

ARSENIC REMOVAL FROM DRINKING WATER BY ADVANCED FILTRATION PROCESSES

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ABSTRACT

All over the world the presence of arsenic in water sources for human consumption has been raising great concern in terms of public health since many epidemiologic studies confirm the potential carcinogenic effect of arsenic. Because arsenic removal is the most frequent option for safe drinking water, the development of more efficient and sustainable technologies is extremely important.

Membrane separation processes are suitable for water treatment because they can provide an absolute barrier for bacteria and viruses, besides removing turbidity and colour. Their application is a promising technology in arsenic removal since it does not require the addition of chemical reagents nor the preliminary oxidation of arsenite required in conventional treatment options. However, since membrane technologies such as reverse osmosis can be a very expensive and unsustainable treatment option for small water supply systems, it becomes crucial that alternative methods are developed.

This work presents a few conclusions based on a laboratorial study performed to evaluate the efficiency of arsenic removal using ultrafiltration, microfiltration and solar oxidation processes under different experimental conditions for relevant parameters. The results showed removal efficiencies higher than 90%.

Key-words: safe drinking water, arsenic removal, membranes, public health.

1 INTRODUCTION

The presence of arsenic in natural waters can occur naturally or result from anthropogenic activities, generally emerging with higher concentrations in groundwater. The contamination of drinking water sources has a wide variety of adverse health effects, including severe skin lesions (Fig. 1), cardiovascular and haematological effects, and neurological disturbances effects have been attributed to chronic arsenic exposure (Yoshida *et al.*, 2004). Furthermore, several epidemiological studies have confirmed that chronic arsenic poisoning causes skin and internal cancers (Lamm *et al.*, 2004).

Acute and sub acute poisoning results from ingestion of large quantities of arsenic with lower exposure time, whereas chronic poisoning occurs due to consumption of arsenic contaminated water for a long time period. Considering the lethal impact of arsenic on human health, environmental authorities have taken a more stringent attitude towards the presence of arsenic in water. In 1993, the World Health Organization (WHO) had decreased the maximum contaminant level (MCL) standard of arsenic in drinking water from 50 to 10 ppb. The drastic reduction of this parametric value has led many impoundments, which serve small and medium water supply systems, to become critical for this contaminant. Consequently, drinking water facilities are undergoing several technical and operational changes induced by the non-compliance (though seasonal) of raw water arsenic levels with the new quality standard (Duarte *et al.*, 2009a).



Figure 1 Skin lesions caused by prolonged hydra ingestion of arsenic
 (<http://www.sos-arsenic.net/english/contamin/index.html>)

When a safer drinking water source is not available or it becomes too expensive to exploit – one that is both low-arsenic or arsenic-free, and exhibits acceptable microbiological quality – treating raw water for arsenic removal is often the sole viable option to explore. In this case, there is ample justification for the development of innovative removal technologies that are more efficient and economically sustainable. This issue is very sensitive in the context of water scarcity and climate change (Duarte *et al.*, 2009b).

Arsenic removal technologies should meet several basic technical criteria, including (1) be robust; (2) not carry any undue adverse effect on the environment; (3) be able to provide supply systems with the capacity to produce water in adequate quantity across different seasons; (4) take into consideration present climate change scenarios, and (5) meet the physical-chemical and microbiological quality requirements.

There are several water treatment technologies that allow the removal of arsenic. Currently, conventional removal technologies more often used are based on physicochemical principles, such as coagulation followed by filtration, softening and lime addition, usually yielding efficiencies below 90%. Since these processes are not always sufficient to reduce concentrations of arsenic in drinking water, advanced technologies were developed that include ion exchange, adsorption and carbonate aluminium and the use of physical separation processes (like membranes) (Johnston & Heijnen, 2001).

Most of the mentioned technologies present a few limitations when applied in water treatment plants. The main drawbacks include (1) the need for adding chemicals to water; (2) the need for additional treatments; (3) the production of large volumes of sludge with high amounts of arsenic, and (4) sometimes, high installation and operating costs. Processes involving membranes for removal of arsenic (and other heavy metals) are a major research area in development. These processes have a great advantage that is not requiring the addition of chemicals to get good removal efficiencies.

Several emerging technologies are being developed showing very satisfactory removal efficiencies, either by adapting and improving conventional processes or by developing new biological processes.

Tam *et al.* (2007) cited membrane separation processes as a suitable technology for water treatment, since they can provide an absolute barrier for bacteria and viruses, besides removing turbidity and colour. Fouling in membrane filtration limits its application because cleaning and frequent substitution of membranes is required, increasing the costs involved. Essentially, fouling is a major constraint in separations using membranes. Its occurrence leads to a decline in the membrane permeability and can occur by the deposition of a new layer onto the membrane surface (cake filtration). Most membrane processes are pressure-driven and require pumps to promote the trans-membrane pressure, resulting in high energy consumptions. Alternatively, membrane processes can be designed to operate with gravity as the driving force. Modified membranes through TiO₂ immobilization could be an alternative for the decontamination of potable water with superior quality, due to reduced fouling (lower cake resistance) and the excellent removal of bacteriological and physical parameters (Silva *et al.*, 2010).

The success of applying an arsenic removal technology depends on the following factors: parametric value to achieve; raw water arsenic concentration; flow rate to treat; regional lithography; water source and existing treatment scheme (Mondal *et al.*, 2006).

To deal efficiently with arsenic removal, regular monitoring is required to identify the factors that control arsenic concentration and arsenic speciation. Such monitoring programmes are not easily established in developing countries and thus, arsenite-oxidizing processes integrated into arsenic removal methods appear as a safety precaution measure in high-risk areas (Katsoyiannis *et al.*, 2007).

In this study, advanced filtration processes were analyzed using two different membranes for microfiltration and ultrafiltration processes designed to separate solute and solvent components in the solution using pressure as driving force. In both cases, their behaviour is similar as the solvent (water) flows through the membrane and the solutes are rejected by the action of a pressure gradient. Compared to ultrafiltration, the microfiltration process has its main advantage on the significant reduction in operating costs (energy and filter material).

The aim of this study is to evaluate the efficiencies of microfiltration and ultrafiltration processes, as emerging technologies for arsenic removal in public water supply systems, at a laboratorial scale. The effects of operating conditions on membranes performance, like pressure gradient, initial arsenic concentration, temperature, pH and Fe:As *ratio* in efficiency results were studied.

2 METHODS

The raw water containing arsenic used in the laboratory tests was collected in a groundwater abstraction point located in Fafe, belonging to the *Águas do Noroeste* Company. Three samplings were necessary throughout the research work. The raw water samples characteristics relevant for this work are summarized in Table 1.

Table 1 Characteristics of raw groundwater used in the laboratory tests

Gathering date	Raw water characteristics			
	pH	Conductivity (μS/cm)	Iron concentration (mg/L)	Arsenic (ppb)
2010.04.22.	6.33	106.9	0	13
2010.05.31	6.82	137.9	0	15
2010.08.07	6.14	218.0	0	10

The experiments were carried out in a laboratory filtration cell (Amicon type – Millipore, model 8400) with a capacity of 400 mL (Fig. 2). This was designed to work with membranes of a diameter of 76 mm.



Figure 2 Laboratory installation used for membrane separation tests

Three different types of membranes were used – two UF membranes of polyethersulfone and one MF membrane of PAN/PVC. Before each run, each membrane was washed with distilled water and permeability of the raw water was measured.

The chemical analysis of the arsenic on the original feed as well as the resulting permeates was carried out with an Atomic Absorption Spectrophotometer (AAS) equipped with a hydride generation module (Fig. 3). The iron concentration was also measured using the same AAS apparatus.



Figure 3 Samples analysis using the AAS technique with the hydride generation module

All laboratory tests were performed keeping the same operating conditions and by adopting the same procedures. The samples were preserved adding nitric acid. The pH was measuring using a *pH* meter and the conductivity with a laboratory conductivimeter.

The filtration tests performed were conducted at 22° C, with a constant agitation speed of 100 rpm, applying pressures between 0.5 and 3 bar, with increments of 0.5 bar. For each of these pressure values filtration experiments with distilled water were performed to characterized the hydraulic permeability of the membranes.

In the experiments with different iron to arsenic *ratios*, a preliminary filtration of the solution was made with a 0.45 μm filter (Fig. 4).



Figure 4 Preliminary filtration procedure and filter appearance after experimental period

Solar oxidation and removal of arsenic (SORAS) is a simple method that uses irradiation of water with sunlight in PET (or other UV-A transparent) bottles to reduce arsenic levels from drinking water. The SORAS method is based on photochemical oxidation of arsenite, As(III), followed by precipitation or filtration of arsenate, As(V), adsorbed on Fe(III) oxides (Fig. 5, Wegelin *et al.*, 2000).

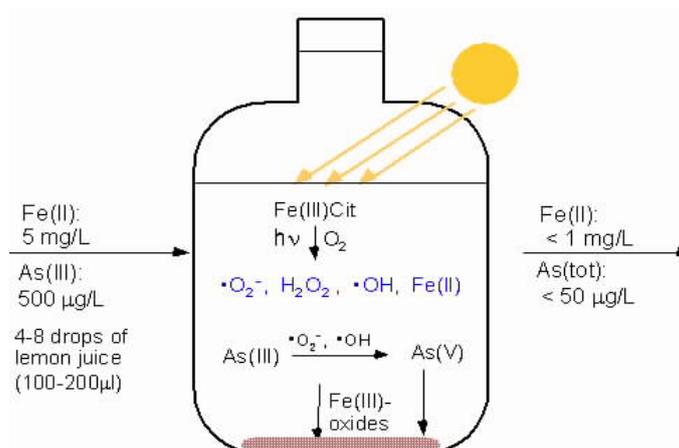


Figure 5 Basic principle of SORAS process: photo-oxidation of AS(III) and precipitation of adsorbed As(V)

SORAS process removes arsenic in a two-step procedure. In the first step, arsenite is oxidized to the strongly adsorbing As(V). In the second step, Fe(III) (hydr)oxides formed from naturally present iron are allowed to settle to the bottom of the container with the adsorbed As(V) and the clear water is decanted (Fig. 6). Instead of adding chemical oxidants such as chlorine or permanganate, reactive oxidants are produced photochemically with sunlight.



Figure 6 SORAS test and a detail of the arsenic residue after sun exposure period

This procedure, worldwide used at household level to treat small quantities of drinking water, could be improved for more frequent application as a low-cost alternative to oxidize arsenite in sunny country areas, in order to increase energy efficiency and to reduce operational costs of small and medium water treatment facilities.

In this work, the experiments of solar oxidation (according to the recommendations of SORAS) were carried out simultaneously with filtration tests. The reagents used in this procedure were citric acid monohydrate, titanium dioxide, and iron (III) sulphate and lemon juice. The samples were also analyzed using the AAS technique.

3 RESULTS

3.1 Hydraulic permeability of membranes

At the beginning of the laboratorial work, a standard run was carried out by filtering distilled water at different operating pressures.

The hydraulic permeability for the membranes (J_v) was calculated from the initial water permeation according the following equation (Mulder, 1996):

$$J_v = L_p \times \Delta P \quad (1)$$

Where,

ΔP is the gradient of hydrostatic pressures across the membrane;

L_p is the hydraulic permeability coefficient.

Figure 7 shows the behaviour of the permeate flux variation with the pressure for the membranes used in this study and described in Table 2.

Table 2 Characteristics of membranes used in the laboratory tests

Membrane	Description
M1, M2, M3	Ultrafiltration membrane PM10 (10 kDa) from <i>Amicom</i>
MU1, MU2	Ultrafiltration membrane PM30 (30 kDa) from <i>Amicom</i>
MC1, MC2	Microfiltration membrane XM300 (300 kD) from <i>Amicom</i>

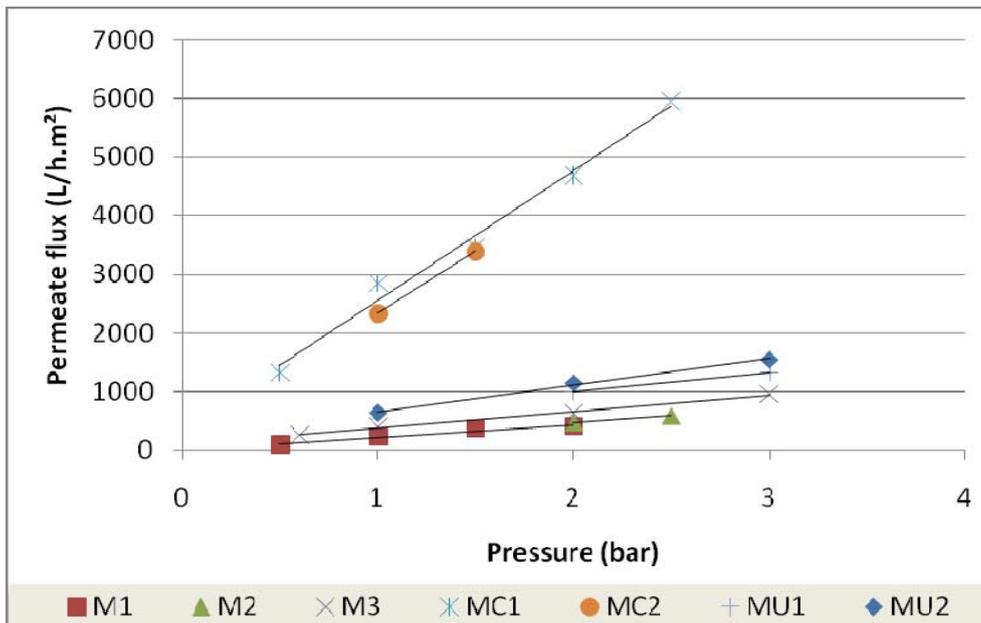


Figure 7 Hydraulic permeability of used membranes to distilled water (at 22 ° C)

The obtained results showed that the hydraulic permeability coefficient of microfiltration membranes is approximately ten times higher than that for ultrafiltration

3.2 Efficiency of the arsenic removal by membrane filtration

For the range of pressure values tested, this operational parameter seems not to play a major role in arsenic removal efficiency (Figure 8). These results were obtained for MU2 ultrafiltration membranes, and an initial arsenic concentration of 15 ppb. Thus, with the objective to reduce the filtration time, all of the following experimental tests were performed using the pressure of 3 bar.

In these preliminary experimental tests it is also possible to verify that when 1 mg/L of iron is added to raw water the efficiency of arsenic removal has a sensitive increase. This phenomenon can be explained due to the formation of macromolecules that react with arsenic and lead to an increase of the ultrafiltration membrane efficiency.

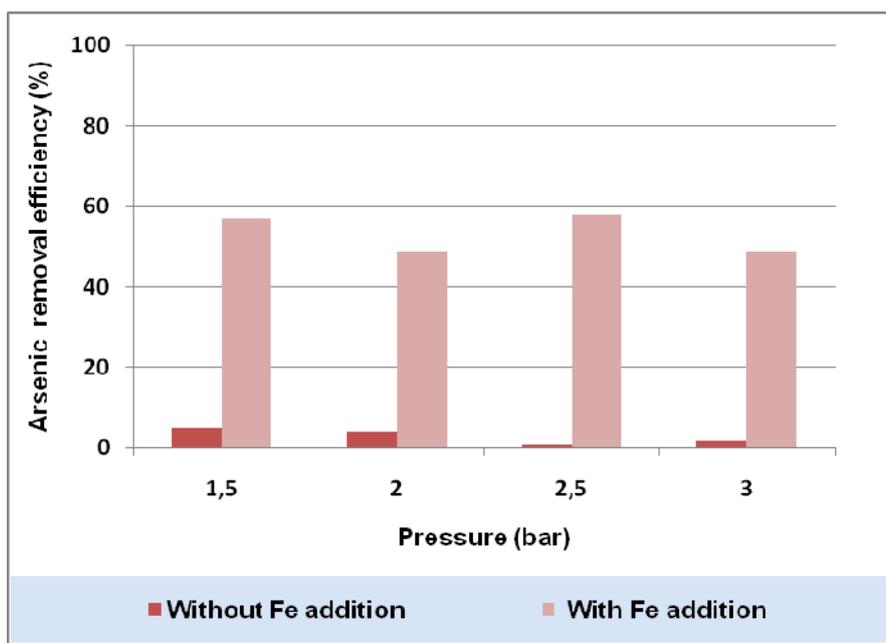


Figure 8 Pressure effect in arsenic removal efficiency using ultrafiltration

The pH value of the raw water solution seems to have a very important role in the arsenic removal efficiency using ultra and microfiltration. It significantly influences the distribution of arsenic species, the affinity of arsenic for iron adsorption and also the charge and formation of iron oxide particles.

Figure 9 shows the results obtained for a raw water with a initial arsenic concentration of 15 ppb that was tested at three different pH values (5.0, 6.8 and 8.5) and two different Fe:As ratios (40:1 and 80:1). The analysis of the results allows the conclusion that the best arsenic removal efficiencies occur at pH 5 in both ultrafiltration and microfiltration processes. The results obtained for the microfiltration process at pH 5 and with a Fe:As ratio of 40:1 was not expected and cannot be explained yet, but trials are under way aiming to clarify the behaviour of the membrane used. The low initial concentration of arsenic (As_0) in raw water may be related to the likely overestimation of this removal efficiency.

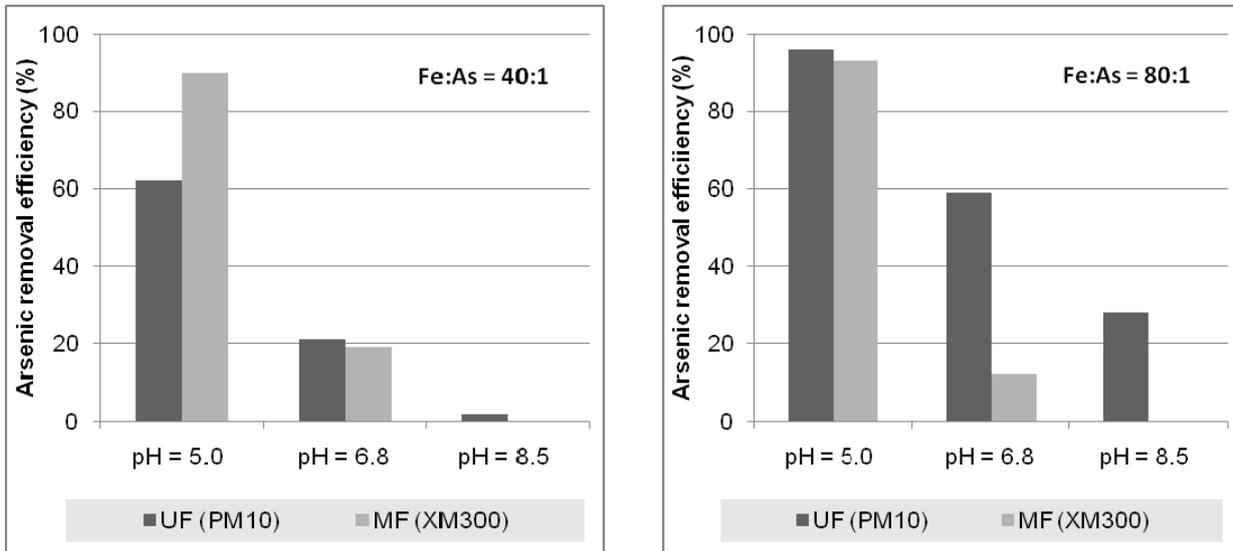


Figure 9 Effect of pH value in arsenic removal efficiency for different Fe:As ratios ($As_0=15$ ppb)

To evaluate the efficiency of arsenic removal with different iron to arsenic ratios, a set of experiments was performed with feed water containing several concentrations of arsenic and iron corresponding to Fe:As ratios of 15:1, 20:1, 40:1, 80:1, 100:1 e 200:1. Feed water was prepared at neutral pH and only aeration was performed. Figure 10 shows that for higher values of Fe:As ratio (80:1, 100:1 and 200:1) higher arsenic removal efficiencies were achieved. The reduction of arsenic removal efficiencies for the lower initial iron concentration in raw water could be explained by the absence of iron in the raw water. So, this can inhibit a more effective adsorption of arsenic or the reduction of the capacity of iron oxidation for the needed arsenite to arsenate conversion (Oliveira, 2010).

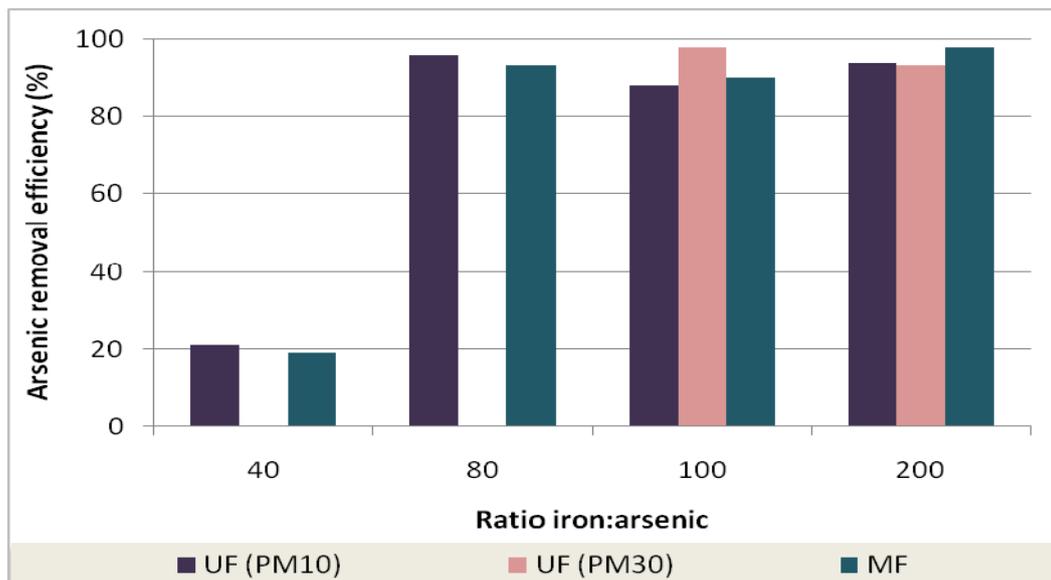


Figure 10 Effect of Fs:As ratio variation in arsenic removal efficiency

The addition of an accurate iron concentration (dependent on pH value) combined with a preliminary filtration of raw water allowed to improve the arsenic removal efficiency, even without the later utilization of membrane filtration. It shows that it is possible to remove more than 60% of arsenic for Fe:As ratios of 80:1, using gravity filtration processes only (Fig. 11). This conclusion is very important because low-rate filtration is a conventional unit process present in the most WTP, which could be improved for arsenical removal propose if the Fe:As ratio is efficiently controlled.

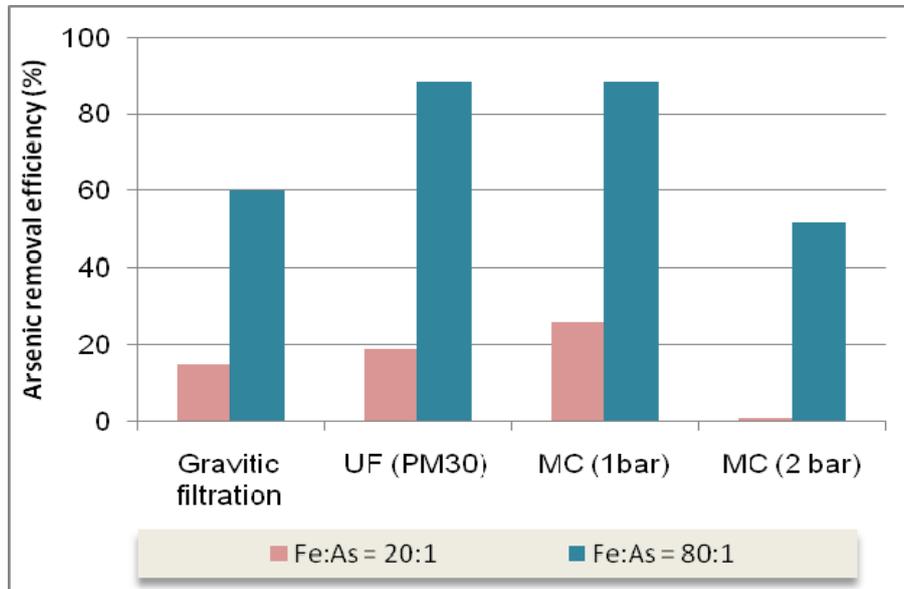


Figure 11 Arsenic removal efficiency comparison between gravity and pressure membrane filtration

3.3 Arsenic removal efficiency applying SORAS technique

Experimental results depicted in Figure 12 show that arsenic removal efficiency using the SORAS method can achieve very interesting results for a sun exposure time of about 4 hours, when an accurate amount of iron is added to raw water, namely if pH value is low (approximately 5). Thus, these operating conditions revealed “ideal” both for membrane filtration as well as solar oxidation process. Therefore, solar oxidation technique could be used more often as a low-cost raw water pre-oxidation step that uses a renewable and clean energy source.

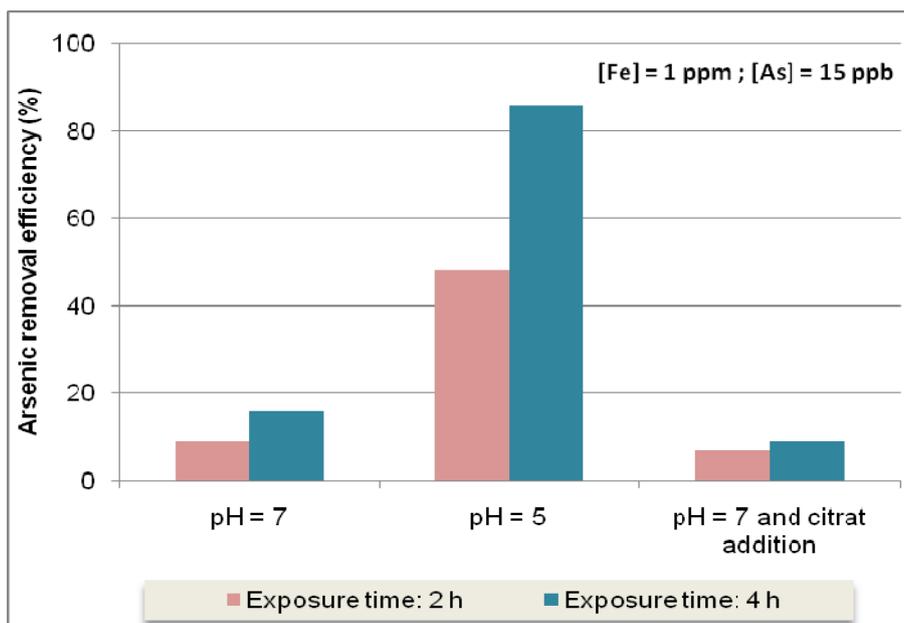


Figure 12 Arsenic removal efficiency using solar oxidation (SORAS technique)

4 CONCLUSIONS

The raw water used in this study (even though from a groundwater catchment) did not present sensitive iron concentrations and made it necessary to add this constituent in the laboratory. However, this phenomenon usually does not occur in groundwater, thus it is possible to obtain the desired arsenic removal efficiencies only with iron that usually exists in the natural water sources.

The methodology used included pilot experiments at a laboratory scale. It appears to be suitable for the optimization of two separation processes based on membrane filtration – ultra and microfiltration – and to improve the knowledge for its real scale implementation in order to reduce water supply treatment costs in view of the characteristics of the raw water.

The experimental results obtained in this research work showed that arsenic removal efficiency using membrane separation processes increases for lower pH values (below 6) and higher Fe:As ratios (above 100:1). On the other hand, preliminary filtration or solar oxidation can be used for a sensitive removal efficiency improvement with low treatment costs increase.

The performances of ultra and microfiltration are excellent and very similar when the ideal operational conditions are presented (pH = 5-6; Fe:As ratios near 200:1) reaching a range between 93 and 98%.

The arsenic removal efficiency was not sensitive to test pressure variation. A similar conclusion had already been obtained in previous research works on micro and nanofiltration processes (Caniyilmaz, 2005; Lazarova, 2009);

The major (and unexpected) conclusion of this work is that microfiltration also led to excellent arsenic removal performance. So, the possibility of selecting membranes with higher permeate flux seems to have the potential for providing enormous gains in energy efficiency and lower construction and operational costs when applied to the real scale.

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