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A Review on: Advances in Membrane Technologies for Heavy Metal Removal from contaminated Water

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Abstract. The contamination of water by various toxic constituents, particularly heavy metals, exerts deleterious effects on both flora and fauna, with potential repercussions for human well-being. Consequently, there exists a pressing imperative to explore methodologies aimed at the elimination of hazardous substances from polluted water. Among the array of extant approaches, membrane-based techniques emerge as notably efficacious for mitigating pollutants, specifically heavy metals, in water systems. The elimination of mineral contaminants from water holds paramount significance for fostering a hygienic environment and safeguarding human health. Polymeric membranes offer an energy-efficient approach to water purification, yet they encounter fouling issues during filtration. Surface modification of the membrane is one avenue for mitigating fouling, aiding in the maintenance of elevated water productivity levels. The present investigation undertakes a comprehensive examination of outcomes derived from diverse experiments conducted over the preceding two decades, with the objective of identifying the most pertinent membrane filtration processes, accounting for varied contaminant profiles.

1. Introduction

Water, an elemental and foundational component of the natural order, stands as the quintessential source of life, intertwined with the very fabric of human existence throughout the annals of history. Its indispensability is so deeply ingrained that the conceptualization of life persisting in its absence becomes a formidable exercise in imagination. Paradoxically, the life-affirming essence of water, when subjected to human actions marked by negligence, can transform into a harbinger of mortality [1]. Against the backdrop of escalating global population dynamics, relentless scientific advancements, and the consequent proliferation of manufacturing and agricultural activities, water pollution has burgeoned into an overarching and inescapable concern on a planetary scale. This surge is concomitant with a contemporaneous reduction in freshwater resources, posing an existential threat to public health [2]. The gravity of this challenge becomes starkly evident when considering that over 150 million individuals worldwide confront imminent peril due to the contamination of their drinking water sources, resulting in a tragic toll of more than 20 million lives annually.

The term "water pollution" encapsulates a multifaceted process involving the introduction of deleterious elements into water, thereby engendering alterations in its quality that prove injurious to both human well-being and the broader environmental ecosystem. Within the purview of water pollution, a panoply of contaminants besieges water supplies, comprising pesticides, detergents, phenolic compounds, organic dyes, and heavy metals. The presence of such substance’s precipitates nuanced and multifaceted alterations in water quality, rendering it unsuitable for consumption as a potable resource [3, 4].

Consequently, the urgency of an expansive and interdisciplinary exploration of water quality assumes paramount importance. The development of efficacious mitigation strategies is imperative to address this intricate and escalating global challenge, necessitating a concerted effort to comprehend, assess, and proactively manage the manifold dimensions of water pollution and its implications for human societies and the broader ecosystem.

2. Classification of water contaminants

Broadly, a variety of pollutants, including thermal, radioactive, pathogenic, suspended particles, nutrients, and agricultural pollutants, can be categorized as water contaminants. The majority of organic and inorganic contaminants that are released into water bodies come from sewage and industrial effluents [5]. Figure 1 shows classification of water contaminants.

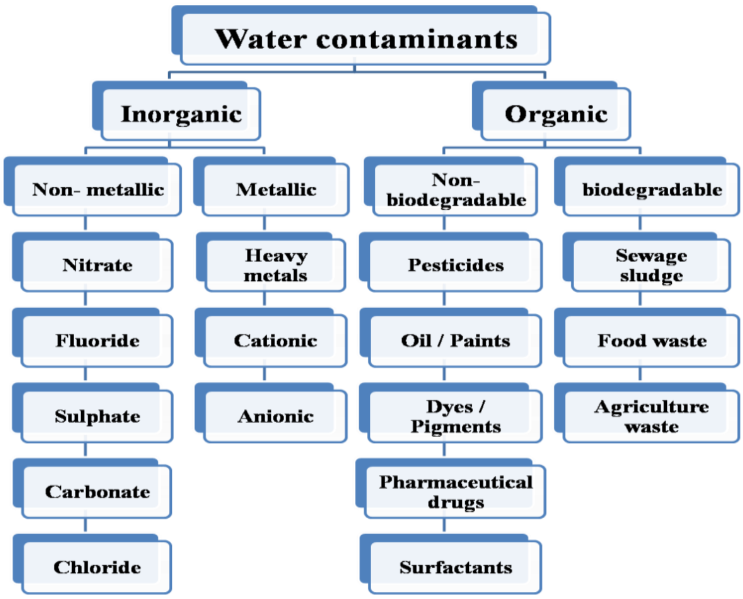

Figure 1. Classification of water contaminants.

2.1. Inorganic contaminants

Diverse inorganic contaminants are being recognized worldwide, raising concerns about their impact on human health when present in wastewater sources. These inorganic pollutants encompass suspended solids, colloidal substances, phosphorus and nitrogen compounds, heavy metals, and more [6].

2.2. Heavy metals

One of the most dangerous types of pollutants in water are heavy metal ions. Transition metals (like Cd, Hg, and Cr), elements in the bottom left section of the periodic table (like Pd and Sn), and some metalloids (like as) are basically considered heavy metals. These elements are dangerous because they can bind to a variety of functional groups in biomolecules, including amino, carboxylic acid, and sulphur -containing groups. In order to interfere with the functioning of proteins and enzymes, they can bind to them. The remediation of wastewater contaminated with heavy metals has garnered significant attention from environmental chemists and chemical engineers, given the inherent toxicity of these pollutants. Although heavy metals typically exist in trace amounts in natural waters, many of them are classified as toxic even at minimal concentrations [7]. Consequently, the imperative to treat wastewater contaminated with metals before its discharge into the environment is underscored by the need to adhere to these regulatory frameworks and safeguard ecosystems and human health.

3. Treatment methods that can be used to remove heavy metals from wastewater and water.

There are several treatment options available for removing heavy metals from industrial wastewaters (see Table 1). These consist of unit activities such membrane separation, ion exchange, coagulation and flocculation, and chemical precipitation. However, the economic viability and efficacy of these processes are predominantly evident when dealing with relatively high concentrations of solutes.

Table 1: Various techniques for eliminating heavy metals from wastewater and water [8].

Method	Description	Advantages	Disadvantages
Chemical Precipitation	This method turns metal ions into insoluble precipitates of carbonate, phosphate, sulphide, or hydroxide using chemical agents.	-High degree of selectivity and simplicity of use; precipitants are reasonably priced.	-Unable to effectively treat water having a high heavy metal concentration. -Needs a significant quantity of precipitating agents.
Coagulation - flocculation	In this technique, the particles' surface negative charge and enable aggregation, a positively charged coagulant is added in this process. After that, an ionic flocculant is given to the positively charged aggregates, reacting with them to produce a bigger group that may be filtered out.	-Alum is a reasonably priced coagulant with an easy-to-use method.	-Inadequate removal of heavy metals; frequently requires combination with precipitation process to ensure removal efficaciously. -Contraction of mud.
Ion exchange	In this technique, solid ion exchange resin) is typically utilized. In order to enable complexation of the metal with the free functional group, reversible ion exchange between the solid and liquid phases may occur, wherein H^+ is liberated from the functional groups.	- Quick motion. - Easy procedure. -Economic procedure since it makes use of inexpensive components and resin that can be recycled.	– Metal ion fouling on ion exchange materials. -Only appropriate for low metal concentrations. - Extremely pH-sensitive. -Low binding affinity may be the result of free acids present.
Membrane processes	Is a method of removing particular components from a solution by forcing feed water through a semi-permeable membrane at high pressure.	- Simple operation - No sludge production - No need for chemicals - High efficiency of heavy metals removal	- High investment cost -Membrane sediment formation - Influence of unwanted ions on the efficiency

3.1. Membrane separation

In order to selectively remove particular elements from the solution, feed water is forced through a semi-permeable membrane under high pressure in the membrane separation process. Purification of a solute-saturated solution is accomplished by means of this non-thermal approach [9]. Diffusion is the process by which molecules or ions move across the membrane, and the rate at which this happens depends on a number of variables, including temperature, pressure, membrane permeability, and the concentration of molecules or ions in the solution. Divided into two groups—low-pressure membranes, which include microfiltration (MF) and ultrafiltration (UF) and pressurized membranes, which include nanofiltration (NF) and reverse osmosis (RO) refer to Figure 2, these technologies provide distinct features and advantages that are described in more detail below Table 2.

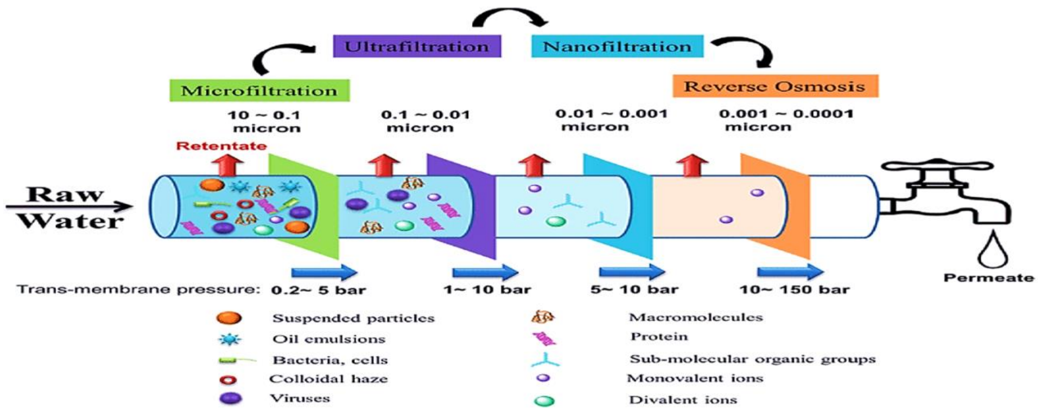

Figure 2. Pressure-driven membrane processes for water treatment technologies [10].

Table 2: Various membrane techniques to extract heavy metals from wastewater and water.

Particular	UF	NF	RO
Membrane	Porous asymmetric	Finely porous asymmetric / composite	Nonporous asymmetric / Composite
Pore size	5–20 nm	1–5 nm	0.5 – 1.5 nm
Transfer mechanism	Sieving and preferential adsorption	Sieving/electrostatic hydration/diffusive	Diffusive (solutes migrate by diffusion mechanism)
Typical solution treatment	Solution with colloids and/or macromolecules	Ions, small molecules	Ions, small molecules
Typical pure water flux (L m^{-2} h)	100–2000	20–200	10–100
Pressure requirement (atoms)	1–10	7–30	20–100
Advantages	High separation efficacy	High rejection of heavy metals in a moderate operating pressure range	Excellent heavy metal rejection
Disadvantages	Secondary pollution production and the need for post-treatment	Lower water permeability and higher energy usage in comparison to the UF process	The limited water permeability and high energy needs

3.2. Ultrafiltration Membrane (UF)

The pores of ultrafiltration membranes typically exceed the size of heavy metal particles. Consequently, additives are introduced to increase the size of heavy metals. This gives rise to the proposals of micellar-enhanced ultrafiltration (MEUF) and polymer-enhanced ultrafiltration (PEUF). MEUF proves particularly suitable for waters contaminated with low-concentration contaminants. In MEUF, a surfactant is introduced into contaminated waters at a concentration surpassing the critical micellar concentration. Surfactants with an electrical charge opposite to heavy metals generally exhibit the highest levels of preservation. The MEUF process schematic diagram is displayed in Figure (3a). On the other hand, PEUF facilitates the penetration of water and ultrafine components into membrane pores, with metal ions binding to polymer traps and subsequently being extracted. Figure (3b) depicts a schematic depiction of the PEUF process. Prior studies on the application of MEUF and PEUF for heavy metal removal are outlined in Table 3.

a b

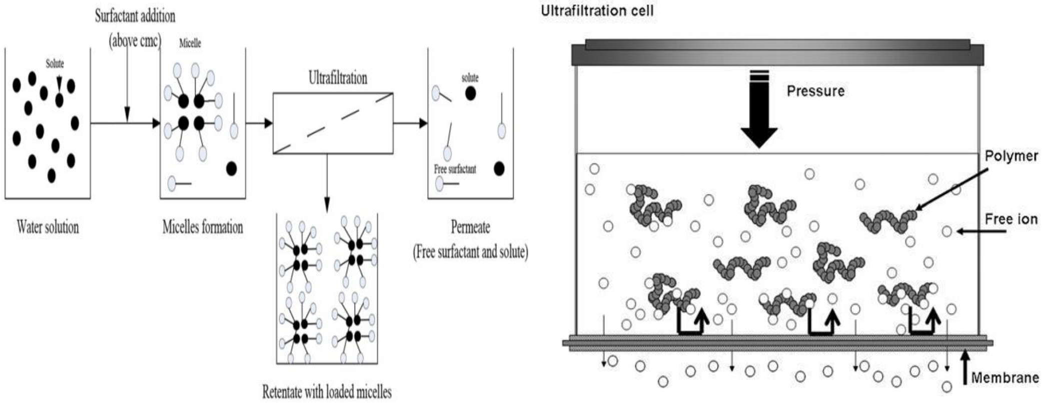

Figure 3 (a). MEUF process schematic diagram, (b). PEUF process schematic diagram .

Table 3. Removal of heavy metals by MEUF and PEUF processes.

Technology	Type of metal	Removal efficiency (%)	Reference
MEUF	As (VII)	19	[12]
	Pb^{2+}	>99.3	
	Ni^{2+}	98.6	[13]
	Cd^{2+}	93.0–98.0	[15]
PEUF	Cu^{2+}	99.5	[11]
	Cr^{3+}	99.5	[14]
	Ni^{2+}	99.1	
	Cd^{2+}	99.0	[16]

3.3. Nanofiltration Membrane (NF)

The inception of NF membrane development dates back to the mid-1980s, initially employed for the separation of small organic molecules and divalent salts [17]. Positioned between UF and RO, nanofiltration (NF) exhibits a pore size within the range of 1–10 nm and/or a Molecular Weight Cut off (MWCO) of 200–800 Da. Consequently, NF operates within the spectrum bridging ultrafiltration and reverse osmosis processes. NF membranes inherently possess a loose, selectively thin film structure with small pore sizes, effectively suited for the separation of metallic ions. The fact that NF membranes reject multivalent ions far more strongly than monovalent ions is one of their distinguishing features. Although the precise ion rejection differs throughout membrane manufacturers, NF membranes typically have a multivalent ion rejection of 95% and a monovalent ion rejection of 20%. An overview of the removal of heavy metal ions utilizing different kinds of NF membranes is shown in Table 4.

3.4. Reverse Osmosis (RO)

In reverse osmosis (RO), only smaller particles are permitted to flow through a semi-permeable membrane with pore sizes ranging from 0.5 to 1.5 nm. Pressure between 20 and 70 bars is required for this procedure. RO membranes differ from NF membranes in that they are denser and have less defined pores.RO works in the opposite direction from osmosis, which is the theoretical principle that governs the net movement of water from a region of low solute concentration to an area of high solute concentration. In this procedure, water molecules are forced to travel against the concentration gradient by applying pressure. The primary challenges associated with reverse osmosis technology include membrane fouling and degradation. Previous studies focused on the application of RO for heavy metal removal are summarized in Table 5.

Table 4. Heavy metal ion removal with different NF membrane types.

Type of NF membrane	Type of metal	Removal efficiency (%)	Reference
Negatively charged	Cu(II)	92	[18]
	Cd(II)	99	[19]
	Cr(VI)	98	[20]
	Pb(II)	98	[21]
	Ni(II)	88.1	[22]
Positively charged	Cd(II)	98.3	[23]
	As(V)	99.5	
	Cr(II)	93.5	
	Pb(II)	99.5	
	Ni(II)	99.7	

Table 5. Removal of heavy metals using RO process.

Technology	Type of metal	Removal efficiency (%)	Reference
RO	Cu^{2+}	99.5	[24]
	Ni^{2+}	99.4	
	As(V)	92–99,2	[25]
	Pb^{2+}	98.9	[26]
	Cd^{2+}	99.3	
	Cr(VI)	96.0	[27]
	Mn	99.48	
	Zn^{2+}	98.8	[28]

4. Surface Modification of Water Purification Membrane.

Currently, polymer membranes stand out as the most extensively employed technology in the realm of purifying polluted water, owing to their exceptional and superior efficacy [29]. Nevertheless, fouling which is defined as the unwanted build-up of solutes on the membrane's surface, internally within the pores of a porous membrane, or both—is a significant problem related to this kind of membrane [30]. To address the issue of fouling, surface structures are modified in various ways. A summary of surface modification techniques employed to enhance membrane resistance to fouling is presented in Table 6. Significantly, surface coating is now the method of choice for reducing fouling in RO and NF membranes; these coatings are strong enough to be regarded as "permanent" [31].

5. Future perspectives

Numerous polymeric materials and an assortment of nanomaterials have been created to improve the effectiveness of heavy metal removal. The pH, temperature, and pressure are some of the factors that impact the membrane technology's removal efficiency and cost. In order to reduce costs and increase efficiency, the parameters should be changed to their proper values.

The goal of recent study has been to create solutions that are economical. However, depending on the wastewater sources and cleanup scope, the total cost can vary depending on the methods used. Therefore, comparing the precise cost of repair for various procedures is a challenging process. This implies that in the future, remedies that would be more beneficial for practical uses should take operational costs into account.

Table 6. An overview of the methods for surface modification utilized to increase the fouling resistance of the membrane.

Modification technique	Membrane types	Advantages	Disadvantages
Adsorbed coatings: uncured	MF, UF, NF, RO	minor adjustment; could lead to more rejection	prone to surface leaching; may reduce the penetration of pure water
Adsorbed coatings: cured		decreased leaching in comparison to uncured adsorbed coatings; rejection could rise	could reduce the permeance of pure water.
chemically induced grafting		lasting alteration of the membrane's surface; could lead to more rejection	could reduce the permeance of pure water.
plasma coating		quick and easy modification that works on a variety of membranes and is more durable than plasma therapy without polymer coupling.	needs a plasma reactor; harsh treatment could harm the membrane

6. Conclusion

Selecting the most appropriate technology for removing heavy metal ions from polluted water involves considering several crucial factors, including operational costs, removal efficiency, and economic feasibility. Although membrane filtration is extensively researched and acknowledged for its high efficiency, the broader implementation is influenced by cost considerations. Reverse osmosis technology has demonstrated the highest efficiency in heavy metal removal, ranging from 98.0% to 99.9%. While characterized by high operational efficiency, reverse osmosis requires a substantial amount of energy. Ensuring the sustainability of this process's high efficiency necessitates the establishment of suitable and intermediate conditions. Polymeric membranes offer an energy-efficient approach to water purification, yet they encounter fouling issues during filtration. Surface modification of the membrane is one avenue for mitigating fouling, aiding in the maintenance of elevated water productivity levels. Many previous studies on polluted water treatment utilized artificially polluted water, revealing a discernible gap in methods for treating actual polluted water. Consequently, there is a need for novel methods and research utilizing real polluted water to address diverse pollutant types. Future studies should also target experimental processes. While technologies for effectively and safely removing metals from contaminated water are continuously under study and development, future research endeavours should take into account these evolving techniques and their potential applications.

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