



# Application of reverse osmosis technology for arsenic removal from aqueous solution

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# **Arsenic - What is it?**

- **Naturally occurring element**
- **Natural sources**
  - **Erosion, dissolution, and weathering of rocks**
  - **Volcanoes**
  - **Forest fires**
- **Manmade/man-affected sources**
  - **Agriculture**
  - **Wood preservatives**

# **Arsenic – MCL**

The new Maximum Contaminant Level (MCL) for arsenic is 10 ppb.

The EPA estimates that 350,000 people in the U.S. drink water containing more than 50 ppb, and nearly 25 million people drink water containing more than 25 ppb.

# Arsenic - Treatment

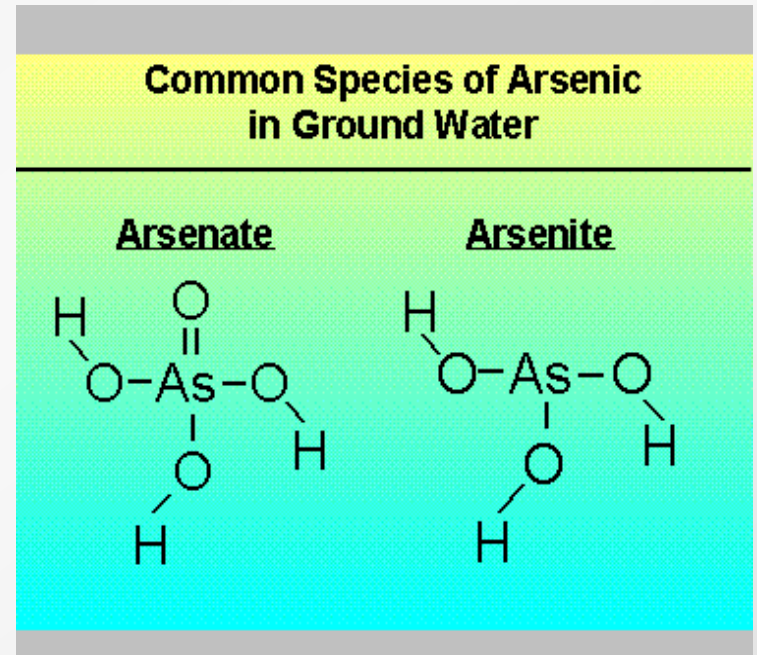
Treatment is dependent on oxidation state

**Arsenate-As(V)**

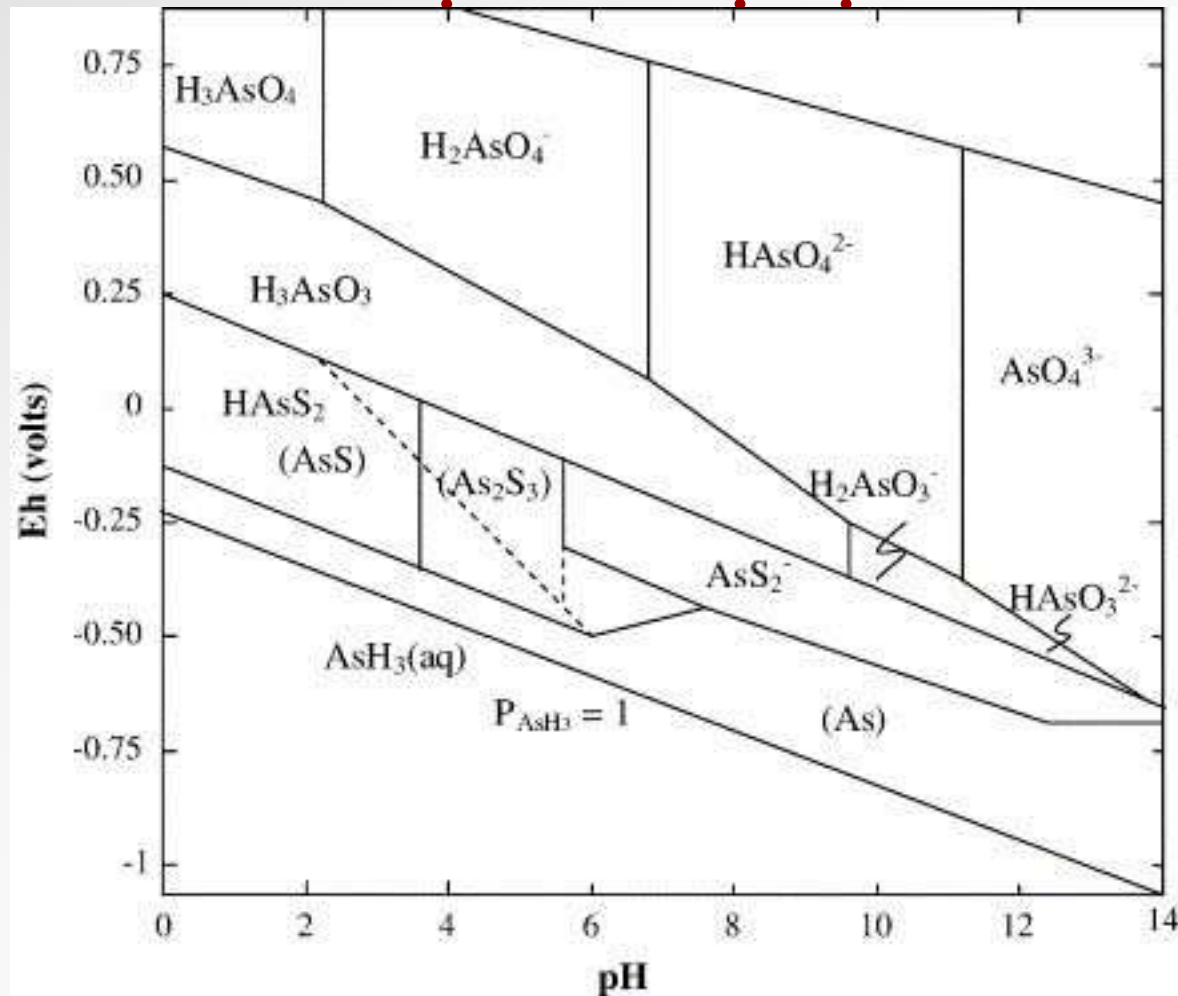
**Effective removal**

**Arsenite-As(III)**

**Must undergo oxidation  
to be effectively removed**



# Redox potential (Eh) and pH control



Arsenic species predominating in various pH ranges have been discussed

# **Arsenic – Treatment Options**

- ***Adsorption***
- ***Reverse Osmosis (RO)***
- ***Distillation***
- ***Ion Exchange (IE)***

*Used methods for removal of arsenic from waters are mainly oxidation/reduction, precipitation, adsorption and ion Exchange, solid/liquid separation, physical exclusion, biological removal processes, and reverse osmosis (RO).*

*The most common technologies for arsenic removal have been coagulation with metal salts, lime softening, and iron/manganese removal.*

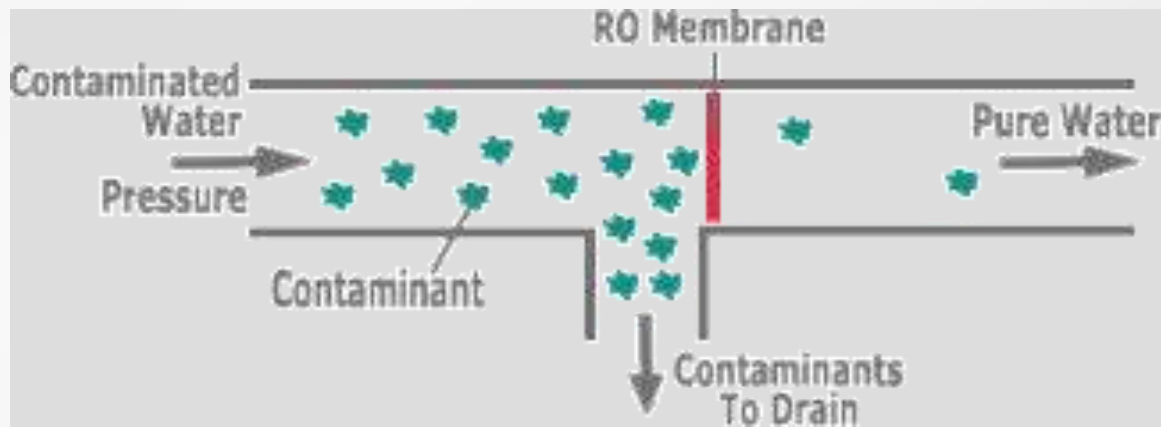
# Removal of Arsenic by Reverse Osmosis

## ➤ Advantage

- Achieves greater than 95% removal

## ➤ Disadvantage

- Relatively poor water recovery
  - Most units designed to achieve 20-30% recovery
  - Used to treat drinking and cooking water only



# OBJECTIVE

The objective of this work was to investigate the removal of arsenate from water by RO with SWHR membrane using model solutions containing arsenate as single solute.

The effect of pH and concentration of feed water and operating pressure on the removal was determined.



Dangerous arsenic concentrations in natural waters is now a worldwide problem and often referred to as a 20th- 21st century calamity.

High arsenic concentrations have been reported recently from the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India.



The application of RO on the natural water samples taken from Kızıldere (Kütahya, Turkey) and Gülbahçe (Nevşehir, Turkey) geothermal areas was performed under optimal conditions.

The chemical composition of the natural (ground) water samples from Kızıldere (pH=9.2) and Gülbahçe (pH=7.1) were determined by three times analyses [ $n=3$ ].

Ionic species	Concentration [ $n = 3$ ]	
	Kızıldere (Kütahya)	Gülbahçe (Nevşehir)
F <sup>-</sup> , mg/L	20.6 ± 0.8	0.7 ± <0.1
Cl <sup>-</sup> , mg/L	76.7 ± 16.5	87.7 ± 5.9
SO <sub>4</sub> <sup>2-</sup> , mg/L	850 ± 18	74.2 ± 6.7
HCO <sub>3</sub> <sup>-</sup> , mg/L	1590 ± 24	98.4 ± 3.5
CO <sub>3</sub> <sup>2-</sup> , mg/L	213 ± 4	200 ± 5
<b>As (total), µg/L</b>	<b>2281 ± 43</b>	<b>62 ± 3</b>
<b>As(V), µg/L</b>	<b>1821 ± 35</b>	<b>50 ± 2.7</b>
<b>As(III), µg/L</b>	<b>460 ± 35</b>	<b>12 ± 2</b>
Li, mg/L	3.8 ± 0.1	0.4 ± <0.1
B, mg/L	24.8 ± 0.3	29.7 ± 0.3
Ca, mg/L	1.2 ± 0.1	not detected
Mg, mg/L	not detected	10.7 ± 3.4
Mn, mg/L	not detected	not detected
Fe, mg/L	not detected	not detected
Al, mg/L	not detected	not detected

# *Reverse osmosis pilot plant*

The reverse osmosis pilot plant (Prozesstechnik GmbH) used in this study was described in our previous work

Accepted Manuscript

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Authors: Yunus Cengeloglu, Gulsin Arslan, Ali Tor, Izzet Kocak, Nesim Dursun

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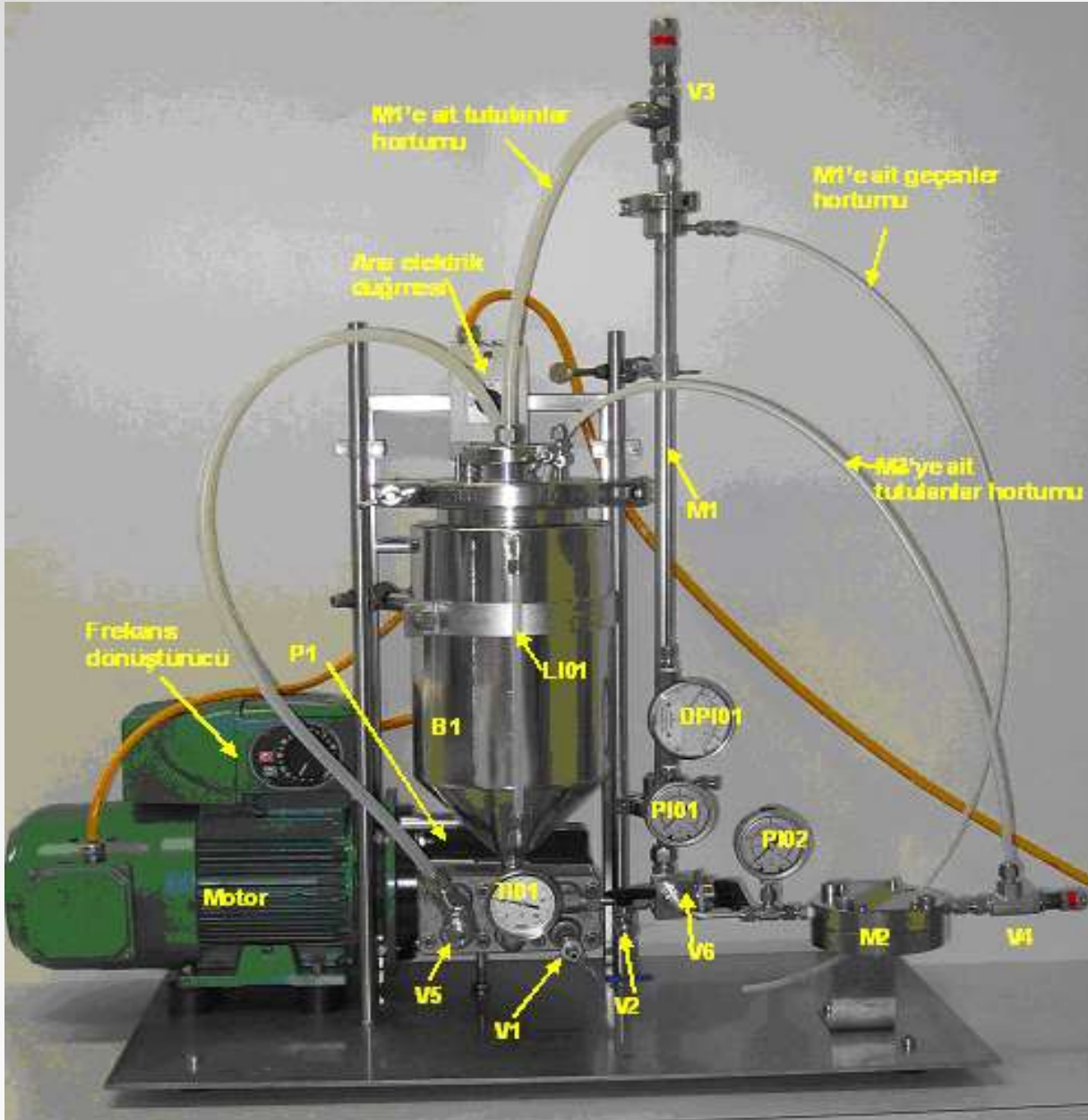
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# Prozesstechnik GmbH *reverse osmosis pilot plant*



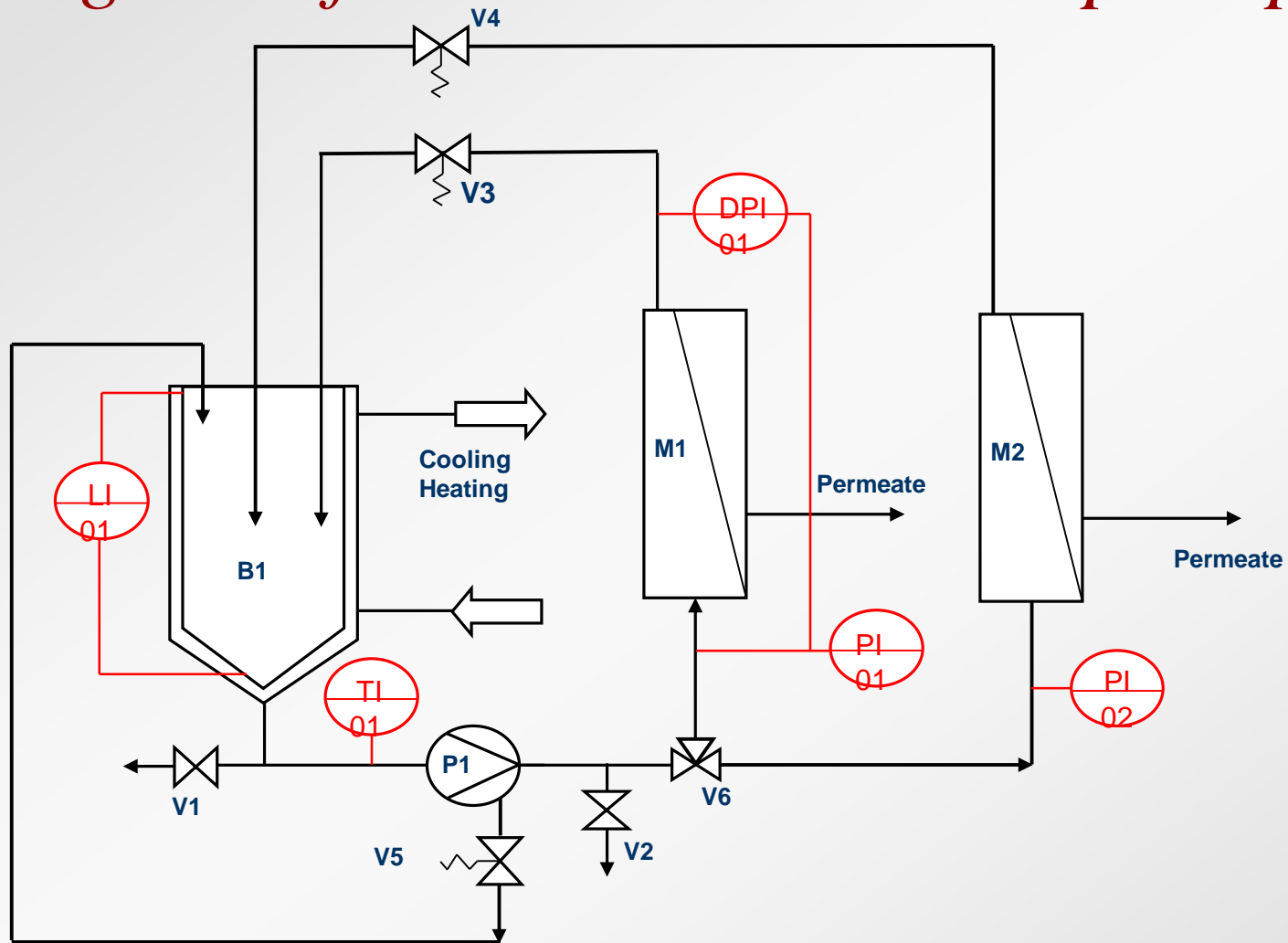
RO pilot plant consists of;

diaphragm pump controlled with a frequency converter (flow range: 1.8-12 L/min, pressure range: max 40 bar),

feed tank with heating/cooling jacket (5 L capacity),

membrane housing for both spiral wound and flat-sheet membranes.

# *Flow diagram of the reverse osmosis pilot plant*



M1 and M2: Membrane housing, B1: Feed tank with heating/cooling jacket, V1 and V2: Emptying valve, V3 and V4: Pressure regulation valve, V5: Spring loaded valve, V6: Three way valve to select which membrane housing, P1: Pump, PI01 and PI02: Pressure gauge, DP1: Differential pressure indicator, LI01: Level indicator on the feed tank, TI01: Temperature indicator.

SWHR membrane having 44 cm<sup>2</sup> exposed area with a flat-sheet configuration was obtained from FILMTEC.

SWHR membrane	
Configuration	Flat-sheet
Max temperature, °C	45
Max pressure, psig	1200
Salt rejection, %	99.6
Chlorine tolerance, ppm	< 0.1

# *Experiments*

The arsenate solutions were prepared in distilled water by diluting the prepared stock solutions (1000  $\mu\text{g/L}$ ) to desired concentrations.  $\text{H}_3\text{AsO}_4$ ,  $\text{NaOH}$  and  $\text{HCl}$  were obtained from Merck Co. (Darmstadt, Germany). All chemicals were the analytic grade reagents.

In specific experiments, composition of the feed water and operating pressure were chosen as below:

- Feed water is an arsenate solution with different concentration (50, 100, 150, 200, 300, 500 and 750  $\mu\text{g/L}$ ), at pH 4.10, operating pressure 20 bar and temperature: 20  $^\circ\text{C}$ .
- Feed water is a 200  $\mu\text{g/L}$  of arsenate solution at nine different pH ranging from 3.56 to 10.40, operating pressure 20 bar and temperature: 20  $^\circ\text{C}$ .
- Feed water is a 200  $\text{mg/L}$  of arsenate solution at pH 3.24 under different operating pressure ranging from 10-35 bar at temperature: 20  $^\circ\text{C}$ .

# *Experiments*

At the beginning of each experiment, pH of the feed water (2 L) was adjusted to the desired pH level by addition of 0.1 M NaOH or 0.1 M HCl and it was placed in the feed water tank. The system was operated in the permeate recycle mode. A new membrane was used for each experiment after conditioning the membrane at least 2 h under the experimental conditions. Then the measuring sequence was started. Every hour, samples of permeate were taken and their arsenic concentrations were determined. The experiments were performed at 20 °C. The arsenic rejection was calculated according to:

$$\text{Arsenic removal (\%)} = (C_{\text{permeate}} / C_{\text{feed}}) \times 100$$

where,  $C_{\text{permeate}}$  and  $C_{\text{feed}}$  are the arsenic concentrations of the permeate and feed water, respectively.



# *Instruments*

The concentration of arsenic and cations in the samples was determined by Hydride Generation (HS-60)-ContrAA 300 Atomic Absorption Spectroscopy (ContrAA 300, Analytikjena).

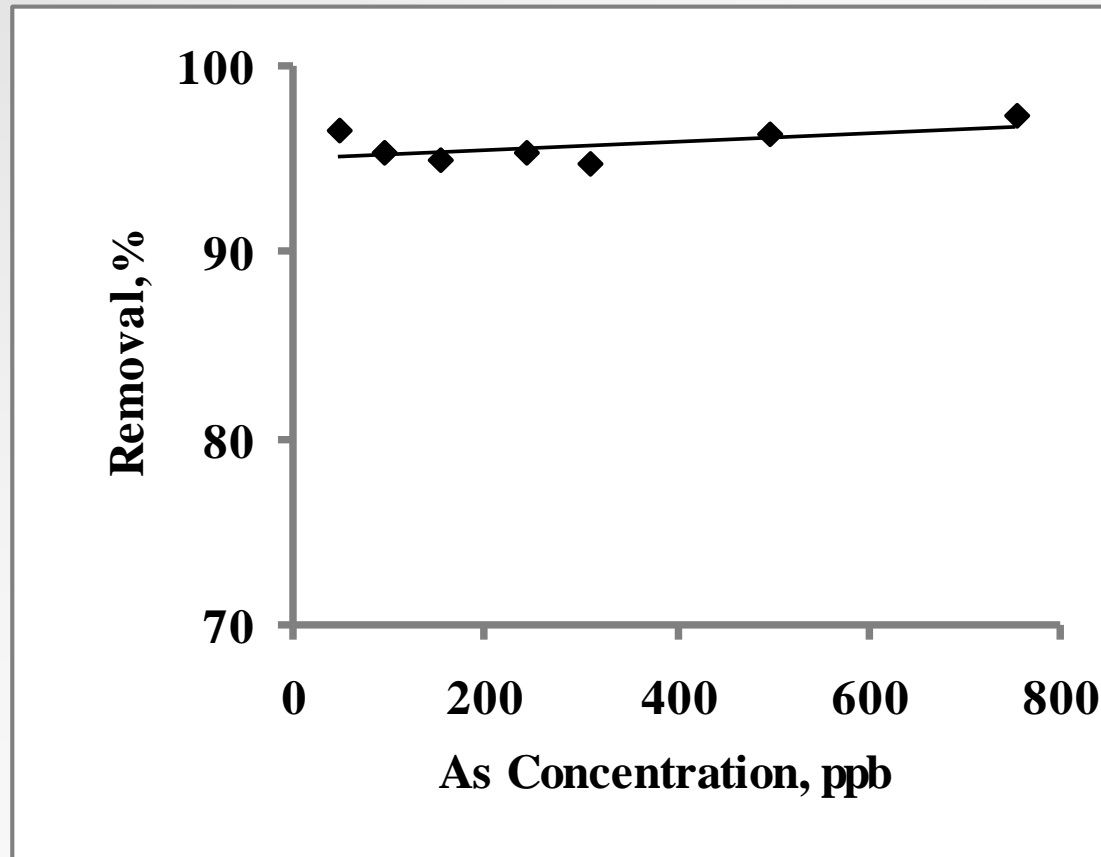
The wavelength utilized for the determination of arsenic was 193.69 nm.

Linearity for arsenic was observed in the concentration range of 0.25-10  $\mu\text{g/L}$ .

Coefficient of regression ( $R^2$ ) for arsenic was  $>0.999$ ,

Limit of detection (LOD) was 0.061  $\mu\text{g/L}$ .

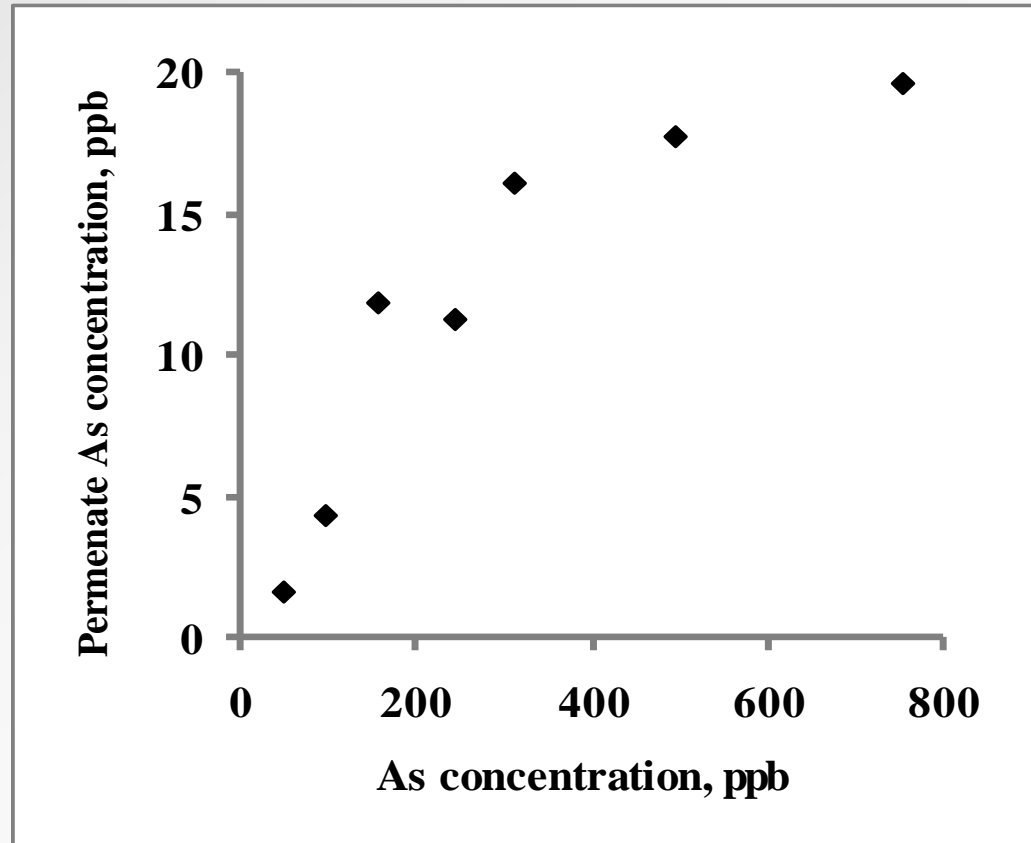
## *Effect of feed water concentration*



Dependency of arsenic removal on the arsenic concentration of feed water. pH of feed water: 4.1, operating pressure: 20 bar, temperature: 20 °C.

It is seen that arsenic concentration of feed water has no significant effect on the rejection.

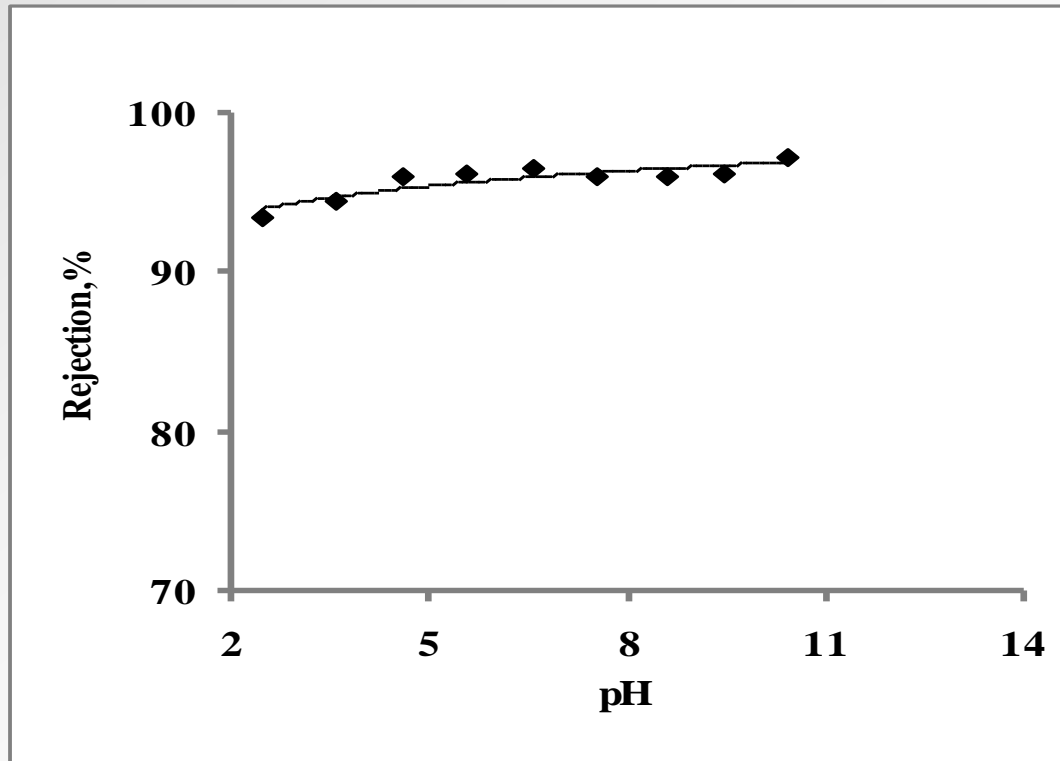
This result can be attributed to that permeate water concentration increases with increasing the feed water concentration.



Dependency of permeate concentration on the arsenic concentration of feed water. pH of feed water: 4.1, operating pressure: 20 bar, temperature: 20 °C.

In other words, arsenic rejection does not depend on the feed concentration.

# *Effect of pH of feed water*

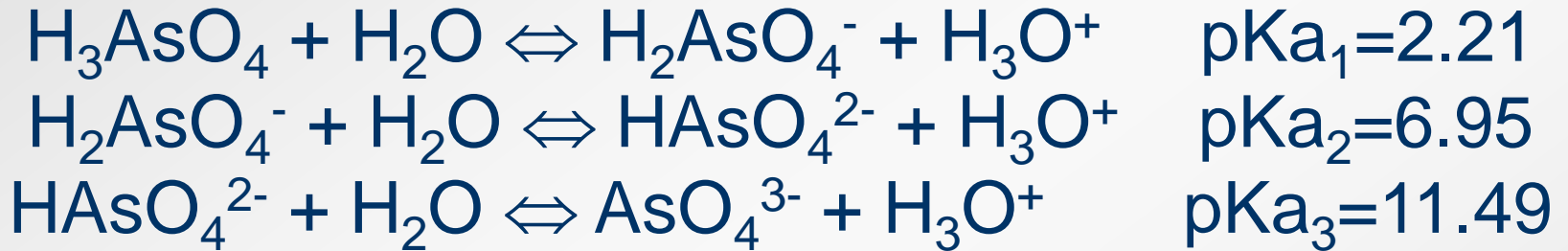


Dependency of arsenic rejection on pH of feed water. Arsenic concentration of feed water: 200  $\mu\text{g/L}$ , operating pressure: 20 bar, temperature: 20  $^{\circ}\text{C}$

The figure indicates that negligible increase in the arsenic rejection was observed with increasing pH.

This results can be attributed to that the arsenate  $\text{As(V)}$  was either in monovalent anion or in divalent anion through all the pH range investigated as following equation.

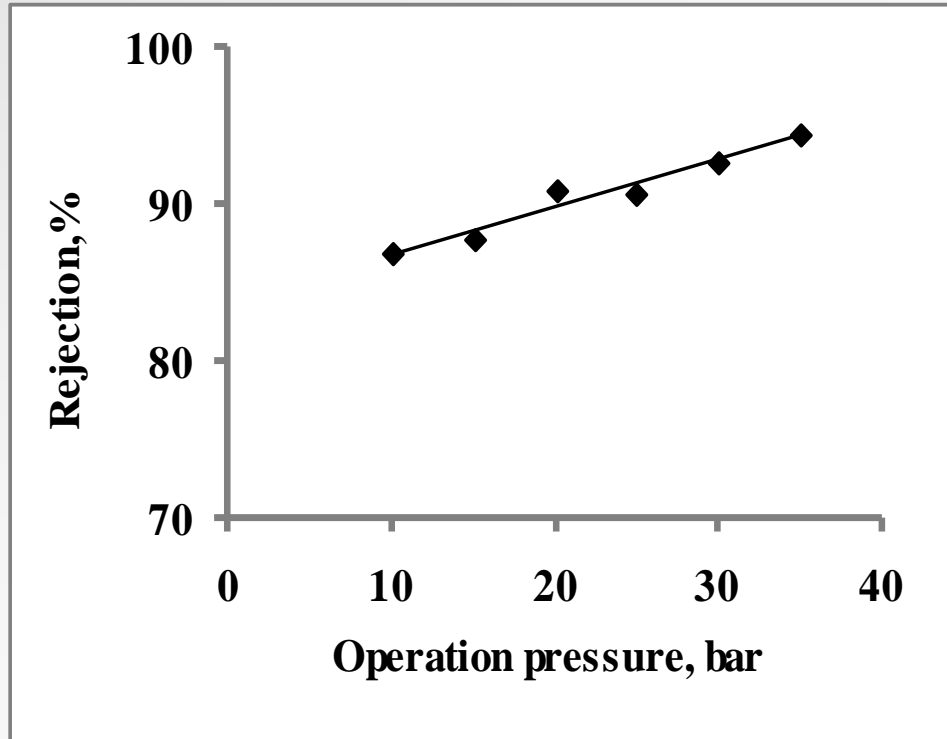
## *Effect of pH of feed water*



The values of the dissociation constant of arsenic acid are  $\text{pKa}_1=2.21$ ,  $\text{pKa}_2=6.95$  and  $\text{pKa}_3=11.49$ , respectively. Therefore, it can be inferred that arsenic predominantly exists as anionic species in aqueous solution at pH above 2.21.

Generally charged species are rejected to a greater extent by many RO membranes due to repulsive forces between membranes and anionic species

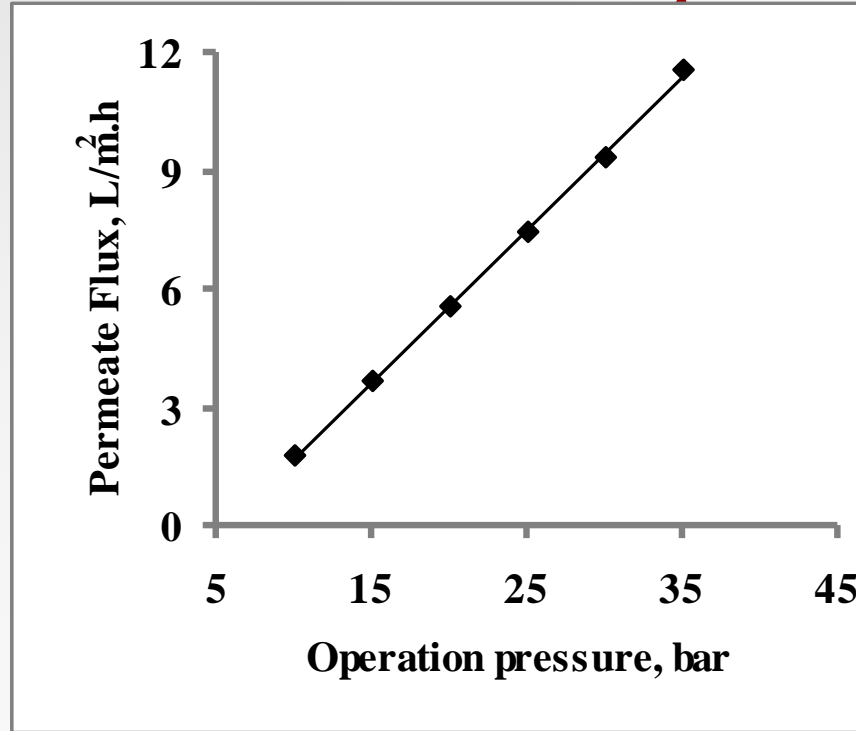
# *Effect of operating pressure*



Dependency of arsenic rejection on the operating pressure. Arsenic concentration of feed water: 200  $\mu\text{g/L}$ , pH of feed water: 4.1, temperature: 20  $^{\circ}\text{C}$ .

As expected, arsenic rejections increased with increasing operating pressure.

*In addition, increasing operating pressure also increased permeate flux*

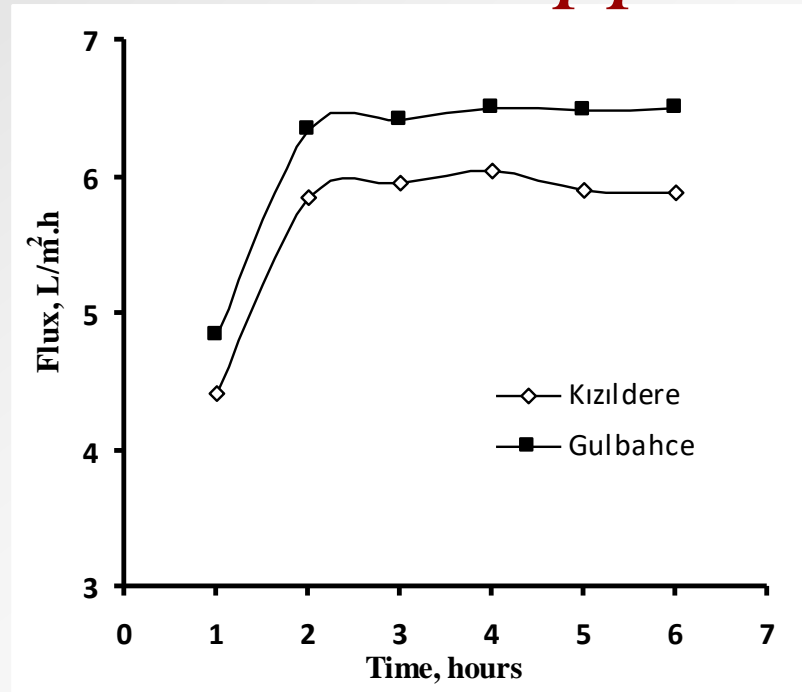


Dependency of permeate flux on the operating pressure. Arsenic concentration of feed water: 200 µg/L, pH of feed water:4.1, temperature: 20 °C

Permeate flux for SWHR membrane was found to be increasing. Because pressure is the driving force in RO system. Thus, higher operating pressure results in higher volume of permeate water.

Permeate flux is important because higher flux gives the short operation time, which reduces the cost of RO system.

# *Natural water application*



Permeate fluxes for natural samples (Arsenic concentrations of samples from Kızıldere and Gülbahçe were 2281 and 62  $\mu\text{g/L}$ , respectively, pH Kızıldere and Gulbahçe were 9.2 and 7.1, respectively, operating pressure: 35 bar, temperature: 20°C).

Permeate fluxes increased during initial 2 h, which may indicate that dynamic membrane conditions were not achieved at initial 2 h. Then, fluxes for both samples reached a steady state values.

Permeate fluxes for Kızıldere sample (4.4-6.0 L/m<sup>2</sup>.h) were found to be higher than those of Gülbahçe (4.8-6.5 L/m<sup>2</sup>.h). This result can be attributed to different chemical composition of the samples.



WHO and EPA require that arsenic concentration  
in drinking water is below 10  $\mu\text{g/L}$

	Kızıldere	Gülbahçe
Arsenate Rejection, %	99	97
Arsenate concentration, $\mu\text{g/L}$	18.2	1.5
Arsenite concentration, $\mu\text{g/L}$	4.6	0.6

For the present study, permeate concentration of Gulbahçe sample (2.1  $\mu\text{g/L}$ ) was lower than WHO and EPA recommendation limit.

However, permeate concentration of Kızıldere sample (22.8  $\mu\text{g/L}$ ) was higher than WHO and EPA limit. As a result, one-stage RO is sufficient for the sample from Gulbahçe, but Kızıldere sample needs additional step, such as dilution of RO permeate with other sources and/or double-pass, to reduce the arsenic concentration.

**1**

Removal of arsenate by RO depends greatly on the pH of the feed water. For studied membrane, it was found that negligible increase in the arsenate rejection was observed with increasing pH.

**2**

Removal of arsenate increases when increasing the operating pressure.

**CONCLUSION**

3

The rejection of arsenate does not depend upon the feed water concentration.

4

Two different natural (ground) water samples containing 2281 and 62  $\mu\text{g/L}$  of arsenic were treated by using RO with SWHR membrane and obtained results showed that RO could be efficiently used (with >95% rejection) for removal of arsenic from groundwaters.

**CONCLUSION**

# Future Work

The objective of future work was to investigate the removal of arsenic from water by RO with hybrid processes.

The proposed membrane-based hybrid process integrates in one step sorption efficiency of adsorbent like red mud with membrane separation.

# Acknowledgment



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