Regeneration of Fouled Nanofiltration Membrane Used in Textile Wastewater Treatment

BY

Radwa Zain Elabedeen Abdel-Maoty

A Thesis Submitted to the

Faculty of Engineering at Cairo University

In Partial Fulfillment of the

Requirements for the Degree of

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CHAPTER 1

INTRODUCTION

Although water is very important for human life, development and environment, its resources are limited and its quality is vulnerable. Water is considered the source of life and development on earth as there is no life without water, air and food, the latter being tied to water. Although water is a regional resource, its lack is a global problem due to the increase in population, economic growth and climatic changes. To avoid any major water crisis, conservation measures should be adopted, in addition to finding new sources of water and using it efficiently. According to PAI 1999 estimation, 458 million people in 31 countries faced water shortage crisis in 1995. By 2025, 48th countries of population over 2.8 billion will face water lack. Egypt is one of the countries facing a scarcity in water demand. (1)

As indication of water shortage, the threshold value of $1000m^3$/capita/year is used. During the nineties, Egypt has passed that threshold. By 2025, expected population increase will bring Egypt down to $500m^3$/ capita/year. The rapid increase in growth rates of population will extend the problems of activities which linked with water sector distribution. The actual water requirements for different sectors are 79.5 BCM/year, while the currently available resources in Egypt for use are 55.5 BCM/year, and 1.3 BCM/year efficient rainfalls on the northern strip of the Delta. Thus the gap between the needs and availability of water is about 20 BCM/year. This gap is minimized by recycling. (2)

In addition to the water shortage the world faces a water quality crisis due to continuous population growth, urbanization, land use change, industrialization, increased living standards and wrong wastewater management strategies. The shortage and mismanagement of wastewater has a direct influence on biological diversity of aquatic ecosystems, and bad influence on life system integrity, which affect a wide range of sectors, from urban development to industry that are dependent on it. It is substantial to consider wastewater management as a part of the integration, full life cycle, and eco-system management that operate across the sustainable development issues (social, economic and environmental). (3)

Different conventional and nonconventional water treatment methods are used. The conventional methods are mainly biological treatment (aerobic, anaerobic or both), physico-chemical treatment (precipitation and coagulation followed by flocculation and sedimentation), adsorption, ion exchange and chemical oxidation (with oxidizing agents like ozone and hydrogen peroxide). A combination of coagulation, sedimentation and filtration is the most widely applied conventional water treatment technology, which has been used since the early 20th century.

The nonconventional water and wastewater treatment methods are mainly based on using membrane technology. As examples of such nonconventional methods are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes. These membrane filtration technologies are efficient processes of water treatment which cannot be treated using conventional treatment methods. The main advantage of membrane technology is its wide field of applications in desalination and several industries like pharmaceutical, textile, food, etc.

Membrane processes have the superiority on the conventional water treatment techniques due to energy savings, ease of coupling with other methods and operations, being an ecologically and environmentally friendly clean technology which produces high quality fluids with variable operating conditions, great malleability in systems design with ease of scale up, high separation efficiency, ease of operation, and absence pollution. [4]

On the other hand membrane processes have some disadvantages due to the operation conditions and physical nature of the membrane like, concentration polarization, fouling and short membrane life-time. Textile industries, well-known for their need for significant amount of water in scouring, bleaching, mercerizing and dyeing processes, produce large volumes of wastewater contaminated with chemicals like dyes and auxiliaries which affect the environment if discharged untreated. The wastewaters of textile dyeing processes have large amounts of complex components containing high concentrations of organic, and high-color. [5]

Fouling is a major disadvantage of membrane treatment; it is a phenomenon that is excessively complicated and has not been exactly determined. Generally, the term is applied to simply explain the unwanted formation of deposition on membrane surfaces. This happens when discarded particulate matters are not transferred from membrane surface back to the bulk stream [6]. Fouling are materials like adsorbed macro-molecules, gels, or deposited particles on the membrane surface or into the pores of the membrane. [7]

In the membrane process industries, cleaning of membrane is one of the most important concerns from the economic and scientific point of view. Membrane cleaning processes are consisted of physical, chemical and physio-chemical methods. Practically, the most widely process sequence applied in membrane cleaning is physical cleaning methods followed by chemical cleaning methods. However, only the chemical cleaning methods are most widely applied in RO membrane. [8]

The chemical cleaning could be applied daily, such as in whey industry, weekly, monthly, or annually, such as in desalination plant, this could be decided according to fouling occurrence and extent [6]. Membrane regeneration is one of the most important techniques use for membrane cleaning; by which fouling and short life time of the membrane could be overcome. Membrane regeneration could be achieved by chemical cleaning of the membrane when it reaches the complete fouling point. This process can be done to extend the membrane life time.

The main aim of this thesis is to examine the possibility of regenerating NF membrane used in textile wastewater treatment. The study is based on solving the high degradation of nanofiltration membrane used during the treatment of wastewater produced from dyeing process.

The study comprises six chapters, the first chapter is the introduction, the second chapter is literature survey and background of membrane technologies used in water treatment; conventional and advanced treatment techniques, membrane transport phenomena, third chapter mention statement of the problem and research objectives which have been identified during studying of the literature review, the forth chapter presents the experimental set-up methods of treatment, tools and methodology, the fifth chapter discusses the experimental results, finally the sixth chapter devoted to the conclusion and recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

By the 1900s, on attempts of using membrane to separate particles began when Bech hold, invented a method for preparing nitrocellulose membranes of graded pore size. Later workers, particularly Zsigmondy, Bachmann, Elford and Ferry, refined these preparatory techniques, and then membranes were used to separate different types of laboratory solutions by dialysis and MF. By time and till the 1930s, micro porous membranes were manufactured commercially on a small scale.

By the 1960s, the new membrane science had been improved, but membranes were still only used in laboratories and in a few small specific industries. Till this time there was no real membrane industry, and total sales did not exceed US$10 million. The weak sales and limited usage of membrane was referred to problems appearing during operation as processes were too slow and membranes too expensive and too unselective. By time, partial solutions of the previously mentioned problems led to the development of the membrane industry which has grown many hundred times during the last century. Now, industry has grown, the sales had been raised, and the usage of membrane spread widely in many industrial applications. (9)

Membrane filtration can remove suspended solid, organic compounds, and also inorganic pollutants such as heavy metals. This depends on particle size that can be detained; various kinds of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis membranes can be used for removing heavy metal from wastewater.

The scientific explanation of the membrane processes is based on the combination of the heavy metals (cations) by a bonding substance so as to increase their molecular weight to be larger than the size of pores of the selected membrane. That technology has the advantages of low-energy requirements, very fast reaction kinetics, and high selectivity of separation over the other conventional technologies.

Filtration membrane treatment technologies are used in drinking water, wastewater and also industrial water treatment. In drinking water filtration, filtration membrane can eject nearly all particles of size larger than 0.2 μm, such as guardia and cryptosporidium. The most effective technology which could be applied when it is desired to reuse water for industry, restricted domestic purposes, or before draining the water into river, is filtration membrane treatment which considered forming a tertiary treatment. While, dissolved substances in water such as phosphorus, nitrates and heavy metal ions cannot be removed filtration. (10)

2.1.1 Membrane Demand

The need for clean water is a problem of global issue. The planet's water resources are limited owing to the fact that the pure water stocks are specified and constant, while global water demand is growing by time. At the same time, the quality of the earth water becoming significantly deteriorated and polluted, this represents great challenges for the major water treatment sectors such as municipal, industrial and environmental sectors.

Treating water becomes a global concern on the level of individuals, communities, industries, nations, and their national institutions seeking to explore methods to maintain this vital resource available and suitable for use. During the last decade, membrane bioreactor systems (MBRs), appear to be an efficient technology converting the polluted waters into high quality water convenient for drain into the water resources like rivers, seas in addition to sewage and increasingly into a reusable product. Desalination technology considered to be a recent source of potable and high quality water, a supplement to water supplies.

By 2005 the value of using (MBRs) become around $216.6 million, the global (MBRs) market is increasing at an average annual growth rate (AAGR) of 10.9% and reached about $363 million in 2010.These systems of treatment are growing more rapidly than the biggest market of advanced wastewater treatment equipments and faster than the markets of other types of membrane system. It is expected that the stricter environmental regulations all over the world will rise sales of (MBRs) and drive industry, municipalities, and prompt maritime sectors to consider (MBRs) technology.

During the prediction time, municipal wastewater treatment will become the first sector using (MBRs). The growth can mostly be due to the increasingly using of (MF) in industrial wastewater treatment. Increasing production quantity and improving technologies quality have minimize filtration membrane technologies capital and operating costs to the limit that made the usage of membrane treatment now an applicable alternative in many water and wastewater applications. Membrane treatment systems' market has grown up due to technological improvements resulting in cost reduction. This led the industrial sector to increase using filtration membrane treatment technologies.

During the past few years, membrane modules price has been minimized, due to firstly raised focus on research and development which improve product offers and secondly increasing competitive markets. (10)

2.2 Membrane Separation Technology

2.2.1 Membrane Terminology

A membrane is a semi-permeable or selectively permeable barrier which allows some molecules or ions to pass through it, on the other hand preventing the others from passing. Membrane separation mechanism is explained as shown in Figure (1), apportion of fluid known as permeate (filtrate) is passing across the membrane, while other constituents are ejected by the membrane and held in the concentrate stream as shown. (11)

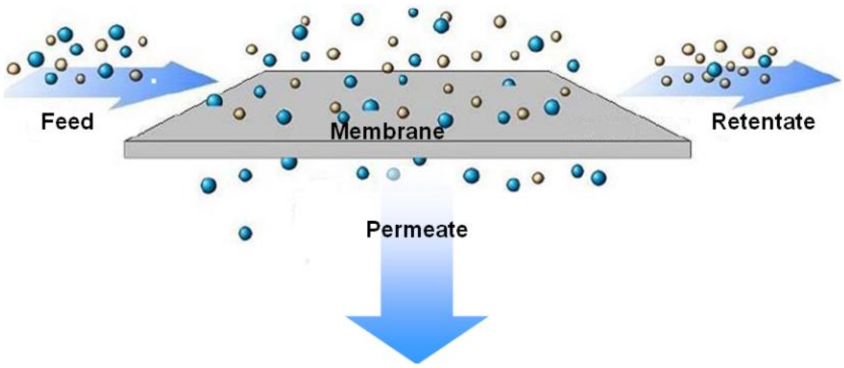

Figure (1) the membrane separation mechanism [12]

The transfer of materials through a membrane needs a driving force. A chemical reaction provides that driving force for material to transfer from one side to the other. The chemical potential gradient can be achieved by applying pressure difference, concentration difference, or temperature difference. Also material transport could happen due to the electric potential which leads to the ion exchange.

2.2.2 Membrane Separation Mechanism

The most important feature of membranes applied in separation processes is their capability to control the permeation of various types of substances. Most membranes fall into one of two major classes of membrane separation mechanisms; the first is pressure-driven and the second is electrically-driven. The most widely used membrane separation technologies are pressure-driven processes. [9,10,11]

A. Pressure-driven membrane

In pressure-driven processes, as shown in Figure (2), a hydraulic pressure forces water molecules known as permeate to pass across the membranes, this permeate water which recovered considered to be the produced pure water whereas the pollutants are held and concentrated in the main stream as retentate, that becomes the ejected or concentrated water flow.

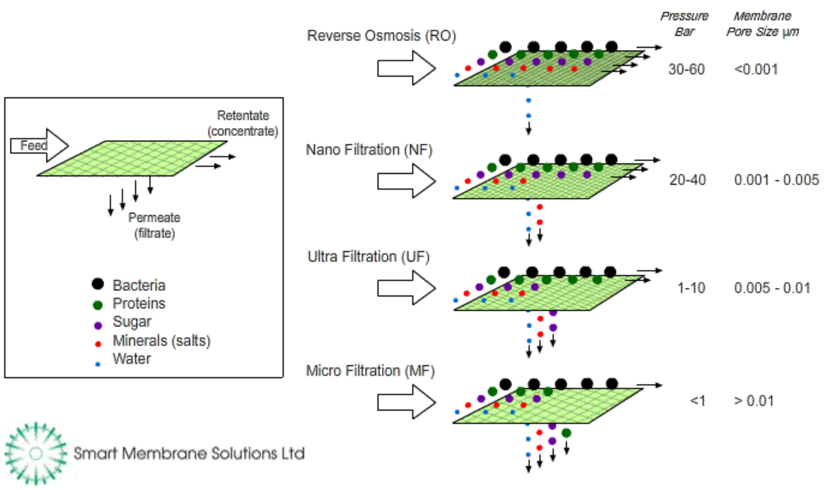

Figure (2) Pressure-driven membrane process and different pore size [13]

Pressure-driven flows are used to separate permeate in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes. The capability of performance of the different (MF) and (UF) and the size range of water and wastewater constituents, facilitate the removing of large organic particles, large colloids, and many different microorganisms.

A microfiltration membrane (MF) considering to be a permeable barrier which reduces turbidity and suspension of many kinds of colloids. Ultrafiltration membranes (UF) allow more removal than microfiltration filtration membranes (MF), however, operate at higher pressures. In wastewater treatment, microfiltration membranes (MF) or ultrafiltration membranes (UF) provide an appropriate grade of treatment. In drinking-water treatment, microfiltration membranes (MF) and ultrafiltration membranes (UF) may be applied together with nanofiltration membrane (NF), and reverse osmosis membrane (RO) to eliminate coarser material, so this sequence could reduce fouling of the less permeable membranes; nanofiltration membrane and reverse osmosis membrane.

For the production of drinking water, (RO) is the most ordinarily technology could be applied. Recently, Nanofiltration membranes (NF) could be used as an applicable alternative to the treatment of conventional water due to their capability of operating at lower pressures and attains higher recovery rates than reverse osmosis membrane (RO) technologies. Another benefit of using nanofiltration membrane (NF) is minimizing the cost of softening groundwater of low turbidity.

B. Electrically-driven membrane

In electrical-driven membrane processes, shown in Figure (3), an electric current is applied to move ions through the membrane from the purified water at the main stream. In this mechanism, the ions are detained in the concentrated stream then disposed. The product is the purified feed waters.

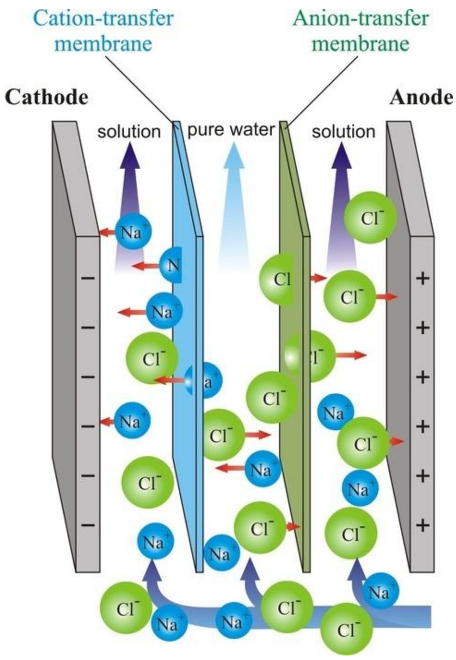

Figure (3) Electrically-driven membrane process [14]

Electro-dialysis reversal process (EDR) is an improvement of the main electro dialysis process and an example of electrically-driven membrane process. In (EDR), the driving force of the emerging direct-current is inverted periodically to prevent fouling and forming of scales on the membrane surface. This innovated process is improving the membrane efficiency and operating conditions. The main part of the process is ion exchange, where cation-selective and anion-selective membranes are placed alternately in a membrane panel. Water passes through the ionic membranes and then an electric current is applied across the panel, where the cathode and anode attract positive and negative ions respectively. The brine solution collected by anode and cathode is disposed concentrate, while desalinated water is collected to the collection system of clarified water.

2.3 Membrane Configuration

Membrane processes have two major flow filtration configurations; cross-flow and dead-end. These configurations are important operational technique affecting fouling kinetics and degree; understanding the basic differences between the techniques may help us explain clearly conflicting data. [15]

2.3.1 Cross-flow filtration

As shown in Figure (4), cross-flow filtration is the flowing of feed tangentially to the membrane surface. Concentrate discharged out of the same direction while the filtered passes across the membrane to the other side. The Cross-flow filtration membrane has advantages such, low tendency to membrane fouling on the other hand the disadvantages are high cost and labor intensity.

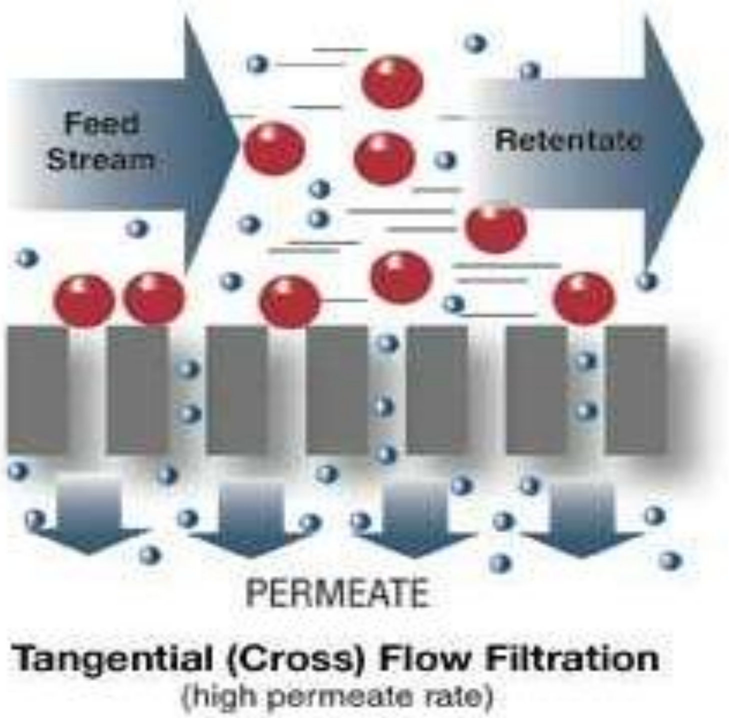

Figure (4) cross-flow filtration [16]

a. At constant pressure operation

As shown in Figure (5-a) the pressure is constant, and the flux is begins high and drops rapidly due to cake formation or retained particles. [15]

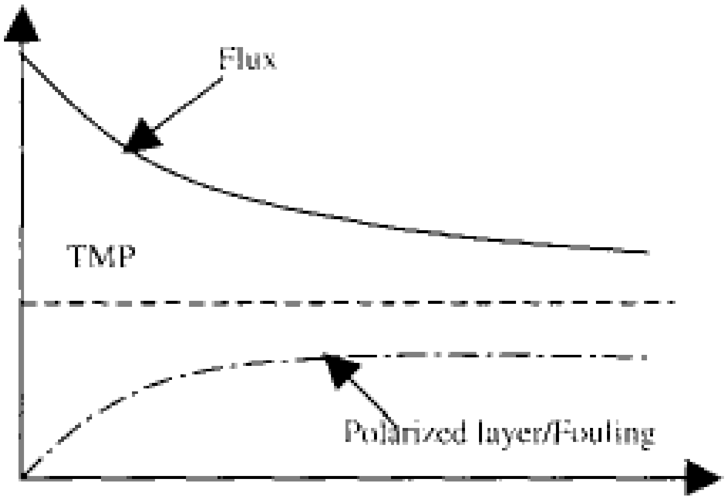

Figure (5-a) Cross flow filtration at constant pressure

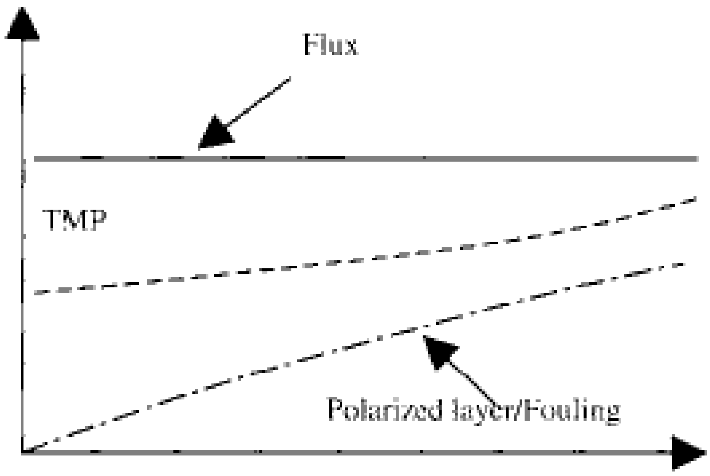

Figure (5-b) Cross-flow filtration at constant flux

b. At constant flux

Figure (5-b) shows the cross flow operation at constant flux, which will result in a gradual rise of the trans-membrane pressure (TMP) if fouling, occurs. For such type of operation occasional cleaning will be required.

2.3.2 Dead-end filtration

For dead-end filtration in Figure (6) the fluid passes across the membrane surface in normal direction. Dead-end filtration membranes have advantages like, the relative ease of fabrication which reduces the cost of the separation process, the ease of implementation and the lower price compared to the cross-flow membrane filtration. However, disadvantages are the extensive fouling, and concentration polarization.

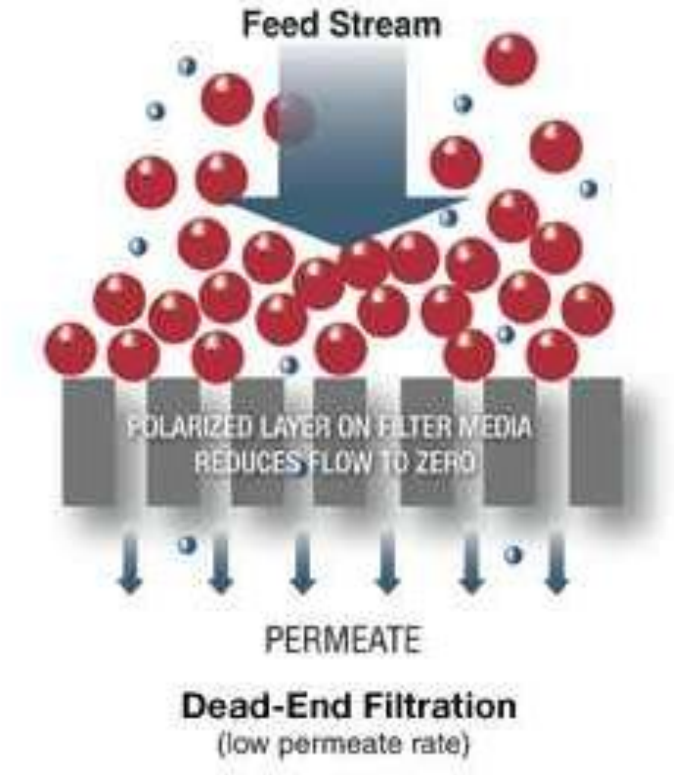

Figure (6) Conventional (Dead-end) [16]

i. Dead-end filtration at constant pressure operation

In dead-end operation at constant pressure as in Figure (7-a) the flux may decline to zero when the cake is formed and will not backwash. Laboratory studies have proffered to conduct experiments at constant pressure. It has been noticed, from observations, that at constant pressure operation fouling rate would be high at the beginning, due to the high flux, but at the end the fouling rate can slow down considerably, although it may not reach a zero rate. [17]

ii. Dead-end filtration at constant flux

As shown in Figure (7-b) the trans-membrane pressure (TMP) steadily increases till backwash occurs, and then the new filtration cycle starts. In dead filtration at constant flux; fouling rate can be relatively slow, but cake formation progresses with time to reach the same rate, this is unlike constant pressure operation. Constant flux operation is more likely used in plants of large-scale where it is required to generate a certain amount of permeate every day.

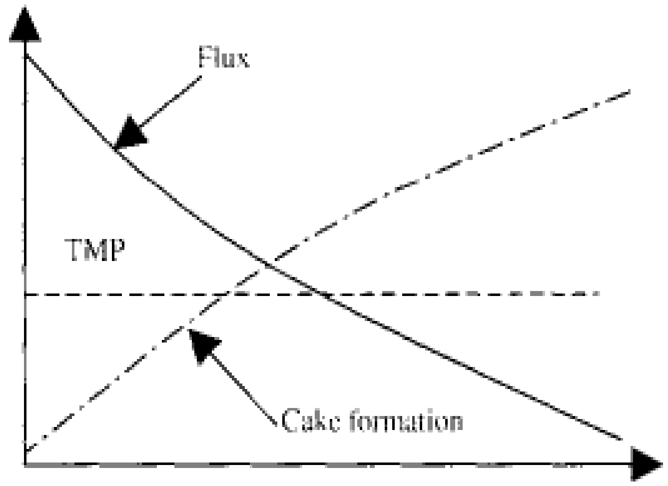

Figure (7-a) Dead-end Filtration at constant Pressure and decline flux

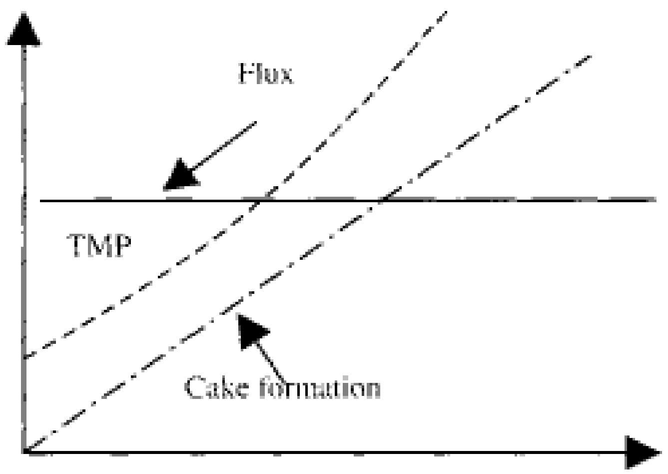

Figure (7-b) Dead-end Filtration at constant flux

2.4 Membrane Processes Types

The membrane is a physical barrier that permits specific materials to flow through; the passage depends on the physical and/or chemical properties of those materials. Membranes usually compose of a thin dense layer on top that forms the actual membrane with a porous support layer under it. Filtration Membrane types, as shown in Figure (8) based on membrane pore sizes, thickness, and membrane material, are classified into four types according to pore sizes as follows:

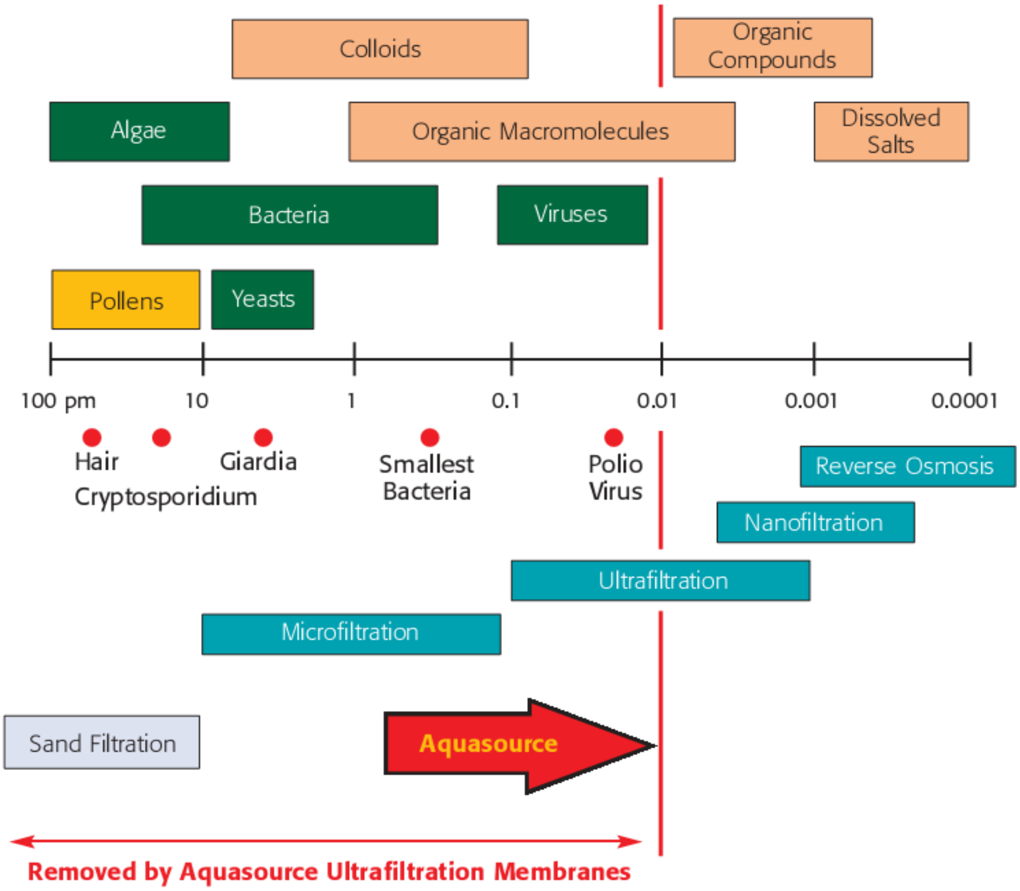

Figure (8) mechanisms of membrane filtration processes according to pore sizes [17]

2.4.1 Microfiltration membrane (MF)

Microfiltration is a process which intakes biological matter particles ranging from0.025µm to 10.0µm from solutions passing through micro porous membranes manufactured from polymeric materials. Microfiltration can be utilized as a pretreatment to nanofiltration and reverse osmosis.

2.4.2 Ultrafiltration membrane (UF)

Ultrafiltration membrane (UF) is a different type of membrane filtration that a hydrostatic pressure is forcing the fluid to flow through a quasi-porous film. Suspended solids and solutes of large molecules are held, while water and solutes of small molecules go across the membrane surface. This filtration procedure is utilized in industry for cleansing water.

2.4.3 Nanofiltration membrane (NF)

Nanofiltration membrane (NF) is an almost new membrane filtration technology applied regularly to treat low total dissolved solids (TDS) in water like surface water and fresh groundwater, and also in softening (polyvalent particle