DESIGN & APPLICATION OF HYBRID MBR TECHNOLOGY IN CONTAMINANTS REMOVAL

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I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Chemical Engineering studies. All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

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To Maa, Baba

To Maa

To my beloved elder sister Supti

To Ishtiaq Jami, Suphal Basak, Kamalesh Roy

&

TO my labmates

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Abstract

This research evaluates the application of advanced hybrid Membrane Bioreactor (MBR) technology to remove contamination such as agricultural waste, biomedical waste, dairy waste, household waste and heavy metals from waste water. A Membrane bioreactor (MBR) processes are mainly used for wastewater treatment (WWT) by using microfiltration (MF) or ultrafiltration (UF) and integrating them with a biological process like a suspended growth bioreactor. In this research different membrane technologies and advanced processes of contamination removal in wastewater have been reviewed. Using chemicals and reagents nano composite materials and brilliant green solution have been prepared. After that 2mg of nano composite material was mixed with every prepared solution for dye removal. To calculate efficiency of the nano adsorbent, UV-visible spectrophotometer was used. From the observational data, 3 graphs have been obtained which summarizes the time vs concentration, time vs ln (concentration) and time vs 1/c. Henceforth, this current study presents a one pot synthesis method for fabrication of Graphene Oxide (GO) based nanocomposite materials; also, batch adsorption experiments were carried out to investigate the removal of cationic dyes e.g., brilliant green from the water using Graphene Oxide (GO) based nanocomposite materials. Further the order of the reaction was determined and it was found to be concurring with second order kinetics. Percentage removal 61.33% and maximum uptake removal 0.092 mg/mg is recorded for brilliant green dye in the batch adsorption experiment.

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Chapter 1: Introduction

1.1 Background

Membrane Bioreactor (MBR) technology is an advanced wastewater treatment process that combines biological treatment (activated sludge process) with membrane filtration. It uses semi-permeable membranes to separate treated water from biomass (microorganisms) and suspended solids, resulting in high-quality effluent suitable for discharge or water reuse applications. MBRs offer several advantages over conventional wastewater treatment processes and have gained popularity for various applications. MBRs provide superior removal of suspended solids, bacteria, pathogens, and even smaller particles like microplastics compared to conventional treatment methods. The membranes act as a physical barrier, producing a high-quality effluent with low turbidity and reduced risk of contamination [1]. The use of membranes ensures consistent and reliable treatment performance, irrespective of fluctuations in influent quality or flow rate. This makes MBRs suitable for meeting stringent water quality standards and regulations. systems can be easily retrofitted into existing wastewater treatment plants or designed as standalone units for various applications, such as municipal wastewater treatment, industrial wastewater treatment, and decentralized wastewater treatment. Nanotechnology has shown significant promise in improving various aspects of wastewater treatment processes. It involves the application of nanomaterials or nanoscale processes to enhance the efficiency, effectiveness, and sustainability of wastewater treatment methods. Nanomaterials such as activated carbon nanoparticles, carbon nanotubes, and nanoscale metal oxides possess a high surface area, which makes them excellent adsorbents for removing contaminants like heavy metals, dyes, and organic pollutants from wastewater [2]. The combination of biological treatment with membrane filtration in MBRs results in higher sludge concentrations, leading to reduced sludge production compared to conventional activated sludge processes. This minimizes the costs associated with sludge disposal and management.

Membrane bioreactors (MBRs), which use membrane filtration instead of sedimentation tanks ,have been used extensively in industrial wastewater treatment to produce high-quality effluent for water reuse. Without using chemicals, solid-liquid separation can be improved by adding membranes to MBR systems. The concentration of biomass in the aeration tank of MBR systems

can reach up to 5,000–20,000 mg/L since bulking, foaming, and sludge settle ability issues are no longer issues in membrane separation [3]. By lowering system footprints, reducing sludge formation, and increasing organic biodegradation rates, high biomass concentrations can strengthen the system.It is reasonable to assume that MBRs could be a feasible alternative to treat P&P wastewater and to meet the new, strict criteria of effluent color given their high organic removal efficiency and improved solid-liquid separation. Nevertheless, membrane fouling remains a chronic issue with MBR systems in spite of their many benefits.

Treatment of wastewater is an emerging issue of global concern especially due to growing industrialization, urban centers and population size. The increasing pressure of water scarcity and the preservation of fresh water for aquatic life has forced the invention of better treatment techniques. From these, Membrane Bioreactor (MBR), technology has proved to be an effective solution to combating wastewater and contamination [4].

MBR technology utilizes principles of conventional biological wastewater treatment while incorporating membrane filtration; has the following benefits;: The benefits are increases in treatment efficiency, reduction in treatment plant size, and increase in effluent quality. It has however received considerable focus in the recent past because of the potential to deliver high quality treated water for reuse.To meet the treatment demanding of MBR or to avoid some of its problems, various types of MBR have been devised. Some of them are submerged MBRs, external MBRs, as well as other MBRs central to various primary and secondary treatment processes. Each proposed configuration boasts definite advantages as for flexibility of operation, energy demands, and the level of contaminant elimination. It is therefore essential to evaluate these different MBR technologies in view of enhancing wastewater treatment and in order to tackle various contamination cases [5].The underlying concept that forms the basis of MBR technology therefore is a combination of biological activities as well as membrane separation. Microorganisms present in the bioreactor carry out the process of oxidation and reduction of organic matter as well as other pollutants, while the membrane filtration part isolates the purified water from biomass and other soluble solids. These processes' general principles are necessary to be understood to get a better perspective of MBRs and improve the current and create new hybrid systems.

The choice and balancing of the microorganisms within the bioreactor are tremendously significant in the effectiveness of MBR systems. Several bacterial communities possess difference ability with

regard to their efficiencies in degrading the contaminants and accommodation making to the type of environment. The microbial population involved in the biological processes is sensitive to change in the process parameters such as hydraulic retention time, sludge retention time and dissolved oxygen levels. This optimization has a significant relationship with microbial ecology and those factors that controls microbial activity in MBR systems.The continuous improvements in hybrid MBR technologies presents one of the major possibilities of improving the removal of contaminant into wastewater [6]. For instance, integrating processes like advanced oxidation, adsorption or any electrochemical process, the hybrid MBR systems have the capability to address a wide customer base and give better treatment outcomes. The formulation and implementation of such systems therefore calls for strategic evaluation of the interdependences that exist in the given treatment technologies and the resulting general efficiency of the system in place [7].

Promising techniques that have to be pursued to improve MBR technology in terms of removing contaminations from the wastewater include the following: Some of these may embrace modification of membrane surface to minimize fouling and to enhance the selectivity, use of new materials in adsorption of contaminants and intelligent control systems for better control of the process. Also, the use of renewable energy resources, energy recovery systems can enhance the sustainability and economy of the MBR systems.These critical areas of MBR technology in wastewater treatment are the focus of this research. As a result, this researh aims at contributing to the knowledge of wastewater treatment technologies as it looks at the identification and performance evaluation of various MBR configurations, microbial process optimisation, as well as the development of better innovative hybrid systems [8]. It is envisaged that the understanding arising from this research will be of immense benefit to enhancing water quality, encouraging the reuse of water and overall global water crisis mitigation.In addition, the study will seek to determine the ability of MBR technology in the elimination of emergent contaminants, including pharmaceuticals, personal care products, and microplastics, which are posing considerable risks to the freshwater sources, and inhabitants. To contribute to the progressive advancement of MBR technology for the treatment of the multifaceted wastewater issues of the 21st century, it is goals of this research to advance new approaches for improving the effectiveness of contamination elimination [9].

1.2 Research rationale

A supply of clean water is an essential requirement for the establishment and maintenance of diverse human activities. Water resources provide valuable food through aquatic life and irrigation for agriculture production. However, liquid and solid wastes produced by human settlements and industrial activities pollute most of the water sources throughout the world.Due to massive worldwide increases in the human population, water will become one of the scarcest resources in the 21st century. In the year 2021 the majority of the global population (some 56% of world population) will live in urban environments. By the year 2021, there will be 44 megacities with a population of over 10 million each, 18 of which will exist in the developing world [18]. Central to the urbanization phenomena are the problems associated with providing municipal services and water sector infrastructure, including the provision of both fresh water resources and sanitation services [10].

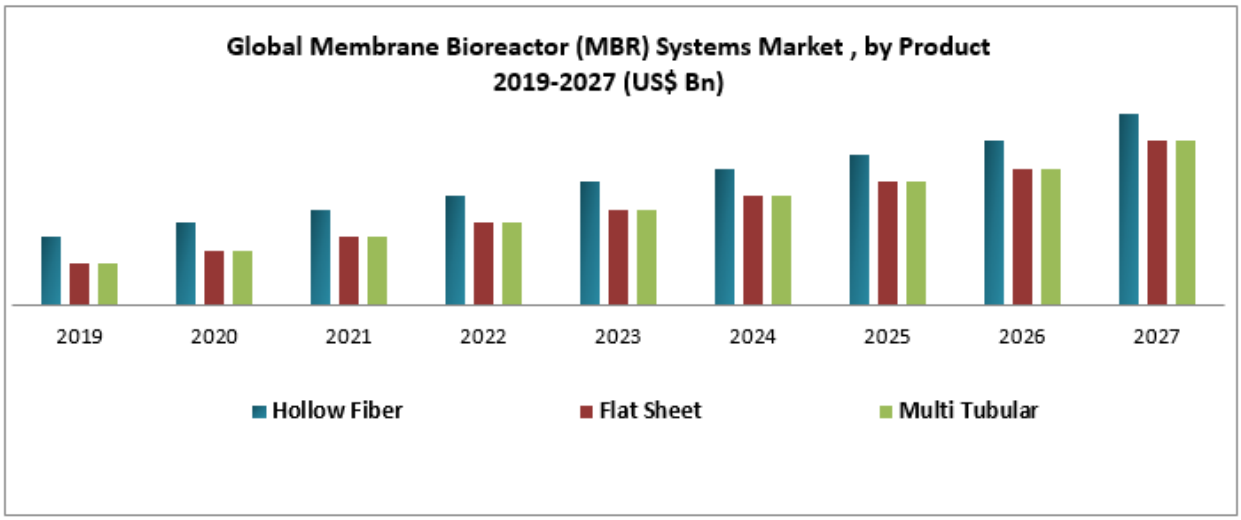
The outbreak of COVID-19 pandemic has created havoc all across the globe causing exponential casualties and tremendous health and economic loss. With increasing COVID-19 cases, the amount of biomedical waste has increased manifolds making more people vulnerable to the pandemic. The developing and underdeveloped countries are already facing the challenges of waste management, and the waste generated during the pandemic scenario has added to the already existing challenges. However, the dark side was that the surging [11].

COVID cases increased the amount of plastic waste produced worldwide by around eight million tons from 2018 to August 2021, 46% of which was contributed by Asia alone. Production and use of single use disposable masks and plastic based personal protective equipment (PPEs) shot up drastically reflected by an increase in its global market of USD 50.9 billion in 2019 to USD 91.6 billion in 2021. As human numbers increase, greater strains will be placed on available resources and pose even greater threat to environmental sources. A report by the Secretary-General of the United Nations Commission on Sustainable Development (1997) concluded that there is no sustainability in the current uses of fresh water by either developing or developed nations, and that worldwide, water usage has been growing at more than three times the world’s population increase, consequently leading to widespread public health problems, limiting economic and agricultural development and adversely affecting a wide range of ecosystems. Although India occupies only 3.29 million km2 geographical area, which forms 2.4% of the world's land area, it supports over

15% of world's population. India also has a livestock population of 500 million, which is about 20% of world's total livestock [19]. However, total annual utilizable water resources of the country are 1086 km3 which is only 4% of world's water resources. Total annual utilizable resources of surface water and ground water are 690 and 396 km3, respectively (Ministry of Water Resources, 1999). Consequent to rapid growth in population and increasing water demand, stress on water resources in India is increasing and per capita water availability is reducing day by day. Total water requirement of the country in 2050 is estimated to be 1450 km3 which is higher than the current availability of 1086 km3. The total wastewater generated by 299 class-1 cities is 16,652.5 MLD. Out of this, about 59% is generated by 23 metro cities [12].

Due to growth in population, the number of industries has exponentially increased. This result in either severe environmental challenges or huge demand for water supply. According to the current status of water resources, it is utmost importance to utilize novel solutions to improve water cycle management in public and industrial areas. Additionally, implementation of the novel sustainable techniques in water cycle is required to consider the true value of water. With this in mind, recovery of the wastewater can be considered as a highly valuable resource which can be accomplished with the aid advanced technologies. One of the alternative technologies for wastewater treatment is the use of membrane biological reactor. It is a combination of biological process with membrane filtration that is called Membrane Bioreactor (MBR). In this case, the degradation of biomass is occurred inside the bioreactor tank, while separation of treated wastewater form microorganisms is completed in a membrane module [13]. Over the last two decades, MBR attracts lots of attention due to its potential to produce high quality effluent and currently considered as a mature technology to treat wastewater.It was reported that 22.4% of Compound Annual Growth Rate (CAGR) was expected for the MBR market. It is considered to have a highest MBR market growth in the world. Fig. 1 summarizes the MBR market growth by region during the period 2019-2027. Due to growth in population, the number of industries has exponentially increased. This result in either severe environmental challenges or huge demand for water supply. According to the current status of water resources, it is utmost importance to utilize novel solutions to improve water cycle management in public and industrial areas. Additionally, implementation of the novel sustainable techniques in water cycle is required to consider the true value of water. With this in mind, recovery of the wastewater can be considered as a highly valuable resource which can be accomplished with the aid advanced technologies. One of the

alternative technologies for wastewater treatment is the use of membrane biological reactor. Recent BCC (Business Communication Company) report showed that the market size of MBR to be 3.0 billion USD in 2019 and is expected, at a CAGR of 7%, to reach 4.2 billion UDS by 2024 [20]. Worldwide, APAC (Asia-Pacific i.e., one segment of MBR market if it is categorized based on the region. It is considered to have a highest MBR market growth in the world. Fig. 1 summarizes the MBR market growth by region during the period 2019-2027 [14].



The reason for this research on a new type of hybrid Membrane Bioreactor (MBR) technology for wastewater treatment is based in the fact that the present methods are not efficient enough to cope with the increasing demand for clean water. As the positive trend in water provisions is distinguished, the population faces severe problems of water deficiency and pollution, so the development of new technologies to treat and reuse wastewater is crucial. The following are some of the factors explaining why this research is relevant and essential in the course of its implementation The factors include:

To begin with, the global population has been on the rise and has been urbanizing at a very high rate hence leading to more generation of wastewater. Current types of treatment cannot fully address the issues of effluent quality that is desired for environmental preservation and water recycling. Since MBR technology yields good quality of effluent, it presents an option out of this challenge. However, there is still a fairly deficit of knowledge on the capacity of MBR systems regarding various pollutants and costs of their work. It is in this regard that this research seek to add to this on-going development by examining intricate other hybrid MBR configurations.

Second, new and more complex pollutants including drugs, biodegradable micropollutants, cosmetic and personal care products have become constituent of wastewater that present a great challenge to current WAS water treatment procedures. Such substances are known as emerging pollutants and contribute to harm of aquatic communities and can also pose a threat to the health of people. The engineering of mishmash MBR technologies that can bail out these stubborn pollutants is paramount to the protection of environmental and public health. This research aims to fill this gap by developing and implementing novel advanced hybrid MBR systems from which would cater for the wide range of pollutants [15].

Thirdly, the emphasis of new trends in water management that implies the extremely important concept of circular economy, including water reuse, requires the advancement in the treatment technologies that will provide the necessary quality of effluent for the attainable reuse options. MBR technology has demonstrated much promise in this area, but there is a need to advance the way it works, in the cost and in the extent of the contaminants it is capable of removing. It is the goal of this study to fine-tune process parameters, along with investigate new hybrid setups with a view to improving the performance of this MBR technology in delivering water with quality fit for reuse [16].

Fourthly, there is still a problem of energy intensity to the processes of wastewater treatment, including MBR systems. However, there is need to enhance the energy efficiency in these systems so as to enhance use and make the systems sustainable. This research rationale also involves elucidation on means of making energy consumption in MBR systems efficient, probably by incorporating renewables or by enhancing efficient functional methodologies. Such advancements would help bring the carbon footprint of wastewater treatment down to satisfaction of sustainability goals of the world [17].

Fifthly, it is vital in the MBR systems that the selection and optimization of microorganisms which are employed have a significant influence. But the microbial ecology of bioreactors and other systems that are useful for pollutant elimination remains largely unknown and has yet to be fine-tuned to its best advantages. This research proposes to fill this gap by studying the selectivity and activity of microorganisms and its relation to process parameters to improve the efficiency and robustnes of MBRs.

Lastly, the continuation of research to create different mechanisms for hybrid MBR technologies indicate that the issue of membrane fouling and ineligible limits of destroying some contaminants in normal MBR systems is still a promising area which has to be improved. Thus, the aim of this research is to enhance the treatment efficiency of wastewater through the integration of comprehensible related treatment processes. It can also be considered that the introduction of such an approach can help in the extension of the possibilities of using MBR technology in other types of wastewater and for other types of treatment. Therefore, this research is aiming at developing efficient and effective methods of treating wastewaters facing ever increasing quizzicalities. In this work, paying specific attention to the improvement of the hybrid MBR technologies, fine tuning of the microbial processes, and upgrading of the contaminant removal technologies, the author endeavors to make a useful input to the body of knowledge in wastewater treatment. Thus, the consequences of this research can influence the water management practices, environmental conservation measures, and the promotion of the well-being of the people throughout the world, so it constitutes a very timely and highly relevant line of inquiry [18].

1.3 Research aim

This research aims to design a hybrid Membrane Bioreactor (MBR) technology and apply it to identify and remove contamination from waste water.

1.4 Research objectives

- To identify different MBR technologies for contamination removal from waste water
- To evaluate the working principle of MBR technologies in waste water treatment
- To Optimize process parameters for selection of microorganism used in bio reactor
- To design and apply an advanced hybrid MBR technology and apply it to identify and remove contamination from waste water
- To recommend different strategies to enhance contamination removal from waste water by MBR technology

Chapter 2: Literature review

2.1 Biological technologies and their challenges in contamination removal

Biological trickling filter and biofilm reactor

A biological trickling filter is a three-phase system with fixed biofilm carriers. Wastewater enters the bioreactor through a distribution zone, trickles downward over the biofilm surface, and air moves upward or downward in the third phase [19]. Bio-trickling filters have been used in wastewater treatment plants (WWTPs) for decades in the removal of biochemical oxygen demand (BOD), chemical oxygen demand (COD), pathogen decontamination, odor and air pollution control, but their application to ECs removal has not become wide practice.

Biological nitrification and denitrification

Nitrification is the biological oxidation of ammonium to nitrite and nitrate, and denitrification is the biological process which is used to reduce nitrate/nitrite to nitrogen gas. Denitrification process is carried out at anoxic (i.e. absence of oxygen) conditions. Differences in results from recent studies may originate from the variation in operating conditions such as hydraulic retention time, sludge retention time, mixed liquor pH and temperature. This kind of process is mostly applied together with MBR for wastewater treatment [4]. The removal of EDCs such as estrone (E1), 17α-ethinylestradiol (EE2), 17β-estradiol (E3), bisphenol A, 4-*tert*-butylphenol and 4-*tert*-octylphenol and PCPs (such as benzophenone, galaxolide, oxybenze, salicyclic acid and tonalide) by denitrification has been found to be 82-100% at μg L^{-1} level influent concentration [20].

Biological activated carbon

The accumulation or artificial immobilization of microorganisms under proper temperature and nutrition condition on the surface of activated carbon produces the biological activated carbon. In that case activated carbon (mostly granular form) acts as a carrier which can exert the adsorption and biodegradation roles simultaneously. The mechanism involves the interaction of granular activated carbon particles, microorganisms, contaminants and the dissolved oxygen in solution. In most cases biological activated carbon process is used after ozonation for the removal of contaminants, and biological activated carbon can be part of a tertiary treatment process for reclamation purpose as it can efficiently remove both nitrogen and organic carbon [21].

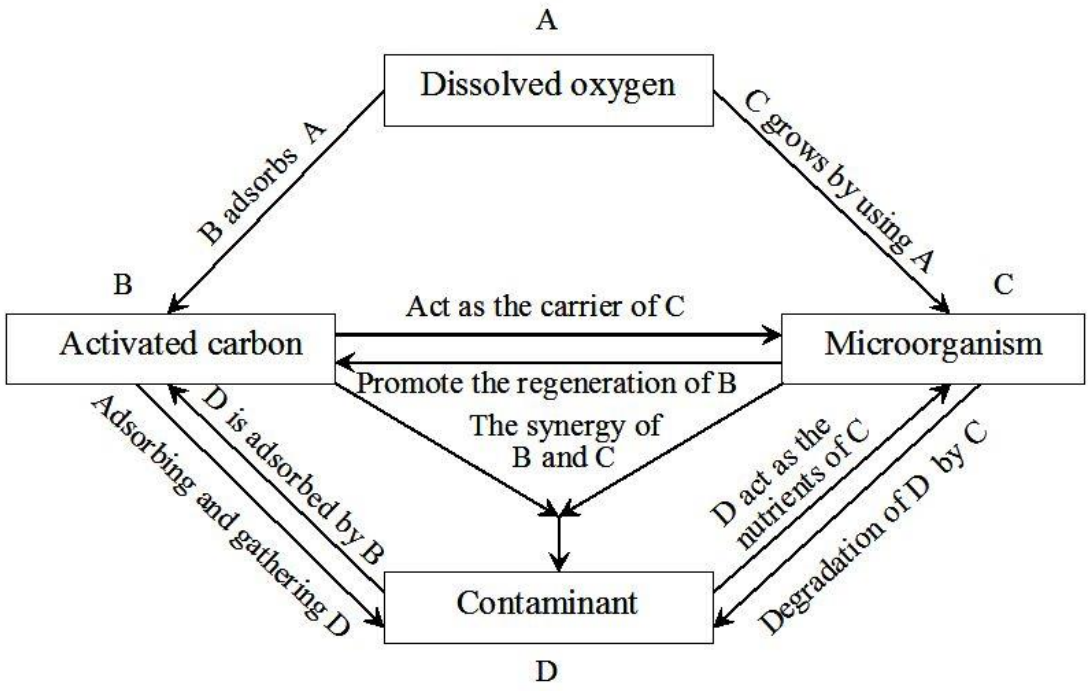


Figure: Biological Activated Carbon Treatment Process for Advanced Water and Wastewater Treatment

Microalgae/Fungi based treatment

Biologically based wastewater treatment by microorganisms (bacteria, algae and fungi) can simulate the ability of natural ecosystems to attenuate pollution from water in a cost effective and sustainable way. Microorganism based treatment systems have been proved to effectively remove some ECs with the mechanism of degradation and phytoremediation. Microorganisms produce some enzymes which are responsible for the biodegradation of the ECs. For example, some fungi produce extracellular enzymes with low substrate specificity and are very suitable for the degradation of some ECs even at low water solubility [22]. On the other hand, microalgae (phytoplankton) based wastewater treatment technologies such as high rate algal ponds has high attention due to the resource recovery of algal biomass, use of fertilizer, protein-rich feed or biofuel and high quality effluent.High rate algal pond is shallow raceway reactors in which microalgae and bacteria grow in symbiosis. Such system is responsible for the degradation of organic matter by heterotrophic bacteria, which consume oxygen by micro-algal photosynthesis. Such system does not require aeration. Some of the ECs such as pharmaceutical beta blockers (atendol, propranolol and sotalol), gastroesophageals and anticancer drugs (crimetidine, famotidine

ranitidine, acridone and citalopram), anti- inflamatory drugs (acetaminophen including stimulant butalbital), and antibiotics (azithromycin, erythromycin, sulfathazole, sulfapyridine and sulfamethazine) can be removed up to 100% by fungal reactors [15]. EDCs such as E1, E2 and EE2 can be removed by more than 95% at a concentration level of 1 $\mu g\ L^{-1}$ in algae based polishing pond treatment based system [23].

Activated sludge process

Activated sludge is a process where biomass produced in wastewater by the growth of microorganisms in aeration tanks takes place in presence of dissolved oxygen. Among all conventional wastewater treatment processes, the activated sludge process is the most widely used and applied in so many ECs removal around the world, and as the proportion of removal by primary setting, chemical precipitation, aerating volatilization and sludge absorption is small, the majority of ECs in wastewater is removed by biodegradation. This process utilizes bacteria and protozoa for treating sewage and industrial wastewaters by the utilization of air and a biological floc. These kinds of microorganisms can break down the organic matter into carbon dioxide, water and other inorganic compounds. It has lower capital cost than advance oxidation processes and generally more environmentally friendly than chlorination process.

Biological technologies are an emerging field in contamination removal that utilize living organisms or their products to remediate polluted environments. These technologies hold promise due to their potential to be cost-effective, sustainable, and capable of targeting a wide range of contaminants [24]. However, they also face several challenges. Ensuring that the chosen biological agent (such as bacteria, fungi, or plants) targets the specific contaminant and efficiently degrades or immobilizes it is crucial. Different contaminants require different biological agents with specific enzymatic capabilities. Environmental contamination can consist of a wide variety of pollutants, including heavy metals, pesticides, hydrocarbons, and emerging contaminants like pharmaceuticals and microplastics. Developing biological technologies that can address this diversity is a significant challenge. Biological remediation processes can be highly dependent on environmental conditions such as temperature, pH, nutrient availability, and oxygen levels. Optimizing these conditions for maximum efficiency is essential but can be challenging in dynamic environments. While biological technologies might work well in laboratory settings, scaling them up for field applications can be challenging. Factors such as establishing appropriate

population densities of the biological agents and maintaining their activity in the natural environment need careful consideration. Ensuring the long-term stability and effectiveness of biological remediation processes can be difficult. Biological agents may lose their activity over time due to predation, changes in environmental conditions, or competition with native microorganisms. Some biological agents can absorb or accumulate contaminants, leading to potential biomagnification in the food chain. This raises concerns about unintended ecological consequences and human exposure to contaminants through the food web.

Biological technologies have been in the forefront for years within wastewater treatment because it is environment friendly and cheap for removal of contamination. These technologies mainly depend on the use of microorganisms to degrade the wastes and to filter out pollutants in the water. Among the most used biological treatment method are the activated sludge processes, sequencing batch reactor (SBR) and anaerobic digestion [25].

Activated sludge processes include the aeration of the wastewater with help of microorganisms which forms flocs and in the process consume organic matter. In this technology, the removal efficiency has been established to be impressive in the removal of organic compounds and nutrients and even some heavy metals. These flow mutations can create an efficient process which can be altered for more enhanced nutrient removal making the application of this process universal in wastewater treatment processes.

Sbrs are fill-and-draw systems, and all the steps of the treatment take place in one vessel. It is flexible in operation and also can be modified in order to suit the changing condition of the wastewater [26]. SBRs since they proved very efficient in the elimination of nitrogen and phosphorus they are ideal for water reclamation expected high nutrient concentrations in wastewater.

Anaerobic digestion has become popular in the recent past; particularly in the treatment of high strength organic wastes. This technology is anaerobic, that is it functions without air and the output is biogas which is a very useful commodity. Anaerobic digestion is especially a good process for reducing the volume of organic sludge and has been applied in the treatment of industrial wastewater.

While being very efficient in contamination removal, the implementation of the biological technologies is hampered with several difficulties. Y the one of the most important topics is the question of microorganisms' sensitivity to toxic compounds and variations in physical conditions. Both pH and temperature fluctuations, as well as the existence of toxic compounds, can negatively affect the performance of the microbial community; these changes destabilise the process and lessen its effectiveness.Another issue is that most of the bacterial processes are but slow to remove some of the newly identified pollutants including pharmaceuticals and personal care products. Evaluations have shown that most of these compounds are not eliminated by conventional water treatment processes hence the threat to aquatic life and human health.The final disadvantage of employing biological technologies is the management of high amounts of sludge produced. The management, utilization, and/or disposal of excess biomass may add a sizable amount towards the expense of operating of sewage treatment facilities.Moreover, biological processes can consume far more space in equipment such as the reactors as well as the settling tanks. This aspect could be quite laborious more so where there is a scarcity of land as is often the case with major cities [27].The formation and stabilisation processes of biological systems may take considerable time particularly when the system is in operation in the treatment of complex industrial effluents. In this case, the treatment can be compromised and hence there can be difficulties in adhering to the set of effluent discharge standards.

Finally, aeration power demands in aerobic biological processes can be excessive, make the processes costly and environmentally unfriendly. The energy recovery from the anaerobic processes is through the production of biogas but this is always followed by some extra post-treatment steps in order to meet the required standard of effluents.To tackle these challenges, much effort has been made by researchers to find several new strategies. These include the development of more robust microbial communities through bioaugmentation, the use of granular sludge technologies which improves on the settle ability and reduces on space requirements and advanced oxidation processes to improve fate of the slow biodegradable compounds.Membrane bioreactors (MBRs) which integrate process of biological degradation with membrane filtration has been found to have potential of addressing some of these challenges [28]. MBRs have a better quality and concentrated effluent, occupy less space and allow excellent regulation of microbial community. Nevertheless, the fouling of the membrane surface is an issue that has been observed to cause a lot of problems in MBR.

The future research areas of biological wastewater treatment are the identification of new microbial seed cultures, improved methods of aeration, and the application of nanotechnology for the purpose of increasing efficiencies of the treatment process. These advancement may also be capable of enhancing the efficiency and effectiveness of biological technologies in contaminants removal from wastewater.

2.2 Chemical technologies and their challenges in contamination removal

Chlorination

Most of chemical oxidation processes have demonstrated high effectiveness in the degradation of ECs present in wastewater system which are oxidized to readily biodegradable and less toxic compounds. Sometime less reactive species such as chlorine (gaseous chlorine and hypochlorite) and bromine have also been used in wastewater treatment. The effect of chlorine on the removal of some ECs has been carried out by Noutsopoulos et al. using 1000 ng L-1 of each ECs pollutant after exposing initial chlorine dose of 11 mg L-1 for 60 min. The maximum removal efficiencies were 95% and 100%, respectively for naproxen and diclofenac.

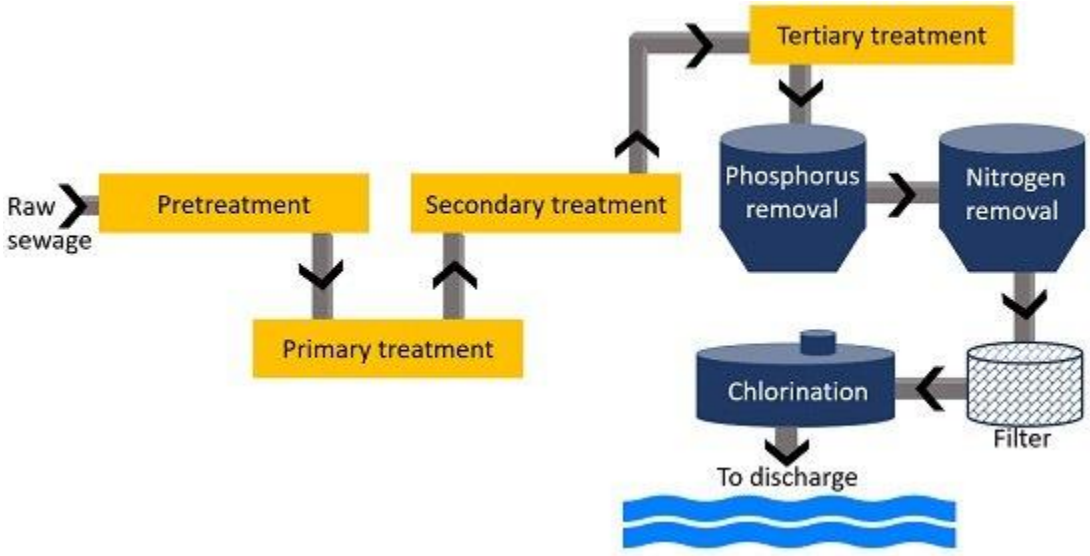


Figure: Chlorination in Wastewater Treatment - Meaning, Factors Affecting & Process

Ozonation

Ozone is a very powerful oxidant that reacts selectively with double bonds and aromatic rings of ECs with a high electron density. Ozonation is also an AOP which involves direct reaction of ECs with ozone molecules through the action of secondary oxidants such as hydroxyl radicals produced from ozone in aqueous solution, which increase the oxidation capacity [29]. Ozonation has been implemented as the principal treatment method or to enhance the biodegradability and efficiency of subsequent treatment. Ozone production is an energy intensive process, therefore making it costly to implement. An ozone treatment system may increase the energy demand over a conventional WWTP by 40-50%. The use of ozone as a means of breaking down pharmaceuticals in wastewater has been the subject of numerous studies over the last decade.

Fenton process

Fenton is an oxidation process that involves reactions of hydrogen peroxide in the presence of iron to produce hydroxyl radicals. Since iron is abundant and non-toxic, Fenton reactions are a viable option for wastewater treatment. Oxidation power of H2O2 is enhanced by its oxidation to $OH^{\cdot}$ and the chain reactions of Fenton chemistry can be represented as:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^-$ (1)

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+$ (2)

Ferrous ion can be regenerated from Fe(III) through above reaction. But reaction 2 is much slower than reaction 1. As a result, Fe(III) accumulates in the solution and then precipitates as Fe(OH)3 sludge. Thus the removal of Fe from solution can decrease the process efficiency. Moreover, it requires a significant amount of reagents that increases the operational costs [30]. Another drawback of classical Fenton process is the unintended consumption of formed $OH^{\cdot}$ by hydrogen peroxide and ferrous ions through the following reactions:

$OH^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + OH^-$ (3)

$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}$ (4)

At high reagent concentrations, these reactions can strongly hinder the efficiency of the process since $HO_2^{\cdot}$ formed is a weak oxidant compared to $OH^{\cdot}$. For the remediation of ECs in wastewater the iron concentrations used, normally added as ferrous sulphate, are commonly in the range of

10–50 mg L-1. As hydrogen peroxide is consumed in the reaction, the added amount of this reagent is strongly dependent on the amount of organic matter and on the intensity of treatment that is required.

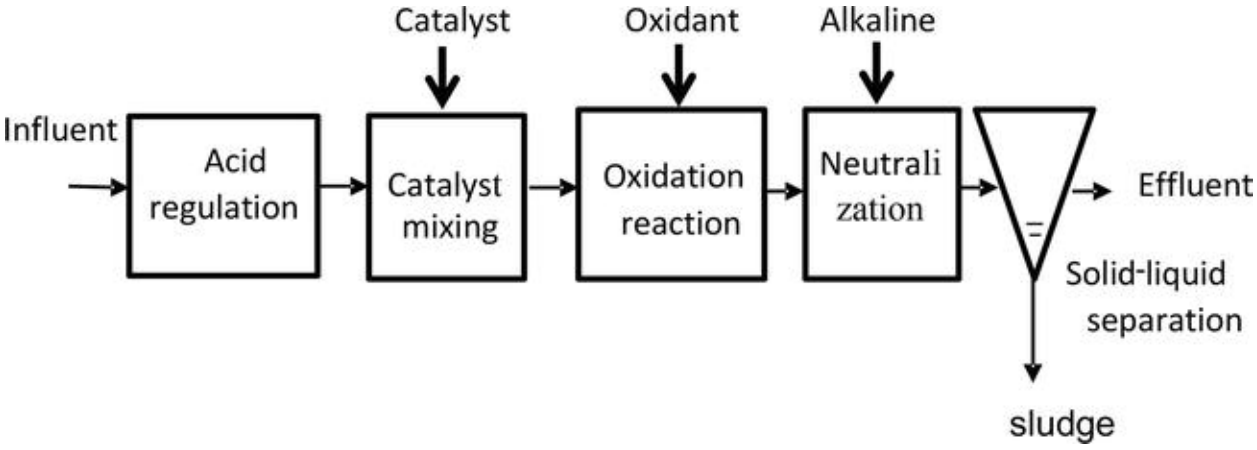


Figure: Advancements in the Fenton Process for Wastewater Treatment

Photolysis

Photolysis is a process in which molecules of ECs undergo decomposition as a result of the absorption of light or radiations. Though different sources of light are utilised, disinfection of water using UV remains as a commonly used technique. There are two types of photolysis, namely direct photolysis where the direct absorption of photons lead to degradation of pollutants and indirect photolysis which occurs in the presence of photosensitisers such as using of hydrogen peroxide or other photosensitisers [31]. In terms of removal efficiencies, UV photolysis in the presence of hydrogen peroxide has been found better than only UV photolysis. UV photolysis/H2O2 process can remove most of ECs successfully by up to 100% with the exception of some ECs such as lincomycin and diclofenac (around 80%), when ECs concentrations were mg L-1. Thus it can be stated that UV photolysis is less effective than UV photolysis/H2O2 for the removal of all ECs except EDCs where they followed the order of UV photolysis > UV photolysis/H2O2 [31].

Chemical technologies for contamination removal involve the use of chemical agents to degrade, immobilize, or extract pollutants from contaminated environments. These methods have been widely used for decades and continue to play a significant role in environmental remediation. However, they also face various challenges. Chemical treatments should be specific to the target

contaminant, minimizing the impact on non-target compounds and avoiding the generation of harmful by-products. In some cases, chemical treatments can lead to the formation of secondary contaminants or by-products that may be equally or more harmful than the original pollutant. Ensuring that the treatment process does not create additional problems is essential. Understanding the fate and transport of chemicals used in remediation is crucial. Some chemicals may persist in the environment, potentially causing unintended consequences, and their long-term effects need to be thoroughly evaluated. Some pollutants, especially persistent organic pollutants (POPs) and emerging contaminants, are resistant to standard chemical treatment methods [32]. Developing effective solutions for these challenging contaminants is a constant struggle. The efficiency of many chemical treatments is influenced by factors such as pH and temperature. Maintaining optimal conditions in the field can be challenging. Translating laboratory-scale success to large-scale applications can be difficult. Factors like cost, logistics, and accessibility play a crucial role in determining the feasibility of widespread implementation.

Chemical technologies are highly significant in managing wastewaters, as these technologies provide efficient and fast ways of water purification from different types of pollutants. These technologies refer to the application of chemical reagents for the elimination, conversion, or stabilisation of pollutants in effluent [33]. Among the commonly used chemical methods for water and wastewater treatment the following can be mentioned: coagulation – flocculation, chemical precipitation, AOPs and ion exchange.

Coagulation-flocculation is a chemical water treatment process that consists in the addition of coagulants that will destabilize colloids in the wastewater and then the process of forming large particles or flocs. This process has been found to be very effective in the removal of suspended solids, turbidity and some dissolved organic matter. Aluminum sulphate, ferric chloride and synthetic polymers are the usual coagulants used for this process.The technique of chemical precipitation is applied to eliminate ions of heavy metals, phosphorus and other inorganic admixtures from wastewater. In this process, chemical reagents are admitted to make their reaction with target pollutants to form solid and non soluble materials that can easily be separated by sedimentation or filtration. Some of the most used precipitating agents are lime, sodium hydroxide, and several metal salts.

Post is a series of processes have received much attention in the last few years due to their efficiency in degrading the refractory organic pollutants and the newly identified chemical substances. These processes produce hydroxyl radicals which are highly reactive and can oxidise almost any type of pollution. Some of the well known AOPs are Fenton's reaction, ozonation and UV/H2O2 process. Since the start AOPs has been identified that is particularly effective in removal of pharmaceuticals effluent water, pesticide and other hard-copy pollutants. Another important chemical technology in the area of wastewater treatment is ion exchange which is particularly useful in the removal of dissolved ions of heavy metals, nitrates, and the ions that cause water hardness. It is the ability to trade a colourful solid resin with the wastewater to take out the selected contaminants through a process of electively trading ions.Although the chemical technologies are quite efficient in the removal of contaminations, the following challenges are associated with them. Perhaps the most outstanding drawback is the possible production of toxic substances in the course of the process. For instance, although chlorine water used for water disinization can work, it has got adverse effects such as forming of the disinization by-products (DBPs) which include trihalomethanes which is recognized to be carcinogenic. Likewise, there are some AOPs that produces toxic intermediates in the case that they are not well regulated [34].

Chemical treatments can be very sensitive to wastewater factors such as pH, temperature, and the presences of other interferents. This variability can make it rather difficult to keep a steady performance from the treatment process and particularly in treating compound or fluctuating wastewater feeds. The second major problem is the high level of chemicals that required to be used in many chemical treatments. This not only increases the cost of operations but also poses some challenges to the environment in as much as production and disposal of these chemicals is concerned. In coagulation processes for instance the use of metals salts results in formation of larger volumes of sludge hence adding to the problem of waste management.The selectivity of chemical treatments can also be a disadvantageous feature, which may sometimes decelerate the processes of remediation. It is therefore important to realise that some processes may be very efficient at the removal of certain of these contaminants while significantly less efficient at the removal of other contaminants. This frequently requires the application of several treatment stages or a combination of various techniques, to guarantee optimal eradication of the contaminants [35].

The possibility of chemical residuals in treated effluent is another which is especially true in the case of strong oxidants or metal-based coagulants. Such residuals may also have an effect on the receiving water bodies and their elimination may be necessary through extra steps.Energy cost is a factor in some of the chemical treatment methods especially in UV-based or ozone-based AOPs. These processes essentially have high energy demands and so they have the potential of pushing the operational costs and even the carbon footprints higher.To overcome these difficulties, there are many ways being investigated by researchers. These are green coagulants from natural sources, catalytic processes to improve AOPs efficiency and nanotechnology for contaminant removal [36]. However, hybrid systems of chemical processes integrated with biological treatment systems have been also described to reduce some of these limitations. For instance, in chemical pre-treatment, biodegradability of compounds that are usually difficult to degrade is promoted hence increasing efficiency of biological stages.

Future areas of focus in chemical wastewater treatment are also likely to involve the use of better selective and ecofriendly chemical reagents, better design options to minimize by products formation during treatment process, and better catalysts to upgrade the whole treatment process. These advancement can also help to enhance the efficiency and efficiency of chemical technologies in removing contamination from wastewater.

2.3 Different membrane technologies for removal of hazardous materials from waste water

Membrane bioreactors (MBRs)

Membrane bioreactors (MBRs) combine biological processes and membrane filtration to achieve better treated effluent quality by exploiting the dual benefits of membrane separation and activated sludge processes (ASPs). In the case of high strength industrial wastewater, operating parameters such as HRT, SRT, and MLSS should be optimized, and suitable pretreatment or neutralization should be provided to preserve the microbial community and prolong the membrane life. Metal sorption on activated sludge takes place as follows:

Cell wall and cell membrane contain various cations like Na+, K+, Mg2+, and Ca2+, and these ions will be exchanged with other dissolved metals in the MBR mixed liquor.

Interaction between metals and the sorption sites on cell surface induces complexation and/or microprecipitation.The removal of metals in MBRs depends on a variety of parameters such as: (i) operating parameters like dissolved oxygen (DO) levels, mixed liquor SS (MLSS), and sludge retention time (SRT), (ii) physicochemical parameters such as metal type, species, and initial concentration, the type and concentration of ligands, the presence and concentration of competing cations, [37] (iii) biochemical parameters such as the concentration and content of extracellular polymeric substances (EPS), ligands produced through bacterial activity, products from cell lysis, and bacterial species that favor metal uptake.

Adsorption on activated carbon (AC)

Activated carbon (AC) for industrial wastewater treatment is usually applied in two forms – powdered (PAC) and granular (GAC). Adsorption unit can either be used before biological treatment for removing toxic compounds or be placed after the physio-chemical treatment steps for ensuring the complete removal of micropollutants. AC can be used to remove organics such as pesticides, phenols, pharmaceuticals, organic halogens, non-biodegradable compounds, dyes, and inorganics such as Hg2+, Pb2+, Cd2+, Cu2+, and Ni2. AC is also an efficient media for microbial growth, and biologically activated carbon (BAC) has been developed for the inactivation of biological pollutants within a short period. Attaching biomass to AC can remove contaminants by both adsorption and biodegradation. However, AC has some disadvantages, such as expensive thermal/ chemical regeneration methods and the loss of a significant fraction of adsorbent during regeneration [38]. Moreover, the adsorption mechanism on AC depends on various factors such as dispersive, electrostatic and chemical interactions; intrinsic properties of the solute and adsorbent and hence the interaction between the pollutants and AC is difficult to predict. Although AC has a high adsorption capacity, it can maintain it only until the adsorption sites become exhausted with pollutants. Other absorbents such as polymeric absorbents are also used when recycling of valuable chemicals is desired.

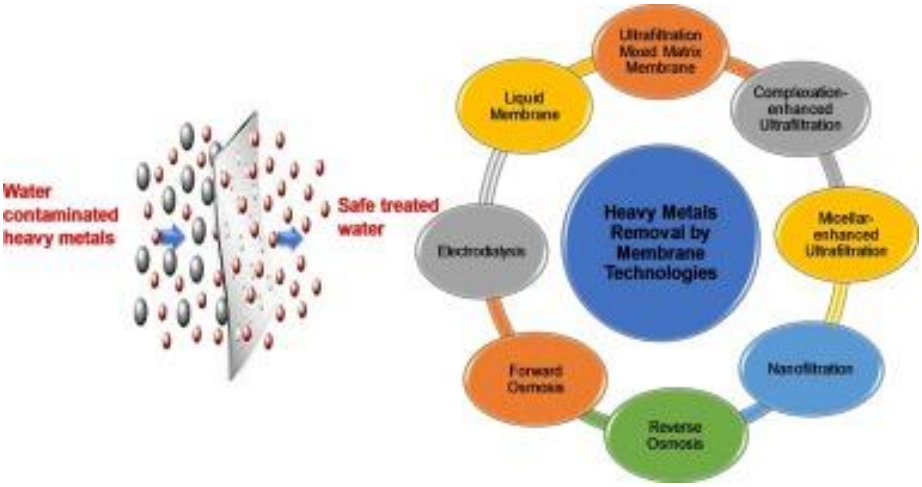


Figure: Recent trends of heavy metal removal from water/wastewater by membrane technologies

Advanced oxidation processes (aops)

Advanced oxidation processes (AOPs) are chemical treatments involving the generation of hydroxyl radicals (OH•) that can efficiently oxidize recalcitrant pollutants. OH• are characterized by their high standard oxidation potential (up to 2.80 V) and their high reaction rate in comparison to common oxidants like chlorine, oxygen, ozone, H O , or potassium permanganate. The dosage of chemicals as it will increase the cost and may give the possibility of by-product formation. Secondly, reactor configuration and contact time, which is often determined when implementing a pilot study rather than a lab-scale, should also be considered. The quality of industrial wastewater and other operating conditions also affect the efficiency of degradation of concerned pollutants. It is known that most of the organic substances would react instantly with the introduced radicals [39]. Turbidity also acts as an influencer to the system performance because the more turbid the industrial wastewater, the lower is the penetration of UV source to the water. Additionally, Fe2+ and Cu2+ or other heavy metals in wastewater may also cause the formation of Fe or Cu organic complexes thus results in fouling for the system. The recently employed AOPs are the Fenton-based processes, electrokinetic treatment, and degradation with metal oxides.

Membrane technologies are relatively new to the water industry breaking the ‘barrier’ in providing very efficient solutions for the removal of a multitude of categories of pollutants. These technologies use membranes that are partially permeable in separating contaminants in water on

the basis of size, charge or other physical chemical characteristics. There are four dominant technologies that are utilized in membrane wastewater treatment and they are microfiltration(MF), ultrafiltration(UF), nanofiltration(NF) as well as reverse osmosis(RO).Among all the membrane filtrations, microfiltration is the least closed and is normally applied to separate suspended solids, bacteria, and some colloidal particles. MF membranes were considered to have pore size of the order of 0. It ranges between 1 and 10 micrometers creating the efficiency of employing them in the treatment of water for diverse purposes, although often used for pre-treatment of water for other membrane processes.Ultra filtration (UF) used membranes with a relatively small pore size of 0. 01 to 0. 1 micrometers and applies for the removal of macromolecules, proteins and viruses in combination with suspended solids. UF is particularly applied in industrial effluent treatment and as a pretreatment to RO in water reclamation.Nanofiltration (NF) lies inbetween UF and RO in terms of pore sizes of membranes used in this process; they are in the range of 0. 001 to 0. 01 micrometers [40]. Free water is obtained by NF because it is efficient in rejecting divalent ions, organic substances and several monovalent ions. It has been used in the removal of hardness, color and in the treatment of textile effluents.This is the most stringent of all the membrane filtration process since it is able to filter out almost all dissolved solids including monovalent ions. RO membranes have a pore size of less than 0. 001 micrometers in size, and function by countering osmotic pressures. It is in wide application in water desalination, wastewater reuse and treatment of very concentrated industrial effluents.Apart from these conventional processes of membrane use for pollutant removal, several novel membrane technologies have been anticipated for elemental removal from the hazardous materials. That is why Forward Osmosis (FO), also operates based on using osmotic pressure difference between feed solution and draw solution to force water flow through a suitable selective membrane. Further, FO has been postulated as being capable to treat high-salinity wastewaters as well as concentrating valuable resources from the wastewaters.

Membrane Distillation (MD) is one of the thermal separation processes that integrates both the membrane separation and phase change. It has been proved to be useful in the treatment of highly saline wastewaters and in the recovery of useful compounds. MD performs at relatively low pressures compared to RO and can use low grade heat, thus its suitability for some applications.

Electrodialysis (ED) and Electrodialysis Reversal (EDR) are techniques where ion-exchange membranes and an electrical field are used to remove ions from wastewaters. They are more applicable in water desalination as well as recovering of ions of value from industrial wastes.

Although various membrane technologies have numerous benefits in hazardous material removal, they have the following difficulties. Membrane fouling is actually the most critical one which affects the flux, energy consumption and membrane's life cycle. Fouling could be as a result of particles getting deposited on the membrane surface, or bio growth on the membrane surface or accumulation of organic materials on the membrane surface [41].

One of the problems in the membrane technology is the difficulty of achieving simultaneously high selectivity and permeability. The membranes with high levels of selectivity are generally those with low permeability which implies that such systems will require high operational pressures and a lot of energy. The development of good membrane systems is highly dependent on the balance of these properties in order to optimize their efficiency at an appropriate cost.Some environmental concerns including those arising from the handling and disposal of concentrate streams produced by the membrane processes; especially in the case of RO systems. These concentrate streams may contain high concentrations of dissolved solids and impurities which has to be treated or properly Eliminated.Power usage is always an issue and more so for high pressure systems as is the case with RO. From the energy demands of membrane filtration it was seen that, membrane filtration consumes a large amount of energy depending upon the kind of application done particularly when done industrially.Chemical compatibility is another with which one has to be specific because some types of membranes might provide poor performance if exposed to specific chemicals found in industrial wastewaters [42]. This in a way constrains the feasibility of using membrane technologies in dealing with specific forms of hazardous waste streams.

To overcome these challenges, researcher are coming up with these strategies: These are; innovations in new memra materials and structures with improved fouling behaviour and selectivity like the mixed matrix memra and bio-mimetic memra. Techniques in surface modification are being developed in a bid to enhance the performance and durability of the membranes.Synergistic combination of membrane processes with other treatment technologies, such as biological treatment in the membrane bioreactor or advanced oxidation processes has been found to give positive signals for some of the limitations of stand-alone membrane systems. These

approaches can provide more exhaustive treatment scenarios of complicated arrays of wastewater feed.

In the future works of the field of membrane technology, there are the self-cleaning membrane, new designs of the membranes to enhance the mass transfer and fouling of the membranes, and the effects of nanotechnology in the present membranes. Such advancements are promising to optimizing and enhancing the efficiency and effectiveness of membrane technologies for the purification of the hazardous substances from the water.

2.4 Membrane bioreactor and integrated membrane bioreactor systems for micro pollutant removal from wastewater

Over the past two decades, membrane bioreactors (MBRs) have been designed and operated for treatment of a variety of pollutants, such as particulates, carbonaceous substances, nutrients and pathogenic microorganisms. Compared with these pollutants, which can be removed easily by conventional methods, the removal of certain other pollutants, particularly the micropollutants (pharmaceuticals, personal care products, steroid hormones, surfactants, industrially generated chemicals, etc.) is often very different. Therefore, examination of the fate and removal of micropollutants during wastewater treatment is very much crucial for any of the treatment process to avoid their dis- charge into the environment [43]. In this section, characterization and different removal processes utilizing MBRs with a focus on the fate and mechanism of micropollutant removal are discussed. Membrane bior- eactor (MBR) systems seem to be promising under this scenario, due to their several advantages, including high performance efficiency com- pared to conventional activated sludge treatment plant (CASP), less space requirement, environment friendliness. Therefore, it has been recognized as a key technology for water reuse and recycling in many developed and developing countries. MBR is a hybrid process in- tegrating the membrane technique with biological treatment, which enables CASP to be operated as a single step process by avoiding the need for a secondary clarifier. Fig. 2 compares the conventional was- tewater treatment process with that employing MBR technology.

In general, MBR system is categorized into two kinds in accordance with the configuration; (1) submerged membrane bioreactor (SMBR) and (2) side stream membrane bioreactor. Fig. 2 shows a brief sche- matic of MBR system. Earlier the side stream MBR was developed where the

membrane module is placed outside the bioreactor for the re- circulation pump. Due to its high energy consumption, in 1980s, sub- merged-MBR system was further developed where the membrane module was submerged within the bioreactor, thus, permitting the ef- fluent to pass through with sludge retention. In a SMBR, aeration maintains the activated sludge in suspended mode, limiting the mem- brane fouling.

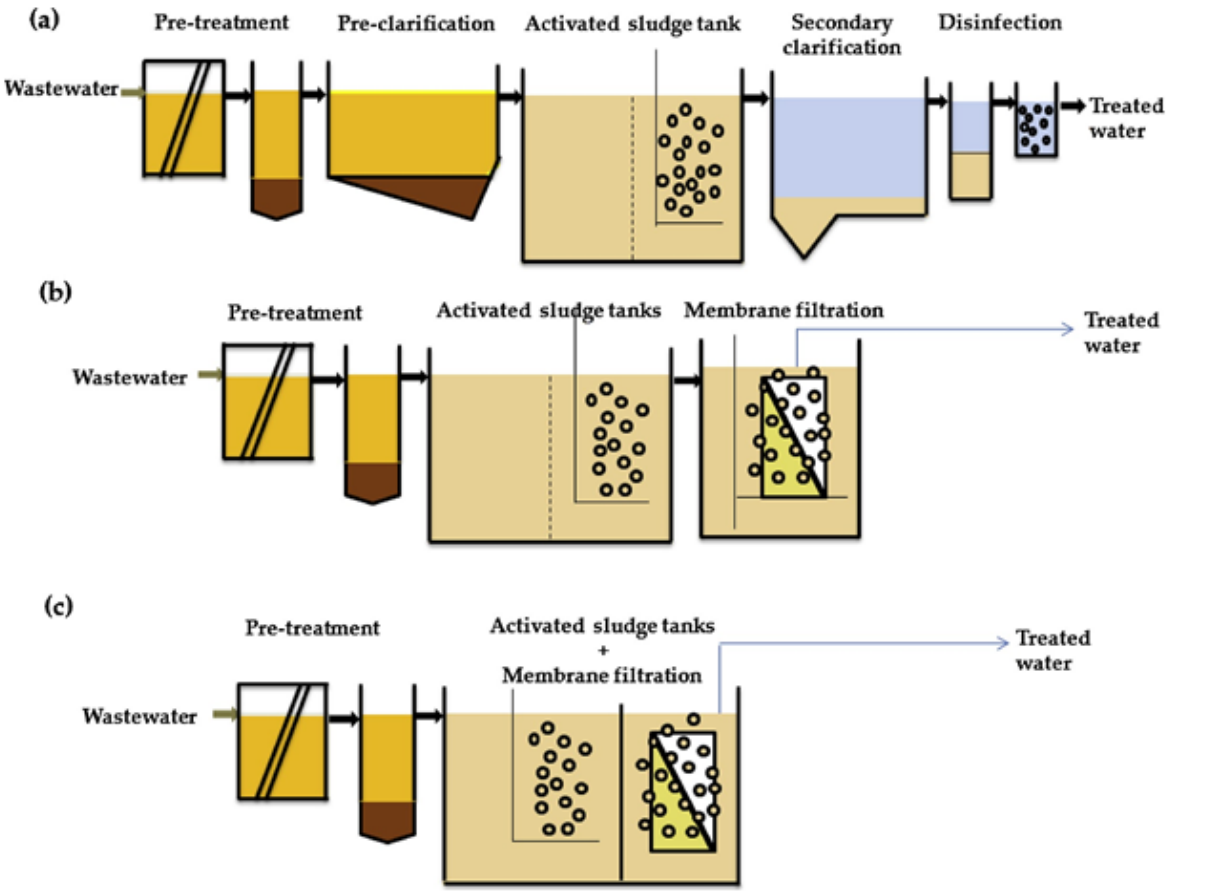


Fig. 2. Scheme of the (a) conventional wastewater treatment process, (b) Side stream MBR (c) submerged MBR [1].

Integrated approaches involving MBRs with some other processes such as advanced oxidation process (AOPs), membrane distillation process, bio-entrapped membrane bioreactor, granular MBRs, etc. are the approaches of integrated MBR system.

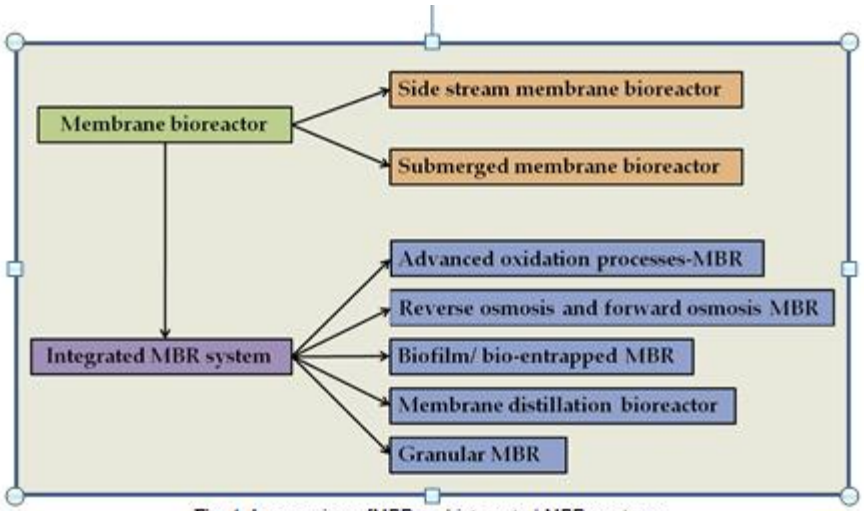


Fig. 4. An overview ofMBR and integrated MBR systems.

Efficient processes at the tertiary level for the removal of micropollutants from Wastewater includes Membrane Bioreactors (MBRs). MBRs consist of both biological processes and membrane filtration, and have the following characteristics than conventional activated sludge systems. Thus, integration of membrane separation with biological treatment gives higher biomass concentrations, better effluent quality along with reduced area [44].

MBRs have been said to have considerable promise in the context of micropollutant removal because of their capacity to support a diverse microbial population, which tend to have the capacity of breaking down a broad array of substances. The high SRTs that are feasible in MBRs enable the development of slow-growing microorganisms that can degrade comparatively biostabile substrates. Besides, the membrane component could ensure the efficiency of particulate-bound micropollutants and most dissolved compounds in water according to the filtration strategy.MBRs have been proven to remove a wide array of macropollutants and different Micropollutants classes such as pharmaceuticals, PPCPs, EDCs and pesticides. The removal mechanisms in MBRs are not simple and these involve biodegradation, adsorption to biomass, and membrane rejection. On most occasions the level of removal depends on the physicochemical properties of the micropollutants and the operational conditions of the MBR.To provide even better treatment of micropollutants, integrated MBR systems have been invented. These systems incorporate a combination of MBR technology with other treatment steps to deal with specific pollutants or enhance the treatment capacity of the system.

Some notable integrated MBR configurations include:

MBR-Activated Carbon: The enhancement of MBRs with powdered or granular activated carbon has also been observed to enhance the removal of hydrophobic micropollutants within the system.

MBR-Advanced Oxidation Processes (AOPs): Pre-treatment methods like ozonation or UV/H2O2 treatment if applied prior to MBRs might be useful in degrading recalcitrant micropollutants.

Anaerobic MBRs (An MBRs): These systems integrate the anaerobic biological treatment with the membrane filtration and hence show fixed advantages such as energy recovery and the treatment of high strength wastewaters having micropollutants.

Forward Osmosis MBRs (FO-MBRs): The use of forward osmosis membranes in the MBRs has been found to enhance the water recovery efficiencies and the removal of the micropollutants.

Membrane Distillation Bioreactors (MDBRs): It is established as a novel technology, which operates by integrating membrane distillation with biological treatment, and can have high removal rates for a huge variety of micropollutants [45].

However, the following limitations are still existent in the application of MBRs and integrated MBR systems for the removal of micropollutants. Issues are still with membrane fouling, which can be a serious operational problem that may influence further running efficiency and energy requirements. The research on the fouling-resistant membranes and the more effective cleaning ways is still on-going.The further destiny of transformation products that are formed in the course of micropollutant degradation in MBRs is another issue. Sometimes the transformation products may be more toxic or even more persistent than the parent compounds and hence there is need to understand how these products are formed and how they can be removed.

Some of the operational factors that should be further investigated include SRT, HRT and characteristics of the membrane on the efficiency of removal of micropollutants. Already, optimizing of these parameters for better micropollutant removal while at the same time considering the general treatment efficiency and cost factor is a challenge.The monitoring

techniques for micropollutants in MBR systems are still in the development stage and highly expensive; hence, it is essential to find convincing methods of online monitoring for such materials which are increasingly regulated [46].Some research areas for future studies in MBR treatment technology of micropollutants are: synthesis of new membranes with high affinity for micropollutants, microbial consortia manipulation with emphasis on degarders, and the application of state of the art modeling technologies for monitoring and regulation of the MBR process.The prospects of MBRs and integrated MBR systems for the solution of the problem of micropollutant removal from wastewater are rather great. Further investigations and advancements in this area suggest the potential to elevate water quality and shelter environmental and health from modern threats posed by contaminants.

2.5 Removal of emerging contaminants from wastewater streams using membrane bioreactors

The process of removing emerging contaminants from wastewater streams using membrane bioreactors (MBRs) involves a combination of biological treatment and membrane filtration. MBRs are advanced wastewater treatment systems that integrate the conventional activated sludge process with membrane technology. Here's a step-by-step overview of the process:

Wastewater Collection and Pre-Treatment: Wastewater from various sources, including domestic, industrial, and agricultural, is collected and undergoes preliminary treatment to remove large debris, grit, and other coarse solids [47]. This step is essential to protect the MBR system from potential damage and to improve overall treatment efficiency.

Biological Treatment (Activated Sludge Process): The pre-treated wastewater is then introduced into the biological treatment tank, where microorganisms, such as bacteria and protozoa, are used to biodegrade organic matter and other contaminants present in the water. The microorganisms consume the pollutants as a food source, breaking them down into simpler and less harmful substances.

Solid-Liquid Separation: After the biological treatment, the mixture of treated water and activated sludge (microorganisms) is separated to clarify the water. Conventional activated sludge systems use gravity settlers or sedimentation tanks for this purpose.

Membrane Filtration: In an MBR, the solid-liquid separation is achieved through a membrane filtration process. The mixed liquor containing the activated sludge is pumped through a set of ultrafiltration or microfiltration membranes [48]. These membranes have fine pores that efficiently remove suspended solids, bacteria, pathogens, and other larger particles from the water, producing a clarified effluent.

Concentration and Sludge Recycling: As the membrane continuously filters the mixed liquor, some solids and organic matter can accumulate on the membrane surface, causing fouling. To control fouling and maintain efficient operation, a portion of the activated sludge (concentrated through the membrane filtration) is periodically recycled back into the biological treatment tank. This process is known as sludge recycling or mixed liquor recycle.

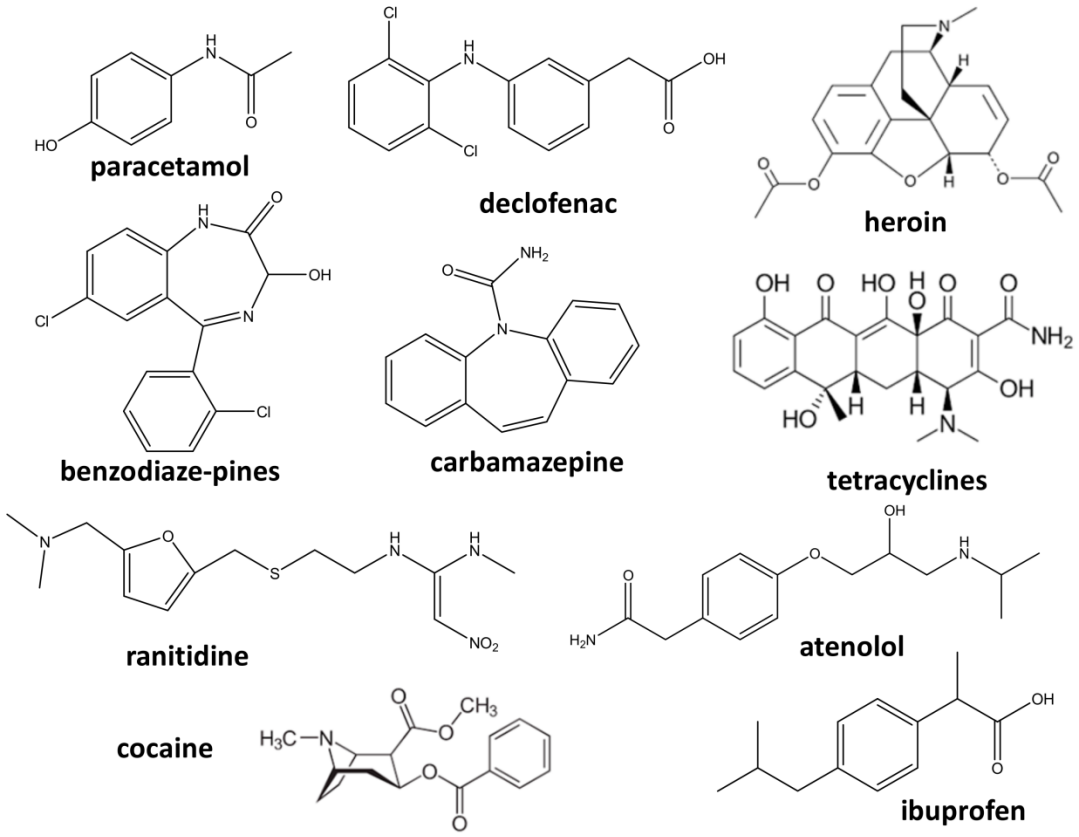


Figure: Different membranes for removal of emerging contaminants from wastewater streams using membrane bioreactors

Recently, experts have been alarmed about the occurrence of some chemicals referred to as emerging contaminants in wastewater streams. These pollutants include pharmaceuticals, personal care products and endocrine disrupting substances, industrial chemicals and most of which are usually not fully degraded by the conventional wastewater treatment systems. MBRs have been successfully implemented for the removal of these new generated contaminants being a process that combines biological treatment as well as membrane filtration.For the removal of emerging contaminants MBRs have several benefits as compared with conventional activated sludge systems. This issue means that there is higher biomass concentration that can be achieved in MBRs that enable the build up of a more effective microbial community, including slow growers, which have the ability to break down compound that are difficult to degrade. Extended SRTs achieved in MBRs also favor the ability of microorganisms for the degradation of emerging contaminants due to improved biodegradation rates.The membrane aspect of MBRs has a major function in getting rid of emerging substances. A number of studies has reported that UF or MF membranes most frequently applied in MBRs can adequately remove particulate-bound pollutants and act as a filter to eliminate certain dissolved species depending on their molecular size. Further, the layer of cake developed on the surface of the membrane can also be another layer of filtration and may improve the rejection of some pollutants.It has also been discovered that MBRs can readily remove a vast assortment of emerging pollutants such as pharmaceuticals (including antibiotics, analgesic and hormones) personal care products like fragrances and UV filters, as well as industrial chemicals like flame retardants and plasticizers [49]. The removal efficiencies are affected by the physicochemical characteristic of the contaminants, and the operational condition of MBR.

MBR provides a complicate fashion of the removal of new emerging contaminants through biodegradation, adsorption on biomass, and rejection by the membrane. Most organic EOCs are believed to be removed through biodegradation since microorganisms incorporate the compounds as a source of carbon and energy, or else metabolize them in parallel with other substrates. For hydrophobic molecules, adsorption to biomass can be considerable while membrane rejection is involved in eliminating large molecules and charged things.

However, some limiting factors that are still apparent in using MBRs for the removal of emerging contaminants are as follows: The presence of residual halogenated organic compound and the observed formation of transformation products are real issues that are associated with biological

treatment. The different transformation products may be even more resilient or dangerous than the initial compounds and that is why more insights into their behaviour and effects must be gathered.The effect of the specific working parameters on the efficiency of the removal of ECA in MBRs has not been adequately explained. Parameters like SRT, HRT; pH; temperature; DO concentration were found to have a direct bearing on the removal efficiency. Finding the right values for these parameters that will result in higher removal of contaminants without a huge compromise in the overall treatment efficiency and cost is still difficult.Sifting of the membranes is again a predominant operational problem in MBRs, which may affect the durability, efficiency, and energy requirements of the system. Novel and unknown compounds and their byproducts can also be implicated in the process of membrane fouling, and therefore require designs of FO membranes that are resistant to fouling and proper methods of fouling removal.More research on the characterization and quantification of emerging contaminants in MBR systems, and the establishment of efficient and affordable tools for their detection, would be relevant to the control of the processes and the satisfaction of the ever-stricter norms [50]. The concentrations of these contaminants in wastewater streams tend to be low thus complicating efforts at detection and measurement.To address these challenges and further improve the removal of emerging contaminants, several innovative approaches are being explored:To address these challenges and further improve the removal of emerging contaminants, several innovative approaches are being explored:

Hybrid MBR systems: Emphasising supplementary processes together with MBRs, for instance, advanced oxidation, activated carbon adsorption, or UV disinfection in order to address particular types of Non-removable organic pollutants.

Membrane development: Studies on the development of new membrane materials and modification of surface for better selectivity on newly appearing compounds and resilience to fouling.

Microbial community engineering: Approaches for the stimulation of growth of particular degraders or improvement of microbial community in MBRs biodegradation capability.

Process intensification: Examining additionally designed reactor structures and potentials for reactor operation that will enhance the possibility of effective purification and decrease energy consumption.

Modeling and control: Mechanistic modeling and stochastic control for enhancing process performances and probable excellence in removing emerging contaminants [51].

As a rapidly developing field of MBR technology for removal of emerging contaminants, future research directions for MBR are: Examination of interactive effects of multiple removal processes, Improvements of MBR system design, energy consumption, integrated anaerobic MBRs for emerging contaminants.MBR systems have a very high potential for the removal of ECA from the wastewaters and thus enhancing water quality and public and environmental health. Further studies in this topic are crucial as it aims at helping to deal with with emerging pollutants that are being posing in water resources.

2.6 Comparison between advanced hybrid MBR and stand-alone MBR in waste water treatment

Advantages of hybrid MBRs compared to stand-alone MBRs are well reported in literature and, among others, are extended lifetime of the old CAS system, lower membrane surface requirement due to treatment of the peak flows outside of the MBR, continuous operation at optimal designed conditions which results in energy efficient operation, cost effective option of WWTP retrofit, less membranes and infrastructure utilization reducing the investments costs [52]. One of the obvious disadvantages of the hybrid concept is the bigger footprint of the plant because of the required surface needed for the CAS system and possibility of incidental discharge of suspended solids, bacteria and viruses due to potential overflow or bypassing of the peak flows. In addition, when less membrane is installed they need to be frequently used and, in consequence, rest periods of the membranes are limited. Therefore, life-time of the membranes due to often shorter ‘out of operation’ periods is probably shorter.The recent full-scale results and experience significantly broadened the understanding of the associated processes. However, despite the increase in applicability, information regarding the influence of a particular design on operation and performance is only scarcely available. Moreover, available information is scattered and hardly

published and thus transfer of knowledge is very limited. Our present work provides information on design concepts and plant configurations, and their impact on operation, performance, energy consumption and economy of the MBR plant [53]. The specific objective of this study is to evaluate a hybrid concept of MBR design, i.e., a combination of a conventional activated sludge (CAS) process and an MBR, in comparison to a stand-alone MBR. Finally, advantages and disadvantages of each particular design are presented and discussed.An advancement of the modern variety of membrane bioreactor systems is the hybrid membrane bioreactor, with which conventional MBR systems are integrated with other treatment steps to optimize general MBR performance and adapt to certain treatment conditions. Overall, this comparison of hybrid MBRs now being proposed to incorporate advanced elements and the conventional stand-alone MBR system underlines the strengths and weaknesses as well as areas of possible application of the two systems in wastewater treatment.SMBRs as distinct from other MBRs have gained significant practicability in wastewater treatment because of their potential for generating high quality effluent as well as it can operate at better biomass loading in contrast to the conventional activated sludge process. Such systems include the biological reactor with integration of membrane filtration where micro filtration (MF) or ultra filtration (UF) is preferred. Essentially, the following are benefits associated with small-scale MBRs: They are compact, have high ability to remove the suspended solids and pathogens, and can be used in water recycling.

However, most MBRs when used as a single unit face a number of challenges on ability to handle some specific wastewater treatments. Some of the drawbacks include the inability in total elimination of some of the stubborn organic matters, low efficiency in nutrient elimination especially phosphorus and ease by which they can be fouled. Also, the energy used for membrane aeration and permeate extraction may also be large at around 0.033 kWh/m3. Some of these problems have been tackled by the development of other sophisticated hybrid MBRs which incorporate other additional treatment steps with the standard MBR system. Some notable hybrid MBR configurations include:Some notable hybrid MBR configurations include:

MBR-Activated Carbon: Filtering with PAC or GAC as an added commodity improves the adsorption procedure, especially of non-degradable organic molecules.

MBR-Advanced Oxidation Processes (AOPs): The process of MBR can be enhanced by using AOPs including ozonation, UV/H2O2, or Fenton's process in the elimination of resistant pollutants.

Anaerobic-Aerobic MBRs: Such systems include a combination of anaerobic and aerobic biological treatment with membrane filtration and include values of energy recovery and nutrient removal.

MBR-Ion Exchange: The integration of ion exchange processes improves also the nitrogen and phosphorus elimination.

Forward Osmosis MBRs (FO-MBRs): The forward osmosis membranes can enhance the ability of water recovery and likewise, the tendency of membrane fouling. Comparing the performance of advanced hybrid MBRs with stand-alone MBRs reveals several key differences:Comparing the performance of advanced hybrid MBRs with stand-alone MBRs reveals several key differences:

Contaminant Removal: Regarding efficiency in removing contaminants, Hybrid MBRs are found to offer higher overall efficiencies compared to conventional MBRs for a wide range of pollutants especially those difficult organic structures and other 'emerging' contaminants. It is thus possible to treat these pollutants that may not be effectively degraded by biological treatment with other treatment processes.

Nutrient Removal: Some hybrid systems like cooperating MBRs-anaerobic-aerobic or MBR-ion exchange have better nutrient removal capacities than simply MBRs. It is particularly useful for one wanting to achieve low levels of nitrogen and phosphorus in their effluent.

Membrane Fouling: Some of the hybrid system arrangements, including MBR activated carbon or FO MBRs have demonstrated an ability to lower the membrane fouling rates than the single MBR systems. It may lead to better long-term result and less cleaning needed for the surfaces.

Energy Efficiency: Further energy cost might be needed for the supplementary treatment process which is absent in some of the hybrid MBR systems such as the anaerobic-aerobic MBR which has the proact of biogas production. As you can imagine, the net energy disposition depends on

the particular HPS hybrid setup employed and the treatment aims. Operational Flexibility: Some of the hybrid MBRs offer higher operational flexibility to cope with changes in the characteristic of influent and/or objectives of the plant. Since it is possible to modify or even exclude some aspects of the treatment, performance and the use of resources can be maximally tuned up.

Complexity and Cost: Integrated MBR systems are in most cases more complicated in terms of design and function compared to individual MBRs. This could however lead to higher capital and operational costs, which have to be put against any improvements in treatment performance that might be gained.

Footprint: Although hybrid MBRs may necessitate extra room for extra treatment processes, which are nevertheless essential in certain applications, the overall secured volumetric eliminations with the hybrid MBRs developed can be slightly better within the same or slightly bigger footprint than the unit standalone MBRs normally provide.

Resilience: Unfortunately, a limited amount of information is available on the removal and effects of hyacinth clogging on hybrid systems, but general considerations of hybrid systems suggest that the multi-barrier approach may provide more robust response to changes in influent quality, or system upsets. The question whether to integrate advanced hybrid MBRs with other systems or install stand-alone MBRs depends on factors such as the treatment goals or treatment needs, the nature of the inflow, legal standards, as well as conditions at the site. Full scale standalone MBRs could be used in applications where there is high demand for high quality effluent mainly for the removal of most conventional pollutants and pathogen. Nonetheless, the hybrid MBRs have some merits when it comes to cases that involve high demand for better removal of difficult to degrade contaminants, stringent nutrients standards and high recovery rates [54].

Given the fact that new issues in the field of wastewater treatment appear frequently – sometimes, they focus on new pollutants and substances contained in wastes, at other times, – on resource utilization and compactness, the advancement of new hybrid MBR systems is expected to proceed. Possible objectives for further research are the enhancement of the design and layouts of hybrid configurations for particular processes, the discovery of new methods of integration, and the search for efficient, environmentally friendly, and low-cost MBR hybrid systems.

In conclusion, it is possible to state that alone MBRs still preserve itself as rather buoyant and commonly used technology, however, the novel hybrid MBRs can provide promising solutions to complicate WWT issues. The further development of these technologies will be instrumental in addressing future requirements for water quality as well as the improvement of water use.

2.7 Nanotechnology in waste water treatment

Nanoscale membranes are used in nanofiltration and ultrafiltration processes to separate dissolved solids, microorganisms, and other pollutants from water. These membranes offer higher selectivity and efficiency compared to conventional filtration methods. Nanoparticles like titanium dioxide (TiO2) and zinc oxide (ZnO) can be used as photocatalysts to degrade organic pollutants in wastewater under UV or visible light [55]. When exposed to light, these nanoparticles generate reactive oxygen species that break down organic contaminants into harmless byproducts. Silver and copper nanoparticles have antimicrobial properties, and their incorporation into water treatment systems can enhance disinfection and help control the growth of harmful microorganisms. Nanobubbles are tiny gas bubbles with diameters in the nanometer range. They can improve the oxygen transfer efficiency in aeration processes, leading to better performance in biological treatment systems. Nanotechnology enables the development of highly sensitive and selective nanosensors capable of detecting low concentrations of specific pollutants in wastewater. These sensors can provide real-time monitoring and data for improved process control. Nanoscale materials have been used to develop efficient adsorbents for the removal of nutrients (e.g., phosphorus and nitrogen) from wastewater, which is essential in combating eutrophication and protecting aquatic ecosystems. Photocatalysis is a promising technique for water purification that uses a light active nanostructured catalyst medium to degrade various pollutants present in the water [56]. Photocatalysis is a process defined as “change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance—the photocatalyst—that absorbs the light and is involved in the chemical transformation of the reaction partners.”11 In a typical photocatalysis system, a semiconductor material is used as catalyst medium, which upon absorption of a light energy higher than its bandgap energy generates an electron–hole (e–h) pair. The photo-generated e–h pair then produces highly reactive oxidizing and/or reducing radicals, such as super oxides (O^{-}_{2} , hydroxyl ions (OH• , or other radicals, in water. These radicals then degrade any organic/inorganic pollutant

molecules present in the contaminated water through some secondary reactions. The degradation of the water contaminants can also occur through direct transfer of the photo-generated electrons or holes from the catalyst surface to the contaminant molecules.

Nanotechnology is one of the most rapidly growing areas in the sphere of water treatment technologies, providing some new ideas for contamination control and real improvements in the existing procedures. The special characteristics of nanomaterials, such as the high SA/VS ratio, reactivity and adjustable surface chemistry explain their potential use in numerous field of water treatment.Among the most diverse areas of nanotechnology application in wastewater treatment the use of new adsorbents for the removal of contaminants is of great importance. Carbon nanotubes, graphene based materials and metal oxide nanoparticles have shown high adsorption potential for different pollutants; heavy metals, organic compounds, and new emerging contaminants. These kinds of nano-adsorbents may have higher adsorption capacity and more favorably kinetic characters than traditional adsorbents, so it may greatly improve the efficiency of treatment in a short contact time.Nanoparticles have also promised a lot as far as catalytic degradation of refractory organic pollutants in wastewaters is concerned. Nano-photocatalysts such as TiO2 and ZnO photocatalyst under light irradiation produce ROS to oxidise and mineralise the organic pollutants. The photocatalytic technology has thus been further extended by the synthesis of visible light-active photocatalysts.There is one more important improvement in the field of wastewater treatment under the title of nanomembrane technology. The incorporation of nanomaterials including silver nanoparticles, carbon nanotube, and graphene oxide into the polymer matrix of the membranes has enhanced permeability, selectivity and antifouling characteristic in contrast to the conventional membrane [57]. Since these properties affect the efficiency of the filtration processes in the membrane-based treatment systems, altering them could increase efficiency and reduce energy consumption in the processes.

Real-time monitoring of water quality parameter and concentrations of contaminants are other factors that are being focused on in nanosensors as well as nanodevices. These incorporating nanotechnology based sensing systems can provide faster, cost effective and sensitive pollutant sensors and hence improving the process control and also ensures adherence to the water quality standards.Nanotechnologies do also demonstrate the positive trends of their usage in the disinfection processes. Particles of silver, copper and other metals have been known to have

outstanding antimicrobial profiles making them receptacles for substitute of chemical disinfectants. Furthermore, among the new technologies, nanobubble technology has been proposed for using in water treatment with such possibilities as oxygenation, disinfection, and pollutant removal.

Despite the numerous advantages offered by nanotechnology in wastewater treatment, several challenges need to be addressed for widespread implementation:Despite the numerous advantages offered by nanotechnology in wastewater treatment, several challenges need to be addressed for widespread implementation:

Environmental and health risks: The concerns arising from the release of nanoparticles into the environment and their impacts on organisms and people raise concerns, and must be evaluated and controlled.

Scalability and cost: Most nanotechnology-based solutions have been proven at the lab scale, but taking such technologies to large-scale wastewater treatment facilities and matching the cost constrain are problems.

Stability and longevity: Stability and performance of nanomaterials are essential factors that determine the effectiveness of the nanomaterials for wastewater treatment application.

Regulatory framework: Prescription of correct policies and rules for using nanotechnology in water treatment is important to avoid compromise of safety with a view of setting this new technology into standard measures.

Future research directions in nanotechnology for wastewater treatment include:Future research directions in nanotechnology for wastewater treatment include:

Creation of advanced materials that enable attainment of various treatment goals at once, perhaps fixing and adsorbing, and catalytic degradation.Exploitation of bio-based and biomimetic nanomaterials to come up with new greener treatment technologies.

Development of new materials and designs for the nanoscale components that are incorporated in a range of advanced treatment processes such as membrane bioreactor or advanced oxidation process.Research on new synthetic strategies and environmentally benign synthesis of NM for

their fabrication in a more economic and eco-friendly manner.Development of high sensitivity and real time detection technologies in nanosensing for monitoring multi parameters in water resources and treatment systems [58].

However, future development of nanotechnology in wastewater treatment it could perhaps serve as solutions to the ever emerging water treatment problems in the future. The improvement of these technologies not only paves the way to advance that field of treatment but also help in the preservation of water resources and restrictions on environmental pollution.

2.8 Different strategies to enhance contamination removal from waste water by MBR technology

Enhancing contamination removal from wastewater by Membrane Bioreactor (MBR) technology involves implementing various strategies to optimize the performance and efficiency of the system. Choosing the right membrane material and configuration is crucial for MBR performance. Advances in membrane technology have led to the development of different membrane types (hollow fiber, flat sheet, etc.) with varying pore sizes and hydrophobic/hydrophilic properties. Selecting membranes with appropriate characteristics can improve contaminant removal and reduce fouling. Proper aeration of the membranes helps reduce fouling by providing air scouring to prevent the accumulation of solids on the membrane surface [59]. Regular and effective membrane cleaning routines, such as chemical cleaning, backwashing, and air flushing, are essential to maintain high permeability and reduce fouling effects. Optimizing nutrient conditions, such as nitrogen and phosphorus, can improve the biodegradation of organic contaminants by the microorganisms in the system. Proper nutrient management ensures adequate biomass growth and enhances the overall removal efficiency of emerging contaminants. Controlling the sludge age and solids retention time in the bioreactor allows the microorganisms more time to break down complex contaminants and increases the efficiency of biodegradation. Implementing a proper MLR strategy helps maintain optimal biomass concentrations in the bioreactor. Higher biomass concentration can enhance the degradation of organic compounds and improve sludge settleability, reducing the risk of sludge washout and potential loss of biomass.

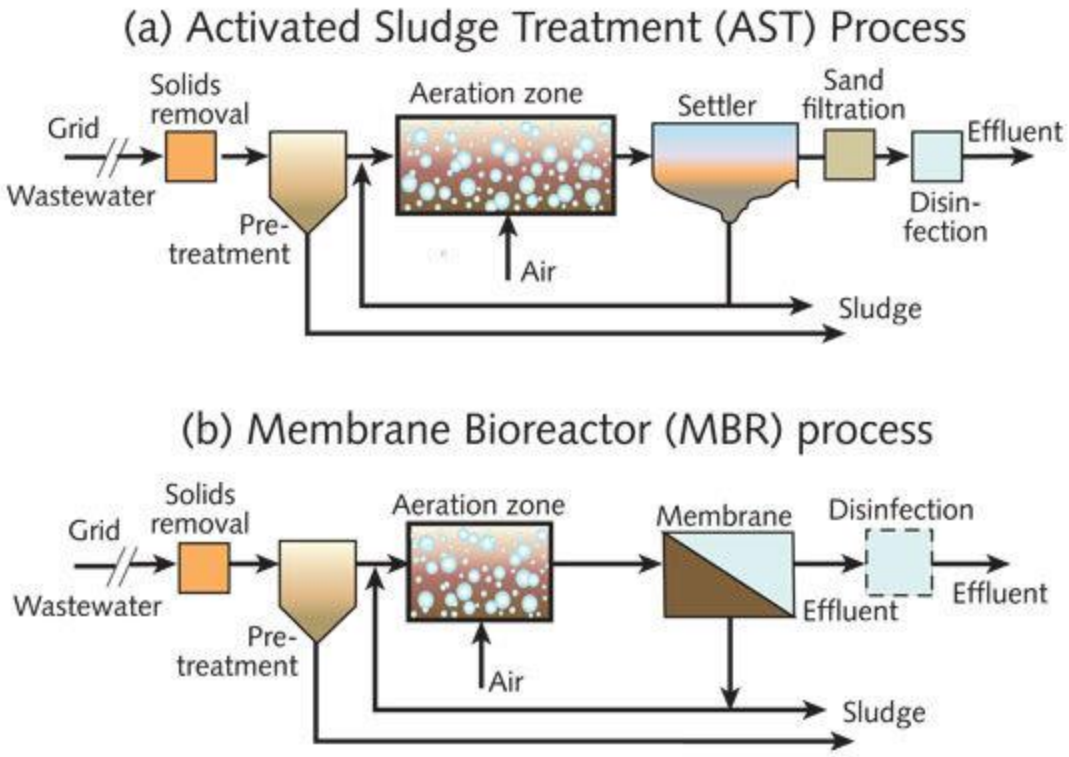


Figure: a) activated sludge process (b) membrane bioreactor (MBR) process

MBR technology is one of the advanced technologies used for wastewater treatment process and the results of applying this technology indicate more benefits than the conventional activated sludge system in terms of effluent quality. Nevertheless, there are some drawbacks, consisting of the removal of specific contaminants, such as refractory organic substances and 'emerging pollutants'. Different techniques have been proposed in order to increase the efficiency of the contamination removal in MBRs with the purpose of optimizing the general performance of the systems and meet the requirements of certain pollutant rejection.

Optimization of Operational Parameters: It is also proven that adjustment of certain operational factors into the MBRs drastically enhance contaminant removal features. Key parameters include:

Sludge Retention Time (SRT): Extended SRTs can facilitate the development of slow metabolizing microorganisms with the potential of breaking down refractory substances.

Hydraulic Retention Time (HRT): At times, the Chilean operators have altered the HRT and this has a direct impact on the contact time of the contaminant with the biomass and hence the removal efficiency.

Mixed Liquor Suspended Solids (MLSS) concentration: It has been also reported that higher MLSS from 1,000 to 2,000 mg/l can improve the rate of biodegradation and adsorption of specific contaminants.

Dissolved Oxygen (DO) levels: DO concentrations, therefore, need to be well controlled for to achieve proper biological treatment, and can be tuned for specific contaminants.

Membrane Modification and Selection: The system performance of the membrane can be achieved by modifying membrane properties of the contaminants:

Surface modification: Measures like grafting, coating or plasma treatment of membrane surface would modify the hydrophilicity of the membrane surface, and therefore, decrease membrane fouling and improvement of the rejection of inclined contaminants.

Novel membrane materials: As for the improvement of selectivity and permeability, new materials can be engineered, for instance, at the nanoscale level, e.g., nanocomposite membranes or biomemetic membranes.

Membrane pore size selection: Selective pore size can be used to improve the removal of specific impurities based on size only mechanisms.

Integration of Adsorption Processes: Integration of adsorbents into MBR systems can improve the index of removal of persistent substances:

Powdered Activated Carbon (PAC): PAC can be added to the bioreactor in order to enhance the efficiency of got rid of hydrophobic and recalcitrant organic components.

Granular Activated Carbon (GAC): The bioreactor may employ GAC either in post-treatment or as the support medium will offer further pollutant removal.

Novel adsorbents: Some of the contaminants can be targeted with the help of using more complex adsorbents like, zeolites, biochar, or engineered nanoparticles.

Advanced Oxidation Process (AOP) Integration: Integrating AOPs with MBRs may improve the destruction of POPs:

Ozonation: That is why pre-treatment or in-situ ozonation can enhance biodegradability of the compounds which are normally recalcitrant to biodegradation.

UV/H2O2: This process involves the use of UV light together with hydrogen peroxide to create hydroxyl radicals for purposes of oxidising contaminants.

Fenton and photo-Fenton processes: These iron based AOPs may be useful in the oxidation of various organic contaminants in water.

Bioaugmentation and Enzyme Addition: By improving the biological aspect of MBRs, the degradation of contaminants will be improved:

Bioaugmentation: The use of specific strains or microbial consortia which are specific in their ability to break down defined pollutants.

Enzyme addition: The addition of enzymes to the system that are known to catalyse the degradation of particular substances.

Anaerobic-Aerobic MBR Systems: The integration of the anaerobic and the aerobic processes in the MBRs is advantageous for some contaminants:

Enhanced nutrient removal: The combined anaerobic-aerobic systems can result in better nitrogen as well as phosphorus elimination.

Degradation of specific pollutants: A few of the contaminants may be mine more efficiently degraded under anoxic conditions.

Membrane Fouling Control Strategies: One only increases contaminant removal on the other hand, reducing membrane fouling can indirectly improve its efficiency by improving operation stability:

Quorum quenching: Employment of QQ bacteria or enzymes to decrease the extent of bio fouling.

Novel membrane cleaning techniques: Increase in better methods of physical and chemical cleaning techniques.

Hydrodynamic optimization: Optimization of the fluid dynamics regime in order to minimize fouling tendency.

Process Intensification: Designing new types of reactors, as well as, optimizing process integration approaches:

Staged MBRs: With multi-stages employing different operating characteristics in order to achieve certain contaminants.

Hybrid systems: Integrating MBRs with other treatment processes for example the moving bed biofilm reactor or fixed-film processes.

Smart Control and Monitoring: Real time monitoring and advanced controls strategies:

Online sensors: Real time monitoring of the contaminant concentration levels and the overall performance of the system through invocation of latest sensors.

Artificial intelligence and machine learning: Creation of the prognosis models and control algorithms for improving the processes.

Resource Recovery Integration: Application of resource recovery procedures to improve the overall sustainability of the systems:

Nutrient recovery: Implementation of Rec.17, integration of processes for phosphorus and nitrogen recovery.

Energy recovery: Could be planning and putting into practice procedures by means of energy recovery for instance biogas through anaerobic digestion.

These strategies depend on some factors such as the type of contaminants it intends to address, various legal requirements as well as cost implication [60]. Sometimes, several methods may be used in sequence to enhance the general level of contamination removal and in a bid to meet the high standards of effluent quality that is being developed.The future researches in MBR technology are expected to target the incorporation of new materials, intensified advanced control

algorithms, and the creation of the improved more environmentally friendly and energy efficient MBR configurations. The continuous effort of improving the efficiency of the contamination removal of MBRs will be instrumental in future challenges faced by the reuse of water and activity in this area.

2.9 Recent developments in physical, biological, chemical and hybrid treatment techniques for removing emerging contaminants from wastewater

Physical Treatment Techniques:

Researchers have been working on improving membrane materials, including nanocomposite membranes, graphene-based membranes, and ceramic membranes, to enhance the removal efficiency of emerging contaminants. These advanced membranes offer better fouling resistance and higher selectivity. Techniques targeting microplastics have gained attention, such as microfiltration, coagulation-flocculation, and advanced oxidation processes (AOPs). These methods aim to effectively capture and separate microplastics from wastewater streams.

Biological Treatment Techniques:

Research has focused on understanding and enhancing the biodegradation capabilities of microorganisms for various emerging contaminants. Metagenomic studies and microbial consortia enrichment have been employed to develop specialized microbial communities capable of breaking down specific pollutants effectively [8]. Bioaugmentation involves the introduction of specific microorganisms or microbial consortia to enhance the biodegradation of emerging contaminants. This technique has shown promise in degrading persistent organic pollutants and pharmaceuticals.

Chemical Treatment Techniques:

AOPs, such as ozone-based treatments, photocatalysis, and Fenton processes, have been investigated to degrade recalcitrant emerging contaminants effectively. These processes generate highly reactive hydroxyl radicals that can break down complex organic molecules. Researchers have explored the use of novel adsorbents, including activated carbon-based materials, graphene oxide, and metal-organic frameworks (MOFs), to adsorb and remove emerging contaminants from wastewater streams.

Hybrid Treatment Techniques:

The combination of MBR technology with AOPs, such as ozonation or photocatalysis, has been studied to achieve a higher removal efficiency of emerging contaminants [61]. This hybrid approach benefits from both biological degradation and advanced oxidation. Researchers have investigated combining different membrane processes, such as nanofiltration or forward osmosis, with AOPs or adsorption technologies to create efficient hybrid systems for removing specific emerging contaminants.The new generation of pollutants such as pharmaceuticals, personal care products, endocrine disruptors and numerous industrial compounds present in the wastewater has been raising new concerns owing to their potential impact of the environment as well as health. Recent advancements in wastewater treatment technologies have therefore been directed towards grappling with this problem as explained in several physical, biological, chemical and advanced hybrid treatment processes. The following review presents particulars on some of the latest developments relating to each of the categories mentioned above.

Chapter 3: Materials and methods

3.1 Materials: Chemicals and Culture media

Some of the standard chemicals used in the study including Kraft Lignin were obtained from TCI while Phenol. red, Azure B from SRL. Mineral salt media compostion (g/L) KH_2PO_4 0.136g, K_2HPO_4 0.346g$MgSO_4$ 2g.$MgSO_4.7H_2O$, 0.8NaCl, 0.006$FeSO_4.7H_2O$, 0.2NH_4Cl, 0.004$Cacl_2.2H_2O$ was used in process of further enhancement of lignin decomposing bacteria. Trace element solution containing (mg/L): FeCl3.6H20, 160, ZnSO4·7H2O, 1 500 ppm, CaCl2·6H2O, 1 60 ppm, CuSO4·5H2O, 1 50 ppm, MnSO4·H2O, 1 500 ppm and Na2MoO4·2H2O. 100. These salts and buffers were purchased from Hi-Media Laboratory Ltd., Mumbai India. The culture media necessary to this investigation, that is, Leuria Bertini, Tryptone media, MR/VP media, Citrate media, Nutrient agar ,potatodextrose agar media,Tryptic soy broth agar media was obtained from HiMEDIA laboratory and Sigma-Aldrich. The used tetracycline was obtained from TCI(Tokyo Chemical Industry CO., LTD). All the chemicals and buffer composition utilized in this study were of.

3.2 Sample collection:

The samples Sludge & Soil were collected from Supreme Paper Mill Kolkata India. The sample was collected in calculable and aseptic conditions and stored in pre sterilized bags and vials. The collected sample was then placed in a cooler and refridgerated at 4°C for future analysis. experimental purpose. These samples were tested for the following wastewater parameters; pH and texture. Colour, moisture content COD, etc. as indicated by the previous study conducted by (source)

3.3 Characterization of sample:

Characterization of a sample then specifies the physicochemical properties of the contaminated soil sample. The Ph of the contaminated soil was only slightly alkaline. There was the realization that the appearance, biochemical and physiological characteristics closer of the crew members, of the company and its employees. than that of the control BOD, COD, chemical oxygen demand , were significantly higher pH indicates has demonstrated how effective the method is in determining the quality of water and the degree of pollution; thus the acidic values at the discharge

point. implies that the effluents could be toxic and no form of life or aquatic life is functionally supported from most of their It is also important because metabolic activities are influenced by pH. and temperature affects behaviour. Features related to organisms, the extent of dissolve ability of gases and salts in water. High BOD and COD values obtained was due to high organic matter in the effluent and this indicates toxicity of the effluent discharge. The increased BOD means that the faster oxygen will be consumed in the stream. Both COD and BOD in general sense are the parameters of comparing the oxygen loss from the contaminated waste.

Parameters	Values
pH	7.77
Appearance	Clear
BOD	54.20
COD	86.44

Table 1:Physicochemical parameters of soil sample

3.4 Enrichment of sample:

Nutrient enrichment process was applied to isolate conceivable strains of bacteria.The 1g collected soil sample was added to 100 ml of Mineral Salt Media (MSM) which contains the following composition; 0.136KH_2PO_4, 0.346 K_2HPO_4, 0.02 $MgSO_4.7H_2O$ 0.8 NaCl,0.006 $FeSO_4.7H_2O$, 0.2 NH_4Cl, 0.004. 1g collected soil sample was added to 100 ml of Mineral Salt Media (MSM) comprising of the composition 0.136 KH_2PO_4, 0.346 K_2HPO_4, 0.02 $MgSO_4.7H_2O$, 0.8 NaCl ,0.006 $FeSO_4.7H_2O$, 0.2 NH_4Cl, 0.004 Concentrations are $Cacl_2.2H_2O$ and trace elements FeCl3.6H20,160, ZnSO4·7H2O,1500, CaCl2·6H2O,160Prepared 0.1M CuSO4·5H2O, 150ml, MnSO4·H2O, 1500ml and 0.1M Na2MoO4·2H2O in a 250ml Erlenmeyer flask.eria. 1g collected soil sample was added to 100 ml of Mineral Salt Media (MSM) comprising of the composition 0.136 KH_2PO_4, 0.346 K_2HPO_4, 0.02 $MgSO_4.7H_2O$, 0.8 NaCl ,0.006 $FeSO_4.7H_2O$, 0.2 NH_4Cl, 0.004 $Cacl_2.2H_2O$ and trace elements FeCl3.6H20,160, ZnSO4·7H2O,1500, CaCl2·6H2O,160, CuSO4·5H2O,150, MnSO4·H2O, 1500 and Na2MoO4·2H2O in a Erlenmeyer flask (250ml). Then, To determine the optimum flasks were shaken at 250rew/min while 100mg/l lignin was supplemented into the MSM media as a carbon source. It was assessed at 37°C under shaking conditions at 120 rpm. At 5th day of incubation, in each tube, 10ml sample was transferred to a new 90ml lignin augmented mineral salt media, and then grown for 72 hours at 37°C at about 120

rpm shaking conditions with 200mg/ L lignin. The enrichment process was further caried on with the increment of length of lignin till 1000mg/l.

3.5 Isolation of microbes:

The broth culture was serially diluted to 10-4 and 10-5 and 100 µl of this broth culture was spread to the lignin augmented MSM agar plates afterward by incubating them at 37 ℃ for 48 hours. The colony morphology and phenotypic characteristics were different when colonies that formed on the plates were chosen, picked up enhanced by streak plate method on the same agar and then recharacterized by streak plate method. The refined colonies were subwas cultured further on MSM agar plates multiplied with the rising concentration of kraft lignin (2001500mg/L). Three bacterial isolates were selected which were potential to grow at the top-flight These concentrations included 0,100, 400, 600, 800, and 1200 mg/L of kraft lignin, each of which was streaked with L-MSM plates containing agar. Likewise, the fungi isolates were grown on Potato Dextrose Agar (PDA) media growth. Thus, three fungal isolates were selected. All those samples where tested to be able to tolerate high concentration of kraft lignin. Bacterial isolate which shows growth towards 1200 concentration of 50mg/L of KL was chosen for further KL degradation experiments since it showed ligninolytic characteristic. A fungal-bacterial consortium was evaluated by biochemical characterization following method also developed.

3.6 Analysis of Ligninolytic enzyme activity

The ability of the isolate to produce Ligninolytic enzymes was further determined qualitatively using plate assay method. with minor adjustments. MSM agar dishes containing phenol red at a concentration of 0.01% and filter sterilized Azure B MnP, LiP, and laccase activities were determined using the substrates: veratryl alcohol (<0.01%), and Guaiacol (<0.05%). order. A single loopful of an over night bacterial culture was grown on the agar plates and then incubate. for 3 to 5 days at a range of temperature 30 ℃. A brown colour colony on the plate containing guaiacol as a substrate was recorded as a positive result for laccase activity while Azure-B and phenol red decolorising confirmed is shown to be associated with a positive reaction for LiP and MnP activity. Determination of the production of ligninolytic enzymes in MSM broth supplemented with 1000 mg/L KL was conducted. A millilitre of the new prepared bacterial suspension with an optical density of 1.0 at 600 NM was grown aerobically on nutrient agar at 30

◦C and 120 rpms for five days. The suspension was then transferred to a 100 mL MSM medium containing 1000 mg/L KL as microsatellite markers. Every 24 hours, the culture to compare bacterial growth and the enzyme activity, the broth was removed from the amperometric cell. To separate the The culture broth of two millilitre from the cell pellets was further centrifugedat 8000 rpm for 10 minutes to obtain clear supernatant. minutes at 4°C For fungi isolates similar experiment was performed. For qualitative estimation, MSM-media was supplemented with the lignin mimicking dyes and 2mm length of fungi mycelium was obtained. was cut and put on the petri plates. The plates were laid in an incubator at 30ºC and were left for 5 days. The amount of enzyme produced by fungal isolates was also analyzed in the same format as that of bacterial isolates. This method was used to determine the Laccase activity and comparison to LiP. 1.0 mL of 4 mM veratryl alcohol wasjson Data added. 1.Crude enzyme solution for test A was made up from 0 mL sodium tartrate buffer (100 mM; pH 3.8), 0.0 mL of sodium substrate solution for the determination of LiP activity." H2O2 (2 mM) was added to the reaction at the rate of 0.2 mL. after 5 minutes of incubation temperature of 30 ◦C. The value of absorptions at 310 nm were recorded via UV–Vis. spectrophotometer This change in the reaction was monitored by using a UV-Vis spectrophotometer (UV-Vis, Varian-50) [62]. The method employed to determine laccase enzyme activity was based on guaiacol oxidation; assay contained 2 mM guaiacol, and 10 mM sodium acetate buffer. The reaction mixture for laccase enzyme estimation was prepared by mixing 50 mM sodium acetate buffer (pH 5.0), and 1 mL crude enzyme. It and then incubated for 2 hours at 30 ◦C, an increase in absorbance at 450 nm was observed. The Thus hydrogen peroxide bleaching of 2,6-dimethyl-phenol (2,6-DMP) at 469 nm wavelength was used to estimate MnP activity.50 buffer mM sodium tartrate pH 4.5, mM MnSO4, mM 2,6-DMP and crude enzyme were and 2 mL of the ligand used in the reaction mixture. The mixture was incubated for 5 minutes at 30 ◦C. The reaction was started with 0.1 mM H2O2. As per suggestions of Mei et al., (2020), enzyme activity was assessed at: in room temperature, and oxidizing 1 umol of substrate per minute. In the following studies: The following experiments were conducted: Experimental work was performed in Self and data was subsequently recorded in tripicates.

3.7 Methodology for membrane filtration

Pre-treatment: Prior to use the pulp and paper industry wastewater as feed in membrane module,the suspended particles were separated using centrifugation process, of 9000g for 30 min.

To avoid any chance of a change in membrane hydraulic resistance during ultrafiltration, the membrane was compressed for approximately one hour with ultra clean water at a pressure of 9 kg/cm2, which was greater than the maximum operational pressure, prior to the trials.

It was determined that complete membrane compaction had taken place once the water flux stabilized and stopped decreasing[63]. Following compaction, water runs at various trans membrane

pressures were used to calculate the membrane hydraulic resistance (Rm).

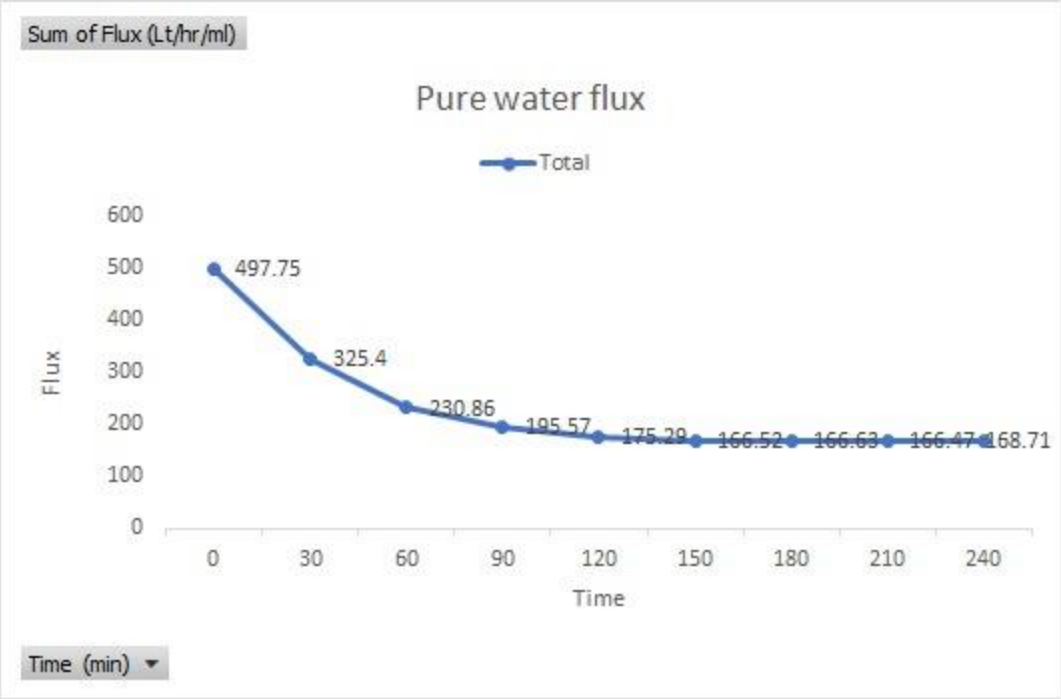
The pure water flux was calculated by

$J= w/\rho At$

Where w is weight of the filtered water, ρ is water density at room temperature, A is membrane area and t is the time interval.

Experiments were done batch wise in the dead end filtration module at different operating conditions starting each time with an initial pretreated feed volume of 350 ml

Following each trial, the membrane was properly cleaned for 20 minutes under running water, immersed for 6 hours in deionised water, and then thoroughly cleaned for another 20 minutes. It was discovered that the water flux returned to almost 98% of its initial value in each instance.



Graph 1: Flux vs Time

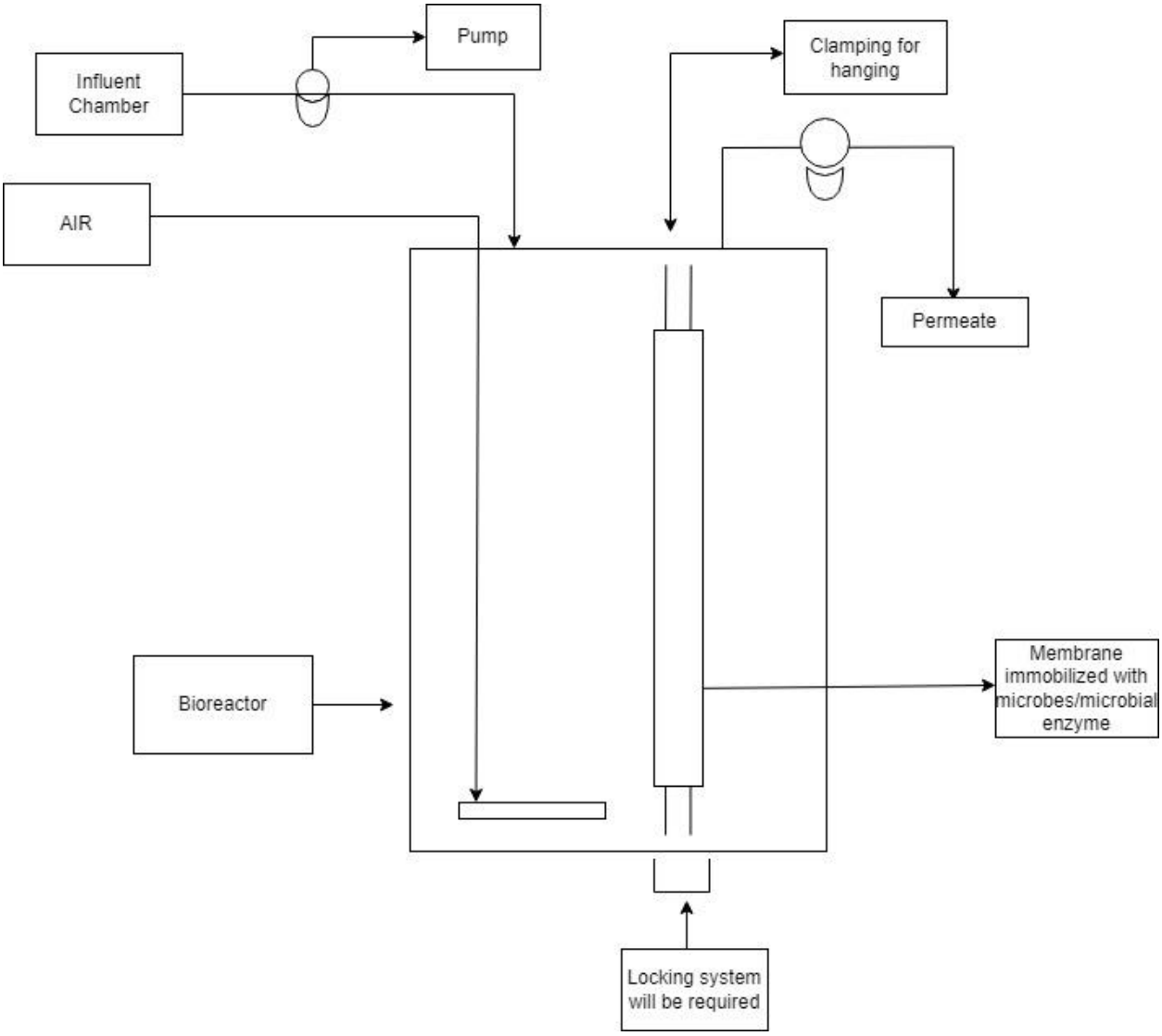
Parameters	Units	Values
pH	-	7.5
Conductivity	µs-cm -1	1250
COD	Mg/L -1	3030
BOD	Mg/L -1	1200

Table 2: The characterization of wastewater of paper industry

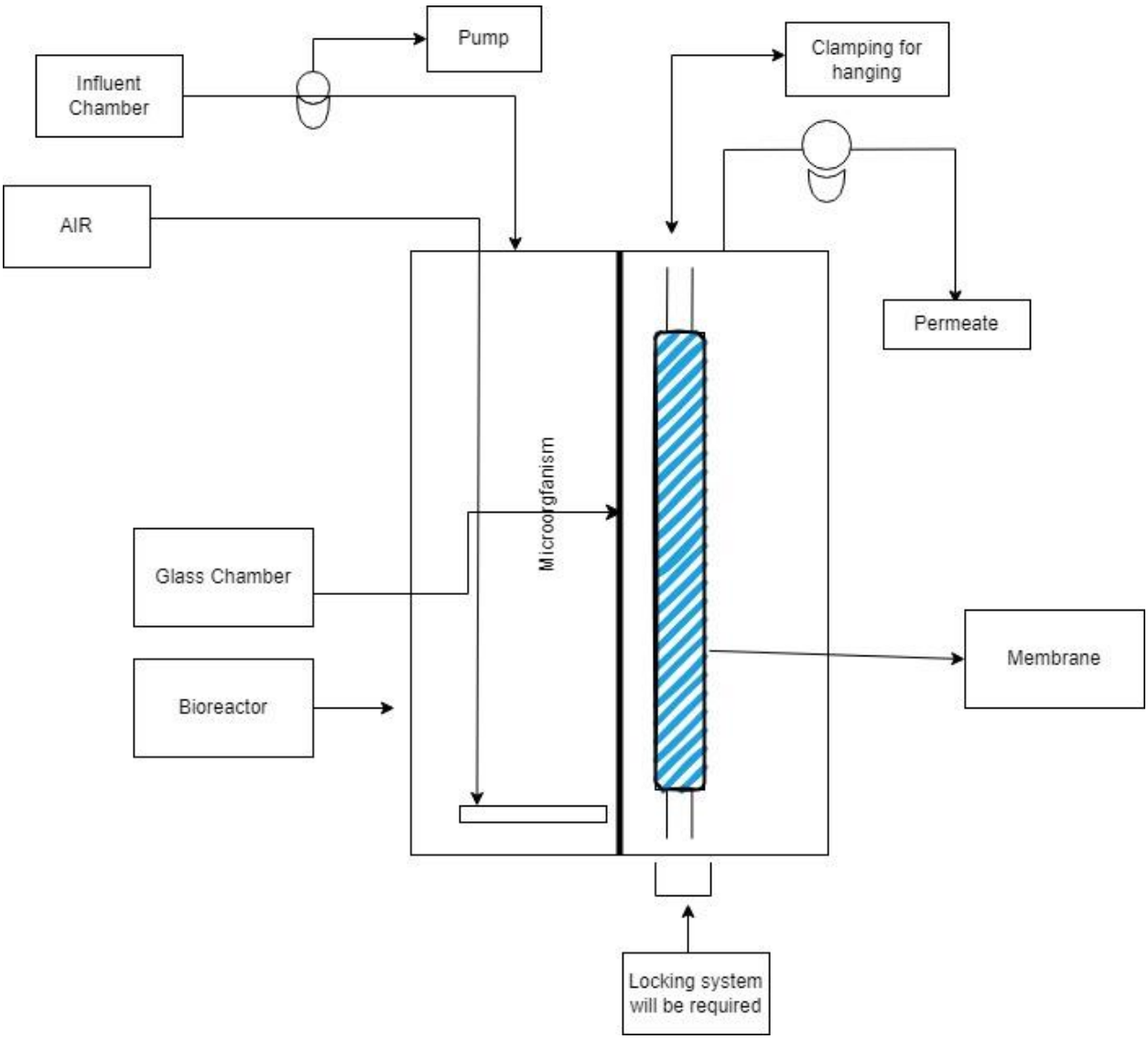
3.8 Design Of Membrane Module

Using cellulose triacetate membrane , batch-wise ultrafiltration of pretreated black liquor was carried out in a q-stirred module membrane. Its special benefits, which include steady effluent quality, good effluent quality, minimal excess sludge generation, high biomass concentration, and no sludge sedimentation issues, membrane bioreactors (MBRs) are frequently employed in black liquor. Membrane screening increases the amount of time that KBL have in touch with the microorganisms in the MBR for degradation by retaining pollutants whose molecular weights above the membrane threshold. Furthermore, the breakdown effectiveness of KBL mostly depends

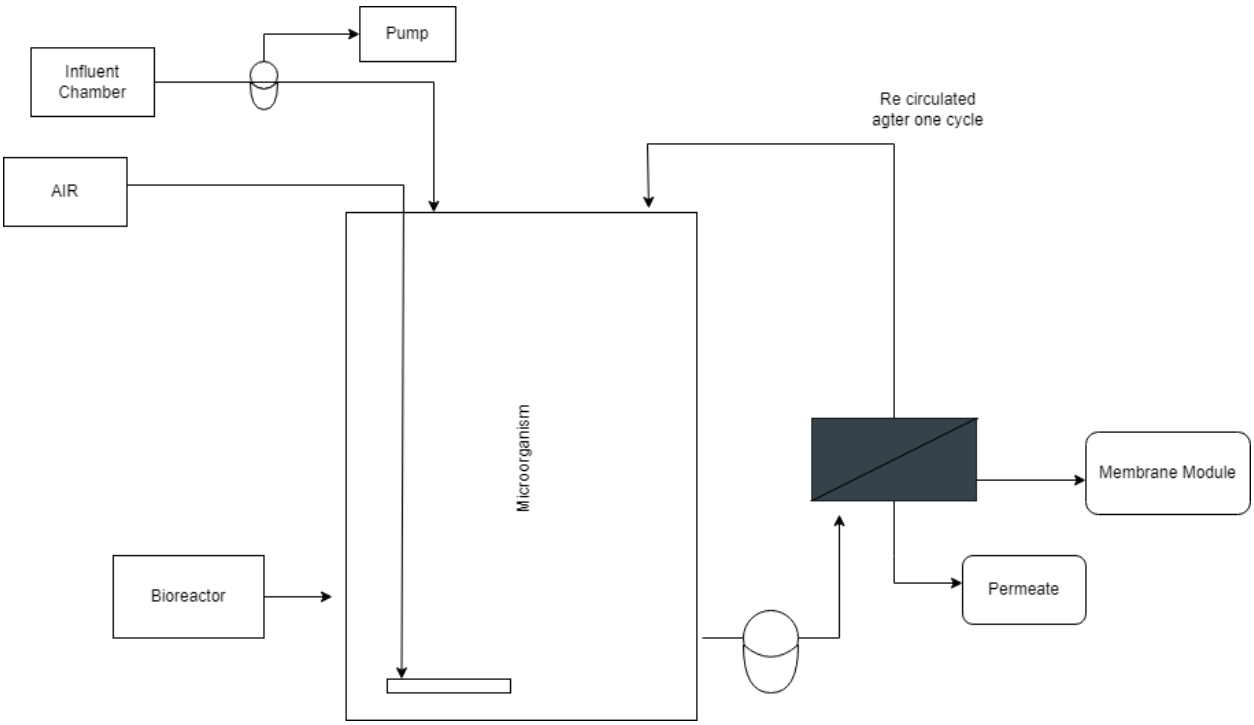
on the kind of microbe may be enhanced in aquatic settings. the effect of KBL on sewage treatment system performance and research on KBL microbial degradation process. The module was manufactured by Gurpreet Engineering Works in Kanpur, Uttar Pradesh, using SS316.(India) in accordance with the design specifications [64]. Two motors with speed controls were included in the module to rotate the membrane enclosure and stirrer.To maximise shear in the membrane's proximity, the stirrer and membrane were rotated in opposing directions. The membrane's and stirrer's rotating speeds were measured using a digital tachometer. The setup has everything needed to recycle the permeate to the feed cell and operate it continuously with a steady supply of composition. This study did not look at the later mode. To stop leaks from the revolving membrane assembly, a sufficient mechanical sealing mechanism was included. Leakage via the top stirrer is prevented by the magnetic drive stirrer mechanism. the whole spinning disc module setup schematic diagram. Sartorious' cellulose triacetate membrane with a 5000 molecular weight cut-off was used for the UF of KBL experiment.sourced from Sartorious Bio-tech India Ltd. in Germany. The actual diameter of the flat sheet membrane, which could operate in the pH range of 4 to 8, was 76 mm, whereas the effective diameter was 56 mm. The membrane may be sterilised by immersing it in 3% formalin, 5% hydrogen peroxide, or 0.1% per-acetic acid for 24 hours. It can be used in both alcohol and aqueous solutions [65].



Design 1: Schematic of submerged MBR module



Design 2 : Schematic of submerged MBR module

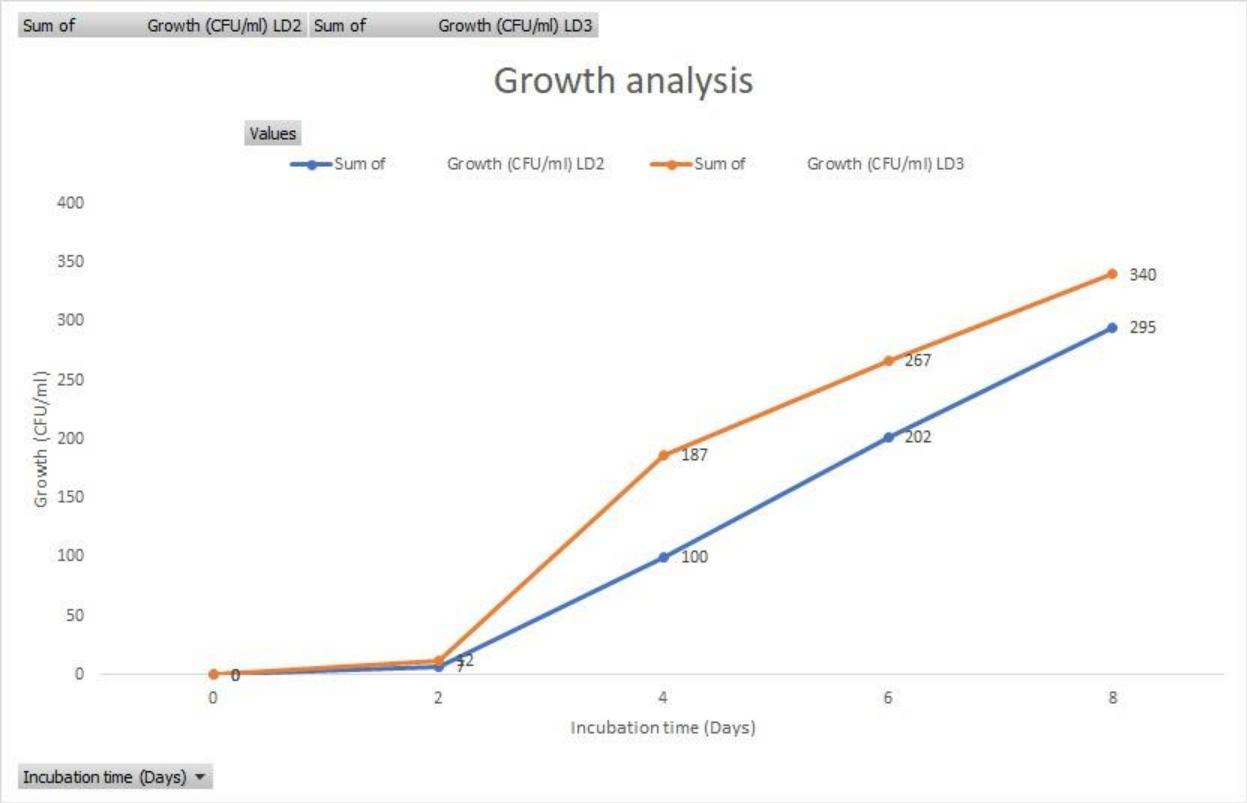


Design 3 : Schematic of aerobic MBR module

Chapter 4: Results and Discussion:

4.1 Isolation, screening and enrichment of ligninolytic bacteria

To separate ligninolytic bacteria,a lignin enrichment procedure was used. One gramme of soil sample was added to 100 millilitres of MSM medium that had been sterilised and adjusted to pH 7 with glucose (0.5%) and KL (1g/L) supplied. The flasks were kept in an aerobic environment during incubation. KL-degrading bacteria are enriched in an incubator shaker set to 37°C and 120 rpm for ten days. The culture broth was severely diluted to 10^{-7}, and 100 µL of this dilution was put on a KL-MSM agar plate in order to collect the ligninolytic potential bacteria that were isolated from the contaminated soil samples. Additionally, plates were cultured for the development of bacteria and fungi at 37°C. Bacterial and fungal colonies that had formed were removed and placed on a new KL-MSM agar plate after 24 to 48 hours. Repeated streaking on nutrient agar plates was used to purify the isolated bacteria and fungus. Consequently, three fungal isolates (KLD1, KLD2, and KLD3) and three bacterial isolates (Raw, LD1, and LD2) were identified and further screening on an MSM agar plate with progressively higher KL concentrations (0.5 g/L, 1 g/L, 1.5 g/L, and 2 g/L). Out of the three bacterial isolates, the one that grew at 452 CFU/ml*10^8 was found to be a possible ligninolytic bacterium that grew opulently at higher KL concentrations. It is clear from graph (1a) that the eighth day saw the highest bacterial growth.



Graph: 1a

Incubation time (Days)	Growth (CFU/ml)	
	LD2	LD3
0	0	0
2	7	12
4	100	187
6	202	267
8	295	340

Table 3: Bacterial growth culture in time of bioremediation of the effluent

4.2 Ligninolytic enzyme activity of bacterial isolates:

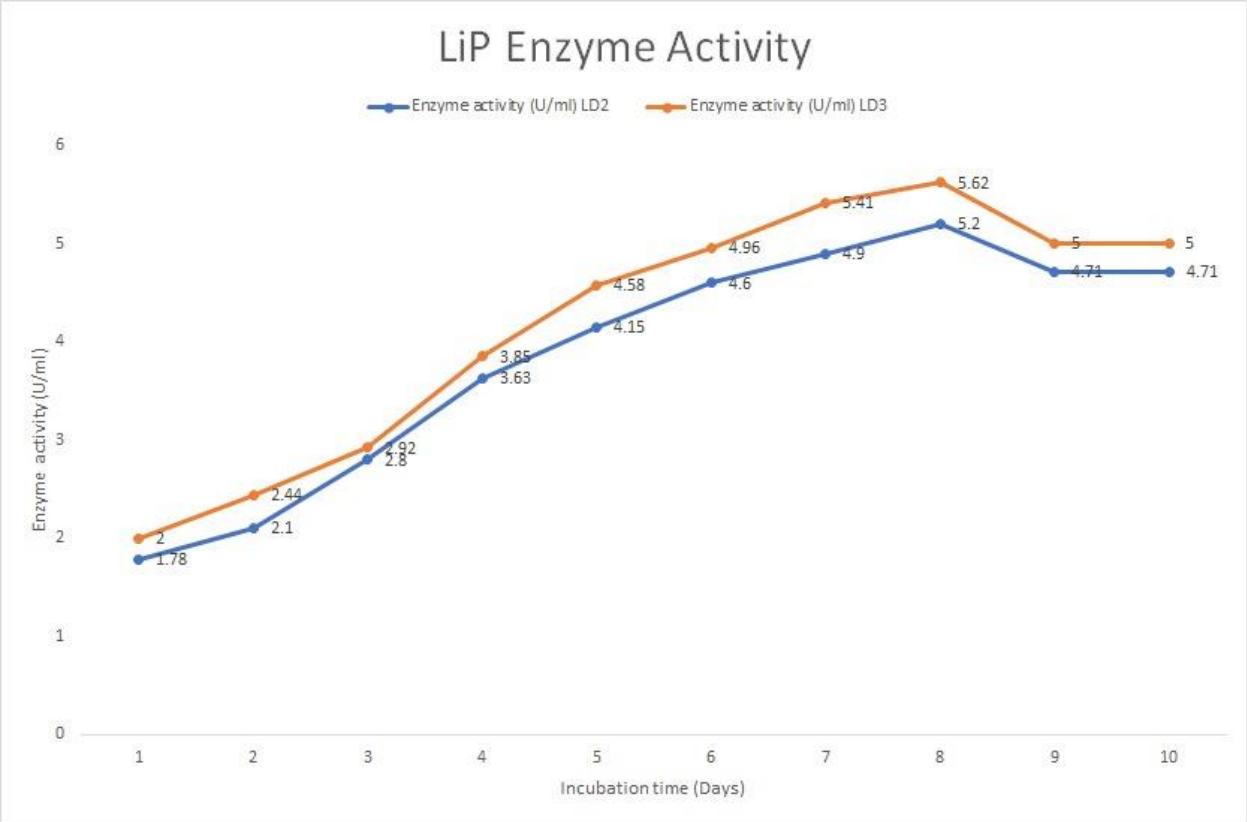
To determine the function of ligninolytic enzyme activity, such as LiP, MnP, and laccase, during KL, the enzymes released by three bacterial isolates (LD2, and LD3) were examined using the plate assay technique. degradation. The bacterium's laccase, MnP, and LiP results were all positive.

The isolate's LiP activity is shown by the elimination of blue colour on the MSM agar plate containing 0.01% Azure-B, whereas the presence of MnP activity is suggested by the change from dark pink to yellow colour. On an MSM agar plate containing guaiacol (0.05%), the brown hue indicated a favourable response for laccase activity. Because of their structural similarity to KL, these compounds were used by ligninolytic enzymes as substrate analogues. Bacteria generate the extracellular ligninolytic enzymes laccase, MnP, and LiP with the purpose of detoxifying and breaking down KL polymer.

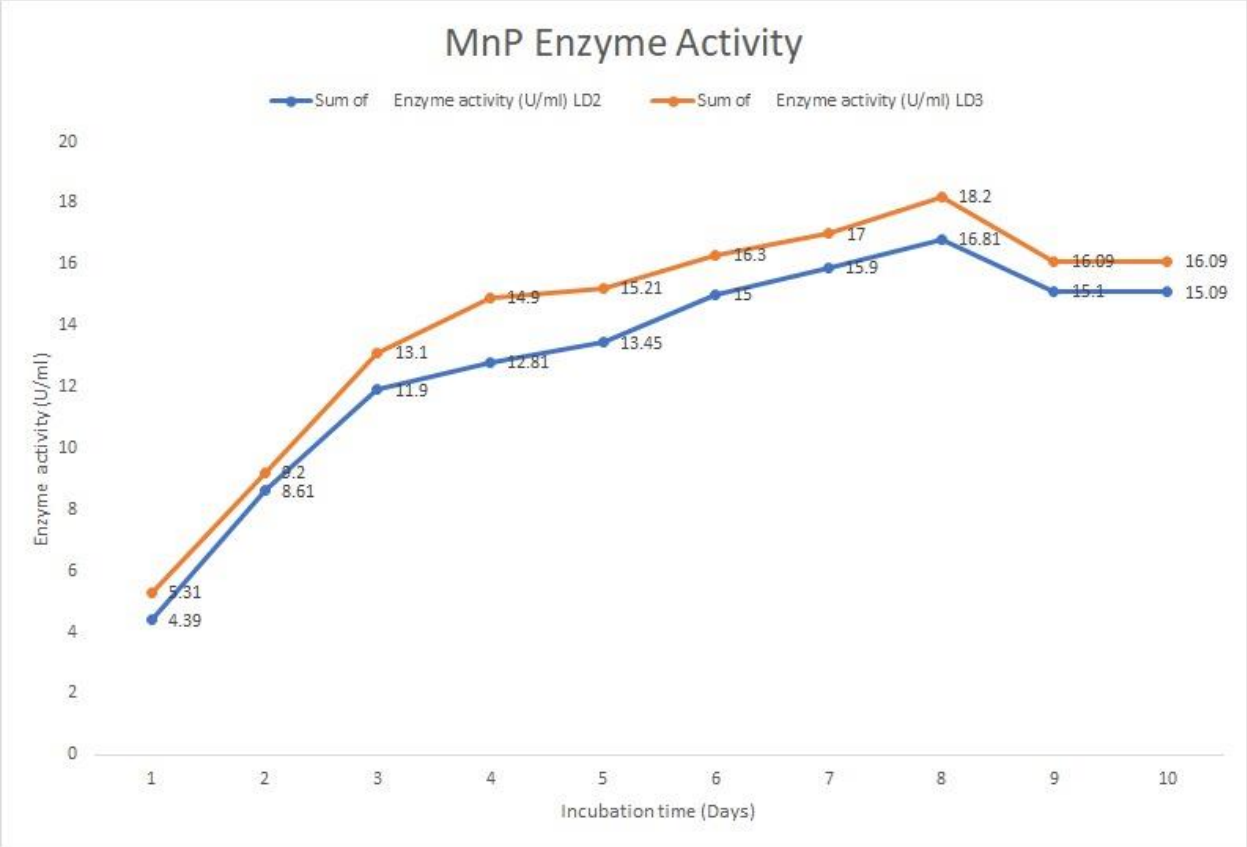
According to the below graph (2 a) it can be stated that on 8th day of incubation LD2 showed maximum LiP enzyme activity (6.2 U/ml) and LD3 showed maximum LiP enzyme activity (5.62 U/ml).

According to the graph (2 b), it can be stated that on 8th day of incubation LD2 showed maximum MnP enzyme activity (16.81 U/ml) and LD3 showed maximum MnP enzyme activity (18.2 U/ml).

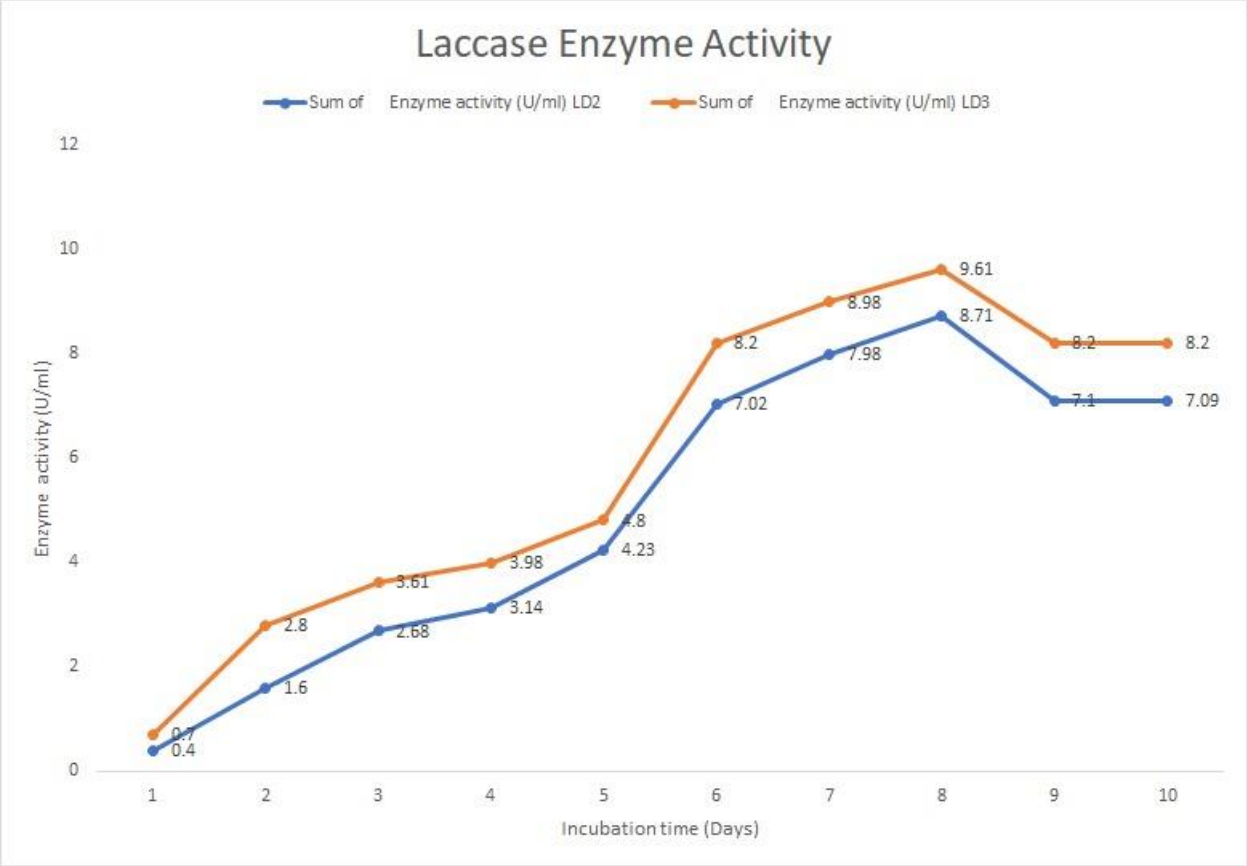
According to the graph (2 c), it can be stated that on 8th day of incubation LD2 showed maximum laccase enzyme activity (8.71 U/ml) and LD3 showed maximum laccase enzyme activity (9.61 U/ml).


LiP Enzyme Activity
Enzyme activity (U/ml) LD2
Enzyme activity (U/ml) LD3
Enzyme activity (U/ml)
Incubation time (Days)
0
1
2
3
4
5
6
1
2
3
4
5
6
7
8
9
10
2
2.44
2.92
3.85
4.58
4.96
5.41
5.62
5
5
1.78
2.1
2.8
3.63
4.15
4.6
4.9
5.2
4.71
4.71

Graph: 2 a


MnP Enzyme Activity
Sum of Enzyme activity (U/ml) LD2
Sum of Enzyme activity (U/ml) LD3
Enzyme activity (U/ml)
Incubation time (Days)
0
2
4
6
8
10
12
14
16
18
20
1
2
3
4
5
6
7
8
9
10
5.31
4.39
8.2
8.61
13.1
11.9
14.9
12.81
15.21
13.45
16.3
15
17
15.9
18.2
16.81
16.09
15.1
16.09
15.09

Graph: 2 b



Graph: 2 c

Incubation time (Days)	Enzyme Activity (U/ml)	
	LD2	**LD3**
1	1.78	2
2	2.1	2.44
3	2.8	2.92
4	3.63	3.85
5	4.15	4.58
6	4.6	4.96
7	4.9	5.41
8	5.2	5.62
9	4.71	5

10	4.71	5

Table 4: LiP enzyme activity for bacteria

Incubation Time (Days)	**Enzyme Activity (U/ml)**	
	LD2	**LD3**
1	4.39	5.31
2	8.61	9.2
3	11.9	13.1
4	12.81	14.9
5	13.45	15.21
6	15	16.3
7	15.9	17
8	16.81	18.2
9	15.1	16.09
10	15.09	16.09

Table 5: MnP enzyme activity for bacteria

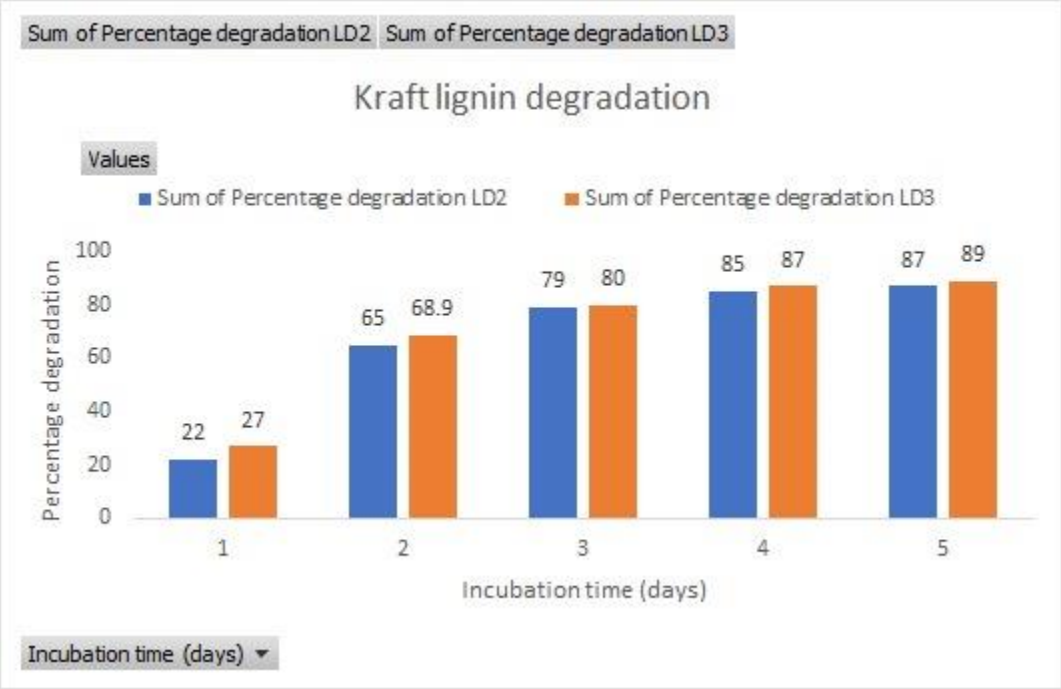
Incubation Time (Days)	**Enzyme Activity (U/ml)**	
	LD2	**LD3**
1	0.4	0.7
2	1.6	2.8
3	2.68	3.61
4	3.14	3.98
5	4.23	4.8
6	7.02	8.2

7	7.98	8.98
8	8.71	9.61
9	7.1	8.2
10	7.09	8.2

Table 6:Laccase enzyme activity for bacteria

4.3 Degradation of kraft black liquor and colour reduction:

Within five days of bacterial treatment, a significant decrease in effluent colour was seen, suggesting that bacterial growth had a considerable impact on both KL degradation and colour reduction. Because bacterial strains could use KL as a source of carbon and protein for development, the effluent's KL content decreased along with its colour. According to the graph (4a) below, the maximum growth was seen at 600 nm on the fifth day of incubation for LD2 and LD3, (mixed culture of bacteria and fungi/consortium). Consequently, the rates of colour decrease and KL degradation also rose.



Graph-4a

Incubation Time (Days)	Percentage Degradation (%)	
	LD2	LD3
1	22	27
2	65	68.9
3	79	80
4	85	87
5	87	89

Table 7: KL degradation

Future Scopes and Planning:

This integrated system has two operational unit.

Bioreactor

This system deals with the biological remediation of the contaminants.

1.Selection of the microorganisms for treating the contaminants

2.Optimizing the growth parameters for enhanced biodegradation

3.Characterization of the selected microbes

4.Performing the removal biodegradation of the contaminants

5.The biodegraded products will be next treated by membrane process in the integrated system

Membrane

The membrane used is modified for increasing the efficiency

Addition of nano adsorbent

Preparation of the nano adsorbent

Characterization of the nano adsorbent

Fabrication of hybrid, modified membrane

Performing the removal experiments

Optimizing the process parameters of the modified membrane

Designing of the hybrid membrane bioreactor for the removal of contaminant

Conclusion:

In conclusion, the lack of pure water and an increase in water shortage day by day confirm the necessity for searching an efficient material for treatment of wastewater. The design and application of Hybrid Membrane Bioreactor technology offer an efficient and sustainable solution for the removal of contaminants from wastewater. The integration of membrane filtration with biological treatment processes leads to enhanced removal efficiencies, reduced sludge production, improved stability, and advanced removal of micropollutants. These advantages make Hybrid MBRs an attractive option for wastewater treatment in various settings, contributing to improved water quality and resource management. However, it is essential to consider site-specific factors, operational challenges, and economic feasibility when implementing this technology. Continuous research and development in this field will further optimize the design and performance of Hybrid MBR systems for future applications.

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