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Fabrication, Characterization, and Application of Clay-Based Ceramic Membranes for Oily Wastewater Treatment: A Review

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Abstract

The rapid growth of the oil mill industry has led to the generation of large volumes of oily wastewater containing high concentrations of oil, grease, suspended solids, and organic pollutants. The discharge of such effluents without adequate treatment poses serious environmental and public health risks. Conventional treatment technologies often suffer from high operational costs, complex process configurations, and limited efficiency when handling emulsified oils and high organic loads. In this context, membrane-based separation has emerged as a promising alternative due to its high removal efficiency, compact design, and potential for water reuse. Among available membrane materials, clay-based ceramic membranes have attracted increasing attention as low-cost, sustainable, and robust alternatives to polymeric and advanced oxide-based ceramic membranes. This review critically examines recent developments in the fabrication, characterization, and application of clay-based ceramic membranes for treating oily wastewater. Emphasis is placed on the selection of raw materials, fabrication techniques, sintering parameters, and key performance indicators, including permeate flux, rejection efficiency, mechanical strength, and fouling resistance. A comparative analysis with polymeric and conventional ceramic membranes is presented to highlight the advantages and limitations of clay-based systems. Current challenges related to fouling, raw material variability, energy-intensive fabrication, and scale-up are discussed, and future research directions are proposed. Overall, clay-based ceramic membranes represent a promising and economically viable solution for treating oily wastewater, particularly in resource-limited regions.

Keywords: *Clay-based ceramic membranes, oily wastewater, membrane fabrication, fouling resistance, sustainable water treatment.*

1. Introduction

The oil mill industry produces significant amounts of wastewater, commonly referred to as oil mill effluent (OME), and in the case of palm oil processing, it is known as palm oil mill effluent (POME). POME is a highly polluted agro-industrial wastewater characterized by an extremely high organic load. Its biochemical oxygen demand (BOD) ranges from 25,000 to 35,000 mg/L, while the chemical oxygen demand (COD) ranges between 50,000 and 100,000 mg/L. Additionally, POME has total suspended solids (TSS) levels between 18,000 and 40,000 mg/L, and its oil and grease content varies from 2,000 to 7,000 mg/L [1]–[3]. The environmental impact of untreated POME is severe, leading to oxygen depletion in water bodies, disruption of aquatic ecosystems, and greenhouse gas emissions [4], [5]. Conventional treatment methods, such as biological processes and coagulation-flocculation, are commonly used. However, these methods often have long retention times and are inefficient at removing emulsified oils [6].

Membrane-based separation processes have emerged as promising alternatives for treating oily wastewater. These processes are favored for their high separation efficiency, compact design, and ability to produce high-quality effluents suitable for reuse consistently [6]. Pressure-driven membrane processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), have shown excellent results in removing emulsified oils, suspended solids, and organic matter [3]. However, the widespread use of membrane technology is limited by issues such as membrane fouling, material degradation, and economic factors.

While polymeric membranes account for the majority of the commercial membrane market due to their low cost and ease of fabrication, they are susceptible to severe fouling, thermal instability, and chemical degradation when exposed to harsh oily wastewater conditions and aggressive cleaning procedures [2]. In contrast, advanced oxide-based ceramic membranes made from materials like alumina, zirconia, or titania offer superior thermal and chemical stability and longer operational lifetimes. However, their high material and manufacturing costs hinder large-scale adoption, especially in developing regions [3].

To address these challenges, clay-based ceramic membranes have gained attention as low-cost and sustainable alternatives. These membranes are made from naturally abundant clays such as kaolin, bentonite, and ball clay, which provide favorable mechanical strength, chemical resistance, tunable porosity, and significantly lower production costs compared to conventional ceramic membranes [2], [7]. Recent studies have demonstrated their

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strong potential for oily wastewater treatment, with oil rejection efficiencies exceeding 95% under moderate operating conditions [3].

This review critically examines recent advances in the fabrication, characterization, and application of clay-based ceramic membranes for oily wastewater treatment. It focuses on material selection, fabrication techniques, membrane properties, separation performance, and fouling behavior. Key challenges and future research directions are also discussed to support the transition of clay-based ceramic membranes from laboratory-scale research to industrial-scale implementation.

2. Membrane Technology for Wastewater Treatment

Membrane technology has emerged as one of the most effective and versatile approaches for industrial and municipal wastewater treatment due to its high separation efficiency, modular design, and capability to produce consistent effluent quality [7], [8]. Unlike conventional physicochemical and biological treatment processes, membrane-based systems rely on selective barriers to separate contaminants, making them particularly suitable for complex wastewaters such as oily effluents [4]. Over the past two decades, membrane processes have been increasingly integrated into wastewater treatment trains either as standalone units or as polishing steps following conventional treatment. Despite these advantages, polymeric membranes suffer from chemical instability, while conventional ceramic membranes are expensive due to high sintering temperatures and raw material costs. These limitations necessitate the development of low-cost alternatives. Clay-based ceramic membranes have emerged as promising candidates due to their natural abundance, low cost, and excellent thermal and chemical stability [6]

2.1 Principles of Membrane Separation

Membrane separation operates on the principle of selective mass transfer through a semipermeable barrier driven by an external force. In wastewater treatment, pressure-driven membrane processes dominate, where transmembrane pressure serves as the primary driving force. Separation mechanisms include size exclusion (sieving), electrostatic interactions, and adsorption of solutes on the membrane surface or within membrane pores [6].

Depending on pore size and operating pressure, pressure-driven membrane processes are classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF and UF membranes typically remove suspended solids, colloids, bacteria, and emulsified oil droplets, whereas NF and RO membranes provide tighter separation, enabling the rejection of dissolved organic compounds, multivalent ions, and salts [3]. For oily wastewater treatment, MF and UF are most commonly employed due to their lower operating pressures and reduced energy demand.

2.2 Classification of Membrane Materials

Based on material composition, membranes are broadly categorized into polymeric, ceramic, and composite membranes. Polymeric membranes are fabricated from materials such as polyvinylidene fluoride (PVDF), polysulfone (PSf), polyethersulfone (PES), and cellulose acetate. These membranes are commercially dominant owing to their low cost, flexibility, and ease of large-scale fabrication. However, polymeric membranes exhibit limited resistance to high temperatures, extreme pH conditions, and aggressive cleaning agents, making them susceptible to fouling and chemical degradation during oily wastewater treatment [2].

Ceramic membranes are typically manufactured from inorganic materials such as alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2). They offer superior thermal stability, chemical resistance, mechanical strength, and longer service life compared to polymeric membranes [3]. These properties make ceramic membranes particularly suitable for treating harsh industrial effluents. Nevertheless, the widespread application of conventional ceramic membranes is constrained by high raw material costs and energy-intensive fabrication processes.

Composite or hybrid membranes have been developed to combine the advantages of polymeric and ceramic membranes. These systems include polymer ceramic composites, surface-modified membranes, and thin-film nanocomposite membranes. While composite membranes demonstrate improved antifouling properties and enhanced separation performance, their fabrication complexity and cost remain significant challenges [7].

2.3 Applications of Membrane Technology in Oily Wastewater Treatment

Membrane processes have been extensively applied for the treatment of oily wastewater generated from oil mills, petrochemical industries, metal processing, and food industries. MF and UF membranes are particularly effective in removing free and emulsified oils, achieving oil and grease removal efficiencies exceeding 95% in many reported studies [3]. NF and RO membranes are commonly employed as downstream polishing units to further reduce COD, color, and dissolved solids, enabling water reuse in industrial operations [6].

In oil mill wastewater treatment, membrane systems are often integrated with biological or physicochemical pretreatment to mitigate fouling and improve overall treatment efficiency. For example, anaerobic digestion followed by ultrafiltration and reverse osmosis has been shown to produce high-quality effluents suitable for reuse while significantly reducing organic loading [4]. Such hybrid configurations highlight the flexibility and effectiveness of membrane-based treatment strategies.

2.4 Advantages and Limitations of Membrane Processes

The major advantages of membrane technology include high separation efficiency, compact system design, modular scalability, and the potential for water recovery and reuse. Additionally, membrane systems can be automated and easily integrated into existing treatment infrastructure [9], [10] Despite these benefits, several limitations hinder their widespread adoption. Membrane fouling, caused by oil droplets, organic matter, and suspended solids, leads to flux decline, increased energy consumption, and frequent cleaning requirements [9]. High capital and operational costs, particularly for ceramic membranes and high-pressure NF/RO systems, also remain critical concerns.

Overall, while membrane technology offers substantial advantages for oily wastewater treatment, material selection, fouling control, and cost optimization are essential considerations. These challenges have motivated the development of alternative membrane materials, such as clay-based ceramic membranes, which aim to balance performance, durability, and economic feasibility.

3. Clay-Based Ceramic Membranes: Materials and Fabrication

Despite the benefits of membrane technology in wastewater treatment, several limitations prevent its widespread adoption. Polymeric membranes are susceptible to fouling, leading to a decline in flux and necessitating increased maintenance. On the other hand, conventional ceramic membranes, while more durable, are associated with high production costs. These challenges highlight the need for alternative membrane materials that are both cost-effective and robust [11], [12].

Clay-based ceramic membranes have emerged as promising alternatives due to their advantages over conventional oxide-based membranes. They are low-cost, abundant in nature, and highly stable thermally and chemically. These membranes are increasingly being recognized as sustainable substitutes, aiming to reduce material and manufacturing costs while maintaining sufficient mechanical strength, chemical stability, and separation performance for wastewater treatment applications.

Natural clays, in particular, are appealing because of their availability, affordability, and favorable physicochemical properties, making them suitable for membrane fabrication in resource-limited regions. The structure of the membranes is influenced by material composition and fabrication conditions, so detailed characterization is essential to evaluate their performance effectively.

3.1 Raw Materials for Clay-Based Ceramic Membranes

Natural clays are aluminosilicate minerals composed primarily of silica (SiO_2) and alumina (Al_2O_3), with varying amounts of iron oxides and alkali or alkaline earth oxides that act as fluxing agents during sintering. The mineralogical composition of clay significantly influences membrane porosity, mechanical strength, and permeability after firing [7].

Kaolin is the most widely used clay for ceramic membrane fabrication owing to its high purity, low plasticity, and excellent thermal stability. Kaolin-based membranes typically exhibit uniform pore structures and good mechanical strength, making them suitable for microfiltration and ultrafiltration applications [1], [8]. Bentonite, which is rich in montmorillonite, is often incorporated to enhance plasticity and green body strength. Its swelling behavior and ion-exchange capacity can also contribute to improved adsorption and separation performance [3]. Ball clay, composed mainly of kaolinite with minor impurities, is frequently blended with kaolin to improve workability during shaping processes [2].

In recent years, several studies have demonstrated the feasibility of utilizing locally sourced clays for membrane fabrication. Although variations in mineralogical composition may affect membrane reproducibility, appropriate pretreatment, blending, and characterization strategies can mitigate these challenges and enable consistent membrane performance [7].

3.2 Fabrication Techniques

The fabrication of clay-based ceramic membranes generally involves raw material preparation, shaping, drying, and sintering. Each step plays a critical role in determining the final membrane structure and performance.

Raw clay → grinding/sieving → pore former addition → shaping (pressing/extrusion) → drying → sintering → finished membrane

Fig. 1. Schematic representation of the typical fabrication steps involved in the production of clay-based ceramic membranes for wastewater treatment, adapted from reported fabrication routes [4]

Raw material preparation typically includes drying, grinding, and sieving of clays to achieve a uniform particle size distribution. Pore-forming agents such as starch, sawdust, or agricultural waste ash are often added to enhance porosity and permeability. These additives burn out during sintering, creating interconnected pore networks [7].

Shaping methods vary depending on the desired membrane geometry. Uniaxial or hydraulic pressing is commonly used to produce flat-sheet membranes with controlled thickness and density. Extrusion techniques are widely applied for the fabrication of tubular or multichannel membranes, which offer higher surface-area-to-volume ratios and are better suited for industrial-scale applications [13]. Slip casting and tape casting enable the production of thin membrane layers for asymmetric or multilayer membrane configurations, while freeze casting has been explored to generate hierarchical and directional pore structures with enhanced permeability [14].

Drying is a critical step that must be carefully controlled to prevent cracking or warping of the green membrane. Slow and uniform moisture removal is essential to maintain structural integrity before sintering.

The fabrication parameters directly influence the structural and functional properties of the membranes, which are evaluated through various characterization techniques.

3.3 Influence of Sintering Parameters

Sintering is a key stage in ceramic membrane fabrication, as it governs densification, pore evolution, and mechanical strength. Sintering temperatures for clay-based membranes typically range from 600 to 1200 °C, depending on clay composition and the presence of fluxing oxides [7].

At lower sintering temperatures, membranes retain higher porosity and permeability but may suffer from insufficient mechanical strength. Increasing the sintering temperature promotes particle bonding and phase transformations, leading to improved strength but reduced porosity and flux [8]. Therefore, optimizing sintering temperature and dwell time is essential to achieve a balance between permeability and durability suitable for oily wastewater treatment.

3.4 Composite and Surface-Modified Clay Membranes

To further enhance performance, clay-based membranes are often modified through material blending or surface functionalization. The incorporation of alumina, silica, or other metal oxides can improve mechanical strength and thermal stability without significantly increasing production cost [3]. Surface modification techniques, such as coating with hydrophilic oxides or functional nanoparticles, have been shown to improve wettability and fouling resistance, which are critical for oily wastewater applications [9].

Overall, the flexibility of clay-based membrane fabrication allows for tailoring of membrane properties to meet specific treatment requirements. Continued innovation in fabrication and modification strategies is expected to further improve the performance and scalability of clay-based ceramic membranes.

4. Characterization of Clay-Based Ceramic Membranes

To assess the effectiveness of fabricated membranes, several characterization techniques are employed to analyze their morphology, structure, and performance-related properties. Comprehensive characterization of clay-based ceramic membranes is essential to establish clear relationships between raw material composition, fabrication conditions, microstructural features, and separation performance. Characterization techniques commonly employed include physicochemical, microstructural, thermal, mechanical, and surface property analyses. These methods provide critical insight into membrane quality, durability, and suitability for oily wastewater treatment applications [15]. These characterization results provide the basis for understanding membrane performance in wastewater treatment applications.

4.1 Physicochemical Characterization

Physicochemical characterization is primarily conducted to determine the elemental composition and crystalline phases present in raw clays and sintered membranes. X-ray fluorescence (XRF) is widely used to quantify major oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, and K_2O, which strongly influence sintering behavior and pore development [7]. High alumina and silica contents are generally associated with improved thermal stability, whereas fluxing oxides facilitate densification at lower sintering temperatures.

X-ray diffraction (XRD) is employed to identify mineralogical phases such as kaolinite, quartz, illite, feldspar, and mullite. During sintering, kaolinite undergoes dehydroxylation to form metakaolin, followed by phase transformation to mullite and free silica at elevated temperatures, significantly enhancing mechanical strength [8]. Fourier-transform infrared spectroscopy (FTIR) is often used as a complementary technique to monitor structural changes and the removal of hydroxyl groups during thermal treatment [2].

4.2 Microstructural and Morphological Analysis

Microstructural characterization provides direct information on pore morphology, grain size, and pore connectivity, which are key determinants of membrane permeability and fouling behavior. Scanning electron

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microscopy (SEM) is the most commonly used technique to visualize surface and cross-sectional morphologies of clay-based membranes. reported SEM observations typically reveal interconnected pore networks formed by the burnout of organic pore formers and partial particle sintering [3].

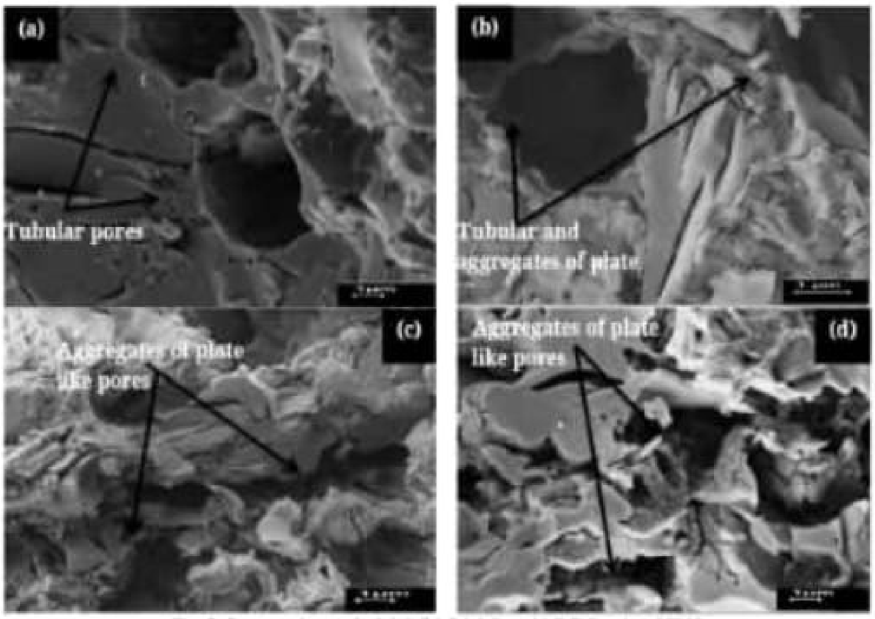

Fig. 2. Schematic illustration of the typical microstructural evolution of clay-based ceramic membranes as a function of sintering temperature, highlighting changes in pore size, porosity, and grain bonding, based on reported SEM observations. (a) Mullite, (b) Mullite-Zeolite, (c), (d) Flexural strength [2].

Energy-dispersive X-ray spectroscopy (EDS), coupled with SEM, is used to assess elemental distribution and homogeneity across the membrane matrix. Atomic force microscopy (AFM) may also be employed to evaluate surface roughness, which directly influences fouling propensity in oily wastewater filtration [9]. Membranes with smoother and more uniform surfaces generally exhibit improved fouling resistance and higher flux recovery after cleaning.

4.3 Thermal and Phase Analysis

Thermal analysis techniques such as thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are used to study mass loss behavior, dehydroxylation, and phase transitions during heating. These analyses provide valuable information for selecting appropriate sintering temperatures and heating rates [8]. Typical weight losses observed in TGA curves correspond to the removal of physically adsorbed water, decomposition of organic additives, and dehydroxylation of clay minerals.

Phase evolution during sintering has a direct impact on membrane performance. The formation of mullite phases at high temperatures enhances mechanical strength and chemical resistance but may reduce porosity and permeability if excessive densification occurs. Therefore, thermal analysis plays a critical role in optimizing fabrication parameters for oily wastewater treatment applications.

4.4 Mechanical Properties

Mechanical strength is a crucial parameter for ensuring membrane durability under operational conditions involving transmembrane pressure, backwashing, and chemical cleaning. Mechanical properties of clay-based membranes are commonly evaluated using flexural strength, compressive strength, or fracture toughness tests [7]. In general, mechanical strength increases with increasing sintering temperature due to enhanced particle bonding and phase transformation. However, excessive densification can compromise permeability. Therefore, an optimal balance between mechanical integrity and porosity must be achieved to ensure long-term operational stability [8]. Compared to polymeric membranes, clay-based ceramic membranes exhibit superior resistance to thermal and chemical stress, making them suitable for harsh wastewater environments.

4.5 Porosity and Pore Size Distribution

Porosity and pore size distribution are critical factors governing membrane permeability and selectivity. These properties are commonly measured using the Archimedes method, mercury intrusion porosimetry (MIP), and Brunauer–Emmett–Teller (BET) surface area analysis [7]. Higher porosity generally results in increased permeate flux but may reduce mechanical strength and rejection efficiency.

Studies have shown that clay-based membranes sintered at intermediate temperatures (700–900 °C) often exhibit an optimal balance between porosity (typically 25–40%) and mechanical stability, making them suitable for microfiltration and ultrafiltration of oily wastewater [3].

4.6 Surface Properties and Fouling Behavior

Surface properties such as hydrophilicity, surface charge, and roughness play a decisive role in membrane fouling behavior. Contact angle measurements are used to assess membrane wettability, with lower contact angles indicating higher hydrophilicity and improved resistance to oil fouling [9].

Zeta potential analysis provides information on surface charge, which influences electrostatic interactions between the membrane surface and oil droplets. Clay-based membranes typically exhibit negatively charged surfaces, promoting electrostatic repulsion of negatively charged oil droplets and suspended solids [9]. Despite these advantages, fouling remains a challenge, emphasizing the need for surface modification strategies to further enhance antifouling performance.

Overall, comprehensive characterization enables systematic optimization of clay-based ceramic membranes, ensuring reliable performance and durability in oily wastewater treatment applications.

5. Performance of Clay-Based Ceramic Membranes in Oily Wastewater Treatment

The performance of clay-based ceramic membranes in oily wastewater treatment is typically evaluated based on permeate flux, oil and grease rejection, chemical oxygen demand (COD) removal, fouling behavior, and cleaning efficiency. These parameters collectively determine the technical feasibility and operational sustainability of membrane systems in real-world applications. Numerous studies have demonstrated that clay-based ceramic membranes can achieve performance levels comparable to conventional ceramic membranes while offering significant cost advantages [16]–[18].

5.1 Permeate Flux and Hydraulic Performance

The separation performance of clay-based ceramic membranes is influenced by pore size distribution, surface chemistry, and operating conditions. Reported permeate flux values range from 50 to 300 $L \cdot m^{-2} \cdot h^{-1}$, while oil rejection efficiencies exceed 95%, reaching as high as 99% in optimized systems. Chemical oxygen demand (COD) removal typically ranges from 70% to 90%. However, fouling remains a significant challenge, primarily due to oil deposition and pore blockage. Despite this, clay-based membranes demonstrate relatively high flux recovery ratios (greater than 85%), indicating that fouling is largely reversible.

Higher porosity and larger pore sizes generally lead to increased flux; however, excessive pore enlargement may compromise oil rejection efficiency. Studies have shown that membranes sintered at intermediate temperatures can achieve an optimal balance between flux and selectivity, making them suitable for treating emulsified oily wastewater. Compared to polymeric membranes, clay-based ceramic membranes maintain more stable fluxes during prolonged operation due to their superior resistance to compaction and chemical degradation.

5.2 Oil and Grease Rejection

Oil and grease rejection is a critical performance metric for oily wastewater treatment. Clay-based ceramic membranes have consistently demonstrated oil removal efficiencies exceeding 95%, with some studies reporting values above 99% for stable oil-in-water emulsions [3], [9]. Separation is primarily governed by size exclusion and surface interactions between oil droplets and the membrane surface.

The intrinsic hydrophilicity and negative surface charge of clay-based membranes contribute to enhanced oil rejection by promoting electrostatic repulsion and reducing oil adhesion. Surface-modified membranes further improve rejection performance by increasing hydrophilicity and reducing fouling tendency [9]. These results highlight the suitability of clay-based membranes for meeting stringent discharge standards.

5.3 Chemical Oxygen Demand (COD) and Organic Matter Removal

In addition to oil removal, clay-based ceramic membranes play an important role in reducing organic load in oily wastewater. Reported COD removal efficiencies typically range from 70% to 90%, depending on membrane pore size, operating conditions, and the degree of pretreatment applied [4]. While MF and UF membranes are not designed to remove dissolved organic compounds completely, their ability to retain oil-associated and particulate organic matter significantly contributes to overall COD reduction.

For enhanced organic removal, clay-based ceramic membranes are often integrated with biological treatment or advanced oxidation processes. Such hybrid systems have demonstrated improved effluent quality and reduced membrane fouling, underscoring the importance of process integration in practical applications [4].

5.4 Fouling Behavior and Cleaning Performance

Membrane fouling remains a major challenge in oily wastewater treatment, as oil droplets, organic matter, and suspended solids can accumulate on the membrane surface and within pores, leading to flux decline. Clay-based ceramic membranes generally exhibit improved fouling resistance compared to polymeric membranes due to their hydrophilic surfaces and rigid pore structures [10], [18].

Fouling behavior is commonly evaluated through flux decline analysis and flux recovery ratio (FRR) after physical or chemical cleaning. Studies have reported flux recovery ratios exceeding 85% after simple hydraulic cleaning, indicating reversible fouling dominance [9]. The high chemical and thermal stability of clay-based ceramic membranes allow for aggressive cleaning using acids, alkalis, or oxidizing agents without significant loss of performance, thereby extending membrane lifespan.

5.5 Operational Stability and Longevity

Long-term operational stability is essential for industrial deployment. Clay-based ceramic membranes have demonstrated stable performance over extended filtration cycles, maintaining consistent rejection efficiencies and mechanical integrity under repeated cleaning and backwashing operations [7]. Their resistance to thermal shock and chemical attack makes them particularly suitable for harsh industrial effluents.

Overall, the reported performance of clay-based ceramic membranes confirms their strong potential for oily wastewater treatment. While further optimization is required to enhance flux and fouling resistance, existing studies indicate that these membranes can deliver reliable and cost-effective treatment performance.

6. Comparative Analysis with Other Membrane Types

A comparative evaluation of clay-based ceramic membranes with polymeric and conventional oxide-based ceramic membranes is essential to assess their relative advantages, limitations, and practical applicability in oily wastewater treatment. Key comparison criteria include separation performance, fouling resistance, chemical and thermal stability, mechanical durability, and economic feasibility.

6.1 Comparison with Polymeric Membranes

Polymeric membranes fabricated from materials such as polyvinylidene fluoride (PVDF), polysulfone (PSf), and polyethersulfone (PES) are widely used in oily wastewater treatment due to their low initial cost and ease of fabrication. These membranes typically exhibit high initial permeate flux and good oil rejection efficiency under mild operating conditions [10]. However, polymeric membranes are highly susceptible to fouling, swelling, and chemical degradation when exposed to high oil concentrations, extreme pH conditions, and aggressive cleaning agents [19].

Table I: Comparison of polymeric, conventional ceramic, and clay-based ceramic membranes for oily wastewater treatment.

Membrane Type	Material	Operating Pressure	Permeate Flux (LMH)	Oil Rejection (%)	Advantages	Limitations	References
Polymeric UF	PVDF, PSf	0.5–3 bar	100–400	90–97	Low cost, easy fabrication	Severe fouling, chemical instability	[11,16]
Ceramic UF	Al_2O_3, ZrO_2	1–5 bar	50–250	>98	Excellent thermal and chemical stability	High material and fabrication cost	[11,12]
Clay-based MF/UF	Kaolin, bentonite	0.5–2 bar	50–300	95–99	Low cost, durable, and use of local materials	Raw material variability	[2,4,6]

The comparative data presented in Table I are compiled from multiple studies reported in the literature [2]–[7], [11], [12], [16].

In contrast, clay-based ceramic membranes demonstrate superior chemical resistance, thermal stability, and structural rigidity, enabling operation under harsher conditions and repeated cleaning cycles without significant performance loss [7]. Although their permeate flux may be lower than that of polymeric membranes under similar conditions, clay-based membranes offer more stable long-term performance and longer service life, which can reduce replacement frequency and overall operational costs.

6.2 Comparison with Conventional Ceramic Membranes

Conventional ceramic membranes are typically fabricated from high-purity oxides such as alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2). These membranes exhibit excellent mechanical strength, narrow pore size distribution, and outstanding chemical and thermal stability, making them highly effective for oily wastewater treatment [9]. However, their widespread adoption is limited by high raw material costs and energy-intensive fabrication processes that require sintering temperatures exceeding 1300°C.

Clay-based ceramic membranes offer a cost-effective alternative by utilizing naturally abundant raw materials and lower sintering temperatures, often below 1000°C [1]. While their pore size distribution may be broader and mechanical strength slightly lower than those of oxide-based ceramic membranes, studies have shown that clay-based membranes can achieve comparable oil rejection and adequate durability for industrial wastewater treatment applications [19]. This balance between performance and cost positions clay-based membranes as attractive candidates for large-scale deployment, particularly in developing regions.

6.3 Economic and Sustainability Considerations

Economic feasibility is a critical factor influencing membrane selection. Polymeric membranes generally have lower capital costs but incur higher operational and replacement costs due to fouling and chemical degradation. Conventional ceramic membranes require significant capital investment but offer long service life and reduced cleaning frequency.

Clay-based ceramic membranes provide a favorable compromise by significantly reducing material and fabrication costs while maintaining acceptable performance and durability [2]. The use of locally sourced clays and waste-derived pore formers further enhances sustainability by reducing transportation costs and environmental footprint. Additionally, the longer lifespan and cleanability of clay-based membranes contribute to lower life-cycle costs compared to polymeric alternatives.

6.4 Overall Comparative Performance

Overall, clay-based ceramic membranes occupy an intermediate position between polymeric and conventional ceramic membranes. They outperform polymeric membranes in terms of chemical and thermal stability and fouling resistance, while offering substantially lower costs than oxide-based ceramic membranes. Although further optimization is required to narrow the performance gap with high-end ceramic membranes, the demonstrated balance between cost, durability, and separation efficiency underscores the strong potential of clay-based ceramic membranes for oily wastewater treatment.

7. Challenges and Future Perspectives

Despite the promising performance and economic advantages of clay-based ceramic membranes, several technical and practical challenges must be addressed before their widespread industrial adoption in oily wastewater treatment. Understanding these limitations and identifying future research directions are essential for advancing this emerging membrane class from laboratory-scale studies to full-scale applications.

7.1 Raw Material Variability and Standardization

One of the primary challenges associated with clay-based ceramic membranes is the inherent variability in natural clay composition. Differences in mineralogy, impurity content, and particle size distribution can lead to inconsistent membrane properties and performance [7]. Such variability complicates process reproducibility and quality control, particularly for large-scale production. Future research should focus on standardized clay characterization protocols, controlled blending strategies, and the development of composition property databases to ensure consistent membrane quality.

7.2 Fouling Control and Surface Modification

Although clay-based ceramic membranes exhibit improved fouling resistance compared to polymeric membranes, fouling remains a significant operational challenge, especially in long-term oily wastewater treatment. Oil adsorption, pore blocking, and cake layer formation can still result in flux decline and increased cleaning frequency [9]. Advanced surface modification techniques, including hydrophilic coatings, functional nanoparticles, and bio-inspired surface designs, should be further explored to enhance antifouling properties without substantially increasing fabrication costs.

7.3 Energy Consumption and Fabrication Efficiency

The fabrication of ceramic membranes, including clay-based systems, is inherently energy-intensive due to high-temperature sintering processes. Although clay-based membranes can be sintered at lower temperatures than conventional oxide-based ceramic membranes, energy consumption remains a concern [7]. Future efforts should

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investigate alternative low-energy fabrication routes, such as microwave sintering, cold sintering, or geopolymer-based approaches, to reduce the environmental and economic footprint of membrane production.

7.4 Scale-Up and Module Design

Most studies on clay-based ceramic membranes have been conducted at laboratory scale using flat-sheet or small tubular configurations. Scaling up membrane fabrication and developing robust module designs suitable for industrial operation remain critical challenges. Research should focus on extrusion-based manufacturing of multichannel membranes, module sealing techniques, and system integration to enable pilot- and full-scale demonstrations [3].

7.5 Integration with Hybrid Treatment Systems

Clay-based ceramic membranes are unlikely to replace conventional treatment processes entirely but rather serve as integral components of hybrid treatment systems. Future research should emphasize the integration of clay-based membranes with biological treatment, advanced oxidation processes, and adsorption systems to enhance overall treatment efficiency and mitigate fouling [4]. Long-term pilot studies evaluating system performance, operational stability, and life-cycle costs are particularly needed.

7.6 Future Research Directions

Despite significant progress, several critical research gaps remain. There is limited quantitative understanding of the relationship between sintering temperature, pore-forming agents, and membrane microstructure, which directly influences permeability and mechanical strength. Most existing studies are based on synthetic oily wastewater, with limited validation using real industrial effluents such as POME, thereby restricting practical applicability. Furthermore, fouling mechanisms at the microstructural level are not fully understood, particularly under long-term operation. There is also a lack of large-scale pilot studies and comprehensive techno-economic analyses, which are essential for industrial adoption [20],[21]

8. Conclusions

Clay-based ceramic membranes have demonstrated significant potential for treating oily wastewater due to their cost-effectiveness, durability, and high separation efficiency. These membranes can achieve over 95% oil removal along with substantial reductions in chemical oxygen demand (COD), making them suitable for industrial applications.

Two key conclusions can be drawn: (i) clay-based membranes provide an optimal balance between cost and performance compared to polymeric and conventional ceramic membranes, and (ii) optimization of fabrication parameters is essential for achieving high permeability and mechanical strength.

Future development should focus on real wastewater applications, fouling control strategies, and large-scale implementation to enable commercialization

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