

Technical Research**EVALUATION OF NITRATE REMOVAL FROM DAIRY WASTEWATER BY MEMBRANE DISTILLATION: A LABORATORY MODEL APPROACH****Ali A. Hasan**

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Abstract: The dairy industry is considered one of the main industries not only in Iraq in particular but throughout the world. Different treatment methods have been used over time and in different countries. Here, membrane distillation has been used to treat wastewater generated by this industry to reduce the burden on the environment. In this paper, direct membrane distillation was used to remove nitrates from wastewater discharged from dairy plants. This method is easy to operate, easy to manage and has many economic benefits. This article has been using the HACH instrument with all kits needed to achieve the tests. For determination of nitrates in samples by the Calmagite Colorimetric method. HACH Method 8030. 100 mL Marked Dropping Bottle. All other instruments have been achieved according to APHA, AWWA, and WEF. On the other hand, scanning electron microscopy (SEM) has been used to watch the formation of nitrate on membrane surfaces. The results obtained in treating the samples that were synthesized and prepared according to the characteristics of dairy wastewater showed the ability of this method to remove nitrates by up to 80-85%, on the other hand temperature affects the value of MD and is directly relative to flux. The temperature of the treated water plays an important role in determining the percentage of nitrate removal through the membrane, as well as the latter's enjoying chemical and physical features that give them positive points in its removal of wastewater when the liquid temperature had been raised.

Keywords: *Nutrients; Nitrate NO_3 ; membrane distillation, removal; dairy wastewater*

1. Introduction

The dairy industry it's one of the main industries that cause water pollution. It is appreciated that the rate per capita use of dairy products increases from 52 liters to over 60 liters within the next three years and then to more than 90 liters by 2025. Bearing in mind that increased milk requires a predictable dairy industry to speed up waste production and related environmental problems [1-3]. The advanced industrial revolution in the early 18th century led to the discharging of a lot of wastewater volume into water bodies. These quantities of wastewater resulted in toxic effects and disruption of the aquatic biological and physicochemical system. Dairy wastewater includes milk solids, detergents, sterilizers, milk waste and cleaning water. It can be described by high concentrations of nutrients, organic and inorganic [4-6]. For example, salinity activities through cheese making may lead to higher salinity levels. Sewage may also consist of acids and alkali contains many active ingredients, disinfectants, as well as a quantity of key microbiology of

pathogenic viruses and bacteria. Therefore, coagulopathy treatment will be applied to pre-dilution samples to prevent coagulation and encephalopathy due to organic and inorganic substances [7-9].

The dairy wastewater besides high demand for chemical oxygen (COD), biological oxygen demand (BOD), nutrients, organic and inorganic materials as well as detergents and cleaners [10-13]. Although the removal of phosphorus was the only condition for nutrient removal in some cases with freshwater discharge recipients, removing jointly phosphorus and nitrogen is usually necessary to meet treatment standards that require nutrient removal. Preliminary research over recent years on the employ of MD technology has focused mainly on salt removal and seawater treatment besides groundwater. Also, other researchers have examined the biological techniques to treat artificial wastewater like the MMBR, which depends utilize plastic models to enable the growth of bacteria and microbiology. However, the use of this treatment did not gain significant attention due to the lack of previous research studies [14-17].

The use of biological processing methods still requires high skills because it requires the use of microbiology like these bacteria. Some factories were constructed in limited spaces, and this happened in different areas in developing countries. These constructions will lead to many obstructions, one of them the mechanism of discharging wastewater into local receivers. For this reason, it's very important to find the specific mechanism for the treatment of this wastewater and relief pollutants before let free the environment [18-21]. There are different mechanisms that may be used in the removal of nitrates specifically related by chemical additives, but membrane distillation has advantages over these mechanisms that rely on the pressure difference between the two sides to pass the steam from the hot side through the membrane openings and condense the vapor collected on the cold side. Figure (1), [22]. This method very economically and cheap for treatment, it's doesn't need a wide area, special abilities of skills, a lot of power, no maintenance, as well as it's can operate with green energy. All these reasons have been motivating to make this article.

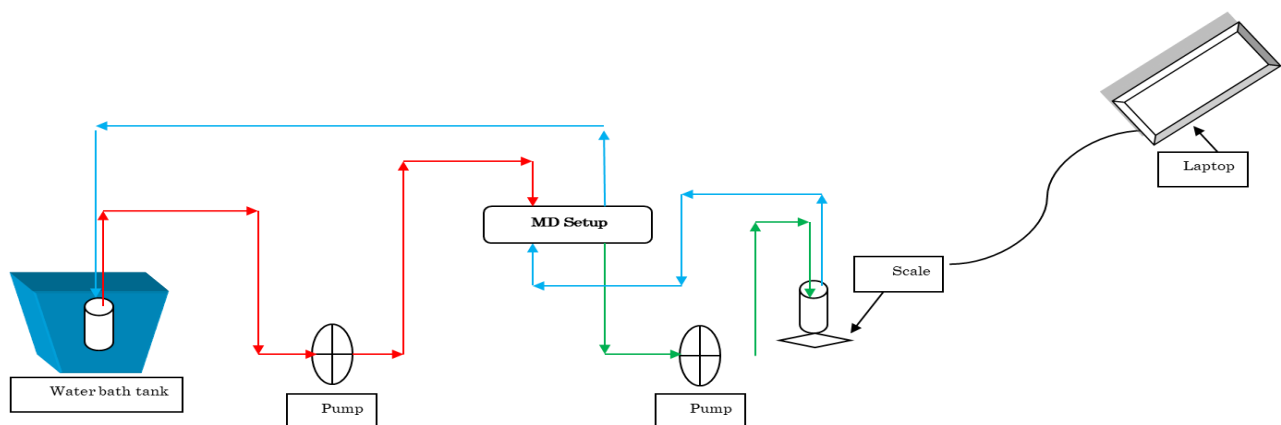


Figure 1. Shows schematic diagram of setup used at the lab.

2. Treatment of dairy wastewater

Numerous methods have been founded and applied for reclaimed water from wastewater. These methods are usually classified as physical, chemical and biological processes. Examples of these methods are reverse osmosis (RO), super filtration (UF), nano filtration, and microfiltration (MF) [23-26].

This process is a non-thermal membrane-based separation used in a different application. It has a wide area of properties such as 100% rejection of inorganic material. MD is selected due to some significant features that it has over other traditional methods resemble biological methods as the latter needs a high level of services and maintenance besides electricity. In MD, chemical treatment can reduce COD by 78% and BOD by 84%. Therefore, researchers and scientists made significant efforts to use this process for recovering freshwater [27-30].

The main disadvantages of chemical phosphorus and nitrate removal are the charge of chemicals and the comparatively excellent sludge creation that raises the price of sludge treatment and the difficulties and cost of sludge disposal [9, 10]. Chemical treatment can reduce COD by 78% and BOD by 84% [31-34].

For this reason, MD come as promising separation technology and gained attention in this space. This process is an uneven membrane. Grounded separation used in a different application. It has ample space of characteristics like 100% rejection of inorganic materials. Therefore researchers and scientists made significant efforts to use this process for recovering freshwater.

3. Using membrane distillation in Milk wastewater treatment

Membrane distillation is considered a promising separation technology and has received considerable research attention for the following main reasons [35-38].

1. MD can deal with higher salt concentrations compared to RO.
2. MD flux is less responsive to feed and fouling compared to RO.
3. MD has a high rebuff of non-volatile components.
4. There is a membrane system to treat most water problems.
5. Ro and NF systems should only be used to remove dissolved solids - they require clean feeding water.
6. UV rays can remove organic colored cancer that causes odors, viruses and other microbiological infections. Salts don't melt.
7. MF can remove outstanding solids, turbines, cryptography and giardia. No colour, virus, or dissolved solids.
8. The advantage of MD over other processes of the membrane driven by pressure like reverse osmosis (RO) is that it needs low temperature and pressure hydrostatic to determine the useful work. Therefore, MD is prospective to be one of the cost-effective processes, which also require lower membrane characteristics.
9. In theory, for a complete separation to occur at MD it requires the size of pore a relatively wider membrane than that used in another membrane for example RO [39, 40].
10. Previously it can be confirmed that MD can be the process of separating steam from water solution through small porous membranes.

In short, MD has many positive features compared with other processes of the membrane driven by pressure such as reverse osmosis (RO). First, it requires low operating temperatures to achieve useful work, that is, and (mainly water) do not heat necessarily until boiling point. Secondly, the hydrostatic pressure you face at MD is less of the pressure used in RO. Therefore, the process is anticipated to be cost-effective and require lower membrane characteristics [41-44].

3.1. Membrane Distillation Process (MD)

The driving force in MD is the partial pressure difference between each side of the membrane pores. The temperature difference causes the vapour pressure to vary across the membrane. Due to the visible nature of the membrane, steam alone can pass through the membrane and not a distilled liquid solution [45-47].

Is the dairy industry being between the most polluting industries in the dairy industry for consumption by large water. Consumption of water to produce milk depends on the size of the plant, usually expressed in terms of a maximum weight of milk held in one day, and the methods complicate. The quantity of water required in the dairy industry is variable due to the management of the plant, however, it will be variable. The main reasons for this are different activities in this industry like washing and rinsing [48-51]

3.2. Economic Technology of Membrane Distillation Process

The process is designed to MD first as a separate process that can operate with minimal power requirements external and less capital and land for the plant. Equipment is required for multiple sclerosis (MD) is much smaller, which means (B) operating temperatures much lower because it is not necessary to heat the working fluid above the boiling point. These benefits result in less heat loss of the environment through the surface of the

device. Besides, enter temperatures in MD typically domain between 35 and 85 ° C. Hence the low level of waste and/or alternative energy sources like solar and wind energy. Geothermal or energy can be combined with economic systems and MD energy efficiency and desalination/wastewater treatments [52-54]. MD solar power plants are cost-competitive with or in remote areas [18]. Easier operating conditions and low operating pressure (usually ambient pressure) increase safety; less contaminated problems are some of the other benefits of MD [55-58].

4. Materials and methods

4.1 Samples:

Artificial samples of wastewater were prepared. 2. Considerations and considerations of making these wastewater samples among the standard characteristics of the global classifications of wastewater.

4.2. Membrane Materials

There are various types of membranes as shown in table 1, are made of different materials such as polypropylene (PP), Polyvinyl fluoride (PVDF), and Polytetrafluoroethylene (PTFE) polyethylene (PE) available in the forms of sheet, tubular, hairy or flat used in the experiments MD [59-62]. (Onsekizoglu 2012)[20].

Table 1. Surface energy and thermal conductivity of commonly used membrane materials

Membrane Material	Thermal Conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	Surface Energy ($\times 10^{-3} \text{ N/m}$)
PTFE	0.25 ~	9-20
PP	0.17 ~	30.0
PVDF	0.19 ~	30.3

These membranes are not the scope of the follicular, ranging from 0.50 - 0.90, the size of the pores as commonly used ranges from 0.4 to 1.0 μm , the thickness ranges between 0.04 and 0.25 mm [63]. Between all materials, PTFE has greater properties like largest, contact angle with water, hydrophobicity, thermal stability and higher oxidation resistance and good chemical compared to PVDF and PP [64-66].

Surface energy and thermal conductivity are properties to be considered while selecting membrane material for use [67-69].

The membrane used at this topic is PTFE part#: MSPTFE 260045B, Lot#: 1801331008, pore size 0.45 μm , wettability: Hydrophobic.

4.3 Setup:

A laboratory model has been built to achieve experiments, and the workflow in experimental implementation can be seen as shown in Figure 1.

4.4 Equipment's and Apparatuses:

The equipment's and apparatuses are stated below: Turbid meter, Scale, COD Reactor, Spectrophotometer, Dryer Oven, Glasses and pipettes, cones, flasks, filter papers, as well as Chemical Kits to measure COD, Scanning Electron Microscopes, EC, pH meter, Total Nitrate meter, HCL acid and other chemicals like NaOH, NaCl salt and other different salts.

4.5 Scanning electron microscopy (SEM)

A bench-top SEM (Nikon/JEOL Neo-Scope JCM-5000) applying a voltage of 10 kV and using a secondary electron detector. Samples were withered in a vacuity kiln overnight and 2 min gold coated (Nikon/JEOL, NeoCoater).

5. Results and discussions

MD phenomenon has become now the head of treatment methods on water and wastewater. The membrane used in this process should have a hydrophobic pattern, and this material will assist in moving vapors from high temperatures to the cool side.

Lots of ways can be employed in running to force vapor pressure difference diagonally across the membrane to produce flux. The permeate transports through the membrane in three steps:

- Vapor is formed at the hot feed solution–membrane Interface;
- The same vapors are transported through the micro porous membrane;
- Steam condensation occurs at the other side of the membrane

Figure. 2. Describe the relation between flux and temperature and as the shown flux will increase with temperature which is confirmed points above.

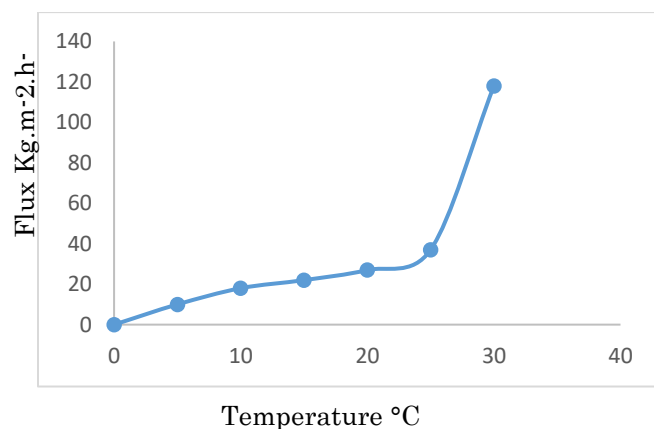


Figure 2. The figure showing the relationship between the flux and different temperatures.

This porosity of the membrane means the volume of pores that will pass vapor through the membrane in the section. The content, which is part of the feed not passing through the membrane perforations, contains a high condensation of nitrate. Mostly this stream is recycled again for higher efficiency. As a result,

the nitrate removal will increase as the feeding temperature increases.

Note from Figure 3 that the nitrate concentration in membrane water treated decreases with increasing temperature. In other words, this increased membrane removal efficiency. This can be achieved if Figure 4 is observed, as the remaining concentration in treated water decreases with increasing temperature. This result can be explained by observing Figure 5, which indicates a decrease in the nitrate concentration with increasing temperature. Nitrates can be emitted to a gaseous degree and attached to the formation of the membrane, or emerge above the liquid.

It depended on this article same concentration of NO_3^{1-} , to clarify the phenomena of removal only. The relationship as shown in Figure 4. Shows that nitrate removal increases with low temperatures due to the susceptibility of nitrate to the membrane surfaces. At higher temperatures, it is noticeable that the removal of this element is reduced because of the disruption of its physical status because it is close to being in a light gas state rather than being in the ionic state. The relationships here in this research show that nitrate removal increases with low temperatures and this is due to the susceptibility of nitrate to the membrane surfaces. At higher temperatures, it is noticeable that the removal of this element decreases due to the physical disruption of its proximity to being in a light gas state rather than being in the ionic state. The reaction formula and the impact of temperature on nitrate removal can be interpreted in Figure 5, which shows the relationship between temperature and concentration of the remain nitrate. If Figure 2 is retrieved with its contents which show the connection between flow and temperature, the increase in flow will be observed by increasing the temperature and the best flux will be observed at a temperature of

approximately 26 to 27.5 °C which will be about 37.5 Kg.m⁻².h⁻¹.

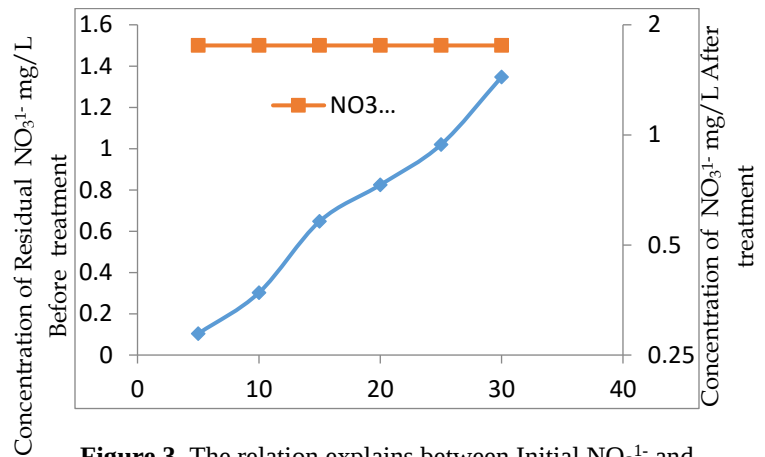


Figure 3. The relation explains between Initial NO_3^{1-} and final concentration after pass samples through MD.

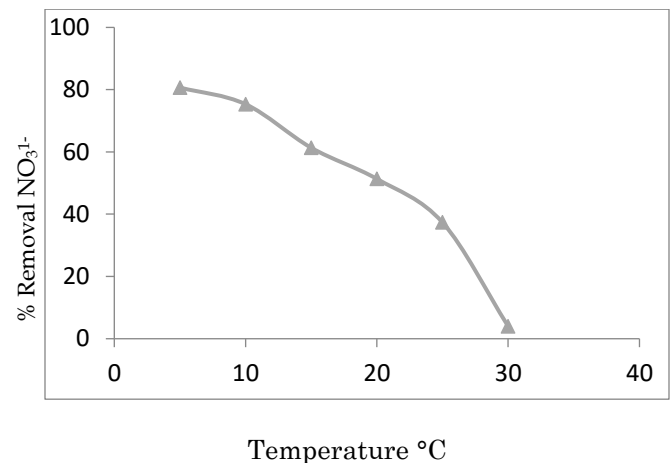


Figure 4. Relation explains between Removal of NO_3^{1-} and Temperature after pass samples through MD.

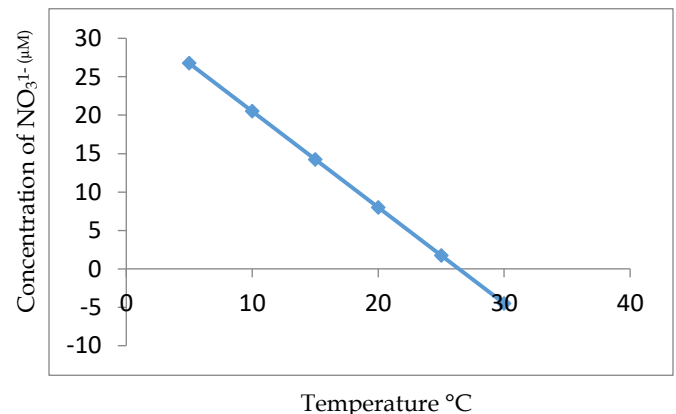
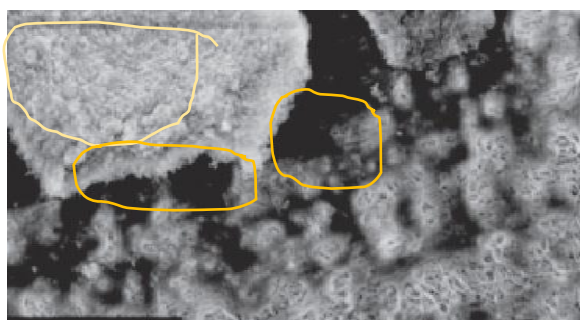
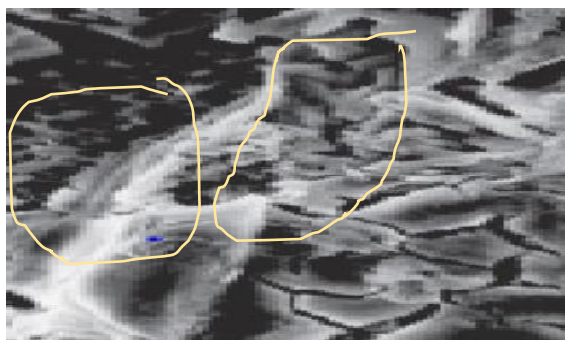


Figure 5. Relation explains between Removal of NO_3^{1-} and Temperature after pass samples through MD.

It is noted from Figure 3 that the best nitrate root removal occurs at a temperature between 20 and 25 °C, at which time the remaining nitrate concentration is within the permissible limits of the world. The removal efficiency begins to increase not because of a state of electrostatic or electrostatic adsorption with diaphragm openings but because of the accumulation of this root, which leads to obstruction of the flow through the holes. Therefore, even the increase in temperature and the mechanism of the difference in pressure between the two sides does not give a significant advantage in the passage of nitrate ions even if the susceptibility to diffusion is large because the diaphragm holes will begin to block. Hence the manufacture of a new secondary sieve that removes nitrates, and as was observed using scan electron microscopy (SEM), note Figure 6 which shows circulated outlines are the accumulation of salts. These groups are surrounded by yellow boundaries.



(a)



(b)

Figure 6. SEM picture of fouling in a membrane layer due to nitrate salts (a, b), when the concentration of salt, when the membrane reach saturation.

The reaction formula and the effect of temperature on nitrate removal can be interpreted in Figure 5, which shows the relationship between temperature and concentration of the remaining nitrate.

6. Conclusion

- 1- The ability of MD to remove NO_3^{1-} from dairy wastewater has reached 80 - 85%,
- 2- Temperature affects the value of MD and is directly relative to flux.
- 3- The temperature of the treated water plays an important role in determining the percentage of nitrate removal through the membrane, as well as the latter's enjoying chemical and physical features that give them positive points in its removal of wastewater when the liquid temperature rises.

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Conflict of interest

The author declares that there are no conflicts of interest regarding the publication of this manuscript.

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