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A review on atomically modified materials by atomic layer deposition for wastewater treatment

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ABSTRACT

The growing global water crisis necessitates advanced wastewater treatment technologies capable of addressing complex contaminants. Adsorbents and membrane technologies provide viable solutions for wastewater treatment, and their performance can be significantly enhanced through surface modification by atomic layer deposition (ALD). ALD enables nanoscale engineering of materials, offering unprecedented control over surface chemistry, pore structure, and functional properties for improved wastewater treatment efficiency. This review critically examines the advancements in ALD-modified membranes and adsorbents for industrial wastewater treatment, highlighting how ALD enhances adsorption kinetics and selectivity in adsorbents, improves hydrophilicity and antifouling behavior in polymeric membranes, and enhances chemical and mechanical stability in ceramic membranes. Despite these advantages, challenges remain in adoption of ALD in wastewater treatment. Future research should focus on optimizing ALD process parameters and exploring synergies with emerging water purification strategies. The continued development of ALD presents a promising pathway towards more efficient and sustainable wastewater treatment solutions.

1. Introduction

Over the past century, global water demand has surged sixfold, driven by population growth, economic development, and evolving consumption patterns [1,2]. The escalating demand coupled with a relatively stagnant water supply, has exacerbated water stress, posing a significant challenge to modern society. Anthropogenic activities contribute to this issue by generating vast quantities of wastewater, which contains suspended, colloidal, and dissolved solids [3]. However, wastewater represents a largely untapped resource for water recycling, with potential to mitigate water stress and contribute to a circular economy [4].

Wastewater treatment methods, such as chemical coagulation, flocculation, distillation, and ion exchange, suffer from high energy consumption and suboptimal efficiency [5,6]. In contrast, membrane- and adsorption-based technologies have emerged as promising alternatives due to their higher filtration efficiency and lower energy consumption [7,8]. However, the transition to these technologies hinges on innovation in the precise engineering of surface properties at the atomic level [9]. Key surface characteristics critical for efficient filtration are pore size, surface charge, catalytic functionality, and material durability [10,

11].

Current approaches to modifying surface properties, such as sol-gel techniques, chemical grafting, and plasma or UV treatments, are limited by high energy demands, substrate compatibility challenges, limited atomic-scale control, and significant capital costs [5]. Furthermore, the porous nature of membranes and adsorbents makes it challenging for conventional methods to uniformly coat surfaces with functional and thin selective layers [12]. Therefore, innovative fabrication techniques are required to develop robust materials tailored for wastewater treatment applications.

Thin films are essential in various technologies, including magnetic storage devices, optoelectronic components, catalysts, and membranes [13]. Vapor deposition techniques, specifically chemical vapor deposition (CVD) and ALD, offer promising solutions for engineering thin films on a wide range of substrates [14]. CVD is a versatile process that enables the deposition of thin films via chemical reactions of gaseous precursors on or near the substrate surface [15]. The fundamental step in preparing CVD is to identify the chemical reaction responsible for the deposition of the desired product. Subsequently, the thermodynamics and kinetics of the reaction should be studied to determine the reaction's feasibility. On the basis of the chemical reaction, gaseous precursors are

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chosen, which are simultaneously flown into the reaction chamber at a particular temperature and pressure to form the desired film on the substrate, whereas the by-product gases are vented. As a result, by choosing the appropriate precursors and deposition parameters, thin films of most metals, non-metallic elements, and a large number of compounds, including carbides, nitrides, and oxides, can be produced [16]. The following are the advantages of CVD:

- Ability to produce dense and uniform films with good reproducibility and adhesion.
- Control over crystal structure and surface morphology by controlling the process parameters.
- Flexibility to deposit a wide range of materials (e.g., metals, carbides, nitrides, oxides, sulfides) due to the wide availability of precursors (halides, hydrides, and organometallics).

There are, however, some disadvantages with CVD as well, which restrict the widespread applicability of CVD. In particular, the inherent limitation of CVD restricts its applicability for modifying pores smaller than approximately 10 nm [17,18]. Moreover, the following limitations are identified:

- Not all CVD reactions yield conformal films.
- Controlling the thickness of grown layers can be challenging due to island-type nucleation mechanisms [19].
- CVD requires high temperatures (typically above 600°C), limiting its use on substrates that cannot withstand such conditions [20].

ALD, a subset of CVD, facilitates conformal thin film deposition with atomic scale precision through sequential and self-limiting chemical reactions of gaseous precursors [21]. The self-limiting nature of ALD reactions ensures that a monolayer is deposited per cycle of ALD [22], even on porous substrates [23]. The unique capabilities of ALD make it particularly advantageous for wastewater treatment applications, as it allows for:

- Precise tuning of pore sizes to nanofiltration and reverse osmosis range (< 2 nm) [24].
- Altering surface charge by depositing a thin layer of targeted material [25].
- Transformation of adsorbent and membrane material's surface areas from hydrophobic to hydrophilic, and vice versa [26].
- Imparting photocatalytic properties to enhance contaminant degradation [27].
- Mitigate fouling in membrane separation [28].
- Convenient separation of adsorbents from the aqueous phase by deposition of magnetic materials.
- ALD operates in a lower temperature range (80–400°C), enabling thin film deposition on a wide range of substrates, even on polymeric materials [29].

Despite widespread applicability of ALD for membrane modification, functionalization, and fabrication, existing reviews remain segmented in focus. They primarily focus on membrane applications for gas/water separation, ALD-based interfacial engineering, or broader functional materials without a dedicated emphasis on wastewater treatment. While some studies have explored ALD's potential for enhancing membrane antifouling or tuning pore size [30–33], and others have reviewed multifunctional materials for aquatic remediation [34,35], a comprehensive review that highlights ALD's role in modifying both adsorbents and membranes for complex wastewater streams is lacking. This review bridges this gap by providing a comprehensive analysis of ALD's role in wastewater treatment, with particular emphasis on its advantages in enhancing adsorption kinetics and selectivity of adsorbents, improving the hydrophilicity and antifouling properties of polymeric membranes, and enabling advanced fabrication routes for robust ceramic

membranes. It begins with an overview of ALD's historical development and fundamental chemistry, highlighting key processing parameters and their influence on thin film properties. While several extensive reviews discuss ALD's mechanisms and broader applications [12,21,35], this manuscript integrates materials science and water process engineering to offer a holistic perspective specifically tailored to wastewater purification, which has not yet been adequately addressed. Key studies from the last decade are examined to showcase ALD's potential in modifying wastewater treatment materials, followed by a discussion of the current challenges and future research directions in the field.

2. Historical perspective and fundamentals of ALD

2.1. Brief history of ALD

ALD evolved from CVD, a well-established thin film deposition technique in use since the 1880s. Early applications of CVD included the enhancement of incandescent lamp filaments through carbon or metal coatings [20]. The conceptual foundation of ALD was first laid in the 1950s in the former USSR, where researchers explored sequential surface reactions for controlled film growth [36,37]. However, its industrial relevance emerged, independently, in Finland in 1970s, when Suntola et al. established the technique under the name of atomic layer epitaxy (ALE) for fabricating thin films in electroluminescent displays [38]. The first Finnish patent for ALE was filed in November 1974, followed by a U.S. patent granted in 1977. Initially, ALE was primarily associated with epitaxial film growth. However, as the technique gained broader applicability beyond epitaxial systems, extending to polycrystalline and amorphous films, the term ALD became widely adopted in the early 2000s.

2.2. Working principle of ALD: The ALD cycle

Thin film formation in ALD results from chemical reactions between the precursor molecules and reactive functional groups on the substrate's surface. To achieve complete surface saturation, the injected dose of the precursors must be sufficient to react with all the available functional groups. Once saturation is reached, further exposure to precursor does not contribute to additional growth, leading to a self-limiting deposition process.

To illustrate the fundamental mechanism, the ALD of alumina (Al_2O_3) using trimethylaluminum TMA ($\text{Al}(\text{CH}_3)_3$) and steam (H_2O) is presented as a model system [39]. The deposition cycle consists of four distinct steps (see also Fig. 1):

- **Precursor exposure:** The substrate is first exposed to TMA, which selectively reacts with the surface hydroxyl ($-\text{OH}$) groups, forming a $-\text{CH}_3$ terminated surface and releasing methane (CH_4) as a reaction byproduct. The reaction proceeds until all accessible $-\text{OH}$ sites are consumed.
- **Purge step:** An inert gas (e.g., nitrogen or argon) is introduced to remove the unreacted precursor molecules and gaseous byproducts, preventing unwanted gas-phase reactions.
- **Co-reactant exposure:** The second precursor H_2O is introduced, which reacts with $-\text{CH}_3$ terminated surface to regenerate $-\text{OH}$ groups while forming a monolayer of Al_2O_3 . CH_4 is again released as a byproduct in this step. This reaction also follows a self-limiting mechanism and it ceases once all available $-\text{CH}_3$ sites have reacted.
- **Final purge:** A second inert gas purge is applied to remove any H_2O and reaction byproducts, preparing the surface for the next ALD cycle.

Each ALD cycle deposits a thin layer, with growth per cycle (GPC) typically ranging from 0.4 – 2.5 Å [21], depending on precursor chemistry and the targeted material. The final thickness is a function of the total number of ALD cycles performed. This GPC deposition ensures

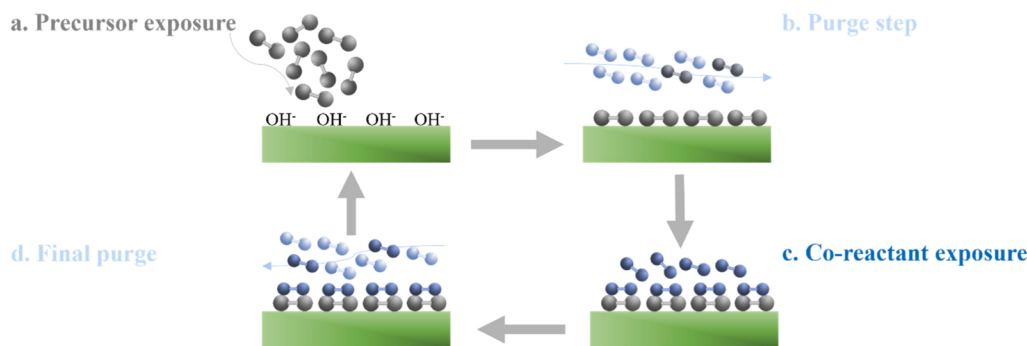


Figure 1. Schematic representation of ALD process.

precise thickness control and conformal coating of complex structures.

2.3. ALD precursors

The selection of appropriate precursors is fundamental to achieving controlled and reproducible ALD. Given that ALD typically operates within a deposition temperature range of 80–400°C [21], precursors must exhibit adequate volatility at the operating conditions while maintaining thermal stability over extended periods.

For an optimal ALD process, precursors must meet the following criteria [9,21,40–42]:

- **Volatility:** The precursor must be sufficiently volatile at the deposition temperature and pressure to ensure transport to the reaction site.
- **Thermal stability:** The precursor should remain chemically stable without decomposition or self-reaction at the deposition temperature.
- **Reactivity:** It must exhibit high reactivity towards the surface functional groups.
- **Inertness to film:** The precursor should not etch or degrade the substrate or the growing film.
- **Safe handling:** Non-toxic and non-corrosive precursors are preferred for safer handling and process reliability.

A practical strategy for identifying suitable ALD precursors involves adapting reactants from a well-established CVD process [41,43]. In this approach, a binary reaction scheme used in CVD is modified to an ABAB... cycle, where reactants are introduced sequentially to achieve self-limiting growth. A key distinction between ALD and CVD lies in GPC, verifying the layer thickness increment per cycle ensures that the deposition follows ALD kinetics rather than CVD-like continuous growth.

2.4. ALD variants: thermal and plasma/radical assisted ALD

Once a chemical reaction has been identified for deposition, the next step is to determine the appropriate variant of ALD. The two primary variants of ALD are thermal-assisted ALD (TALD) and plasma/radical-assisted ALD (PALD), each distinguished by the energy source used to drive the surface reactions.

In TALD, heat energy provides the activation energy for precursor-surface reactions. Common materials deposited using TALD include binary metal oxides (Al_2O_3 , TiO_2 , ZnO , ZrO_2 , HfO_2 , Ta_2O_5), binary metal nitrides (TiN , TaN , W_2N), and certain metal sulfides (ZnS , CdS) [44,45].

In contrast, PALD relies on radicals generated in plasma to facilitate chemical reactions that may not be energetically favored under thermal conditions alone. The radicals enhance surface reactivity, allowing for deposition of materials such as metals (e.g., Ta, Pt, Ru) and semiconductors (e.g., Si, Ge) that are challenging to achieve using TALD.

PALD is particularly advantageous for depositing films at lower temperatures, making it suitable for coating thermally sensitive substrates. However, the high recombination affinity of radicals in PALD may limit penetration into porous structures, challenging its applicability to membrane and adsorbent structures [46].

2.5. Deposition temperature of ALD: The ALD window

Deposition temperature is a key parameter in ALD. The GPC is influenced by temperature, and within a specific temperature range, the deposition process exhibits a stable and self-limiting behavior. This temperature range, known as the ALD window, represents the optimal conditions for achieving consistent and reproducible film growth [47, 48].

As illustrated in Fig. 2, at temperatures below the ALD window, precursor condensation or incomplete surface reactions may occur due to insufficient activation energy, leading to non-uniform or inhibited film growth. Conversely, at temperatures above the ALD window, precursor decomposition can result in CVD-like growth, i.e. deposition is not self-limiting [21,42]. Maintaining deposition within the ALD window is crucial for ensuring uniformity, reproducibility, and the desired film properties.

3. Atomically engineered materials by ALD for wastewater treatment

3.1. Characteristics of wastewater and treatment technologies

Industrial wastewater contains a complex mixture of various organic and inorganic micropollutants, necessitating efficient and selective treatment technologies. Conventional treatment methods often fail to completely remove contaminants. As a result, advanced techniques, such as adsorption and membrane filtration, have emerged as promising alternatives for efficient wastewater treatment.

Adsorption-based treatment relies on high-surface area materials to

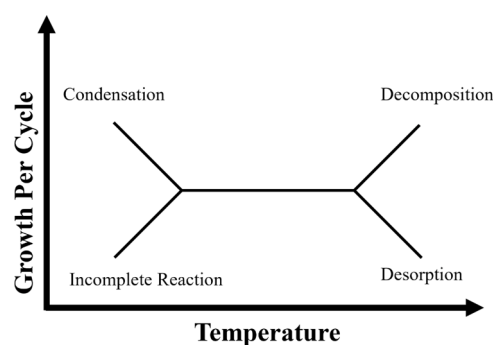


Figure 2. Schematic representation of growth per cycle as a function of process temperature, i.e. the ALD window.

capture contaminants, while membrane filtration enables selective separation based on size exclusion and surface interactions. The performance of adsorbents and membranes is largely dictated by their surface properties, which govern adsorption affinity, permeability, and selectivity. ALD had been extensively explored as a post-modification strategy to enhance these properties, enabling precise atomic-level control over surface characteristics (Fig. 3).

The post-modification by ALD involves the deposition of thin films to coat adsorbents and membranes, thereby tailoring their surface chemistry, pore size, and hydrophilicity/hydrophobicity. This single-step modification approach offers significant advantages over conventional methods, such as sol-gel processing, which often require multiple preparation steps and are associated with high material and processing costs. Moreover, ALD allows for the deposition of a wide range of function materials, including metal oxides, nitrides, and sulfides, onto both organic and inorganic substrates.

In this section, we systematically summarize the applications of ALD-modified adsorbents and membranes for wastewater treatment, emphasizing their improved performance in contaminant removal, selectivity, and long-term stability.

3.2. ALD-modified adsorbents

3.2.1. ALD-modified inorganic adsorbents with single photo-catalysts

A variety of ALD-modified adsorbents have been reported in the literature for removal of (i) dyes (methylene blue, phenols); (ii) toxic, heavy metal ions (Arsenic, Chromium, Copper, Lead); (iii) antibiotics (ciprofloxacin); and (iv) oil from water (Fig. 4) [34]. The primary research focus has been ALD of photo-catalytically active materials, such as titanium dioxide (TiO_2) and zinc oxide (ZnO), onto adsorbents to facilitate their in-situ regeneration via UV irradiation. This approach enhances the long-term stability and reusability of the adsorbents, thereby improving their service life and operational efficiency in wastewater applications. However, Dey et al. concluded that, after growing thin films of TiO_2 on carbon fibers by ALD [49] and compared to both TiO_2 and bare carbon fibers, the TiO_2 films on carbon fibers also improved methylene blue (MB) adsorption on the surface, thus facilitating higher removal from water. Additionally, due to the photocatalytic properties of the deposited TiO_2 films, the exposure to the UV-light photo-catalytically degraded the adsorbed MB, thus regenerating the adsorption sites for the next cleaning cycle. Seo et al. have conducted a similar study in which they deposited TiO_2 films on a porous silicon dioxide (SiO_2) by ALD [50]. Although TiO_2 deposition

results in a decrease of the total surface area, compared to bare SiO_2 , it shows the same MB adsorption capacity as that of bare SiO_2 . However because after saturation, the active adsorption sites of the TiO_2 deposited SiO_2 could be regenerated by annealing at 500°C , the overall performance of the ALD modified surface improves. Wang et al. coated SiO_2 particles with TiO_2 to compare the adsorption of metal and metalloid ions on as-deposited TiO_2 and annealed TiO_2 [51]. It has been concluded that the, as-deposited TiO_2 removes metal and metalloid ions more effectively than the annealed TiO_2 , which has been attributed to the larger surface area. Furthermore, the $\text{TiO}_2/\text{SiO}_2$ particles have a high sedimentation rate compared to the commercial TiO_2 nanoparticles, facilitating the separation of the adsorbent from the wastewater. Jeong et al. deposited another photocatalytic material, ZnO thin films, on mesoporous SiO_2 particles by ALD. ZnO/SiO_2 particles have a lower surface area than SiO_2 particles, but they show a higher adsorption capacity for MB compared to the bare SiO_2 particles [52]. The photocatalytic properties of ZnO also degrade and desorb the adsorbed MB upon exposure to UV light, thus regenerating ZnO/SiO_2 .

3.2.2. ALD modification in organic adsorbents with composite catalysts

An adsorbent that possesses a high density of functional adsorption sites for pollutants may not also possess photocatalytic activity to degrade the adsorbed species and regenerate the adsorbent for the next cleaning cycle, and vice versa. Therefore, Li et al. have come up with a composite catalyst ($\text{Mn}_3\text{O}_4@\text{ZnO}/\text{Mn}_3\text{O}_4$), which consists of a $\text{Mn}_3\text{O}_4@\text{ZnO}$ photocatalyst and a Mn_3O_4 adsorbent [53]. Mn_3O_4 nanoparticles have been prepared using a hydrothermal method, and subsequently, the nanoparticles were coated with ZnO by ALD. The photocatalyst shows a high activity towards the reduction of Cr (VI) species under sunlight irradiation, and the adsorbent facilitates the migration of the reduced species away from the active sites of the photocatalyst, finally resulting in a Cr (VI) reduction efficiency of 94% and total Cr removal of 92% in 70 minutes under simulated sunlight irradiation. By employing the same preparation method, Li et al. have prepared a magnetic $\text{Fe}_2\text{O}_3@\text{ZnO}$ composite photocatalyst for ciprofloxacin degradation [54]. The $\text{Fe}_2\text{O}_3@\text{ZnO}$ composite photocatalyst exhibit a high adsorption and degradation efficiency, i.e. 92.5%, towards ciprofloxacin as compared to bare iron oxide (Fe_2O_3) and ZnO nanoparticles, stemming from the enhanced surface area and zeta potential. A challenge in water purification by adsorbent powders is the complete separation of the powder from the liquid phase, e.g. to reuse it for further purification cycles. However, the $\text{Fe}_2\text{O}_3@\text{ZnO}$ composite photocatalyst has magnetic properties, and, after each filtration cycle,

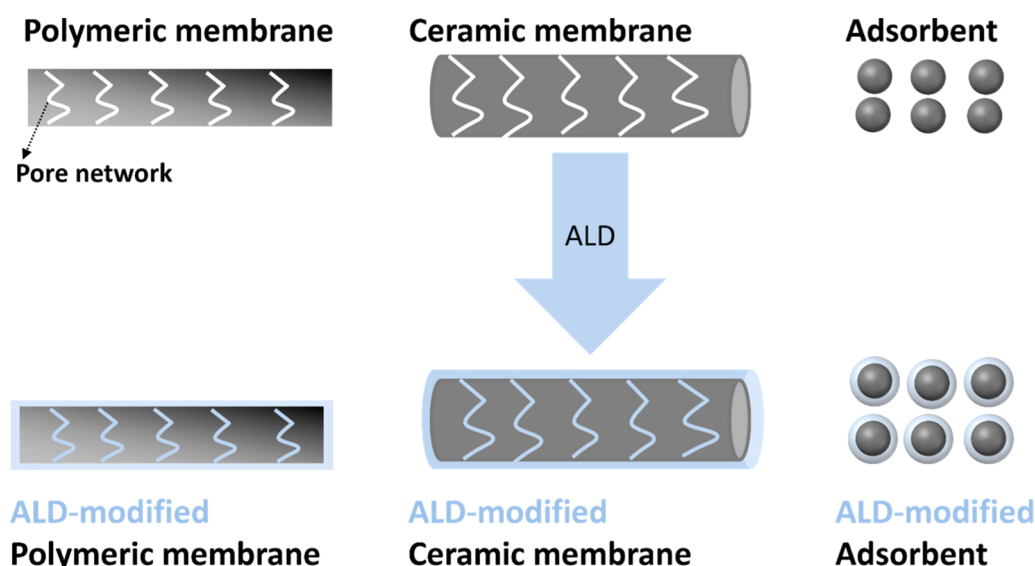


Figure 3. A schematic of atomic-scale modification of polymeric, ceramic membranes and adsorbents by ALD.

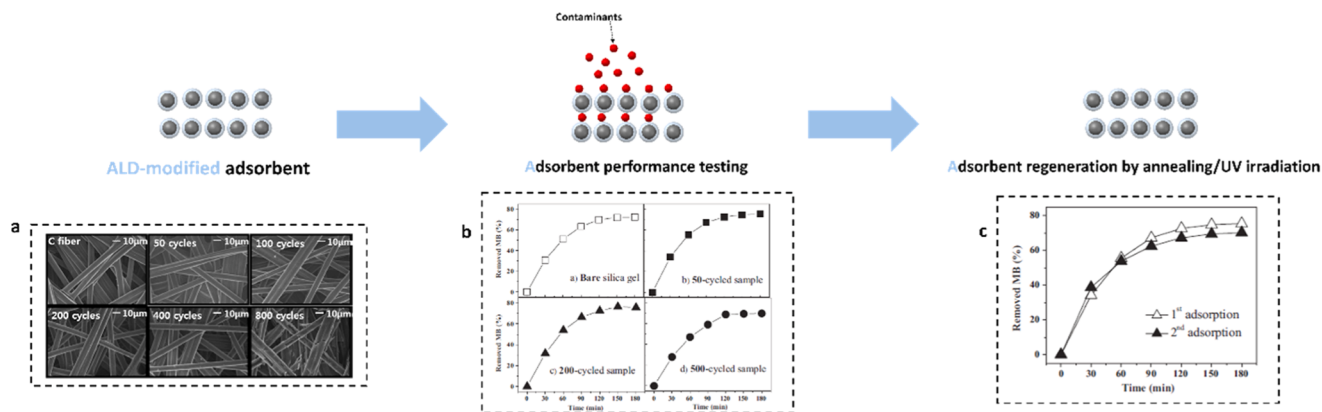


Figure 4. Enhanced performance and regeneration of ALD-modified adsorbents for contaminant removal.

(a) SEM images showing conformal TiO_2 coatings deposited on carbon fibres by ALD. Adapted with permission from [49].

(b) MB adsorption capacity of TiO_2 -coated SiO_2 adsorbents as a function of ALD cycle number, illustrating the tunability of surface properties. Adapted with permission from [50].

(c) Regeneration of TiO_2 -coated SiO_2 adsorbents through annealing at 500°C , demonstrating sustained adsorption performance. Adapted with permission from [50].

the photocatalyst could be collected by applying a magnetic field, while retaining the photocatalytic degradation efficiency after six cycles.

3.2.3. ALD modification of organic adsorbents

Recently, ALD has also been utilized to modify organic adsorbents and carbon nanotubes for metal ions removal and oil-water separation. Mauro et al. have deposited ZnO on polyethylene naphthalene (PEN) by ALD [55]. They have elucidated the properties of the ZnO films, deposited at different temperatures, and have observed that ZnO films can be grown even at a low deposition temperature of 40°C . Their results show that ZnO-modified PEN have a larger affinity towards MB and phenol degradation than pristine PEN. Short et al. ameliorated the oil sorption capacity of cellulose by ALD of Al_2O_3 [56]. Compared to the untreated cellulose, modified cellulose exhibits a 35 times larger oil sorption capacity. Xiong et al. have deposited ZnO on melamine foams by ALD for oil adsorption [57]. They have observed that the deposited ZnO film also incorporates organic components. As a result, the film becomes hydrophobic (water contact angle: 86°), whereas, smooth wurtzite ZnO films are typically hydrophilic with a water contact angle of less than 20° . Therefore, they have subsequently carried out a calcination step at 600°C , changing the surface properties to hydrophilic (water contact angle of 16°). However, they have used the organic moieties-induced hydrophobicity to their advantage and have produced oil adsorbents of high stability and capacity. You et al. have modified multiwalled carbon nanotubes (MWCNTs) firstly by ALD of Fe_2O_3 , in order to introduce magnetic properties, and then subsequently by polyethyleneimine (PEI) [58]. PEI provides a high density of amine groups for adsorption of Cr(VI). The adsorption capacity of the modified MWCNTs has been reported to be 42.8% higher than MWCNTs modified with Fe_2O_3 nanoparticles alone.

3.2.4. ALD modified adsorbents from waste materials

ALD has also been employed to modify industrial waste materials to use them as adsorbents for wastewater treatment. Iakovleva et al. compared the arsenic (III) and (V) removal efficiencies of two solid waste materials, i.e. industrial sand and sulfate tailings, by modifying them with two different techniques: (i) NaOH modification; and (ii) ALD. TiO_2 and Al_2O_3 deposited on industrial waste materials by ALD show a two-times higher arsenic removal efficiency than the materials modified with NaOH to activate iron compounds and generate hydroxide functional groups [59]. Wang et al. have deposited Al_2O_3 on biochar by ALD to improve its surface hydrophilicity [60]. Although the results demonstrate that the Al_2O_3 coating result in an increase in adsorption sites at the expense of surface area, the Al_2O_3 -modified biochar show a

higher removal efficiency for MB than the pristine biochar. In this study, the effect of the surface charge of modified biochar on the interaction of MB has also been analyzed with the conclusion that at a low pH of 5, the high concentration of H_3O^+ ions competitively saturates the adsorption sites, resulting in a decrease of MB adsorption, whereas at a high pH of 9, the concentration of H_3O^+ ions decreases, and the adsorption of MB is relatively high, i.e. ca. 90%. Iakovleva et al. have also employed ALD to modify the surface of metallurgical solid waste materials, i.e. sulfate tailings, but this time with Al_2O_3 [61], with the conclusion that the modified adsorbent selectively removes 97% of cyanide compounds from synthetic acidic wastewater.

The aforementioned applications highlight the importance of ALD for modification of both organic and inorganic adsorbents. Table 1 presents a comparison of these adsorbents.

3.3. ALD-modified organic membranes

Because ALD can be performed at low-deposition temperatures, typically in the range of $50\text{--}400^\circ\text{C}$ [29], the modification of materials with low thermal stability such as polymeric materials is enabled (Fig. 5). In membrane technology, polymeric membranes have the highest market share in the industrial wastewater treatment industry. Numerous research groups have attempted to ameliorate the surface properties of the polymeric membranes by ALD post-treatment [62]. ALD on/in polymeric membranes was found to: (i) enhance hydrophilicity [27], (ii) reduce pore size [63], (iii) modify surface charge [26], (iv) improve fouling resistance [64], and (v) improve mechanical properties. As a consequence, ALD-modified polymeric membranes offer higher contaminant rejection than unmodified membranes.

3.3.1. Enhanced permeability: ALD of Al_2O_3

To the best of our knowledge, Li et al. have published the first report on the ALD of Al_2O_3 on polymeric substrates for wastewater treatment [63]. They have utilized track-etched polycarbonate membranes of a nominal pore size of ca. 30 nm. After 100 cycles of ALD of Al_2O_3 , the pore size has been reduced to ca. 20 nm with an enhancement in surface hydrophilicity. The reported growth rate of $0.8 \text{ \AA}$ per cycle confirms that the deposition process proceeds in a self-limiting manner, characteristic of ALD. This study has further shown that the membranes modified with less ALD cycles (<50) results in an around 20% increase in bovine serum albumin (BSA) retention compared to unmodified membrane, and at only a slight expense of pure water permeability (PWP). However, further increase in the number of ALD cycles results in a gradual increase in BSA retention at the cost of a larger decline in PWP. However, after

Table 1

ALD-modified adsorbents and their properties for degradation of various water contaminants.

Adsorbent	Material Deposited by ALD	Contaminant Targeted	Contaminant Removal in Dark (%)	Contaminant Removal Time in Dark (min)	Contaminant Removal in UV/Normal light (%)	Contaminant Removal Time in Light (min)	Adsorbent Regeneration Method	Adsorbent Regeneration time (min)	Reference
Carbon Paper	TiO ₂	Methylene Blue	-	-	-	-	UV light	60	[49]
Silica	TiO ₂	Methylene Blue	ca. 70	180	ca. 80	180	Annealing 500°C	120	[50]
Silica	ZnO	Methylene Blue	-	-	-	-	UV light	420	[52]
Silica Gel	TiO ₂	Arsenic	-	-	92	-	-	-	[51]
		Selenium			85				
		Molybdenum			99				
		Lead			94				
Polyethylene Naphthalate	ZnO	Phenols			30	240	-	-	[55]
Type 1: Industrial Sand	TiO ₂ & Al ₂ O ₃	Arsenic (III)	-	-	97 & 99	-	-	-	[59]
Type 2: Sulphate Tailings	TiO ₂ & Al ₂ O ₃				92 & 95				
Biochar	Al ₂ O ₃	Methylene Blue	-	-	60	1440	-	-	[60]
Manganese Oxide	ZnO	Chromium	-	-	92	70	UV light	-	[53]
Iron (III) Oxide	ZnO	Ciprofloxacin	18.3	30	92.5	60	UV light	30	[54]
Sulfate Tailings	Al ₂ O ₃	Cyanide	-	-	99	210	-	-	[61]
Type 1: caFe-Cake					99	210			
Type 2: SuFe									
Cotton Balls	Al ₂ O ₃	Oil	-	-	-	-	-	-	[56]
Melamine Foams	ZnO	Oil	-	-	-	-	-	-	[57]
Multi-walled Carbon Nanotubes	Fe ₂ O ₃	Chromium	-	-	ca. 90	-	-	-	[58]

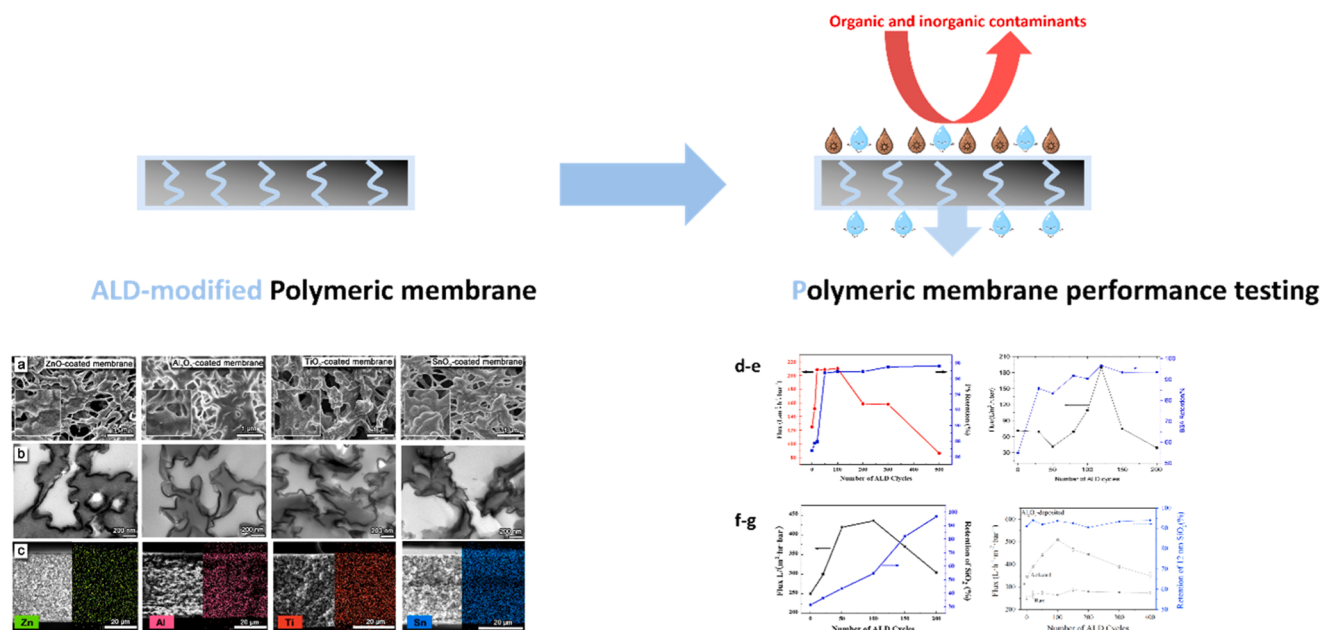


Figure 5. Performance enhancement of polymeric membranes via ALD for contaminant removal.

- (a-c) SEM, TEM, and EDS images of ALD coated membranes with ZnO, Al₂O₃, TiO₂, and SnO₂. Adapted with permission from [72].
 (d) Pure water flux and PS retention of Al₂O₃-coated PTFE membranes as a function of ALD cycle number. Adapted with permission from [26].
 (e) Pure water flux and BSA retention of TiO₂-coated PVDF membranes as a function of ALD cycle number. Adapted with permission from [68].
 (f) Pure water flux and SiO₂ retention of TiO₂-coated PP membranes as a function of ALD cycle number. Adapted with permission from [67].
 (g) Pure water flux and SiO₂ retention of Al₂O₃-coated PP membranes as a function of ALD cycle number. Adapted with permission from [69].

100 ALD cycles, the PWP was reduced only to 5 L·h⁻¹·m⁻²·bar⁻¹, compared to ca. 12 L·h⁻¹·m⁻²·bar⁻¹ for unmodified membranes. Xu et al. have attempted to explore this phenomena further by depositing Al₂O₃ on polytetrafluoroethylene (PTFE) membranes with a pore size of 200 nm [26]. They have found that during the initial 10-50 ALD cycles, Al₂O₃ nucleation and growth occurs predominantly within the pores; while at 50-200 cycles, nucleation shifted to the surface. After just 20 cycles, the PWP increases, by 67.7% compared to the pristine membrane, due to improved hydrophilicity from Al₂O₃ growth on the pore walls. When increasing the ALD cycles to 50 the modified membrane still maintains the PWP but the retention of polystyrene nanospheres (kinetic diameter: 190 nm) is enhanced to 96.7%; whereas, increasing the ALD cycles beyond 100 drastically reduced the PWP (Fig. 5d). This study highlights the importance of choosing ALD parameters carefully to optimize the properties of membranes. Attempts have also been made to convert hydrophilic surfaces to hydrophobic ones; Kong et al. have converted the surface of a filter paper sheet (pore size: 20-25 μm) from hydrophilic to hydrophobic in two steps [65]. First, they have performed ALD of Al₂O₃, and secondly coupled silane molecules onto the precoated Al₂O₃ layer. After 90 ALD cycles, the modified filter paper then shows a lower PWP but a higher permeability to various oils than the unmodified filter paper.

3.3.2. Enhanced selectivity: ALD of TiO₂

In another study, Alam et al. have deposited TiO₂ exclusively on the surface of the polyethersulfone membranes [66]. The deposition has resulted in a smoother membrane surface, with sodium chloride (NaCl) rejection improving more than fourfold to over 90%, albeit with ca. 30% reduction in pure water flux. PTFE is highly inert and hydrophobic without the presence of functional groups, which can result in island-type growth during ALD. To circumvent this problem, Xu et al. have, therefore, introduced an intermediate plasma treatment step to activate the PTFE membrane before ALD of TiO₂ [64]. They have used the same PTFE membrane of pore size of 200 nm as used by Xu et al. [26]. Compared with the untreated PTFE membrane, the 150 cycles of ALD deposition on the activated membrane has resulted in a continuous

thin film of TiO₂ with an increase in PWP by 154% compared to the pristine membrane. Additionally, the retention of monodispersed SiO₂ nanospheres (kinetic diameter: 142 nm) has increased to ca. 33%. In a similar study, Xu et al. have also deposited TiO₂ in the form of conformal thin layers on polypropylene (PP) membranes (pore size: 45 nm) by ALD [67]. This was achieved by the aforementioned plasma pre-treatment to activate the surface of the pristine PP membranes by the formation of active groups on the pore walls. As a result, the film growth was highly conformal and the plasma-treated ALD membranes had a higher hydrophilicity than the non-treated ALD membranes (Fig. 5f). Wang et al. have deposited TiO₂ on polyvinylidene fluoride (PVF) ultrafiltration membranes via ALD [68]. They observed that upon increasing the number of ALD cycles, the PWP first decreased, followed by a sharp increase, which peaked at 120 cycles, and then finally decreased (Fig. 5e). They thus concluded that the optimum number of ALD cycles for obtaining a membrane with the best PWP and BSA retention is 120 cycles. They also elucidated the effect of exposure time on the formation of the TiO₂ film. Their results have shown that even a very short exposure time of 0.5 seconds facilitates greater diffusion of the precursors into the substrate membrane, which results in a thicker film deposition but at the expense of PWP.

The aforementioned plasma activation of the inert porous substrates is an energy-intensive process. Therefore, Chen et al. have invented an alternative activation step for PP membranes (pore size: 43 nm) by using a nitric acid bath [69], which enriches the surface with oxygen and nitrogen-containing active groups that can readily react with the precursors of the ALD process to produce conformal thin films on inert surfaces. It can be seen in Fig. 5g that compared to the bare membrane, the modified membranes have shown a higher PWP and a higher retention of SiO₂ nanospheres (kinetic diameter: 12nm).

3.3.3. Enhanced separation performance: ALD of ZnO

In a different pre-treatment approach, Li et al. have deposited ZnO on PVF membranes (pore size: 200 nm) by employing a pre-treatment step in the ALD chamber [70]. In the first case, a ZnO-like layer has been deposited on the surface of the PVF membrane by employing 10 cycles of

nitrogen dioxide and diethyl zinc precursors prior to the actual deposition of ZnO by diethyl zinc and H₂O precursors. In the second case, the ALD has been carried out without the deposition of the ZnO-like layer beforehand on the surface. Results show that the activation step prior to the ALD results in the formation of uniform films with a high PWP and BSA retention compared to the membranes that were modified by ALD without pre-treatment.

Juholin et al. have treated mine wastewater by modifying commercial nanofiltration membranes, NF90 (polyamide) and NF270 (poly-piperazine), with ALD to deposit a ZnO thin film [71]. The modified membranes are less susceptible to reversible fouling; however, the ZnO thin film has not any effect on irreversible fouling. ALD modified membranes are also used for oil/water separation. Yang et al. have prepared oil-repellant membranes by ALD of several oxides (ZnO, Al₂O₃, TiO₂, and SnO₂) on PVF membranes (pore size: 200 nm) [72]. They have found that, among all the oxides, TiO₂ and SnO₂ surfaces have higher water molecule densities near the surface and thus stronger interactions with water (Fig. 5a-c). Consequently, a hydration layer is formed, which acts as a crude oil-repellant, hence limiting fouling by restricting direct contact between oil and surface. Zhou et al. have deposited TiO₂ on commercial RO and NF membranes [25]. The ALD cycles have been kept low to minimize the loss of PWP while maximizing the selectivity towards salts such as NaCl, CaCl₂, and Na₂SO₄. Their results have demonstrated that high ALD cycles result in the formation of a nonporous dense layer, which greatly reduces the PWP. However, low ALD cycles (< 5) result in a high PWP and a high salt rejection. Huang et al. have used ALD in conjunction with the hydrothermal method to prepare ZnO nanowires on copper mesh for oil/water separation [73]. Under gravity-driven oil/water separation, a ZnO modified copper mesh have achieved a high separation efficiency of 97% coupled with a good stability in acidic, salty, and alkaline solutions.

3.3.4. ALD integration with computational fluid dynamics

Most of the ALD studies have aimed to find the optimum ALD condition (precursor dose time, exposure time, etc.) via the trial-and-error method. Xiong et al. have taken a systematic approach and have employed computational fluid dynamics to find the optimum conditions for ALD of Al₂O₃ on PTFE membranes [74]. After 100 cycles of ALD, hydrophobic membranes have been converted into hydrophilic membranes. By keeping the ALD cycles to a minimum, the trade-off between permeability and selectivity has been reduced, and the modified membranes have had both improved permeability and selectivity. Itzhak et al. have deposited alumina on two polymeric ultrafiltration membranes, namely polyacrylonitrile and polyetherimide [75]. They have examined the effect of precursor exposure time on membrane performance. With short exposure times, a substantial layer of Al₂O₃ is formed primarily at the membrane surface, leading to pore blockage and a corresponding reduction in PWP. In contrast, longer exposure times allows the Al₂O₃ to distribute more uniformly across the membrane cross-section, preventing pore blockage and resulting in improved PWP. Membranes, modified with a low number of ALD cycles (10-30) and longer exposure times (10 seconds), exhibit a reduced oil coverage during oil/water emulsion separation and demonstrate effective fouling removal during crossflow cleaning.

The aforementioned applications and Table 2 highlight the usefulness of ALD for modifying the properties of polymeric membranes. Depending on the application, hydrophilic, hydrophobic, highly permeable, or highly selective membranes can be tailored. However, care must be taken to keep the ALD cycles to a minimum and allow the precursors to diffuse through the porous membrane to achieve both a high permeability and selectivity.

Table 2
ALD-modified organic membranes and their water filtration characteristics.

Substrate	Substrate Pore Size (nm)	Material Deposited by ALD	ALD Exposure Mode Included	Optimum ALD cycles*	Pore Size After ALD (nm)	Pure Water Flux L/(m ² .hr.bar)	Contaminant Targeted	Rejection (%)	Reference
Polycarbonate	30	Al ₂ O ₃	No	100	ca. 19	5	Bovine serum albumin	ca. 77	[63]
PTFE	200	Al ₂ O ₃	Yes	100	NR	210	Polystyrene	97	[26]
PTFE	200	TiO ₂	Yes	150	NR	ca. 4000	Silica nanospheres	35	[64]
PVDF	NR	TiO ₂	Yes	125	NR	ca. 190	Bovine serum albumin	97	[68]
PP	43	TiO ₂	Yes	100	NR	430	Silica nanospheres	55	[67]
Filter Paper (cotton fibers)	20k	Al ₂ O ₃	Yes	90	NR	ca. 10	Diesel Oil	90	[65]
PP	43	Type 1: Al ₂ O ₃ Type 2: TiO ₂	Yes	100	NR	Type 1: ca. 600 Type 2: ca. 570	Silica nanospheres	Type 1: 95 Type 2: 92	[69]
PVDF	220	ZnO	Yes	100	NR	ca. 5000	Bovine serum albumin	96	[70]
polyethersulfone	NR	TiO ₂	No	100	NR	ca. 47	Sodium Chloride	90	[66]
NF90 (polyamide) NF270 (poly-piperazine)	NR	ZnO	No	-	-	-	-	-	[71]
PVDF	200	ZnO, Al ₂ O ₃ , TiO ₂ , SnO ₂	No	-	-	-	-	-	[72]
Type 1: SW30 XLE Type 2: NF270	NR	TiO ₂	Yes	5	NR	(normalized permeability reported)	Sodium Chloride Calcium Chloride Sodium Sulfate	ca. 70 ca. 60 ca. 95 (reported for NF270 only)	[25]
Copper Mesh	NR	ZnO	Yes	100	NR	NR	Mineral Oil	99.7	[73]
PTFE	200	Al ₂ O ₃	No	100	NR	185 (reported as PWP, LMH/bar)	Silica microspheres	ca. 93	[74]
Type 1: Polyacrylonitrile Type 2: Polyetherimide	16 21	Al ₂ O ₃	Yes	50	10.6 14.1	ca. 120 ca. 100	-	-	[75]

3.4. ALD-modified inorganic membranes

The application of ALD for the modification of ceramic membranes is in its early stages of development (Fig. 6). From a wastewater treatment applications' perspective, ceramic membranes have gained attention due to their stability across temperature, pH, and pressure gradients [10]. Additionally, they offer a high PWP in comparison to organic membranes, which is highly desirable for large-scale industrial applications [11].

3.4.1. Tailoring pore structure and selectivity: ALD of Al_2O_3

In comparison with the sol-gel technique, the application of a selective layer on ceramic membranes by ALD can result in (i) processing costs reduction, (ii) precise structural control of the selective layer, and (iii) precise pore size reduction of the ceramic membranes [42]. To the best of our knowledge, the pioneering work on the modification of commercially available ceramic membranes for wastewater treatment has been performed by Li et al. in 2012 [76]. They have utilized a commercially available Al_2O_3 microfiltration membrane with a zirconia (ZrO_2) selective layer (pore size: 50 nm), produced by JIUWU HI-TECH China, and have modified its pore size by the ALD of Al_2O_3 . They have coated the membranes with different ALD cycles and have observed that upon 600 cycles, an ultrathin layer of Al_2O_3 is formed adjacent to the surface of the ZrO_2 layer. Scanning electron microscopy analysis has revealed that the new layer consists of a dense sublayer in tandem with a transition sublayer, forming a selective layer in the form of a thin film coating around the ZrO_2 particles. Additionally, they have discovered that greater exposure times allow the precursors to diffuse into longer depths in the pores (Fig. 6a-i). Membrane performance tests show that the modified membrane has a PWP of $118 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ and a BSA retention of 97%, thus proving the presence of small pores in the newly formed selective layer. Consistent with previous studies, trade-off between selectivity and permeability has been observed, because the membranes, modified at a lower number of ALD cycles, i.e., 100, 200, 300, and 400, have a comparatively high PWP but a lower BSA retention.

3.4.2. Engineering nanoporous selective layers: ALD of TiO_2

If the kinetic diameter of the precursors is larger than the pore size of the substrate, then precursors do not diffuse into the membrane pores. Similarly, if the pore size is slightly larger than the kinetic diameter of precursor molecules, then once a thin film is formed in the pores of the support membrane, after the first few ALD cycles, further diffusion of the precursor molecules is hindered due to narrowing of the pore aperture [12]. The subsequent thin film layer, deposited on the surface of the membrane, then leads to pore blocking, adversely affecting the PWP. Thus, either the thin film is only formed in the pores of the membrane or the newly formed surface layer must be sufficiently porous to avoid huge reduction of the PWP of the membrane. Chen et al. have developed a strategy to convert the dense surface layer into a microporous layer [77]. They have utilized a modified ALD process that relies on alcohols rather than water as the oxidizing precursor and have deposited a thin film of titanium alkoxide in the pores and also on surface of the $\alpha\text{-Al}_2\text{O}_3$ ultrafiltration membrane, having a TiO_2 selective layer (pore size: 5 nm). In a subsequent calcination process, they have burned off the organic moieties, thus generating a microporous TiO_2 layer. They have observed that after 300 cycles of ALD and a calcination step at 400°C for 2 h, the initial ultrafiltration membrane is converted into a nanofiltration membrane having a pore size of 1.3 nm, water permeability of $30 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$, and polyethylene glycol molecular weight cut-off of 680 Da. Shang et al. have modified the active pore size of the commercial Al_2O_3 nanofiltration membranes having a TiO_2 selective layer (pore size: 0.7 nm) by atmospheric pressure atomic layer deposition (APALD) [24]. They have reported that after 1-3 cycles of APALD of TiO_2 , the size of the active pores, present on the surface of the membrane, decreases from 0.7 nm to 0.5 nm. Consequently, after 3 cycles, the PWP reduces from $26 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ to $11 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$, and the polyethylene glycol molecular weight cut-off reduces from 490 Da to 277 Da. The reported PWP values are higher than the commercial polymeric NF90 and NF270 nanofiltration membranes and sol-gel-made tight ceramic nanofiltration membranes, thus proving the effectiveness of ALD for ceramic membrane modification.

ALD has also been used to impart photocatalytic properties to

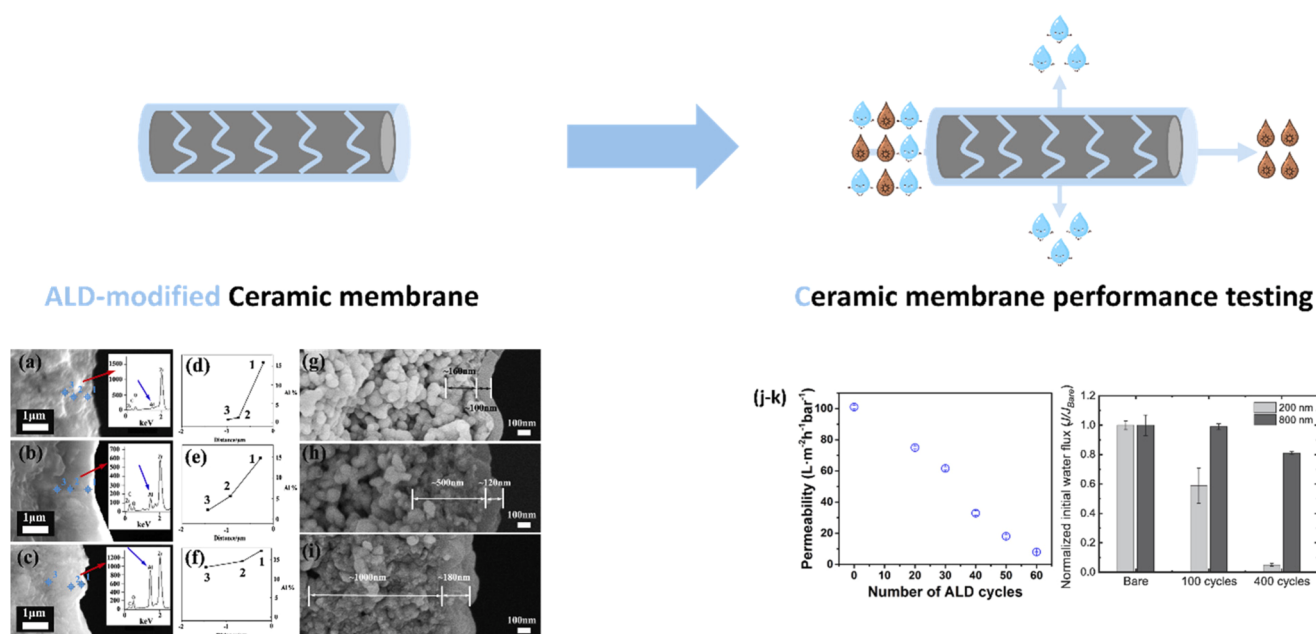


Figure 6. Performance enhancement of ceramic membranes via ALD.

(a-i) Cross-sectional SEM images and corresponding EDS spectra of Al_2O_3 -coated $\text{ZrO}_2\text{-Al}_2\text{O}_3$ membranes deposited with 600 ALD cycles at varying precursor exposure times: (a, d, and g) 0s; (b, e, and h) 10s; (c, f, and i) 40s. Adapted with permission from [76].

(j) Water permeability of TiO_2 -coated $\text{TiO}_2\text{-Al}_2\text{O}_3$ membranes as a function of ALD cycle number. Adapted with permission from [79].

(k) Pure water flux of ZnO -coated $\text{ZrO}_2\text{-TiO}_2$ membranes of different nominal pore sizes as a function of ALD cycles. Adapted with permission from [80].

ceramic membranes for degradation of organic dyes. Berger et al. have coated commercially available anodized Al_2O_3 microfiltration (pore size: 200 nm) and ultrafiltration (pore size: 20 nm) membranes with TiO_2 by ALD for photocatalytic degradation of MB [78]. The PWP of the microfiltration membrane decreases from $3800 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ to $2300 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ upon coating a TiO_2 layer of 6 nm in thickness, and that of ultrafiltration membrane from $1100 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ to $400 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ upon coating a layer of 15 nm in thickness, respectively. Subsequently, they have observed that the removal of the MB from the feed increases with increasing thickness of the coating layer up to a certain extent. For the ultrafiltration membrane, the removal efficiency increases up to a coating thickness of 6 nm, but beyond that point, the layer thickness is no longer the limiting factor. In another report, published by Chen et al., TiO_2 has been deposited on a commercial $\alpha\text{-Al}_2\text{O}_3$ ultrafiltration membrane having a titanium dioxide selective layer (pore size 5 nm) [79]. They have operated ALD in the non-exposure mode, avoiding the diffusion of the precursors in the pores of the membrane, allowing the deposition to take place in the near-surface region only, and avoiding pore narrowing and the resultant decrease of the PWP. After 40 cycles of ALD, the polyethylene glycol MWCO decreases from 7200 Da to 890 Da, and the PWP decreases from $100 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ to $32 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$, respectively (Fig. 6j). Furthermore, they have observed that if the membrane and target molecules have the same charge, it results in a higher retention of the molecules due to electrostatic repulsion. After 40 cycles of ALD, the membrane exhibit a rejection of ca. 93% for negatively charged dyes (Rose Bengal and Reactive Black 5), whereas, the rejection for positively charged dye (Cationic Yellow X-2RL) is only 42%, respectively.

3.4.3. Emerging applications in photocatalysis: ALD of ZnO

The studies on ALD of ZnO are scarce. Recently, Park et al. have deposited a photocatalytically active ZnO film on the Sterlitech USA $\text{ZrO}_2\text{-TiO}_2$ membrane (pore size: 200 nm, 800 nm), and have tested it for the degradation of the 4-chlorobenzoic acid [80]. They have observed a

decrease of the PWP of the membranes after the ZnO deposition (Fig. 6k). However, the deposited ZnO has shown a higher degradation activity compared to the bare membrane. In addition, the accumulation of the 4-chlorobenzoic acid on the bare membrane has resulted in the formation of a biofilm, which greatly reduces the PWP of the bare membrane. In contrast, the ZnO deposited membrane alleviates the formation of biofilm, consequently maintaining the intrinsic PWP.

The aforementioned studies highlight the importance of ceramic membrane modification by ALD. The current research focus has been on oxide ceramic materials. Furthermore, a comparison of these membranes is presented in Table 3.

4. Challenges and opportunities

The applications, highlighted in this review, depict that atomically engineered materials for wastewater treatment can be realized with the help of ALD. Highly conformal coatings ranging in thickness from several angstroms to nanometres can impart desirable properties to materials without changing the fundamental chemistry of the materials [81]. Based on the literature review, the following sub-sections serve as a guide for interested researchers highlighting potential research areas.

4.1. Structural considerations

The ALD on/in porous structures comes with its own challenges. Unlike flat non-porous substrates used in the semiconductor industry, porous substrates are characterized by having: (i) high aspect ratios [82–84]; (ii) varying pore size distribution [85]; (iii) different geometry of pores on the surface and in the bulk of the material [86]; and (v) accessible/inaccessible (open/closed) pores [87]. Therefore, before proceeding to ALD, the aforementioned characteristics of the material must be studied with available characterization techniques. Once a proper understanding has been established, then precursors with adequate kinetic diameter (smaller than pore aperture) should be

Table 3
ALD-modified ceramic membranes and their water filtration characteristics.

Substrate	Substrate Pore Size (nm)	Material Deposited by ALD	ALD Exposure Mode Included	Optimum ALD cycles*	Pore Size after ALD Modification (nm)	Contaminant Targeted	MWCO (Da)	Rejection (%)	Pure Water Flux $\text{L}/(\text{m}^2\cdot\text{h}\cdot\text{bar})$	Reference
Al_2O_3 with ZrO_2 selective layer	50	Al_2O_3	Yes	600	NR	bovine serum albumin	NR	97	118	[76]
Al_2O_3 with TiO_2 selective layer	5	Titanicone	No	300	1.3	polyethylene glycol	680	97 (for PEG of 1000 Da)	30	[77]
Al_2O_3 with TiO_2 selective layer	0.7	TiO_2	Yes	3	0.5	polyethylene glycol	277	95	11	[24]
Al_2O_3 with TiO_2 selective layer	5	TiO_2	No	40	1.5	polyethylene glycol	890	90 (for PEG) 93 (for Rose Bengal & Reactive Black 5) 42 (for Cationic Yellow X-2RL)	32	[78]
Al_2O_3	Type 1: 200 Type 2: 20	TiO_2	No	NR	-	-	-	-	Type 1: 2300 Type 2: 400	[79]
$\text{ZrO}_2\text{-TiO}_2$	Type 1: 200 Type 2: 800	ZnO	No	NR	-	4-chlorobenzoic acid	-	Type 2: 85% (for light intensity $10 \text{ mw}/\text{cm}^2$) 30% (for light intensity $10 \text{ mw}/\text{cm}^2$)	(reported as normalized flux)	[80]

selected to ensure sufficient diffusion of the precursors [88,89]. To facilitate greater diffusion of precursors, ALD must be operated in exposure mode [90]. In principle, this would result in the formation of a conformal thin film on/in the substrate. The deposition cycles should be set to a minimum so that there is not a high loss of PWP, and an optimum between permeability and selectivity can be achieved.

4.2. Pre-treatment of substrate

The precursors in ALD half-cycles react with functional groups of the surface. If a material's surface has a high density of functional groups, then the deposition will proceed in the form of a continuous thin film. However, the absence of functional groups will lead to the growth of material in the form of distinct islands, which will subsequently coalesce to form a film, mainly when the material-to-be-deposited differs from the substrate [19,91].

We found only a few studies that reported the adhesion strength of the film on the substrate [92–94]. This element should not be ignored while designing experiments and should be tested and reported.

ALD can be carried out at low-deposition temperatures, so various materials can be modified. If the substrate material is inert, e.g. polymeric material, then a pre-treatment step should be included to render the material reactive. Several strategies could be utilized for this purpose, namely, plasma pre-treatment step, chemical activation, or even an activation step in the ALD chamber utilizing different precursors.

4.3. ALD materials of focus

Critical analysis of the ALD literature for wastewater treatment applications shows that the main focus of the majority of research groups is on oxide materials (Al_2O_3 , TiO_2 , ZnO) [95]. However, expanding the list of deposition materials to carbides and nitrides could have the advantage of preparing adsorbents and membranes with improved hydrophilicity, highly negative charge, and low fouling [41,96].

4.4. Simulation studies

Most of the conducted studies try to find the optimum deposition conditions via the trial-and-error method. This is a time-consuming process and often results in suboptimal deposition conditions. Therefore, we propose that simulation studies should precede ALD experimental studies. The simulation studies, e.g. through computational fluid dynamics and density functional theory, would give insights about: (i) suitable precursors; (ii) the behavior of the precursors in the reaction chamber; (iii) reaction kinetics; and (iv) confirm self-limiting nature of reactions [40,43]. This allows to select the best precursors and deposition conditions for the particular application.

4.5. In-situ characterizations of thin films

The porosity and pore size of the porous materials decreases as a function of the deposition cycles in the ALD furnace/chamber. However, currently, in situ measurements of pore size are not available. Usually, a silicon wafer is placed next to the substrate in the ALD chamber, and the thickness of the film as a function of deposition cycles is measured on the silicon wafer via ellipsometry [97,98]. The growth behavior on a silicon wafer will be different than a porous material due to different: (i) coefficient of thermal expansion; (ii) functional groups; and (iii) lattice constants. We therefore propose that ALD chambers must be manufactured with in-situ techniques that can measure the change in porosity, pore size, or stoichiometry of the film.

4.6. Scalability for mass production

ALD has already been commercialized for the production of wafers. However, the commercialization of ALD for manufacturing membranes

or sorbents will still need considerable efforts. In our opinion, atmospheric pressure-ALD has the highest potential to be scaled-up to mass production for wastewater treatment applications [24,99].

5. Conclusions

Urban and industrial sectors produce millions of cubic meters of wastewater per annum, which frequently undergoes minor or no treatment before it is discharged. This, in conjunction with water scarcity, leads to water stress which, is a major societal concern. This problem can be tackled by nanoscale engineering of wastewater treatment materials (membranes and adsorbents). Recent breakthroughs in manufacturing methods have paved the way to coat porous materials with ultrathin films to alter their surface properties and pore size. Consequently, rationalizing the design of porous materials with exceptional filtration capabilities.

ALD can deposit a thin film of variety of materials on a substrate of any geometry, for instance porous materials. The technique is, therefore, being currently explored for modification of membranes and adsorbents. ALD is employed as a post-modification step to coat wastewater treatment materials with a functional thin film of a desired material. The material to be coated is chosen on the basis of the properties required for a particular application, for example hydrophilicity, pore size, and surface charge. This opens up new routes for preparing wastewater treatment materials with precise pore size, surface charge, permeability, and selectivity.

All the advances reported in this review illustrate the potential of ALD to obtain porous materials with high filtration efficiency. Results of various studies demonstrate that ALD-modified materials possess superior wastewater filtration characteristics than unmodified materials. The interest of wastewater treatment research groups all over the world in ALD has pushed forth the boundary of knowledge. However, there are challenges and opportunities to be addressed for commercialization of ALD processes for modifying membranes and adsorbents.

CRediT authorship contribution statement

Asif Jan: Writing – original draft, Visualization, Formal analysis, Conceptualization. **Melike Begum Tanis-Kanbur:** Writing – review & editing. **Luuk C. Rietveld:** Writing – review & editing, Validation, Supervision. **Sebastiaan G.J. Heijman:** Writing – review & editing, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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