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MERCURY REMOVAL FROM DAIRY WASTEWATER BY USING MEMBRANE DISTILLATION

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Abstract: Milk is one of the essential and necessary nutrients and maybe a basic substance in some places and all stages of human life. Milk is rich in many important elements for life and durability. Toxins and heavy elements may enter the milk and then into the human body due to pollution, and mercury is one of these pollutants. This product, despite being important, the production process is accompanied by a lot of liquid waste, which may lead to significant environmental damage. All small tests and misilianiuse works as well as the test of characteristics have been achieved according to American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). Mercury concentration has been achieved according to HACH procedure. In this topic, the membrane distillation process has been used to remove mercury, and the results were the ability of the membrane distillation mechanism to remove mercury 89.044% at the start of the operation, which would decrease due to obstruction. The temperature affects work efficiency and removal by MD, but to some extent, when removal reaches the maximum temperature of 15 ° C. The study came out with a set of recommendations, including a broader study on the possibility of cleaning the membrane used in this mechanism when a blockage occurred without stopping the work of this mechanism. Emphasis should be on what was found more than what was done.

Keywords: *Mercury, membrane distillation, dairy industry, industrial wastewater*

1. Introduction and Scientific Background

Milk is an essential material in the formation of human structure in general and in the growth of the child, and it is a biologically active and excellent medium for the growth of microorganisms and pollutants [1-3]. Milk is the main source of calcium, which greatly helps children grow and reduce osteoporosis in the elderly [4, 5]. Calcium is one of a group of elements that play an important role in strengthening bones and these elements such as potassium (K^{1+}), phosphorous ($P^{5+,3+,-3-}$). Some microelements and heavy metals are also found in milk. Microelements such as copper (Cu^{2+}), iron, selenium ($Se^{6+, 4+, 2+, 2-}$) and zinc (Zn^{2+}) are known to be necessary for human growth. However, heavy metals such as arsenic ($As^{5+,3+,3-}$), cadmium (Cd^{2+}), mercury ($Hg^{2+, 1+}$), and lead ($Pb^{4+, 2+}$) have no beneficial effects on human well-being [6-8]. Despite the great importance of this food source rich in vitamins, but it has environmental side effects that can lead to the consequences of environmental disasters in the

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event of increasing the disposal of environmental sources [9-11].

It is a highly consumed food and the average annual milk production rate in Bangladesh is 22, 64,000 tons, and the average available per person is 13 kg per year (according to the Food and Agriculture Organization). It is estimated that the average per capita consumption of dairy products in some countries like Iraq, Syria, Jordan will rise from 52 litres to more than 60 litres over the next three years, then to more than 90 litres by 2025 [12-14].

Minamata disease was first discovered in Minamata city in Kumamoto Prefecture, Japan, in 1956. It resulted from the release of methylmercury in the industrial wastewater from the Chisso Chemical Plant, which lasted from 1932 to 1968. It was also suggested that some Mercury sulphate has also been metabolized in wastewater to methylmercury by bacteria in sediments [15-18].

Mercury: Hg and atomic number 80; It is in the periodic table within the carbon group (group four ten). Lead is a heavy metal with a high density. Its has molecular weight reaches 200.5 [19-21]. The concentration of Hg in milk is not affected by thermal processes during the process of pasting, condensation and drying of raw milk of livestock may even increase. The concentration of these elements is a result of contamination of milk through tools, metal machines, casings, bags and cans [22-24]. The concentration of Hg in raw milk may reach Hg (5.76±0.53 ppb [25-28].

2. Characteristics of Dairy Wastewater

Volume, concentration and composition of the effluent generated In a dairy plant depends on the type of product being processed, Production program, operating methods and design treatment plant and degree of wastewater management [29-32].

The management of the dairy factory, in addition to the quality of the products required in the market, plays a major role in the quantity and quality of the wastewater generated in the dairy plants. The main pollutant in dairy plants water is whey, which is the main volume in the disposal of these laboratories in terms of the amount of the pollutant and the type of effect. It accounts for about 85-95% of milk volume and 55% of milk ingredients [33-35].
Whey consists of carbohydrates (4-5%), most of which are lactose. Proteins and lactic acid are less than 1%. Fat is about 0.4 - 0.5%, while salts vary from 1 to 3% (2,15,26) [10]. Milk handing out effluents have a bigger temperature, big variations in pH, TSS, BOD, COD, TN, TP and FOG, Table 1, it can be seen the characteristics of dairy wastewater which suggested preparing the synthetic samples in this article [36-40].

Table 1. Illiterates the characteristics of dairy wastewater factories

Chemical compositions	Synthetic Samples
COD (mg/l)	1000-3000
Nitrate (NO_3^-) (mg/l)	0.2-16
TP (mg/l)	18-27
Chloride (mg/l)	20-100
Sodium (Na^+) (mg/l)	50-750
Turbidity (NTU)	40-50
TSS (mg/l)	200-1200
TS (mg/l)	150-2500
TDS (mg/l)	150-450
EC (µ mhos/cm)	300-4000
pH	6.5-7.5
Temperature (°C)	25 – 35

3. Effect of Mercury on Health and Environment

Mercury is one of the most dangerous ecosystem. When mercury is released into the environment, it evaporates and travels through air currents and then returns to the stove, near its source and sometimes away from it depending circumstance condition such as wind and heat [41-44]. Mercury may enter the aqueous environment and here it will turn into a dissolved state that is easily ingested by microorganisms and then into microorganisms and converted into methylmercury which is considered a mercury compound toxic (and at low doses) and more than mercury itself in a way that affects both element mercury and methylmercury [45-48], on the central nervous system in the human body, and the peripheral nervous system dangerously, on the other hand, exposure to inorganic salts of mercury leads to skin erosion, affects the eyes, gastrointestinal tract, and increases kidney toxicity. When exposed to mercury compounds it appears in humans various neurological and behavioral disorders; these include tremors, insomnia, memory loss, neuropathy, headache, difficulty in movement, and perception [49-52]. The most dangerous issue is the transition of mercury to the human body through the food chain, as aforementioned in the Minamata accident.

4. A Simple View on Membrane Distillations

Interested in this applied science now many countries that suffer from water shortages, as some statistics indicate the death of hundreds of thousands annually due to the scarcity of clean water for human use. The Gulf countries, and before them the developed countries, pay great attention to water treatment and the use of membrane removal technology [53-56].
Membrane therapy may be called torment or salt removal due to the high concentration in using this technique to remove salinity from water. This technology may be new today, but it is expected to have a significant impact in the next ten years due to its economic and technical advantages in achieving treatment. It differs from its peers from membrane technologies because it uses less energy, which leads it to employ solar radiation to operate it [57-60]. It also does not need a large technical staff and a large number of employees, and in this way reduced the number of employees and the financial and career effort. It can benefit from low operating temperatures even at 30 -80 ° C, and thus it is superior to other membrane methods such as reverse osmosis (RO), ultrafiltration (UF), nanofiltration and microfiltration system (MF), and it does not need addition of chemical or biological materials, and thus, they have agreed to physical, chemical and biological treatment methods, [61-64]. Membrane distillation (which has been applied on this article), is an emerging non-isothermal membrane process which uses thermal energy in order to provide a vapor phase of volatile molecules present in the feed stream (i.e. mostly water) and condensing of the permeated vapor in the cold side see Figure (1).

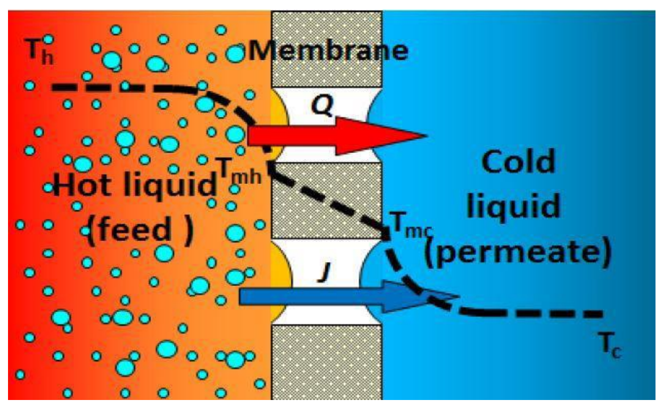


Figure 1. Basic principles of the MD process [65].

5. Advantages of Using MD

This process is the simplest type of MD, has recently gained more attention. It can explain the characteristics of this type briefly:

1- Total (100%) rejection,

2- Intensive to feed concentration,

3- Mild operating conditions,

4- Stable performance at high contaminant concentrations,

5- Osmosis characteristics play a big role in achieving treatment.

The most important advantages of this technique are:

Lower operating temperatures than evaporation

Lower operating pressure than RO

100% rejection of non-volatiles

Membrane distillation (MD) has Featured during the past years as an attractive and computative alternate technique [65- 68].

This simple technique has proven to be highly efficient since salt rejection rates around 99–100% are frequently obtained in desalination. Besides, a relatively low temperature of a maximum of 100 °C and pressure (1 atm) are needed [69, 70].

The major advantage of membrane distillation is that, with compact modules equipped with hollow fibres, a high surface area per unit liquid volume for mass transport is accessible and thus high overall permeation rates are attainable even at relatively low temperature [71, 72].

6. Materials and Methods

6 1. Synthetic Samples:

1. Synthetic samples of wastewater were prepared. The mercury has been added very careful with taking all safety conditions. All steps have been done inside the hood.

2. Considerations and consideration of making these wastewater samples among the standard characteristics of the global classifications of wastewater. The synthetic samples were prepared similar to real samples discharged from dairy factories; these samples were prepared from salts below regarding be similar real samples.

- Sucrose hydrate $C_{12}H_{22}O_{11}.H_2O$
- SodiumPhosphateDodecahydrate $Na_3PO_4.12H_2O$
- Ammonium sulfate$NH_4.2SO_4$
- Mercury(II) sulphate, $HgSO_4$, and it is in the form of white crystals.

6.2 Mercury Test

It has been used Cold Vapor Mercury Concentration Method Method 10065 HACH apparatues [73].

6.3 Membrane Materials

It's common to know that there are various types of the membrane and these can be classified into Hydrophobic and Hydrophilic membranes. These membranes made of numerous materials like polypropylene (PP), polyvinyl iodine fluoride (PVDF), Poly tetra fluoro ethylene (PTFE) and polyethylene (PE) available in tubular, capillary or flat sheet forms which have been used in MD experiments.

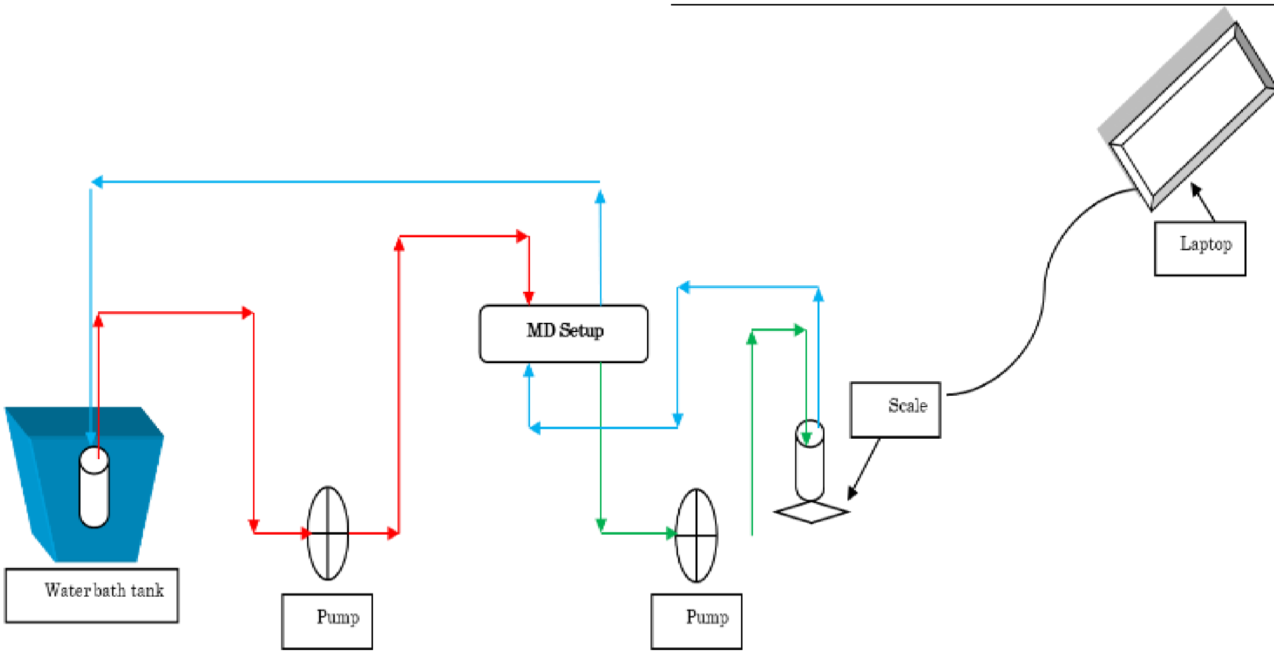
The most important figure of these membranes is porosity. The porosity of these membranes may range 0.5-0.9 μm. However, the most common size is 0.4 -1.0 μm, while the thickness of these membranes is in the range of 0.04 to 0.25 mm [74-76].

Among the different types of membranes materials, PTFE overcomes on other types due to different characteristics like biggest contact angle with water, hydrophobicity, thermal stability and higher oxidation resistance and good chemical compared to PVDF and PP.

The main characteristics which led to using a membrane in this topic are Surface energy and thermal conductivity [77-79].

Table 2. Surface energy and thermal conductivity of commonly used membrane materials

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



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

6.4 Setup:

The setup for the MD application is shown in Figure (2).

The setup used at this experiment was consist of pumps, hoses, valves, scale, laptop to watching fluency of liquid and record readings, different instruments like cones, pipettes, flasks, and differenr glasses.

A laboratory model has been built to achieve experiments, and the workflow in experimental implementation can be seen as shown in "Fig. 2".

The pumps used are 2 pumps of peristaltic pumps,

• Powerful and long-lasting motors • Robust pump heads • Large clear display screens • Wide flow rates available from micro to industrial • Dispensing pumps with optional dosing footswitches and PC control • Compact design to

Figure 2. Shows schematic diagram of

easily move around the lab • Foot pedal switch for quick and easy dosing - press to dose.

7. Results and Discussions

Mercury includes a large atomic number and a molecular weight, which will increase its ability to paste to the membrane. This feature gives this element due to the weight of this feature over the rest of the periodic table. The large atomic number in this element gives it another advantage, which is in addition to its diminution and its ability to cling to it, giving it the characteristic of speed in propagation. This other feature gives it the ability to spread over the membrane and form a layer. Here, and at a certain point, a layer of Mercury will be created that may prevent the rest of the element from penetrating through the membrane and may cause fouling. The cow's milk models were used in the research, as they are the most widely used in the social field.

The mercury concentration was confined in the cow milk models between 2.164 and 0.0.85 mg per kg of milk with an average of 1.125 mg/kg of milk. These measured concentrations helped prepare samples for laboratory experiments. While these levels are very small, they remain worrying because these carcinogenic groups are capable of accumulating.

When you start the pumps and begin to release water molecules and move as steam from the hot medium to the cooler medium, you will notice an increase in the flow value due to the increased escape of water molecules from the side of the large mass. Pressure to minimum pressure and this is shown in Figure 3. This figure is an overview of the state of transport in water molecules, leaving behind atoms of mercury or whatever element was mixed with it in the aqueous medium. At a temperature of the water atoms ionize into two ions, which are two ions: hydronium + H_3O and hydroxide - OH. On the other hand, When you start the pumps and begin to release water molecules and move as steam from the hot medium to the cooler medium, you will notice an increase in the flow value due to the increased escape of water molecules from the side of the large mass. Pressure to minimum pressure and this is shown in Figure 3, as mentioned. This figure is an overview of the state of transport in water molecules, leaving behind atoms of mercury or whatever element was mixed with it in the aqueous medium. At a temperature of the water atoms ionize into two ions, which are two ions: hydronium + H_3O and hydroxide - OH. The Empirical Atomic Radius: 155 picometres (pm). This figure is relatively small compared to the rest of the elements, giving it an advantage in being able to access through the membrane openings.

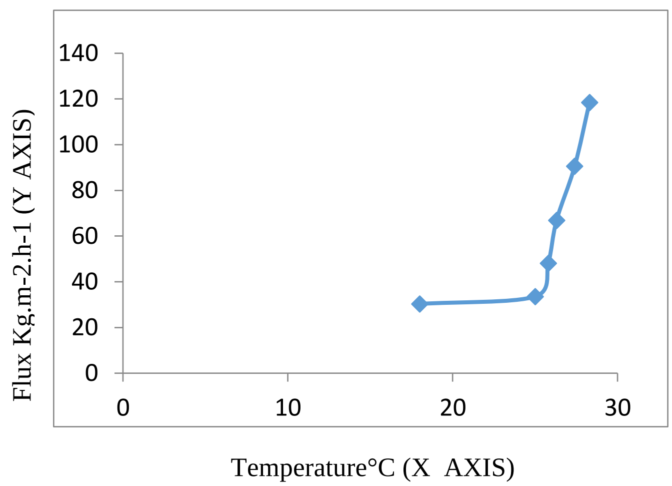


Figure 3. A relationship that shows the variability of temperature with the flow when passing dairy wastewater

From Figure 4, It is noted that the removal of mercury occurs at the beginning of the operation of the system and this is due to the effectiveness of the diff

erence in pressure between the sides of the liquid. After a short time, the mercury atoms start to attach to the membrane walls, which leads to clogs in the holes. It is noted that the mechanism of removal in this way is not completely clear. Here a case of fouling will begin, indicating the necessity of performing a membrane wash to re-work

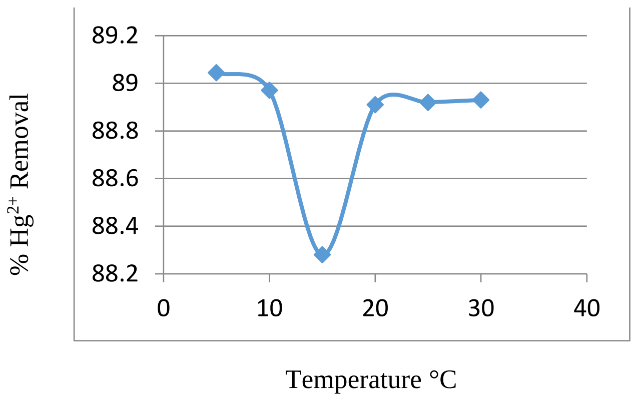


Figure 4. A figure showing the relationship between temperature change and the percentage of Hg ion removal.

From Figure (5), it is noted that the best removal occurs at a temperature of 10-15 ° C. This was due to the pressure difference between the two sides. After that, the percentage of removal will be fluctuating, not large, and this is due to the occurrence of clogs and fouling. In general, the largest removal of this element was 89.044%, after which the role of the mechanism for the difference in pressure between the hot and cold sides will be very little.

Using the equations shown in Figure 5 and shown in the curves, the resulting concentration value can be expected at the flow temperature if it is 15 °C.

If the equation is applied

$$P = 0.0.08\,x - 0.356 \qquad (1)$$

$$Y = 0.008x - 0.038 \qquad (2)$$

Where:

P = Hg concentration before MD,

Y = Hg concentration after MD.

If the inner portion of mercury is 0.828 mg/kg of milk, then the outer portion at a temperature (15 ° C) is 0.097 mg/kg of milk, which is an excellent and acce Tempurature ˚C is noted from Figure (4) that the nature of the treatment mechanism depended heavily on the molecular weight of mercury, which was instrumental in achieving a removal efficiency of 88.28%. But this action is not an excellent positive change, as the particles will begin to accumulate on the membrane wall, leading to fouling and blockage, as noted from Figure (5) as the removal efficiency will decrease.

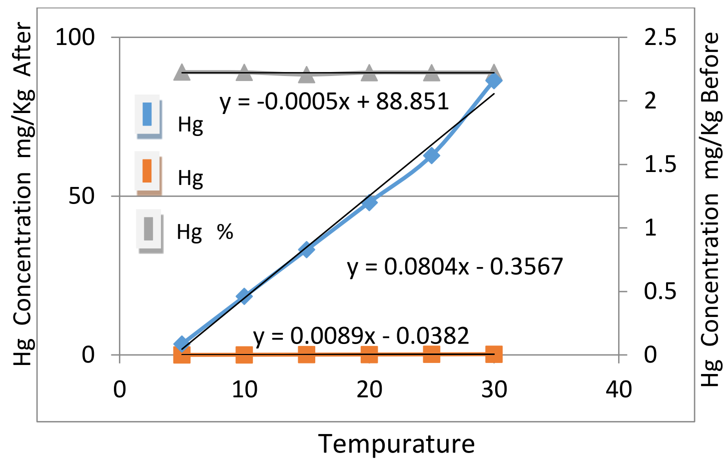


Figure 5. A figure showing the behavior and behavior of the Hg during the passage of the models into the MD at different temperatures.

The capacity of the membrane distillation mechanism to remove mercury is 89.044%, and this occurs at the beginning of operation where the pressure difference due to the temperature difference between the two sides of the membrane plays a major role in the work.

8. Conclusion

- The capacity of the membrane distillation mechanism to remove mercury is 89.044%.
- The temperature affects the work efficiency and the removal by MD, but to some extent, when the removal reaches its maximum and at a temperature of 15 °C.
- The presence of organic or inorganic substances in the laboratory water causes the membrane function to become blocked quickly and may lead to the emission of odours and fouling, and may even lead to its blockage and then stop.

- Providing a pre-treatment process before applying MD to remove suspended soluble organic and inorganic materials to reduce the hydraulic load on the MD, thus reducing the blockage in the membrane.

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Conflict of interest

Ethical Conduct: No Ethical Conduct Required

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