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Membranes, Microbial Fuel Cell and Nanomaterials in Water and Wastewater Treatment

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Abstract

Water purification and re-use from secondary effluents is gaining traction as a viable solution to the growing challenge of water scarcity and declining water quality. Suspended particles, microorganisms, and a variety of organic contaminants make up the majority of secondary effluents from waste water treatment plants. In terms of eliminating contaminants from secondary effluents, membrane filtering and separation methods outperform classic wastewater treatment technologies like coagulation, flocculation, advanced oxidation, ion exchange, and activated carbon adsorption etc. They are the most efficient pollutant removal processes.

Key Words: Membranes, effluent, wastewater treatment, microbial fuel cells, nanomaterials.

1. Water Pollution

Industrial wastewater discharges and oil spills have caused chaos on water supplies in recent years. Water pollution not only causes ecological imbalances, but it also has a direct impact on human health. As a result, scientists must create effective wastewater purification technologies as soon as possible in order to address these serious concerns. High energy use, secondary pollutants, and unpredictable usage, on the other hand, appear to be unavoidable (Bhatia S C. 2010). Water contamination is due to the release of waste products and toxins into river sewage systems, such as the dumping of industrial wastes, incorrect disposal of human and animal wastes, and residue from agricultural operations, such as fertilizers and pesticides. (Woodard F. 2001)

Figure 1, 2: Water Pollution

2. Membranes for Wastewater Treatment

Membrane technology has long been acknowledged as a vital technique for separating toxins from contaminated sources in the water and wastewater treatment industries. Membranes are selective barriers that separate two phases, allowing certain components to flow while preventing others from doing so. Transport in membrane processes can be driven by a pressure gradient, as well as a chemical or electrical potential across the membrane.Membrane procedures rely on physical separation and typically do not require phase change or chemical addition in the input stream, making them a viable alternative to traditional wastewater treatment methods. The membranes have been subjected to extensive testing in order to increase their flux and selectivity. Furthermore, some studies have concentrated on reducing membrane fouling, which is the most serious issue with membranes in wastewater treatment. As a result, membrane performance and commercial markets have grown significantly in recent years. (Mai. Z, 2013)

2.1 Membrane Theory

Membrane separation techniques are defined by the instantaneous retention of organisms and product flow via a selectively permeable membrane. Membrane quality is influenced by a number of characteristics, including high permeate flow and selectivity, strong mechanical, chemical, thermal properties of membrane materials, less fouling during operation, and good compatibility with the working environment. A membrane is partially selective barrier between two homogeneous phases.For many wastewater treatment operations, the membrane rejects suspended or dissolved pollutants while allowing “purified” water to pass through.Based on their structure, membranes are split into two categories: symmetric and asymmetric. Asymmetric membranes feature at least two layers, whereas symmetric membranes have a virtually homogeneous structure across their thickness. The membrane's separation behaviour is determined by the active layer on top, while the porous layer below serves as the top layer.The membrane's mechanical stability is ensured by the supporting layer, which has a low resistance to permeate flow.

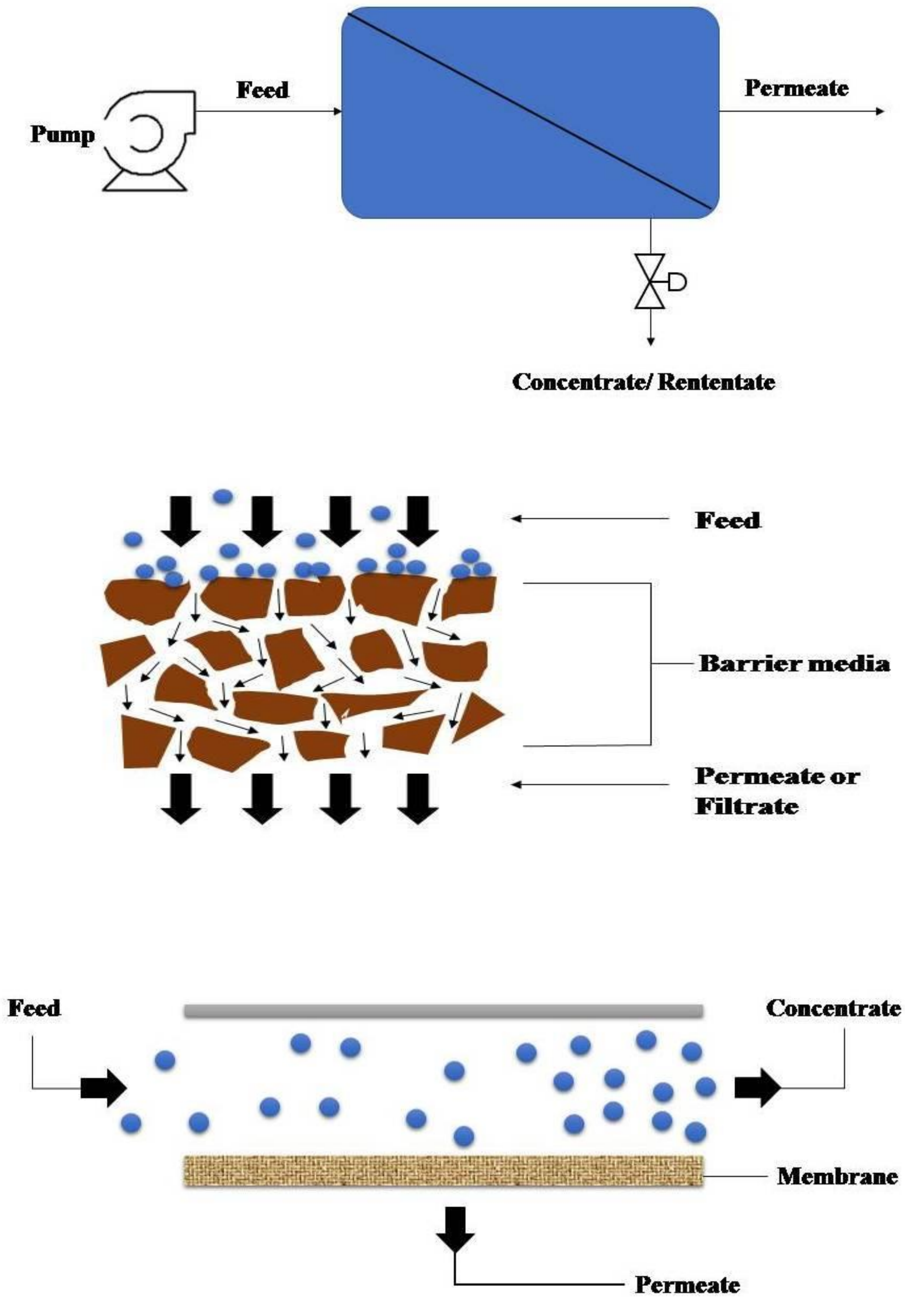

Figure 3,4,5: Conventional "dead-end" Filtration

Membrane processes consist of 3 streams: feed, retentate, product. The membrane, which is a semipermeable barrier, permits certain components to pass through but not other components, and some components pass through faster than others.There are two types of filtration operating modes: cross-flow and dead-end. The feed is pumped parallel to the membrane surface in cross-flow mode, whereas the membrane is fed orthogonally in dead-end mode.

2.2 Features of Membrane Separation Technologies

A quality membrane separation must possess the following features: continuous process that results in automatic operation, no phase or temperature fluctuations, the least amount of energy is usage, no substantial size limits due to the modular design, few moving parts (and thus require less maintenance), no influence on the form or chemistry of the pollutant, physical separation is ensured by a discrete membrane barrier, no chemical additions are required.

2.3 Membrane Separation Techniques in Industry

Over the last two decades, membrane technologies have emerged as one of the most important contributors to the resolution of water-related issues.Membranes for water and wastewater treatment have become more popular as a result of rising water shortages and strict regulations in industrialised countries.Municipalities, industries, and water firms now treat about 60 million m3/day using thousands of membrane plants. The most commonly utilised membrane separation techniques in industries for wastewater treatment are microfiltration , ultrafiltration, nanofiltration and reverse osmosis.The membrane pore size is the primary distinction between these processes .Table 1 summarizes the recognized membrane separationtechnologies in water and wastewater treatment.

Table 1. Summary of the recognized membrane separation technologies

Process	MF	UF	NF	NF
Driving force	0.1-3bar	0.5-10 bar	2-40 bar	7-75 bar
Separation mechanism	Molecular sieve	Molecular sieve	Molecular sieve	Molecular sieve
Material Retained	Suspended solids, bacteria	Macromolecules colloids	Micropollutants,salt,glucose,lactose	Dissolved salts
Material passed	Water dissolved solutes	Water dissolved salts	Water, monovalent salts	Water
Membrane type	Symmetric polymer of ceramic membranes	Asymmetric polymer composite or ceramic membrane	Asymmetric polymer or thin-film composite membrane	Thin-film composite membrane

2.4 Nano based filtration process

Nanofiltration is a special type of filtration in which the dynamic force is pressure.Nanofiltration sheaths have a higher thrust or resistance to multivalent ions, pesticides, and heavy metals than traditional behaviour approaches.It has now produced the most cutting-edge machinery in the field of water purification, which is currently available for use in your house, workplace, or engineering skills.The presentation of the nanofiltration sheath has been the subject of numerous reports Since its discovery in the late 1980s, nanofiltration (NF) membranes have come a long way.NF membranes have a pore size of 1 nm, which corresponds to a molecular weight cut-off (MWCO) of 300–500 Da, and have properties that fall in between ultra filtration (UF) and reverse osmosis (RO).Due to the dissociation of surface functional groups or the adsorption of charge solutes, NF membranes in contact with aqueous solution are also mildly charged. In the presence of a feed solution, polymeric NF membranes, for example, include ionizable groups such as carboxylic and sulfonic acid groups, resulting in a charged surface.NF membranes, like RO membranes, are effective at separating inorganic ions and small organic compounds. When compared to RO membranes, NF membranes have a lower rejection of monovalent ions, a larger rejection of divalent ions, and a higher flow.These characteristics have enabled NF to be used in a variety of specialty applications, including water and wastewater treatment, pharmaceutical biotechnology, and food engineering.

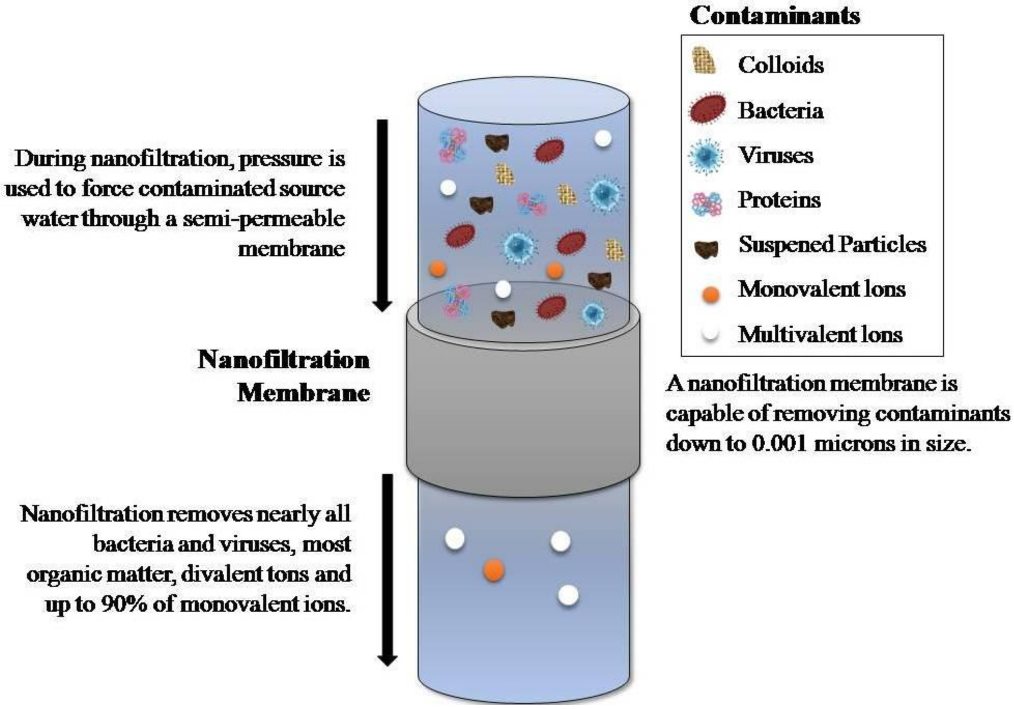

Figure 6: Nanofiltration Process

NF (Nanofiltration) membranes have a performance that is halfway between that of RO and UF (Ultrafiltration) membranes, which can be helpful in certain applications.Because salt rejection is limited when employing NF membranes for drinking water production, post-treatment costs such as demineralization are reduced. Membrane technology provides a number of advantages.The benefit of removing pollutants selectively based on their dimensions. Membranes with a wide range of pore sizes. Their physical properties are effective at removing a variety of pollutants. MFMembranes for (Membrane Filtration) have the biggest pore size. They reject big particles, as do other membrane technologies as well as bacteria and other microorganisms. The rejection is influenced by exclusion based on size, charge and physiochemical interactions between the solute, the solvent, and the membrane.The fraction that occurs in the final product is commonly expressed as coefficient of membrane's rejection. The salt rejection of an ideal RO membrane is greater than 99 percent.

5.2 Reverse Osmosis

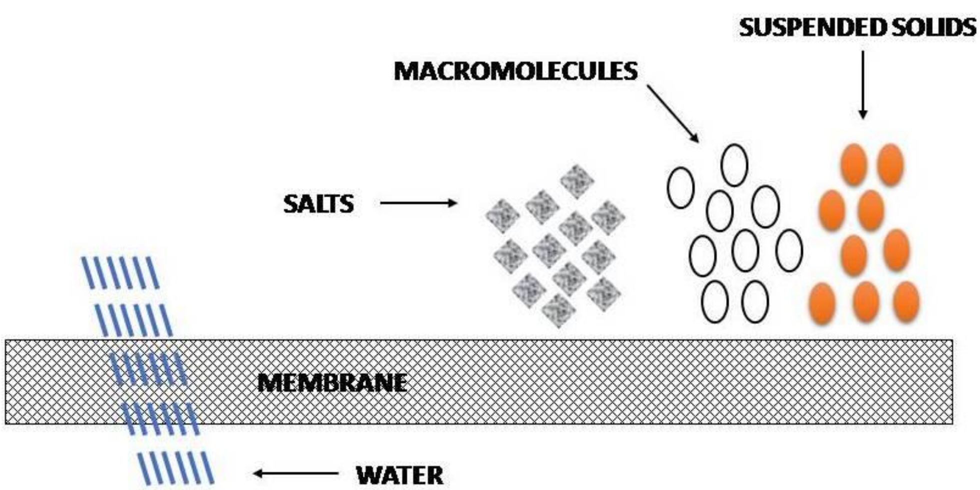

Figure 7: Removal of impurities in RO

Impurities are removed by a semi-permeable membrane using two mechanisms: 1) Mineral salts are repelled by dielectric and molecular forces. 2) Seiving - Does not allow particle matter larger than 0.0005 microns to pass through. Only the tiniest chemical and gas molecules are allowed to pass.

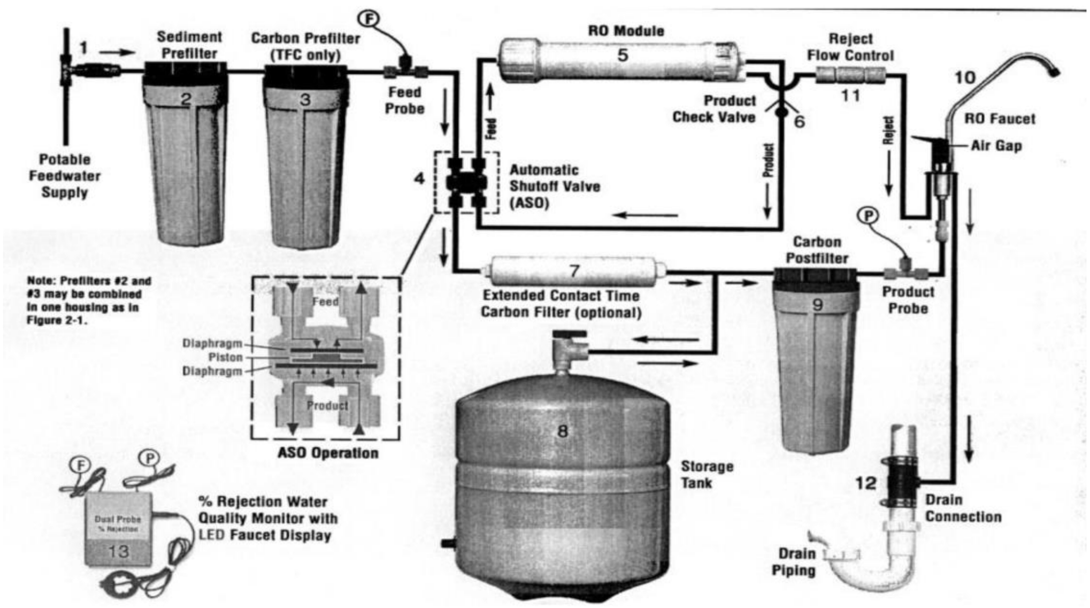

Figure 8: RO System Flow Diagram

The RO System Controls are product water check valve (that prevents back pressure on the membrane), automatic shut-off valve (that keeps the pressure in the storage tank between 12 and 2/3 of the feed line pressure), brine flow restrictor (that keep reject rinse flow at 3x to 5x product flow, maintain membrane life, water quality and avoid water waste).

2.5 Ultrafiltration and Microfiltration

Ultrafiltration (UF) membranes having pores as small as 0.1 m in diameter. Whereas, membranes having pore diameters lies from 0.1 -10 µm are referred as Microfiltration. Molecular sieve is a common mechanism in which particles are separated.It flows readily through membrane pores with a smaller diameter than the membrane pore diameter. Smaller particles are trapped in the pore, while the bigger particles are expelled.

Figure 9, 10: Ultrafiltration and Microfiltration for Wastewater Recycling

The particles to be separated, on the other hand, are typically adsorbed on the surface of pore, resulting in the reduction in pore size. As a result, the particles that are rejected by the membrane are typically much smaller than the pores' size. Both ultafiltration and microfiltration membranes are porous and can be classified into two types: screen membrane filters and depth membrane filters.

2.6 Membrane Bioreactor (MBR)

Membrane bioreactors (MBRs), which combine membrane filtration with biological treatment, are one of the most successful hybrid membrane systems in wastewater treatment. Membrane bioreactor (MBR) technology has risen to prominence as a preferred wastewater treatment method over the activated sludge process (ASP), which has been the standard municipal wastewater treatment method for the past century.MBR is one of the most important breakthroughs in wastewater treatment since it solves the shortcomings of traditional ASPs, such as the need for a lot of room for secondary clarifiers, issues with liquid–solid separation and excess sludge generation. However, there are some drawbacks to using MBR technology, such as greater energy costs, the necessity to manage membrane fouling issues, and the possibility for high membrane replacement costs. (Zirehpour A. 2016)

3 Case study: Microbial Fuel Cell and Proton Exchange Membranes

3.1 Heavy Metals

Heavy metal is defined as any metallic chemical element having a relatively high density that is harmful or deadly at low doses.Chromium, for instance, is one of the heavy metals. Poisonous compounds include arsenic, mercury, and lead. They are components of the Earth's crust that are naturally occurring. They are incapable of being destroyed or degraded in any way.Copper, selenium, and zinc, for example, are heavy metals, required to sustain the metabolism of the human body and can be found in minute amounts in food, drinking water, and the air.They can, however, cause toxicity in higher amounts.Poisoning from heavy metal arises as a consequence of tainted drinking water and significant levels of ozone in the atmosphere near the source of pollution.

3.2 Hexavalent Chromium (Cr (VI)) in Industrial Wastewater

Cr (VI) is present in the wastewaters of a number of industries producing steel, chrome plated products, tannery products, dye stuff, paints. (Mwinyihija. 2010)

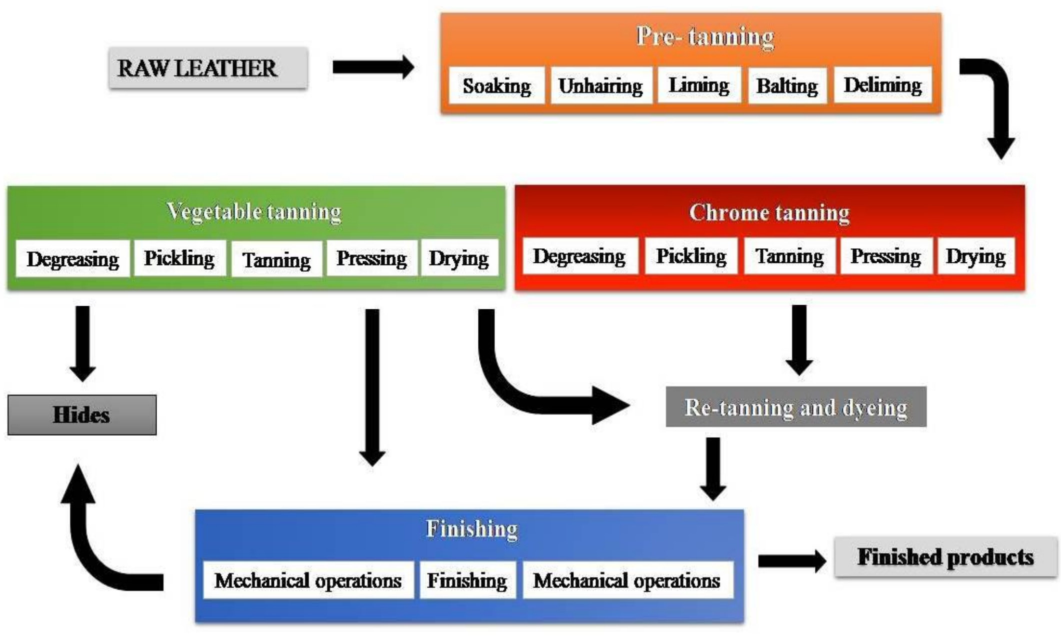

Figure 11: Chromium Discharge in Tanning Industry

3.3 Tanning Process

Process industries are taking up pollution prevention methods in their manufacturing technologies. Hence a of research is taken up on finding alternate solutions for chrome tanning. The leather tanning primarily employs inorganic tannins viz., chromium, aluminium, ferrous and zirconium; organic tannins such as, vegetable tannins aldehydes; synthetic and above combinations are usually the conventional tanning methods . These methods give robustness, decay prevention and prevent resistance, thermal and biodegradations. On the other hand, their negative factors include the disadvantages of the known chrome tannins are limited available source, poor exhaustion and minimal recoverable or reusable from leather wastes Further disadvantages, chromium and other inorganic tannins include the complicated process for waste treatment with net increase in biochemical oxygen demand chemical oxygen demand, total solid, dissolved solids, suspended solids, chromium and salts content The pollution problems of trivalent chromium in waste are due to insufficiency of the treatment systems and formation of hexavalent chromium , carcinogenic and mutagenic, which led to the search for an eco-friendly greener option to tanning process. The wastewater discharged by the tannery industries in water bodies contains one of the major sources of pollutant concentration such as organic contaminants and heavy metals especially Cr (VI). The organic contaminants are discharged after the fleshing process and Cr(VI) after tanning process. The Cr(VI) concentration present in tannery effluent that is discharged into the water bodies is 3mg/L, but the permissible limit as per PCB norms is 0.1mg/L only. (N. Manivasakam. 2003)

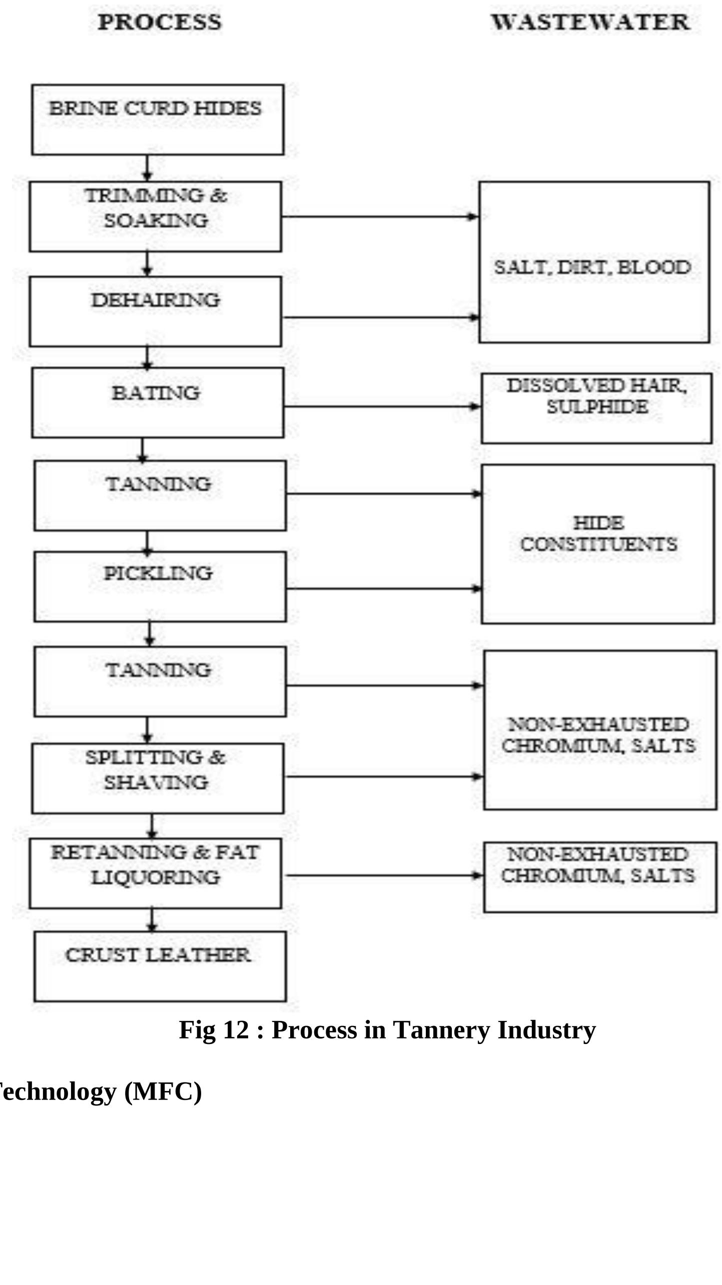

Fig 12 : Process in Tannery Industry

3.4 Microbial Fuel cell Technology (MFC)

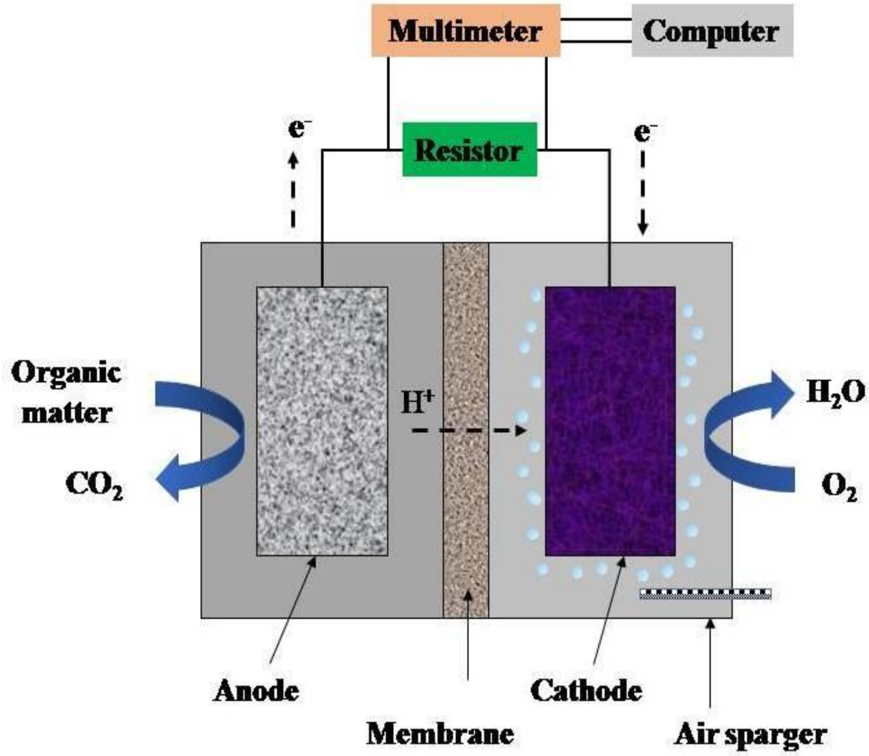

Figure 13: Pictorial Representation of MFC

MFC is a suitable technology for organic contaminant removal, heavy metals reduction and electricity production. A MFC is a bioelectrochemical reactor that converts chemical to electrical energy through catalytic and enzymatic reactions of microorganisms in the absence of oxygen. MFCs can simultaneously be used in the treatment of wastewater which enables the breakdown of organic contaminants. The basic components of MFC are anode, cathode, a PEM and external electrical circuit. In MFC, the organic substrates are used as fuels by the bacterial community present in the anode compartment and electrons and protons are produced through biological process. The electrons transferred by the bacteria reach the cathode through an external electrical circuit and enter into the cathode chamber and are absorbed by the terminal electron acceptors that reduce the heavy metal concentration. The protons penetrate through the PEM to the cathode compartment and eventually combine with the electron acceptors in order to form water molecules (Carmalin Sophia . 2016)

3.5 Principle behind MFC operation:

Based on anodic oxidation and cathodic reduction reactions.

$C_6H_{12}O_6$ (glucose) + $6H_2O$ (water) = $6CO_2$ (carbon dioxide) + $24H^+$ (hydrogen ion) + $24e^-$ (Anode)

$4e^- + 4H^+ + O_2$ (oxygen) = $2H_2O$ (Cathode)

$C_6H_{12}O_6$ (glucose) + $6H_2O$ (water) + $6O_2$ (oxygen) = $6CO_2$ (carbon dioxide) + $12H_2O$ (Overall)

3.6 Membrane Processes for Tannery Wastewater Treatment

Several studies have decribed that crossflow microfiltration, ultrafiltration , nanofiltration , reverse osmosis and supported liquid membranes can be used to recover chromium from spent liquors in the leather industry. Nafion, Ultra Filtration membranes, Ultrex, Salt bridge, and Clay are some of the proton exchange membranes (PEMs) used in MFC. Nafion is valued above all because of its high proton conductivity and ability to generate electricity.
(S. Porchelvi. 2018).

Figure 14: Nafion membrane (Ion Power, Inc.)

3.7 **Proton Exchange Membrane** (PEM)

Nafion is also known as a proton exchange membrane since it is designed to transfer H+ ions, but in an MFC, it preferentially conducts other positively charged substances like sodium, potassium, ammonia, calcium and magnesium ions that are typically 10 times more abundant than protons in solution. SPEEK – Sulfonated Polyether ether ketone (PEEK) is a suitable candidate for the fuel cell community to address the disadvantages of Nafion. PEEK is a low-cost polymer that has excellent thermal and mechanical qualities. This polymer's proton conductivity is achieved through sulfonation, hence the name SPEEK. The inclusion of an aromatic group in SPEEK results in a higher mechanical rigidity of the polymer backbone. Electrolytes of this type have the potential to impact MFC performance. The MFC is a novel technology that can produce power while also treating wastewater. The utilization of Nafion 117 as a Proton Exchange Membrane (PEM) and Pt as a cathode catalyst for oxygen reduction raises the operational cost of this approach. The PEM in this investigation was sulfonated poly ether ether ketone (SPEEK). (Putra H E. 2018)

According to research studies, using SPEEK in power generation is about two times more cost effective than using Nafion 117. Furthermore, SPEEK's COD elimination (88%) is more than Nafion 117's (76%); as a result, with significant increases in power density, SPEEK could be a potential PEM in MFCs on an industrial scale Heavy metal reduction is a common use for Dual Chambered MFCs using Nafion 117 as PEM and the same is expected for SPEEK. (Parnian M.J. 2016, Ghasemi M. 2016)

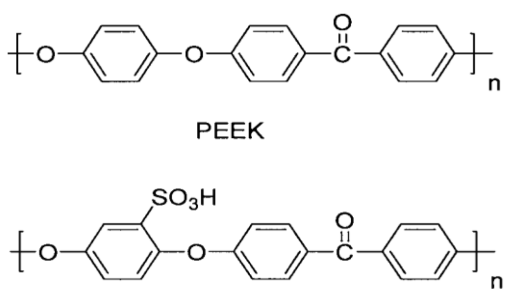

Figure 15: Chemical Structure of SPEEK

4 Nanocomposite Membranes

Nanomaterials have been intensively studied and developed globally in recent years due to the extraordinary qualities that come from nanoscale size, such as increased catalysis and adsorption properties, as well as high reactivity. Nanomaterials have been successfully employed in water and wastewater after numerous studies have demonstrated that they can effectively eliminate various impurities in water. Zerovalent metal nanoparticles (like silver, ferrous and zinc), metal oxide nanoparticles (titanium dioxide, zinc oxides, and iron oxides), and carbonanotubes, are the most investigated nanomaterials. (Boddu V. 2003., Giagnorio M. 2018).

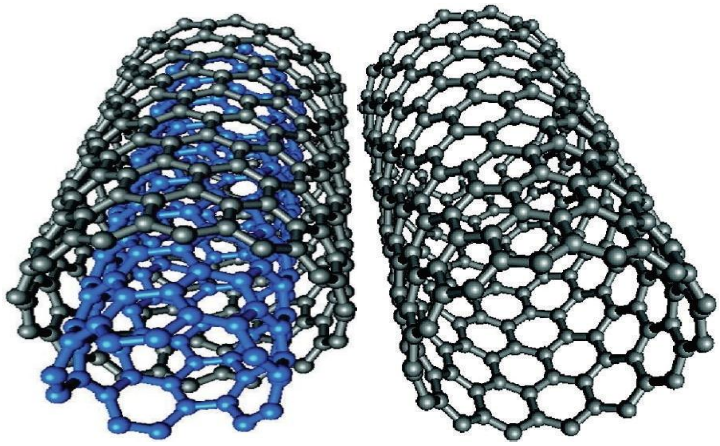

Figure 16: Superstructure representations of (a) MWCNTs and (b) SWCNTs

Carbon nanotubes are made up of graphene sheets folded into cylinders as small as 1 nm in diameter. Because of their unique features, carbon nanotubes (CNTs) have piqued interest as a potential adsorbent. CNTs have outstanding adsorption efficiencies due to their enormous specific surface area and abundance of porous structures. CNTs can be cateorized into two types (Figure 10): (1) MWCNTs, which are made up of numerous layers of concentric cylinders with a spacing of about 0.34nm between the adjacent layers, and (2) SWCNTs, which comprise of single layers of graphene sheets seamlessly rolled into cylindrical tubes . Both MWCNTs and SWCNTs have been used to remove pollutants from water in recent years. In order to improve power output and heavy metal reduction activities, such nanocomposites can be incorporated to to SPEEK membrane. (Mitra S. 2017., Gehrke. I. 2015)

SPEEK Nanocomposite Membrane can be used as PEM (Proton Exchange Membrane) instead of expensive proton exchange membrane like Nafion 117. PEEK (Polyether ether ketone) is actively researched in fuel cell community as a superior candidate to that of Nafion. PEEK is relatively less costly than Nafion membrane with excellent thermal stability and mechanical properties. Proton conductivity for this polymer is obtained by the process of sulfonation and hence the name SPEEK. Addition of nano materials like titanium dioxides (TiO_2) or carbon nanotubes (CNTs) can be incorporated in the SPEEK membrane to increase proton conductivity and to reduce biofouling on the membrane surface. (Hasham. A. 2018).

5 Conclusion

Fabrication of membranes made of a variety of materials has yielded promising results for water an wastewater treatment process. In membrane technology, selectivity and scalability are critical issues. The development of membrane selectivity is critical for enhanced and high-quality water separation. Synthetic membranes' strength and endurance are also desirable qualities for developing next-generation high-efficiency membranes. Membranes with nanocomposites yield better filtration efficiency. In this review we have read various aspects of the existing membrane filtration technologies in the commercial and industrial arena, and the upcoming membranes and wastewater treatment technology in the research and development arena. Furthermore, it is high time to focus research efforts on developing multifunctional membranes with a broader range of uses. It is believed that proton exchange membranes incorporated with nanocomposites will yield better heavy metal reduction efficiency in wastewater when compared to the exiting proton exchange membranes without nanocomposites. However, more experimental research findings are needed to establish this hypothesis.

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