow rate 50 L/hr are below, points with rate 100 L/hr - the principal amount of the points are above, at 200 - respectively, also. It should also be noted that with increasing the initial concentration removal rates are also increased in general.

Conclusions

The treatment from arsenates gave a removal efficiency of 97-99 % after one filtration and it is evident that removal of As(V) is close to 100 % efficient.

Arsenite (III) removal is normally 30-60 % during RO processes. However, the double filtration process give arsenic removal up to 85 %. The total arsenic removal after two filtrations was found to be between 75-92 %. The removal of arsenite in the first filtration was in the range 55 - 65 % and in the second filtration between 40 % and 55 %. For test water consisting both with arsenite and arsenate, the RO system gave a total arsenite removal between 81 - 92 %.

Double filtration is not so efficient method to treat water that contains arsenite. The concentration after two filtrations was higher than the recommended limit of 10 µg/L and was sufficient only with initial concentrations 50 µg/L.

One of the theories for the removal efficiency of As(III) through double filtration RO was oxidation. Tests of the reject water were tested and showed oxidation rates 0 - 38 % in the first filtration and between 0 - 35 % in the second. Many samples had zero content of pentavalent arsenic, so generally difficult to judge by what principle arsenic is oxidized in the system.

There is no correlation between pH and removal efficiencies in the pH rate of 6 to 8, however, the removal rate is noticeably higher at pH 10 when As(III) is ionized.

Further experiments should look into the oxidation process and examine it more closely. Also I recommend to test the forms of As present in water, through potentiometric titration, for example.

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