Membrane Distillation Process for Pure Water and Removal of Arsenic

M. Sc. thesis for the International Master's Program in
Applied Environmental Measurement Techniques

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Abstract

Safe drinking water is very important for human beings. Human life has been under threat in many parts of the world because of high arsenic contamination in ground water. Arsenic is tasteless, colourless and odourless even if its concentration is very high in water. Health effects start to emerge after a long time use of arsenic contaminated water making the problem more serious. So many methods have been tried to get rid of arsenic problem. But these methods have been showing complexities and inefficiency resulting from use of chemicals, careful control of pH, sludge handling, bacteriological growth, requirement of expertise for proper operation etc. Moreover, implementation of a technique or method only for removal of arsenic is not feasible in most cases. The HVR house-hold water purifier, which is based on membrane distillation process, is an effective tool for production of pure drinking water. It can effectively remove all non-volatile impurities including arsenic from water.

In this thesis work, theoretical studies on membrane distillation process were done. Different arsenic removal methods and there comparison with HVR water purifier were investigated. Experiments were done on the HVR water purifier to see its impurities removal capacity. Results were quite satisfactory which justify the effectiveness of the membrane distillation process and the purifier for safe drinking water production.

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1. Introduction

Membrane distillation (MD) is a process in which a liquid (such as water) is separated from impurities by heating and evaporating the liquid and allowing the vapour to pass through a micro-porous hydrophobic membrane. Then the vapours are allowed to condense into liquid by cooling in the other side of the membranes. The membrane pores are sufficiently small that capillary forces prevent direct mixing of the phases on either side of the membrane. The vapour pressure difference across the membrane caused by the corresponding temperature difference provides the driving force that causes diffusion of vapours through the membrane pores.

Membrane distillation process can be used for efficient purification of drinking water, which can remove all sorts of non-volatiles. Currently, there is no commercial product available in the market, which is based on the membrane distillation process. HVR Water Purification AB is a Stockholm based company, which has commercialized a house-hold level drinking water purifier. The purifier is based on membrane distillation process. The purifier has been proved to be very efficient in removing all sorts of non-volatiles from drinking water including arsenic. This purifier can be an effective tool for efficient removal of arsenic from arsenic contaminated ground water. This purifier offers a number of advantages over other impurities and arsenic removal process.

The objective of the project were to make a theoretical study on the membrane distillation process, to study arsenic removal methods used in Bangladesh and to compare them with the HVR water purifier, to conduct experiments on the HVR purifier, and to make a feasibility study of it. Project activities were in Sweden and Bangladesh.

2. The membrane distillation process

In a membrane distillation process, a heated, aqueous feed solution is brought into contact with one side (feed side) of a hydrophobic, micro porous membrane. The hydrophobic nature of the membrane prevents penetration of the aqueous solution into the pores, resulting in a vapour-liquid interface at each pore entrance.

Fig. 1 shows a cross sectional view of a hydrophobic membrane with straight cylindrical pores in contact with an aqueous solution to illustrate how the vapour-liquid interfaces are supported at the pore openings.
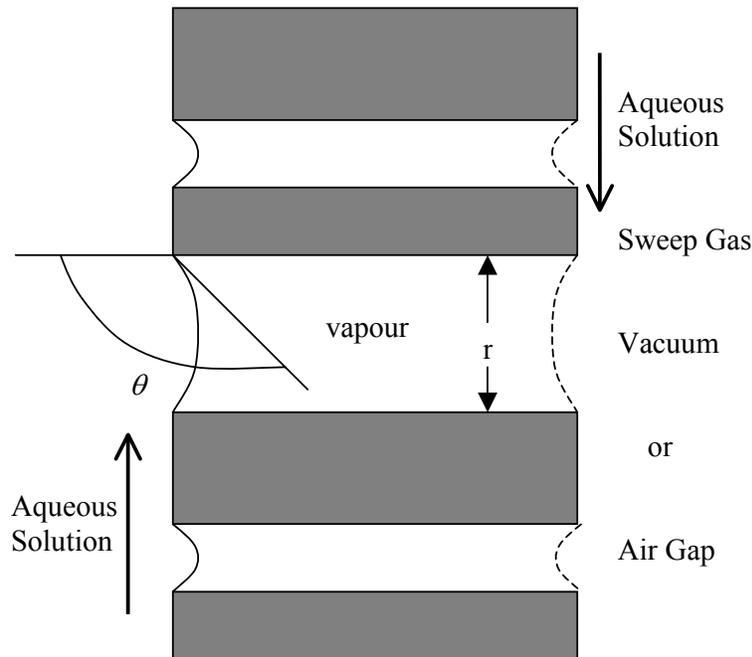
Figure 1. Vapour-liquid interface in MD

Various types of methods may be employed to impose a vapour pressure difference across the membrane to drive the flux. There are mainly 4 configurations of the MD process, which are mainly dependent on how the condensing surfaces are separated from the membrane. They are:

(i) DCMD (Direct Contact Membrane Distillation): The permeate side of the membrane may consist of a condensing fluid in direct contact with the membrane (see Fig. 2(i)).

(ii) AGMD (Air Gap Membrane Distillation): The condensing surface is separated from membrane by an air gap (see Fig. 2(ii)).

(iii) SGMD (Sweeping Gas Membrane Distillation): The condensing surface is separated from membrane by a sweeping gas (see Fig. 2(iii)).

(iv) VMD (Vacuum Membrane Distillation): The condensing surface is separated from membrane by a vacuum (see Fig. 2(iv)).
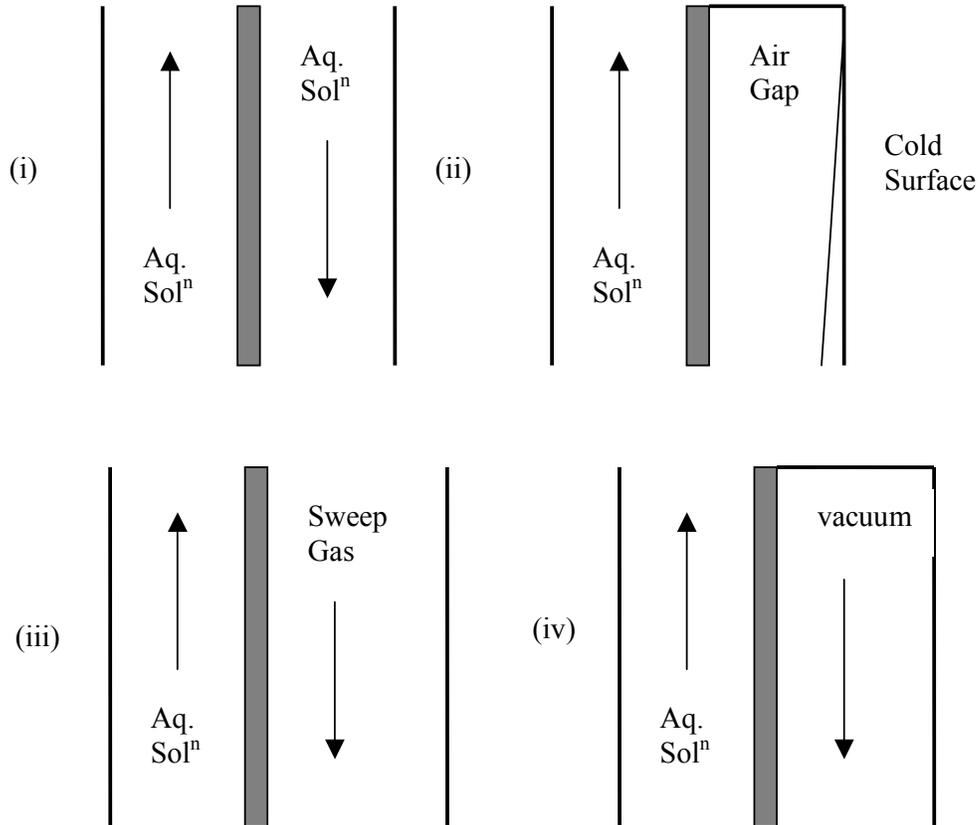
Figure 2. Types of MD process: (i) DCMD; (ii) AGMD; (iii) SGMD; (iv) VMD.

The membrane distillation process is based on the following conditions of parameters:
  (1) The membrane should be porous.
  (2) The membrane should not be wetted by the process liquids.
  (3) No capillary condensation should take place inside the pores of the membrane.
  (4) The membrane must not alter the vapour-liquid equilibrium of the different components in the process liquids.
  (5) At least one side of the liquid should be in direct contact with the process liquid (see article 4).
  (6) For each component the driving force of this membrane operation is a partial pressure gradient in the vapour phase.

The advantages of membrane distillation process over other prominent separation process are:
  (1) 100% (theoretical) removal of ions, macromolecules, colloids, cells, and other non-volatiles.
  (2) Lower operating temperature than the conventional distillation.
  (3) Lower operating pressure than the conventional pressure-driven membrane separation processes.
  (4) Reduced chemical interaction between membrane membranes and process solution.
  (5) Less membrane mechanical requirement in terms of pressure and heat sustaining capabilities.
  (6) Reduced vapour spaces compared to conventional distillation process.
The advantages of membrane distillation over some other membrane separation process are discussed in the article 7.

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3. The air gap membrane distillation (AGMD) process

Among the different membrane distillation processes the air gap membrane distillation (AGMD) is the main focus in this thesis work.
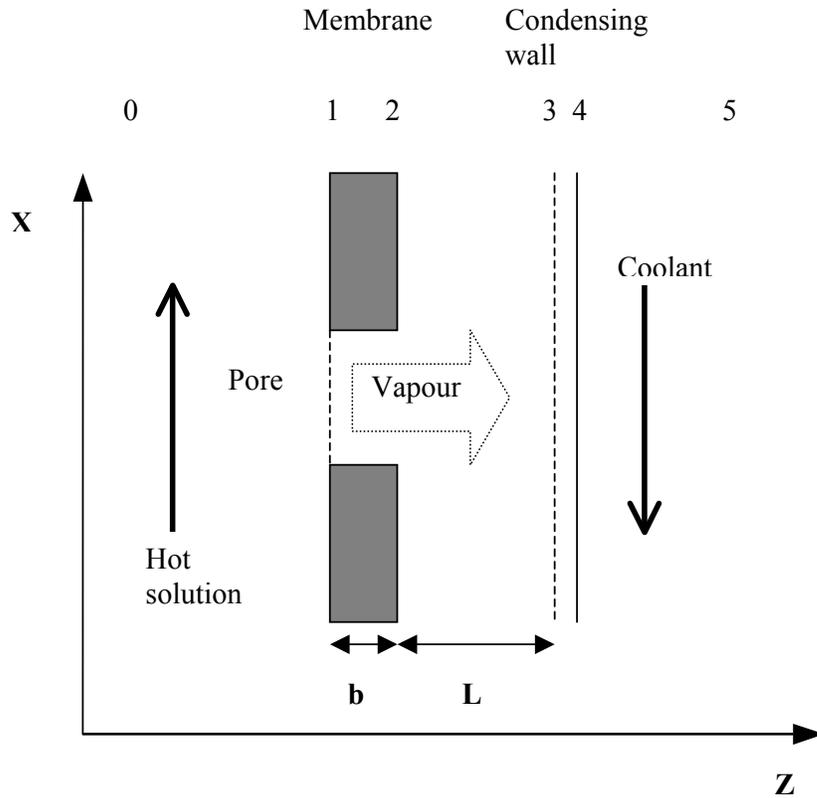
Figure 3. Schematic representation of the membrane distillation module.

The figure shows the air gap membrane distillation system.
"0-1": a flow channel for the hot solution
"1-2": highly porous membrane
"2-3": an air gap
"3-4": a thin condensate layer
"4-5": a channel for the coolant

The mechanism is explained in the following:
(1) Heat transfer from the bulk to the membrane surface at 1.
(2) Evaporation of water from the hot solution surface 1.
(3) Diffusion of vapour from the membrane, from 1 to 2.
(4) Diffusion of water vapour through the air gap, from membrane surface to the condensate film 3.
(5) Condensation of water vapour on the condensate film 3.
(6) Heat transfer from through the condensate film to the coolant, from 3 to 4.

4. Characteristics of the membrane

The membranes used in MD modules are highly hydrophobic polyolefine or fluoroplastic membranes.

For MD, the typical average pore diameter is in the range 0.1-5 μm [2]. Selection of pore size depends on two factors, the pore-size must be large enough to allow the required flux and the pores must be small enough to prevent liquid penetrating through the pores under operating conditions.

The porosity of the membrane is the value determined by dividing the total volume of pores by the total volume of the membrane.

Molar flux through a pore, N is related to the average pore size $<r^{\alpha}>$, the membrane porosity ϕ, membrane tortuosity τ, the membrane thickness b,

$$N \infty \frac{<r^{\alpha}> * \phi}{\tau b} \tag{A}$$

Equation (A) illustrates the importance (in terms of molar flux) of maximizing the membrane porosity and pore size while minimizing the transport path length through the membrane, τb, for MD systems, porosity can be the most influential factor affecting mass transfer rates across the membrane [1]. For pure water, molar flux in DCMD across a relatively thick membrane is proportional to $1/b$ as predicted by equation (A). However, flux becomes independent of membrane thickness at small thicknesses (that is, when $b << k_m/U$ where k_m is the thermal conductivity of the membrane and $1/U = 1/h_f + 1/h_p$, the combined feed and permeate boundary layer resistance). This phenomenon is a result of the increased conductive heat loss associated with thinner membranes ($Q_m \infty 1/b$) [1]. For aqueous solutions with significant osmotic pressures, the effect can become so pronounced that a negative flux(from permeate to feed) results if the membrane is too thin. Porosity can also become important in terms of reducing the amount of heat lost by conduction.

$$Q_m = h_m \Delta T_m$$
$$h_m = \phi h_{mg} + (1-\phi) h_{ms}$$

Where ϕ is the membrane porosity, and h_{mg} and h_{ms} represent the heat transfer coefficients of the gas (vapour) within the membrane pores and the solid membrane material, respectively. Since h_{mg} is generally an order of magnitude smaller than h_{ms}, the value of h_m can be minimized by maximizing the membrane porosity.

Table 1. Commercially available membrane commonly used in MD[1]:

Manufacturer	Trade name	Material	Thickness (μm)	Average Pore size (μm)	Void fraction
3M		PP	<100	a	a
Enka(Akzo)		PP(Tube)	150	0.43	0.70
		PP	140	0.10	0.75
		PP	100	0.20	0.75
Gore	Gore-Tex	PTFE[b]	<50	a	a
Gelman Inst. Co.	TF 200	PTFE[b]	60	0.20	0.60
	TF 450	PTFE[b]	60	0.45	0.60
	TF 1000	PTFE[b]	60	1.00	0.60
Hoechst-Celanese	Celgard 2400	PP	25	0.02	0.38
	Celgard X-20	PP (tube)	25	0.03	0.35
Millipore	Durapore	PVDF	110	0.45	0.75
	Durapore	PVDF	140	0.22	0.75

a = Membranes with a wide range of parameters have been used in MD
b = Membrane supposed on polymer fabric. Reported values of thickness and porosity do not include support.

5. Advantages of membrane distillation process over other membrane technologies

Some of the advantages of the MD process over other membrane technologies are as following:

Less vapour velocity
Conventional distillation column relies on high vapour velocities to provide intimate vapour-liquid contact. MD employs a hydrophobic micro porous membrane to support a vapour-liquid interface.

Less vapour space
The large vapour space required by a conventional distillation column is replaced in MD by the pore volume of a micro porous membrane, which is generally on the order of 100 μm thick [1].

Smaller equipment
In membrane distillation membrane surface per unit volume is high, thus the equipment can thus be made very dense [2].

Lower temperature
The required operating temperatures are much lower, because it is not necessary to heat the process liquids above their boiling temperatures. Feed temperatures in MD typically range from 60 to 90°C, although temperatures as low as 30°C have been used [1].Therefore low grade, waste and/or alternative energy sources such as solar and geothermal energy can be coupled with MD systems for a cost efficient, energy efficient liquid separation system.

Less heat loss
Lower operating temperature combined with reduced equipment surface area results in less heat lost to the environment through the equipment surfaces.

Lower pressure
MD is safer, more efficient process than RO for removing ionic components and non-volatile organic compounds from water. Since MD is a thermally driven process, operating pressures are generally on the order of zero to a few hundred kPa, relatively low compared to pressure driven processes such as RO [1].

Higher rejection of impurities
Since MD operates on the principles of vapour-liquid equilibrium, 100% (theoretical) of ions, macromolecules, colloids, cells, and other non-volatile constituents are rejected; pressure driven process such as reverse osmosis (RO), ultra filtration (UF), micro filtration (MF) have not shown to achieve such high levels of rejection. When applied to desalination, a well designed MD system typically achieves water fluxes as high as 75 kg/ m^2.h, which is comparable to RO [1].

Less mechanical demands
Since MD operates at pressures significantly lower than those encountered in the pressure-driven processes, the mechanical demands (that is, resistance to compaction) on these micro porous membranes is greatly reduced [1].

More chemically resistant membrane
An advantage of MD over RO, UF, and MF arises from the minimal role that the membrane plays in the actual separation. In MD the membrane acts merely as a support for a vapour-liquid interface and does not distinguish between solution components on a chemical basis, nor does it act as a sieve. Therefore, MD membranes can be fabricated from chemically resistant polymers such as polytetrafluoroethylene (PTFE), polypropylene (PP), and ployvinylidenedifluoride (PVDF) [1].

Less fouling
Membrane fouling is less of a problem than in the other membrane separations because the pores are relatively large compared to the pores or diffusional pathways in other membrane separations because the pores are relatively large compared to the pores or diffusional pathways in RO or UF [1].

6. Theoretical model for mass and heat transport [2]
The assumption, that membrane distillation can be described as a process in which a hot condensable vapour is diffusing at steady state through a stagnant film of noncondesable gas to a cold surface where the vapour condenses, is the basis for the calculations.

The molar flux of a vapour diffusing at steady state through a stagnant air film is given by (see fig. 3),

$$N = -\frac{cD}{1-x}\frac{dx}{dz} \qquad (1)$$

Where, N is the molar flux, c is the molar concentration, and D is the diffusion coefficient for the water vapour-air mixture. Although the molar flux is only affected to a minor degree by

the simultaneous mass transfer, the rate of heat transfer is directly affected by the simultaneous mass transfer. The sensible heat, E, is made up of one term describing the conductive energy flux and one term describing the energy flux caused by diffusion.

$$E = -k\frac{dT}{dz} + NC_p(T - T_c) \tag{2}$$

Solving the differential equations (1) and (2), in the membrane region and in the air gap region, the mass and heat transport may be calculated for different membrane parameters and processes.

The coefficients for diffusion D, and the thermal conductivity k depend on both temperature and concentration. In order to simplify the calculations approximate expressions for D and k:

$$cD = 6.3 * 10^{-5}\sqrt{T} \tag{3}$$

$$k_{air} = 1.5 * 10^{-3}\sqrt{T} \tag{4}$$

The effective coefficient for the membrane region can be written as,

$$k = k_{air} * \phi + k_{membrane}(1 - \phi) \tag{5}$$

If these equations are substituted into equations (1) and (2) the molar and energy flux in the membrane region may be expressed as,

$$N = \phi * \frac{6.3 * 10^{-5}\sqrt{T}}{1 - x}\frac{dx}{dz} \tag{6}$$

$$E = -\{1.5 * 10^{-3}\sqrt{T} * \phi + 0.22(1 - \phi)\} * \frac{dT}{dz} + 1.86 * 10^3 N(T - T_c) \tag{7}$$

and in the air gap region as,

$$N = -\frac{6.3 * 10^{-5}\sqrt{T}}{1 - x}\frac{dx}{dz} \tag{8}$$

$$E = -\{1.5 * 10^{-3}\sqrt{T} * \phi + 0.22(1 - \phi) * \frac{dT}{dz} + 1.86 * 10^3 N(T - T_c)\} \tag{9}$$

The above equations may not yield the exact analytical solution. But N and E can be obtained from the following good approximations,

$$N = 6.3 * 10^{-5}\frac{1}{b/(\phi * \sqrt{T_h}) + L/\sqrt{T_c}}\ln(\frac{1 - x_c}{1 - x_h}) \tag{10}$$

$$E = \frac{1.5*10^{-3}(T_h - T_c)}{(b/\gamma * \phi * \sqrt{T_h}) + L/\sqrt{T_c}} * \{1 + 1.14 * \ln(\frac{1-x_c}{1-x_h}) * \frac{b/(\gamma * \phi * \sqrt{T_h})}{(\frac{b}{\phi\sqrt{T_h}}) + (L/\sqrt{T_c})}\} \qquad (11)$$

where, $\gamma = k_{membrane}/(\phi * k_{air})$ and k should be evaluated at T_h.

The mass flux equation can be obtained from the molar flux equation. It can be used to calculate the theoretical pure water production rate.

$$Q = 4.1*10^{-3} * \frac{1}{b/(\phi * \sqrt{T_h}) + L/\sqrt{T_c}} * \ln(\frac{1-x_c}{1-x_h}) \qquad (12)$$

Equation (12) is used in the theoretical calculations where, T_h and T_c is the average bulk temperature in hot and cold sides,

$$T_h = \frac{T_{h,in} + T_{h,out}}{2}$$

$$T_c = \frac{T_{c,in} + T_{c,out}}{2}$$

7. Graphical representation of heat and mass transfer in AGMD

The rate of evaporation or mass flux can be calculated from equation (12) for a number of different processes and membrane parameters.

In an air gap membrane distillation (AGMD) the diffusion path is the summation of the thickness of the membrane, b, and the length of the diffusion path in the air gap, L (see fig. 3).

The temperature of hot solution, T_h and the coolant, T_c can strongly influence the rate of evaporation.
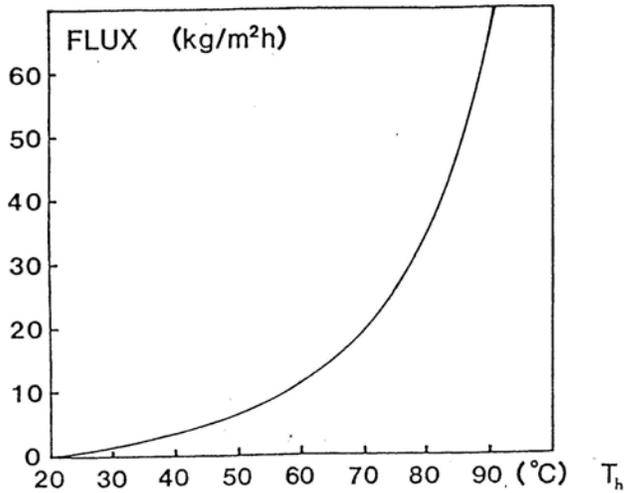
Figure 4. The mass flux as a temperature of the hot solution at $T_c = 20°C$, $b = 0.2$ mm, $\phi = 0.8$, $k_{PTFE} = 0.22$ W/m. K and L= 1 mm [2].

With the decrease in diffusion path, the rate of evaporation increases (see fig 5, 6). The increase is more pronounced as the temperature of hot solution, T_h increases (fig 5).

The vapour pressure increases as the temperature increases, which result in the increase of the driving force. That is why, the rate of evaporation increases if the temperature of the hot solution is increased (see fig 4), even if, the temperature difference, $\Delta T = T_h - T_c$, remains constant (see fig. 5).
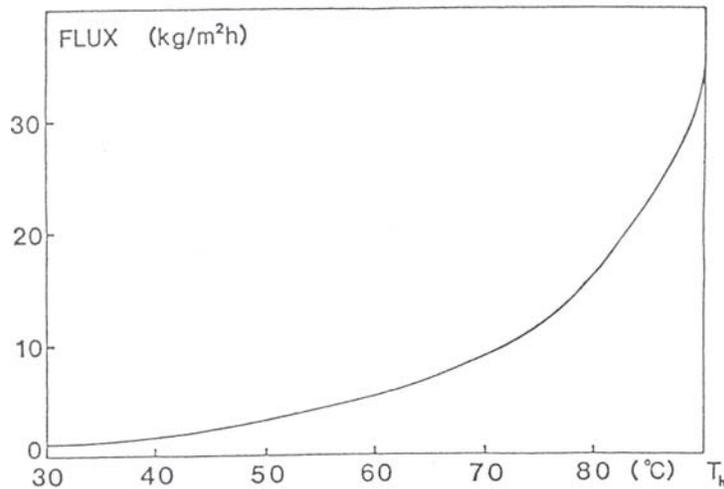
Figure 5. The flux as a function of the temperature of the hot solution at the constant temperature difference, $\Delta T = 10\ °C$ at $b = 0.2$ mm, $\phi = 0.8$, $k_{PTFE} = 0.22$ W/m. K and L=1 mm [2].

If the hot solution temperature remains constant, evaporation increase with the increase in temperature difference between hot and cold side but the rate of the evaporation decreases (see fig. 6).
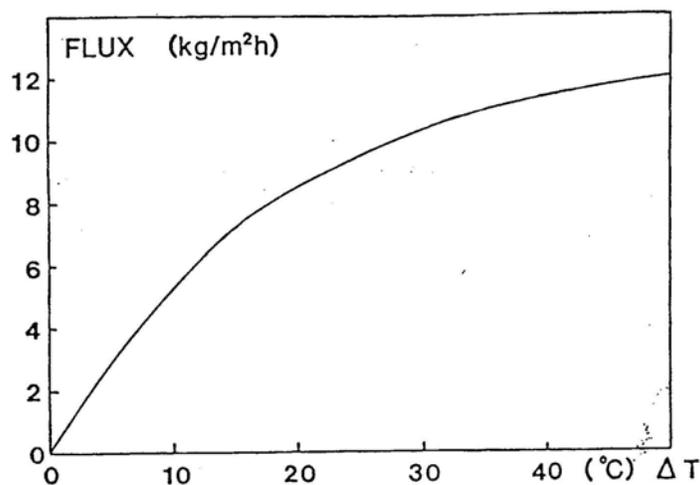
Figure 6. The mass flux as a function of the temperature difference, $\Delta T = T_h - T_c$ at $T_h = 60°C$, $b = 0.2$ mm, $\phi = 0.8$, $k_{PTFE} = 0.22$ W/m. K and L=1 mm [2].

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With the decrease of air gap the flux increases (see fig. 7, 8, and 9).
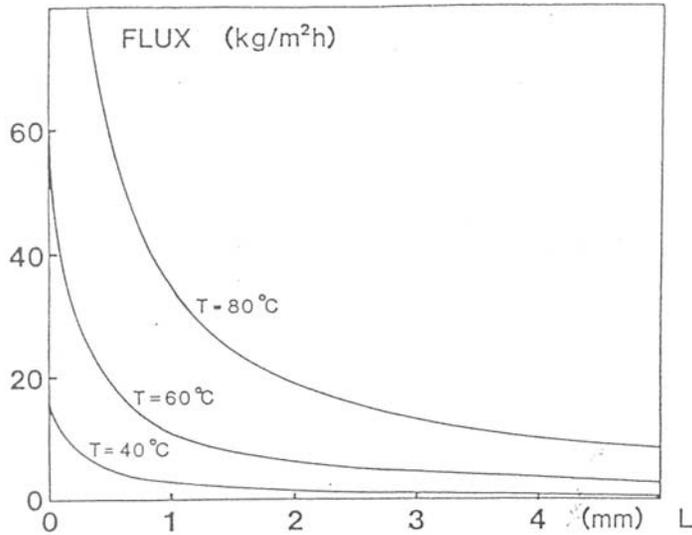
Figure 7. The mass flux as a function of the length of the diffusion path, L in the air gap at $T_h = 60°C, T_c = 20°C, b = 0.2$ mm, $\phi = 0.8$, $k_{PTFE} = 0.22$ W/m. K [2].

Flux decreases with the increase of membrane thickness (see fig 8). As shown in the equation (12), for the calculation of mass flux in AGMD, the denominator consists of the "membrane term", $b/(\phi\sqrt{T_h})$, and the "air gap term", $L/\sqrt{T_c}$. The air gap term is much larger than the membrane term and hence can changes in L can have much more effects than changes in b (see fig. 8).
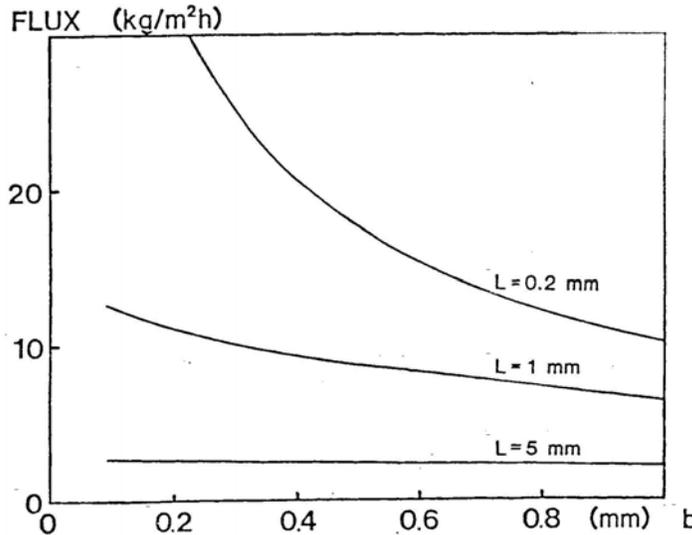
Figure 8. The mass flux as a function of the membrane thickness, b at $T_h = 60°C, T_c = 20°C$, $b = 0.2$ mm, $k_{PTFE} = 0.22$ W/m. K [2].

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Increase of porosity increases the flux (see fig. 9).
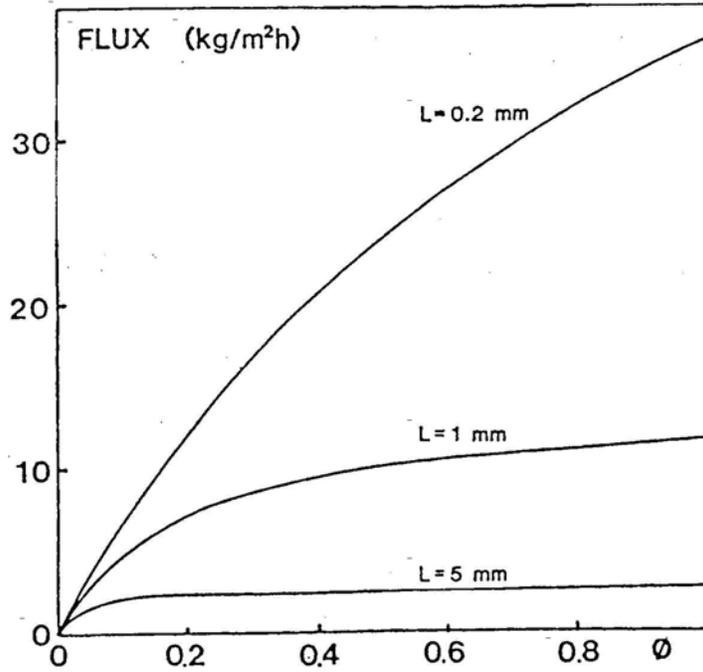
Figure 9. The mass flux as a function of the effective net pore area at $T_h = 60\,^\circ\text{C}$, $T_c = 20\,^\circ\text{C}$, $b = 0.2$ mm, $k_{PTFE} = 0.22$ W/m. K [2].

8. Factors affecting heat and mass transfer in MD
8.1. Membrane wetting
The relationship between a membrane's largest allowable pore size and operating conditions is given by the Laplace (Cantor) equation [1]:

$$P_{liquid} - P_{vapor} = \Delta P_{int\,erface} < \Delta P_{entry} = \frac{-2B\gamma_L \cos\theta}{r_{max}} \tag{B}$$

where γ_L is the liquid surface tension, θ is the liquid-solid contact angle, r_{max} is the largest pore radius, and B is a geometric factor determined by pore structure.

Even though equation (B) is not implicit in operating temperature and process solution composition, these parameters can have significant effects on the liquid-solid contact angle and the liquid surface tension. These affects must be taken into consideration during selection of membrane. In general, the contact angle θ must be greater than 90º for the system to be used in MD. For a typical water-hydrophobic membrane contact angle of 130º, the penetration pressure of a cylindrical ($B=1$) pore of diameter 1μm is only 185 kPa (27 psi) [1].

The presence of strong surfactants can greatly reduce the value of $\gamma_L \cos\theta$, therefore care must be taken to prevent contamination of process equipment and process solutions with detergents or other surfacing agents.

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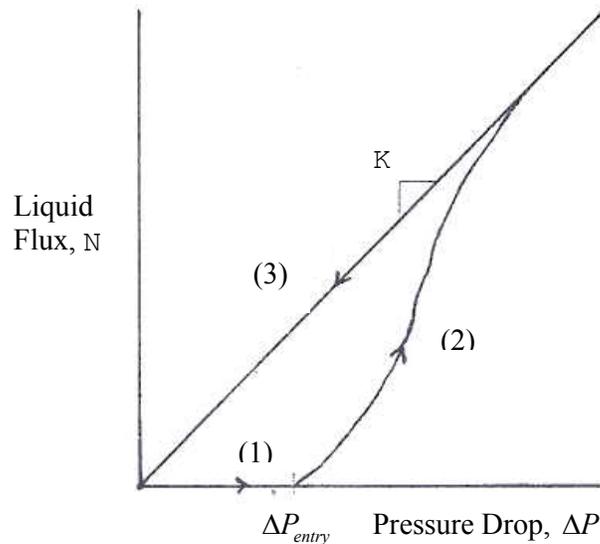
Figure 10. Characteristic graph of liquid flux versus pressure drop in porous hydrophobic membranes [1].

If $\Delta P_{int\,erface}$ exceeds ΔP_{entry} the liquid can penetrate into and through the membrane pores which means the membrane is wetted and needs to be completely dried and cleaned before it can be used once again as a support for vapour-liquid interface.

As the pressure is increased no liquid can flow through the membrane until ΔP_{entry} is exceeded. At this point liquid begins to penetrate the largest pores and is able to pass through the membrane. As the pressure is increased further, more and more pores and become flooded and the liquid flux across the membrane obeys Darcy's law ($N = K\Delta P$), and decreasing the pressure results in a linear decrease in flux. It is evident from the figure that once that once the membrane is wetted the decrease in the hydrostatic pressure on the membrane will not restore the membrane to its un-wetted state. Deterioration of permeate quality increases with the increase in number of wetted pores. Therefore, the goal of any MD system design should be to completely prevent pore wetting.

8.2. Flux decay

One hypothesis made by Franken et al(1987) that flux decay was caused by membrane wetting [1].They hypothesized that as time progressed, more and more pores become wetted, which results in back flow of permeate to the feed. They validated their hypothesis by varying the hydrostatic pressure of the permeate and noting that as the permeate pressure increased the flux decreased. But Franken's explanation is not sufficient for the case where the hydrostatic pressure of the feed is higher than that of the permeate, in which case pore wetting leads to enhanced flux (with reduced selectivity or rejection) as described in the membrane wetting section.

Another mechanism for flux decay is membrane fouling, which has not been thoroughly examined in the MD process. There are several types of fouling such as (1) biological fouling,(2) scaling, (3) particulate or colloidal species. Biological fouling or growth of bacteria on the membrane surface is easily avoided with UV treatment or the addition of the appropriate chemicals to process liquids. Scaling can build up on the membrane surface if the concentration of minerals or salts becomes too high. Scaling can lead to both pore clogging and pore wetting, but has only been observed with saturated process solutions. Particulate or

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colloidal species in the process liquids can lead to membrane fouling as well. These particles or colloids tend to become trapped at the membrane-liquid interface by interfacial tension forces.

There is a lot of theoretical and experimental work to be done in this area of flux decay [2].

8.3. Resistance to heat transfer
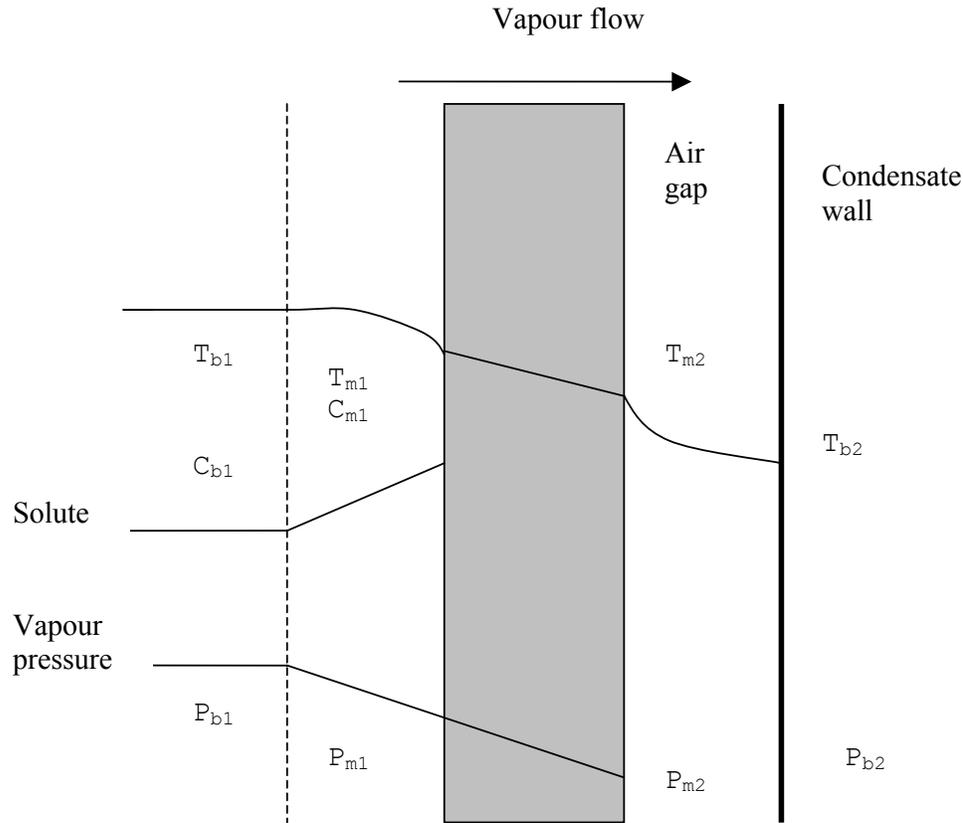
Figure 11. Profile diagram of air gap membrane distillation

As a large quantity of heat has be supplied to the surface of the membrane to vaporize the liquid, heat transfer across the boundary layers is often the rate limiting step for mass transfer in MD. A commonly used measure of the magnitudes of the boundary layer resistances relative to the total heat transfer resistance of the system is given by the temperature polarization coefficient,

$$\Theta = \frac{T_{m1} - T_{m2}}{T_{b1} - T_{b2}}$$

where, T_{m1} is the interfacial feed temperature, T_{m2} is the interfacial permeate temperature, T_{b1} is the bulk feed temperature, and T_{b2} is the bulk permeate temperature. The value of Θ approaches unity for well-designed systems that are mass transfer limited, and it approaches zero for poorly designed systems that are limited by heat transfer through the boundary layers. Temperature polarization coefficient varies between 0.2 and 0.9 [5].

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Temperature polarization can have a significant affect on the flux. Low feed stirring rates or low feed velocities, which result in low Reynolds numbers, can reduce the flux by orders of magnitude relative to the high Reynolds number case [5].

8.4. Heat loss across the membranes
There are two important mechanisms of heat transfer across the membrane: (1) conduction through the membrane material and the vapour within the membrane pores, and (2) transfer of the latent heat of vaporization associated with the mass flux.

The rate of heat transfer across the membrane is given by,
$Q_v = N\Delta H_v$, where N is the molar flux and ΔH_v is the molar latent heat of vaporization.
Conduction of heat across the membrane,
$Q_m = h_m \Delta T_m$, where $h_m = \phi h_{mg} + (1-\phi)h_{ms}$;

$$\phi = \text{membrane porosity,}$$
$$h_{mg} = \text{heat transfer coefficient of gas within membrane,}$$
$$h_{ms} = \text{heat transfer coefficient of membrane solid materials.}$$
$$\Delta T_m = \text{temperature drop between the both side of the membrane.}$$
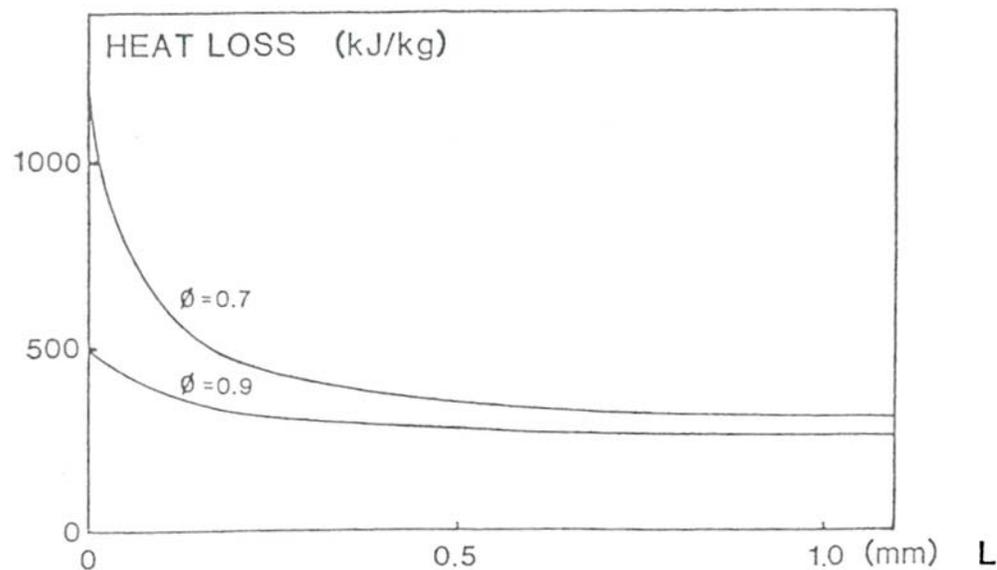
Figure 12. The heat loss as a function of the length of the diffusion path in the air gap at
$T_h = 60\,°C, T_c = 20\,°C, \ b = 0.2 \text{ mm}, k_{PTFE} = 0.22$ W/m. K [2].

Both investigators recommended using thicker membranes to decrease the problems caused by heat loss [1]. But it is surprising that the heat loss is diminished when the thickness of the membrane is reduced (see fig. 13). This is due to the large increase of the mass flux when the membrane thickness is decreased.
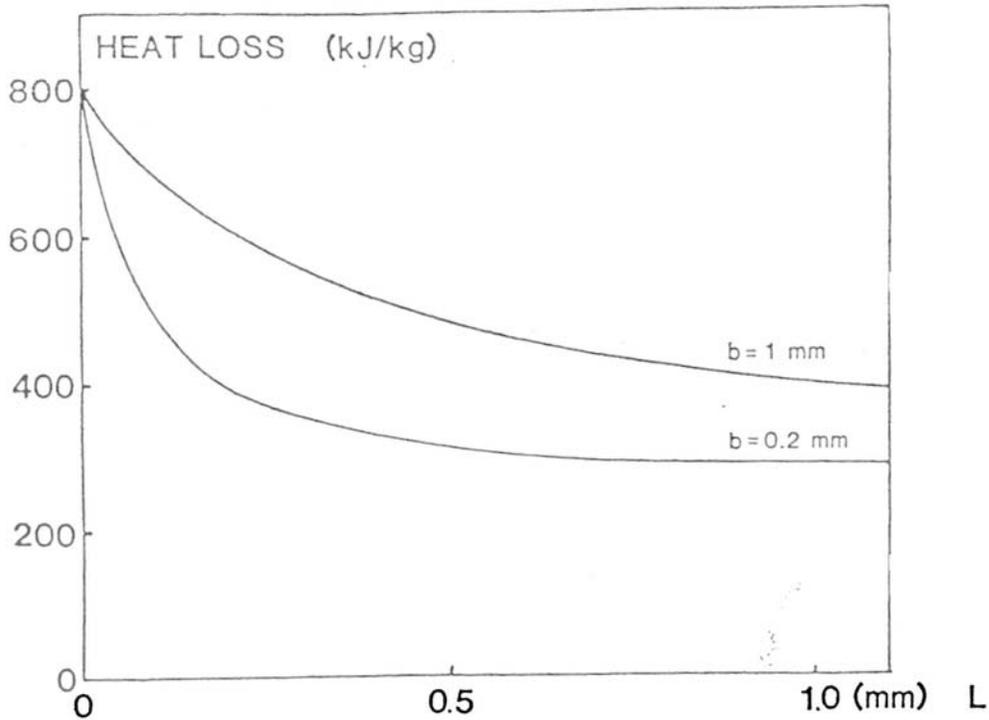
Figure 13. The heat loss as a function of the length of the diffusion path in the air gap at $T_h = 60\,°C, T_c = 20\,°C,\; k_{PTFE} = 0.22$ W/m. K [2].
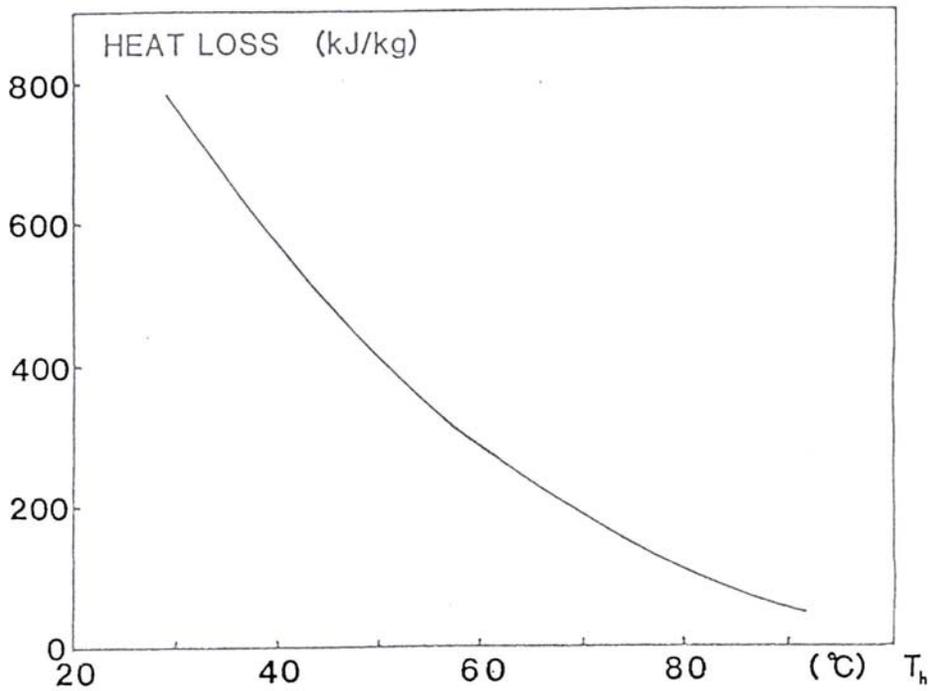
Figure 14. The heat loss as a function of the temperature of the hot solution at $T_c = 20\,°C$, $b = 0.2$ mm, $k_{PTFE} = 0.22$ W/m. K (ref. 2) and $L = 1$ mm [2].

Fane et al.(1987) found that 20 to 50% of the total heat transferred in the MD process is lost by conduction. Gostoli et al (1987) and Findley (1969) showed that if heat conduction across

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the membrane is too great, flux can be diminished and even reversed(from permeate to feed)[1].

Heat transfer coefficients for polymeric materials and vapours are readily available from the thermal conductivities [1].

$h = \dfrac{k^T}{\delta}$, where k^T is the thermal conductivity, and δ is the membrane thickness.

Then thermal conductivities for water and air are respectively [1],

$k^T_{H_2O} = 2.72*10^{-3} + 5.71*10^{-5}T$,

$k^T_{Air} = 2.72*10^{-3} + 7.77*10^{-5}T$

where k^T is in W/m.K and T is in K. The thermal conductivities of polymers are dependent upon both temperature and the degree of crystallinity [1]. As a result, the reported values of can vary, such as for polypropylene 0.15-0.20 W/m.K, for PVDF and PTFE 0.22-0.45 W/m.K [1]. So it is easily understandable that water heat conduction through the pores is less compared to the heat loss through membrane materials. Therefore, heat lost by conduction through the membrane can be reduced by increasing the membrane porosity [1].

9. Extent of arsenic problem
Naturally occurring arsenic in groundwater has become a global problem. In the sedimentary aquifers of the Bengal Delta Plan(BDP) in Bangladesh and neighboring Indian state of West Bengal, As is mobilized in groundwater by natural processes, which is an issue of major environmental health concern[5]. Widespread exploitation of groundwater from the BDP aquifer system, which began in the 1970's, currently supplies drinking water for a population of more than 150 million. Elevated As concentration in groundwater is however is not unique to the BDP, but has been reported in several other countries, including Argentina, Canada, Chile, China, Hungary, Japan, Mexico, New Zealand, Taiwan, Thailand and the United states [5].

The recent decision by US Environmental Protection Agency that the Maximum Contamination Level (MCL) for As in drinking water will be lowered from 50 µg/l to 10 µg/l reflects reevaluation of health risks associated with ingestion of this metalloid (NRC, 1999) [6].

Currently, Bangladesh employs a drinking water standard of 50 ppb (or µg/l) which is based on some earlier guidelines established by the World Health Organization (WHO, 1993). Many countries including Bangladesh have either kept this as the national standard or as an interim target, with the realization that significant impacts may also exist at lower concentrations in the 10-50 ppb range. It should also be noted that based on scientific information available on health impacts of arsenic contaminated water, a value lower than 10 ppb is advisable (WHO, 1999). However, such a value is still considered provisional in part due to the lack of widely acceptable analytical techniques. Existing scientific evidence should be weighed carefully and the drinking water standard for arsenic should be revised downwards [3]. Scientific research has to be emphasized to reduce uncertainty, with due consideration to local conditions. Drinking water standards have to be modified in view of the scientific research [3].
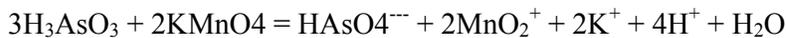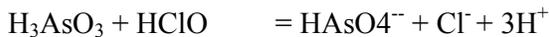
10. Arsenic removal methods or techniques
10.1. Oxidation
Air Oxidation

Arsenic is present in groundwater in As(III) and As(IV) forms in different proportions. Most treatment methods are effective in removing arsenic in pentavalent form and hence include an oxidation step as pretreatment to convert arsenite to arsenate. Arsenite can be oxidized by oxygen, ozone, free chlorine, hypochlorite, permanganate, hydrogen peroxide but atmospheric oxygen, hypochloride and permanganate are commonly used for oxidation in developing countries.

Chemical Oxidation

The processes remove only a part of arsenic.

$$H_3AsO_3 + {}^1\!/_2\, O_2 \quad = H_2AsO_4^- + 2H^+$$

$$H_3AsO_3 + HClO \quad = HAsO4^{--} + Cl^- + 3H^+$$

$$3H_3AsO_3 + 2KMnO4 = HAsO4^{---} + 2MnO_2^+ + 2K^+ + 4H^+ + H_2O$$

Passive Sedimentation

Oxidation of water during collection and subsequent storage in houses may cause a reduction in arsenic concentration in stored water. Arsenic reduction by plain sedimentation appears to be dependent on water quality particularly the presence of precipitating iron in water. Most studies showed a reduction of zero to 25% of the initial concentration of arsenic in groundwater. In rapid assessment of technologies passive sedimentation failed to desired level of 50% µg/l in any well [3].

10.2. Co-precipitation and adsorption processes

Water treatment with coagulants such as aluminum alum, $Al_2(SO_4)_3.18H_2O$, ferric chloride, $FeCl_3$ and ferric sulfate, $Fe_2(SO_4)_3.7H_2O$ are effective in removing arsenic from water. Ferric salts have been found to be more effective in removing arsenic than alum on a weight basis and effective over a wider range of pH. In alum coagulation, the removal is most effective in the pH range 7.2-7.5 and iron coagulation, efficient removal is achieved in a wider pH range usually between 6.0 and 8.5 [3].

As trivalent arsenic occurs in non-ionized form, it is not subject to significant removal. Oxidation of As(III) to As(IV) is thus required as a pretreatment for efficient removal.

Alum dissolution:
$$Al_2(SO_4)_3.18H_2O = 2Al^{++} + 3SO_4^{--} + 18H_2O$$
Alum precipitation (acidic):
$$2Al^{++} + 6H_2O = 2Al(OH)_3 + 6H^+$$
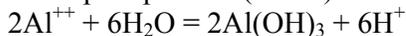
Co-precipitation (Non-stoichiometric, non-defined product):
$$H_2AsO_4^- + Al(OH)_3 = Al\text{-}As(complex) + Other\ products$$
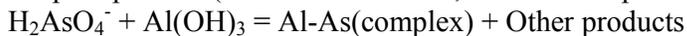
Arsenic is absorbed on aluminum hydroxide flocculates as Al-As complex removed by sedimentation.

10.3. Sorption techniques

Sorption media that are mostly used to remove arsenic are activated alumina, activated carbon, iron and manganese coated sand, kaolinite clay, hydrated ferric oxide, activated

bauxite, titanium oxide, silicium oxide and many natural and synthetic media. The efficiency of all sorptive media depends on the use of oxidizing agent as aids to sorption of arsenic. Saturation (the point when the efficiency in removing the desired impurities become zero) of media by different contaminants and components of water takes place at different times of operation depending on the specific sorption affinity of the medium to the given component.

10.4. Ion exchange

The process is similar to that of activated alumina, just the medium is a synthetic resin of more well defined ion exchange capacity. The process is normally used for removal of specific undesirable cation or anion from water. As the resin becomes exhausted, it needs to be regenerated. The arsenic exchange and regeneration equations with common salt solution as regeneration agent are as follows:

Arsenic exchange:
$$2\mathbf{R}\text{-Cl} + \text{HAsO}_4^{--} = \mathbf{R}_2\text{HAsO}_2 + 2\text{Cl}^-$$

Regeneration:
$$\mathbf{R}_2\text{HAsO}_4 + 2\text{N}^+ + 2\text{Cl}^- = 2\mathbf{R}\text{-Cl} + \text{HAsO}_4^{--} + 2\text{Na}^+$$
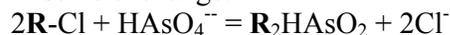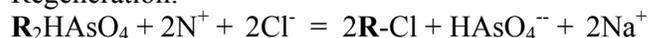Here $\mathbf{R}$ stands for ion exchange resin:

The arsenic removal capacity is dependent on sulfate and nitrate contents of raw water as sulfate and nitrate are exchanged before arsenic. The ion exchange process in less dependent on pH of water. The efficiency of ion exchange process is radically improved by pre-oxidation of As(III) to As(V) but the excess of oxidant often needs to be removed before the ion exchange in order to avoid the damage of sensitive resins.

10.5. Membrane techniques

A reverse osmosis and a combined nanofiltration and reverse osmosis process for the treatment of arsenic were tested in Bangladesh. Those are in the experimental phases, have not hit the market.

MRT-1000 and Reid System Ltd.

A household reverse osmosis water dispenser MRT-1000 are manufactured by B & T Science Co. Limited, Taiwan. This system was tested at BUET and showed a arsenic(III) removal efficiency more than 80% [3].

Low-pressure nanofiltration and reverse osmosis

Oh et al.(2000) applied reverse osmosis and nanofiltration membrane processes for the treatment of arsenic contaminated water applying low pressure by bicycle pump. A nanofiltration membrane process coupled with a bicycle pump could be operated under condition of low recovery and low pressure range from 0.2 to 0.7 MPa. Arsenite was found to have lower rejection than arsenate in ionized forms and hence water containing higher arsenite requires pre-oxidation for reduction of total arsenic to an acceptable level [3]. In many arsenic affected areas, arsenic removal may be the only option in the absence of an alternative safe source of water supply [3].

11. Acceptability of an arsenic removal technology

It showed that arsenic removal is just one small element in the production of a successful and acceptable technology. Many would argue that, given that the technologies are mainly designed to be a short/medium solution, bacteriological contamination is potentially a far more serious and immediate hazard to health than drinking untreated water. There are recommendations made for each of the technologies where there are problems with bacteriological contamination. These principally concern regular cleaning with hypochlorite

to minimize contamination and a hygiene education program as a part of the distribution of technologies. This adds further stages to the water treatment process and potentially further reduce acceptability of the technologies to users [3].

There is some rooms for a trade off between cost and performance. However, lower cost should not be made the priority if it results in a technology which is unacceptable to users, does not produce sufficient water and which may deliver water of a lower quality and containing faecal coliforms [3].

In Bangladesh arsenic removal technologies will be scored based upon the established criteria as to their suitability for use in Bangladesh. The screening will consider the following aspects of the treatment system [3]:
A. Treatment/process – including chemical/physical mechanisms, expected treatment performance, potential limitations on performance, process chemical requirements, power requirements, flow dynamics, hardware requirements, servicing requirements, media regeneration and waste disposal requirements.

B. Social/cultural compatibility – including feasibility of distributing the equipment and materials, ease of system use by women, and feasibility of local system maintenance.

C. Capital/operating costs – including installation/startup costs, operating and maintenance costs, and costs related to disposal of spent units and/or chemical wastes

12. The HVR water purifier
The membrane material is PTFE (Polytetrafluoroethylene) with a porosity of 80% and thickness of 0.2 mm. The length of air gap is 1 mm. There are two membranes used with an area of 42 cm * 24 cm. HVR developed different models of the household water purifier.
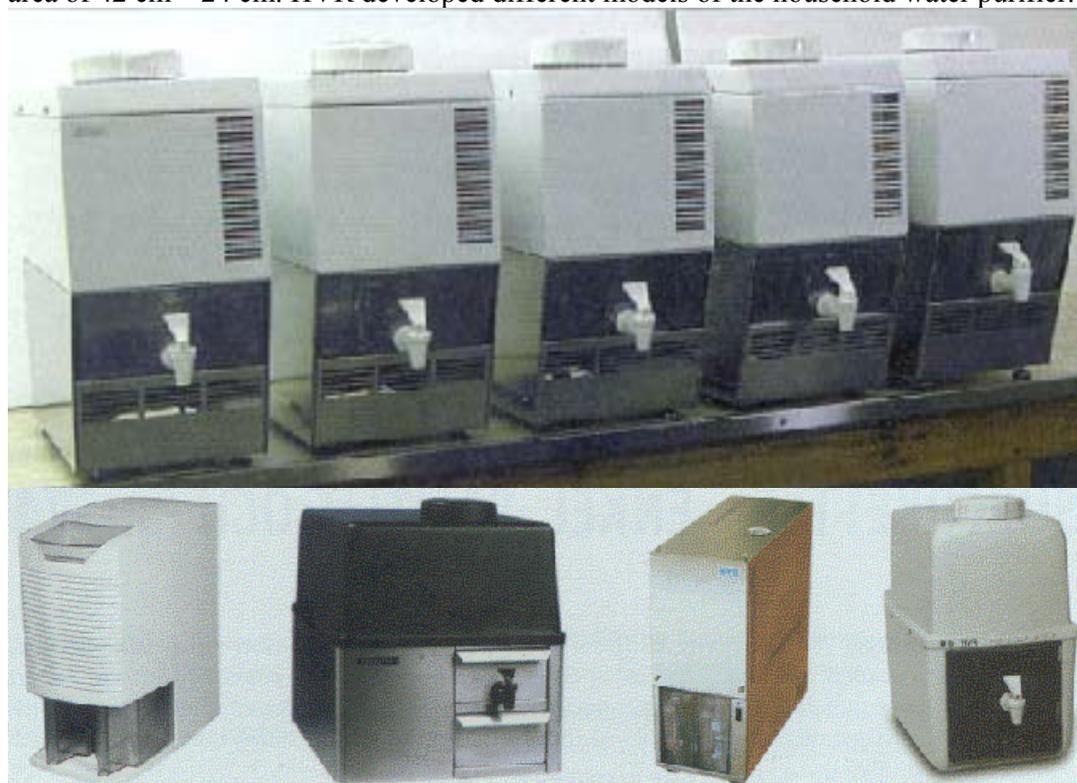
Figure 15. Some models of HVR water purifier

13. Experimental study on HVR purifier and the results

Figure 16. The lab unit of HVR water purifier (side view)

The procedure for operating the lab unit of the purifier was as follows:
1. To connect to electricity supply.
2. To connect to chill water supply.
3. To open the cap of the corrosion-free tank.
4. To pour approx. 4.5 to 4.8 l test feed water through fluid inlet.
5. To connect test vessels to permeate/ treated water outlet.
6. To set temperature of the heater at a temperature between 60-99°C.
7. Start the process by pressing the start button. Let the feed water heated for 15 min.
8. Start the chill water supply approx. 1.5- 2 l/min.
9. If the process is discontinued before approx. 1- 1.3 l permeate is produced, then press the stop button.

Figure 17. Schematic diagram showing the procedure of HVR water purifier
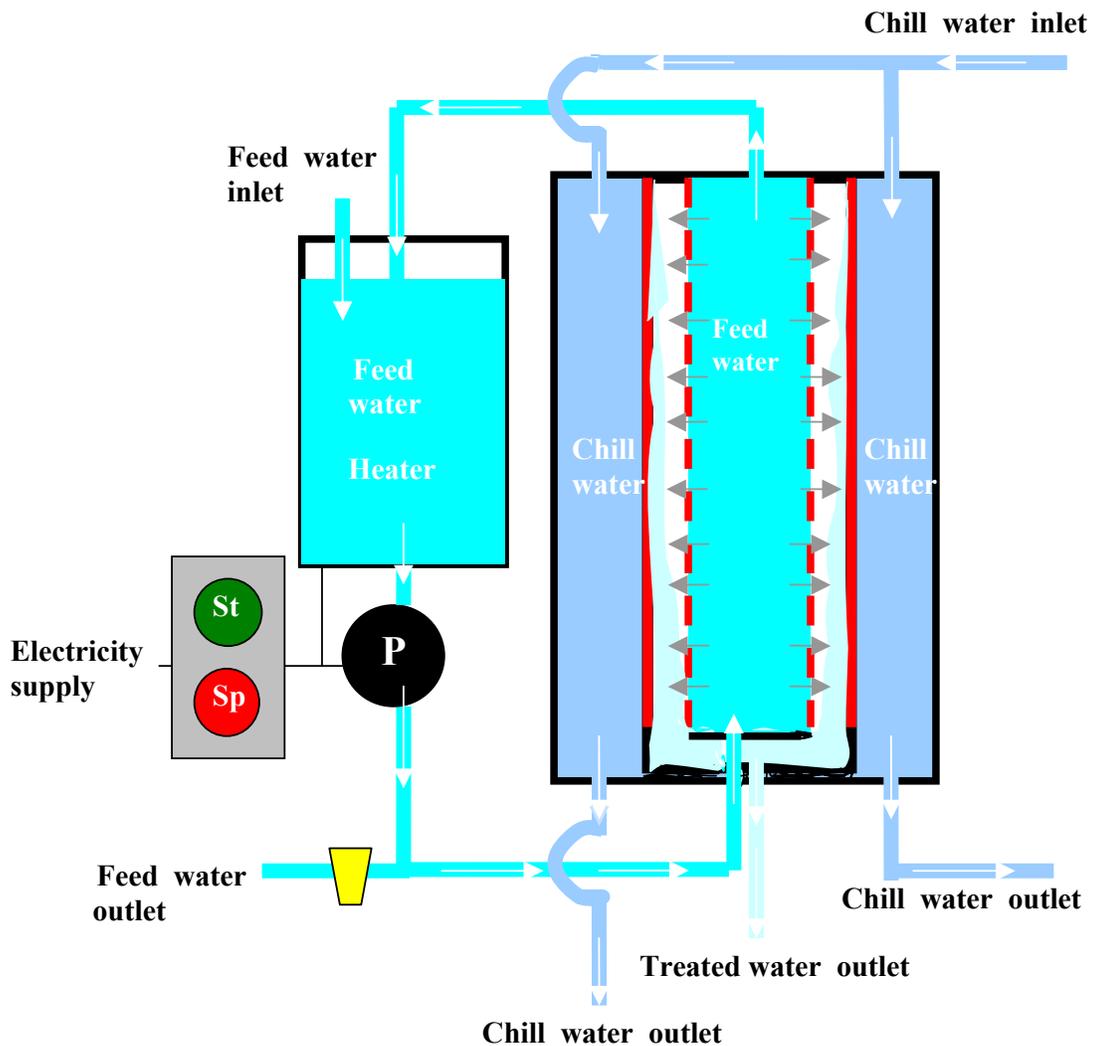(cross-sectional side view)

Experiments were conducted at Royal Institute of Technology (KTH), Sweden and Bangladesh University of Technology (BUET), Bangladesh.

Feed water used were KTH and BUET supply water, water from arsenic contaminated site in Sweden, well water in Bangladesh with extremely high naturally occurring arsenic content etc. Several experiments were also conducted by using those supply water mixed with NaCl salt up to 4% (wt/wt) concentration. Highly arsenic contaminated (0,24 mg/l) water from contaminated surface water in Högsby kommun in Sweden was treated in the lab unit. The concentration found in the treated water was less than 0,0005 mg/l. For 4% NaCl (wt/wt) solution the conductivity in the treated water was 0,94 µS/cm. In all the cases TDS was zero. The exception came only for a water sample (sample A) where TDS were found 30, 40 and 50 mg/l and the conductivity 98 µS/cm. Further study needs to be done to find out the element causing the unexpected (for the lab unit) level of TDS and conductivity. It is to be mentioned

here that there is no percolator or evaporator in the storage tank in the lab unit unlike the commercialized model. That might have caused some volatiles other than water to remain in the feed solution. Another hypothesis may be the presence of old membranes (about 4 years). But still the removal efficiency of the purifier is really excellent for the same sample. The The tests conducted in the Environmental Engineering Laboratory at BUET (Bangladesh University of Engineering & Technology) for sample A in Table 2. All other parameters except Electrical conductivity showed good results.

Table 2. Laboratory experiment results for sample A

Parameter	Unit	Concentration in Raw Water	Concentration in Treated Water
Arsenic (As)	µg/L	334	< 1.0
Manganese (Mn)	mg/L	0,102	0.001
Phosphate (PO4)	mg/L	3,28	0.03
Electrical Conductivity	µS/cm	845	98

Experimental results for two samples (sample A & B) are described here.
Sample A:
The feed water was collected from a tube well located at
          Village:Bhashail Bhogh
          Thana(subdistrict): Srinagar
          District: Munshigonj
          Bangladesh

  Heater temperature = 85°C;
  Chill water flow rate = 1.5 l/min
  Chill water started 15 min after the starting time.
  Room/chill water temp. = 29°C
  The feed water TDS = 270 mg/l
  pH of the raw water = 7,5

Table 3. Experimental results for sample A

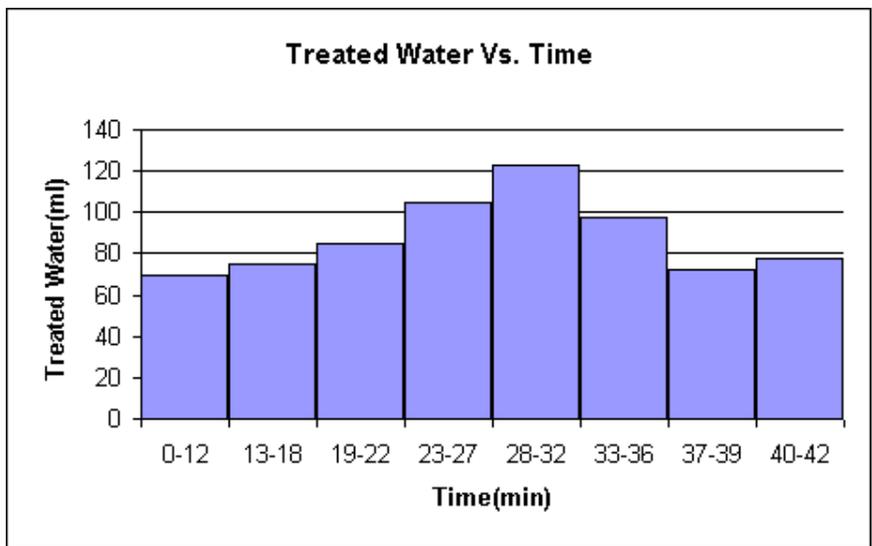|	Treated water volume (ml)	Treated water flow rate (l/h)	Treated water temp. (°C)	TDS (mg/l)	pH
0-12	70	0,35	34	30	6,5
13-18	75	0,75	39,5	30	6,5
19-22	85	1,275	41	30	6,5
23-27	105	1,26	41	40	6,5
28-32	123	1,476	41	40	6,5
33-36	98	1,425	46	40	6,5
37-39	72	1,44	47	50	6,5
40-42	78	1,56	47	50	6,5

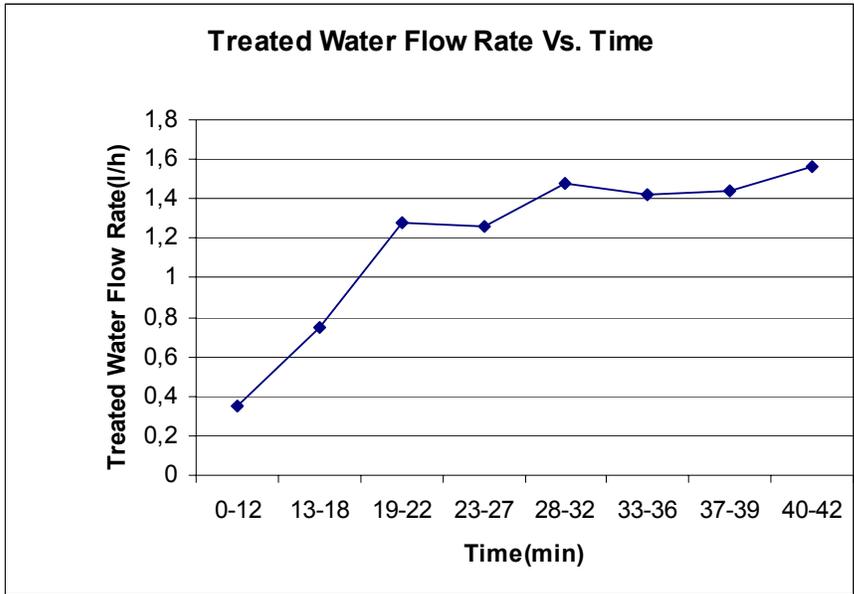**Figure 18.** Treated water vs. time graph for sample A

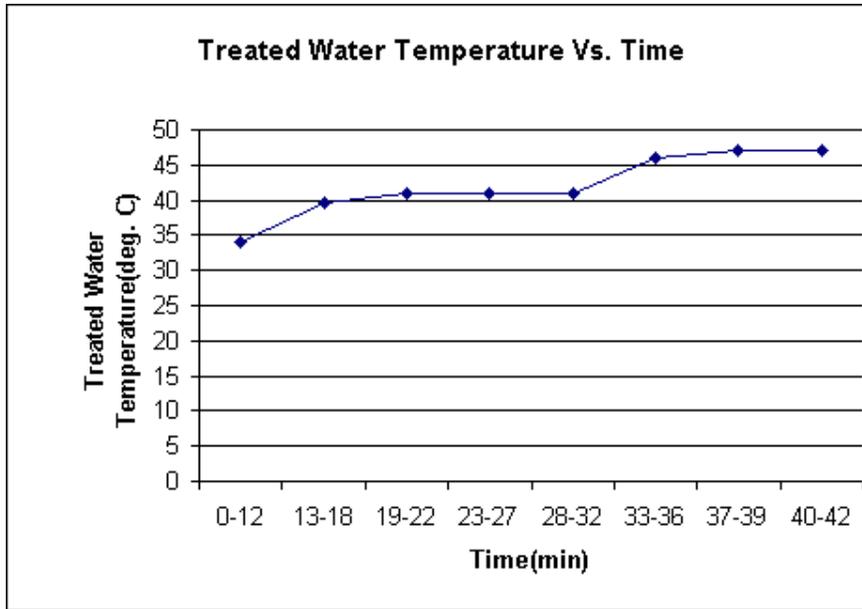**Figure 19.** Treated water flow rate vs. time graph for sample A

Figure 20. Treated water temperature vs. time graph for sample A

Sample B:
The feed water was collected from the BUET (Bangladesh University of Engineering & Technology) supply water which is extracted with deep tube wells located at BUET.

Heater temperature = 85°C;
Chill water flow rate = 1.5 l/min
Chill water started 15 min after the starting time.
Room/chill water temp. = 29°C
The feed water TDS = 280 mg/l
pH of the raw water = 7,5

Table 4. Experimental results for sample B

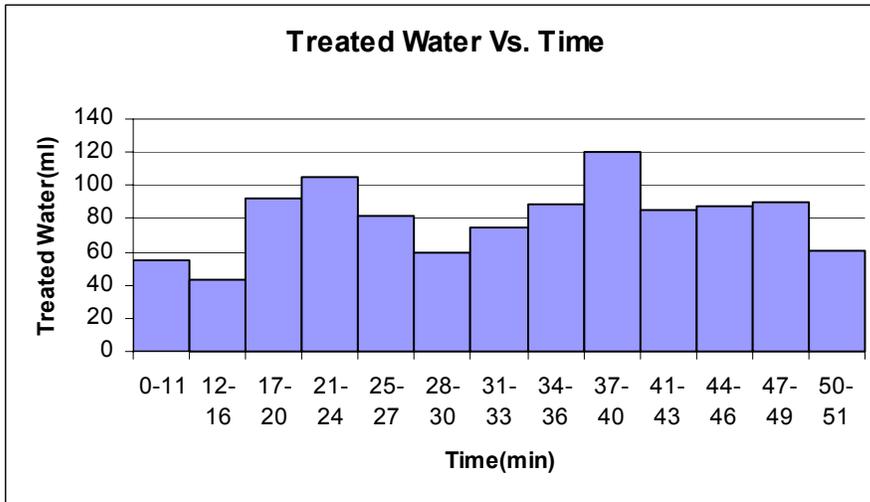| Time (min)	Treated water volume (ml)	Treated water flow rate(l/h)	Treated water temp. (°C)	TDS (mg/l)	pH
0-11	55	0,3	33	0	6
12-16	43	0,516	39	0	6
17-20	92	1,38	42	0	6
21-24	105	1,575	43	0	6
25-27	82	1,64	44	0	6,5
28-30	60	1,2	44,5	0	6,5
31-33	75	1,5	44,5	0	6,5
34-36	89	1,78	46	0	6,5
37-40	120	1,8	46	0	6,5
41-43	85	1,7	46	0	6,5
44-46	87	1,74	46,5	0	6,5
47-49	90	1,8	46,5	0	6,5
50-51	61	1,83	47	0	6,5

25

Figure 21. Treated water vs. time diagrams for sample B
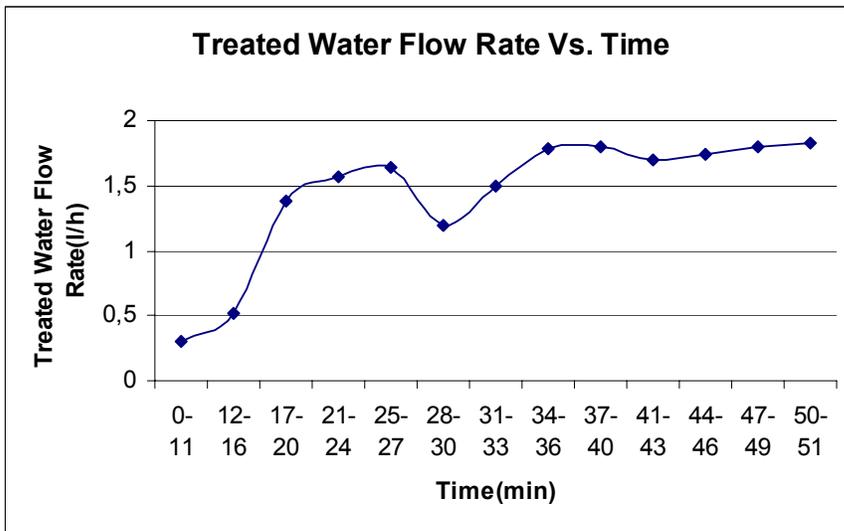

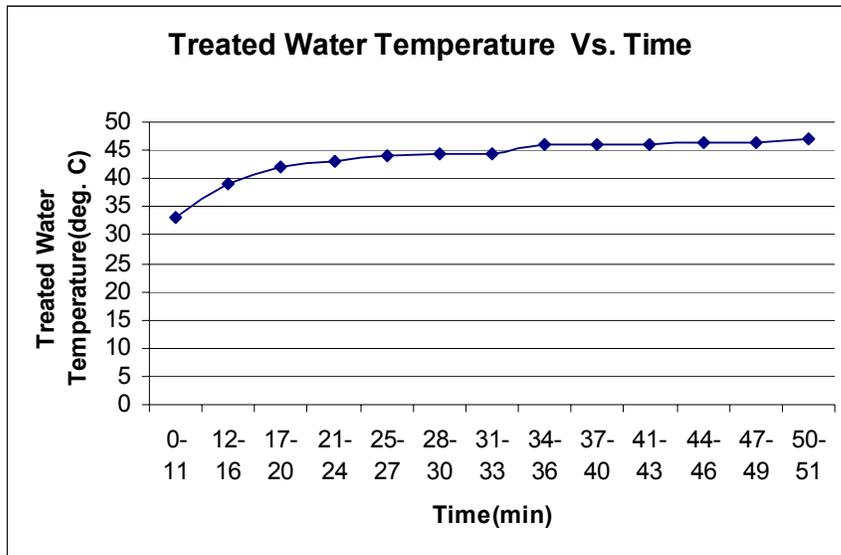**Figure 22.** Treated water flow rate vs. time graph for sample B

Figure 23. Treated water temperature vs. time graph for sample B

It is recommended that to have better results or graph (which can well represent the actual situation) the following things can be followed:

(1) The feed water should be run separately for each parameters like flow rate, volume, temp etc.
(2) Treated water sample should be collected more frequently like in every 5 min(if possible 3 min) until the chill water starts (until 15 min), and then in every 3 min until the machine stops.
(3) It is quite necessary to have more than one person while running the purifier, collecting samples and readings if samples are to be taken frequently.

14. Advantages of the HVR water purifier in removal of arsenic
1. No chemical needs to be used.
2. No need to control the pH of the arsenic contaminated water.
3. No bacteriological growth in the membrane to contaminate the water.
4. No expertise is required to know whether the purifier is working properly.
5. All other impurities are removed along with arsenic.
6. Water purification system is compact and portable, so easy to transport.
6. Low pressure is required, so low energy demand, less vulnerability of the membrane
   and solar energy or waste heat can be used.
7. Easy to handle wastes.
8. Less maintenance cost.
9. Easy to change the membranes.

15. Disadvantages of HVR purifier
1. Higher initial costs than the chemical techniques.
2. Electricity is required.
3. Limited storage tank.
4. Restart is required after 40 to 60 minutes from each start for further treated water.

16. Conclusions

In this thesis work, much more time should have been given to conduct tests on HVR the purifier in Bangladesh, which could not be done for different constraints. In almost all the cases, test results were quite satisfactory. Wide range of cost/benefit analysis can be done and social acceptability can be assessed in future. So much money and time have been spent to get rid of arsenic problem, but unfortunately no real solution has been found. So the membrane distillation process and its application like the HVR purifier deserve much attention from various international agencies, NGO's etc. so that further study and assessment can be done for its wider implementation. Larger community level purifier can be built and placed in the arsenic affected areas in countries like Bangladesh where ground water arsenic problem exists. As most of the power is used for heating the feed water, solar heat, natural gas (which is abundant in Bangladesh) can be utilized. Low-grade waste heat can be used, if possible. As, there is no chemical requirement, no big sludge handling problem, no health risk for bacteriological growth in the purification system, the membrane distillation process has a big advantage in reducing costs for efficient purification of drinking water. In such cases, power supply can be properly managed. It should be mentioned here that the process is not only removing arsenic, it is removing all other impurities from water. It can be a very attractive solution to the arsenic problem. If due attention is given for its proper development and implementation, this new technology can become a real lifesaver.

Symbols

b = membrane thickness, m

c = molar concentration, mole/m^3

C_P = heat capacity, J/mole K

D = diffusion coefficient for the water vapour- air mixture, m^2/s

E = energy flux, J/m^2 s

k = thermal conductivity, W/m K

k_{air} = thermal conductivity, W/m K

k_{PTFE} = thermal conductivity; W/m K

L = length of the diffusion path in the air gap, m

N = molar flux, mole/m^2

Q = mass flux, kg/m^2 h

T = absolute temperature, K

T_c = absolute temperature, K

T_h = absolute temperature, K

x = mole fraction of water vapour

x_c = mole fraction of water at the condensate surface

x_h = mole fraction of water

z = diffusion length, m

ϕ = effective net pore area

Θ = temperature polarization co-efficient

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