

A blue-toned molecular structure, possibly representing a protein or a complex crystal lattice, is visible in the background of the cover. It features interconnected spheres and rods, creating a complex, three-dimensional network.

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IntechOpen Series
Environmental Sciences, Volume 41

Advances in Water Resources Science

*Edited by Jamila Tarhouni,
Muhammad Akhyar Farrukh and Shaista Ali*



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Published in London, United Kingdom

Advances in Water Resources Science

<http://dx.doi.org/10.5772/intechopen.1005965>

Edited by Jamila Tarhouni, Muhammad Akhyar Farrukh and Shaista Ali

Contributors

Aishvarya Hariharan, Arquimedeiz Tolentino-Rojas, Arumugam Sonachalam, Carlos Villalobos, César Torres-Segundo, Emmanuel Kangoma, Erum Khalid, Hifza Rasheed, Hugo Albeiro Saldarriaga-Noreña, Josefina Vergara-Sánchez, José Gustavo Ronderos-Lara, Khirbet López-Velázquez, Krunal Patel, Mario Alfonso Murillo-Tovar, María Luisa García-Betancourt, Mohamed Matthew Blango, Muhammad Dilshad Arshad, Navo Yambasu, Nirmal Kumar Balaraman, Pablo Tello, Pablo Álvarez, Sebastián Norambuena, Zurisaday Villegas-González

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First published in London, United Kingdom, 2025 by IntechOpen

IntechOpen is the global imprint of INTECHOPEN LIMITED, registered in England and Wales, registration number: 11086078, 167-169 Great Portland Street, London, W1W 5PF, United Kingdom

For EU product safety concerns: IN TECH d.o.o., Prolaz Marije Krucifikse Kozulić 3, 51000 Rijeka, Croatia, info@intechopen.com or visit our website at intechopen.com.

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

Advances in Water Resources Science

Edited by Jamila Tarhouni, Muhammad Akhyar Farrukh and Shaista Ali

p. cm.

This title is part of the Environmental Sciences Book Series, Volume 41

Topic: Water Science

Series Editor: J. Kevin Summers

Topic Editor: Yizi Shang

Print ISBN 978-1-83634-863-4

Online ISBN 978-1-83634-862-7

eBook (PDF) ISBN 978-1-83634-864-1

ISSN 2754-6713

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Environmental Sciences

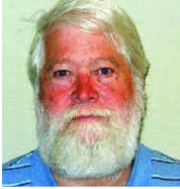
Volume 41

Aims and Scope of the Series

Scientists have long researched to understand the environment and man's place in it. The search for this knowledge grows in importance as rapid increases in population and economic development intensify humans' stresses on ecosystems. Fortunately, rapid increases in multiple scientific areas are advancing our understanding of environmental sciences. Breakthroughs in computing, molecular biology, ecology, and sustainability science are enhancing our ability to utilize environmental sciences to address real-world problems.

The four topics of this book series - Pollution; Environmental Resilience and Management; Ecosystems and Biodiversity; and Water Science - will address important areas of advancement in the environmental sciences. They will represent an excellent initial grouping of published works on these critical topics.

Meet the Series Editor



J. Kevin Summers is a Senior Research Ecologist at the Environmental Protection Agency's (EPA) Gulf Ecosystem Measurement and Modeling Division. He is currently working with colleagues in the Sustainable and Healthy Communities Program to develop an index of community resilience to natural hazards, an index of human well-being that can be linked to changes in the ecosystem, social and economic services, and a community sustainability tool for communities with populations under 40,000. He leads research efforts for indicator and indices development. Dr. Summers is a systems ecologist and began his career at the EPA in 1989 and has worked in various programs and capacities. This includes leading the National Coastal Assessment in collaboration with the Office of Water which culminated in the award-winning National Coastal Condition Report series (four volumes between 2001 and 2012), and which integrates water quality, sediment quality, habitat, and biological data to assess the ecosystem condition of the United States estuaries. He was acting National Program Director for Ecology for the EPA between 2004 and 2006. He has authored approximately 150 peer-reviewed journal articles, book chapters, and reports and has received many awards for technical accomplishments from the EPA and from outside of the agency. Dr. Summers holds a BA in Zoology and Psychology, an MA in Ecology, and Ph.D. in Systems Ecology/Biology.

Meet the Volume Editors



Prof. Tarhouni received her DEA in Hydrodynamics, Hydrology, and Geophysics from the University of Grenoble, France, and a Ph.D. in Water and Land Management from the University of Ghent, Belgium. She is Professor of Groundwater Modeling and Hydraulics and Director of Sciences and Technologies for the Water Laboratory at the National Agronomic Institute of Tunisia.



Prof. Dr. Muhammad Akhyar Farrukh is Head of the Department of Basic and Applied Chemistry and Director of ORIC at UCP, with over 25 years of experience in research, teaching, and academic leadership. He is the Chairman of the Technical Committee on Nanotechnology at the PSQCA, Government of Pakistan, and a Member of ISO/TC 229 Nanotechnologies (ISO, Switzerland). He has earned three gold medals in Chemistry and six more, including one from the Minister of HED and the Governor of Punjab, as well as the SATHA Innovation Award 2018 with a Gold Medal. His national and international recognitions include representing Pakistan at UNESCO (Morocco); Young Chemist Award by IUPAC (Italy); Young Scientist Awards by TWAS (Egypt), IAP/GYA (Germany), and the World Economic Forum (China); Young Researcher Award by the Council for Lindau Nobel Laureate Meetings; IUPAC 2015 Award for Chemists (South Korea); and the Research Productivity Award (Category A, PCST, Pakistan). He has published over 140 papers, presented more than 150 papers at conferences in 25 countries, won 3 industrial projects and 13 major research grants in nanotechnology, and established the first Nano-Chemistry Laboratory.



Dr. Shaista Ali is an Assistant Professor at Government College University Lahore, Lahore, Pakistan. She has more than 15 years of experience in teaching and research in various organizations. She recently received an NRF fellowship and joined the Institute of Catalysis at the University of Cape Town, South Africa, as a Postdoctoral Fellow. She completed her Ph.D. in chemistry with a specialization in nanotechnology. Her areas of expertise are physical chemistry, nanocchemistry, photocatalysis, adsorption, green chemistry, biomedical applications, and latent fingerprinting. She supervised 17 undergraduate and 20 postgraduate students. She has 38 publications with an impact factor of over 70 and a 10 h-index.

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Preface

This Edited Volume is a collection of reviewed and relevant research chapters on developments in Water Resources Science. The book includes scholarly contributions by various authors, edited by a group of experts in the field. Each contribution is a separate chapter, complete in itself but directly related to the book's topics and objectives.

The book includes the following chapters:

1. Green Synthesis of Nanoparticles and Their Application in Nanofiltration Membranes for Drinking Water Treatment
2. Perspective Chapter: Desalination as a Strategic Response to Pakistan's Water Scarcity – Analyzing Opportunities, Challenges, and Pathways for Sustainable Solutions
3. Water Allocation Rules in Semi-Arid Zones of Chile
4. Endocrine-Disrupting Compound in Mexican Aquatic Environments
5. Automation in the Water and Wastewater Industry with Artificial Intelligence
6. Enhancing Water Productivity in Inland Valley Swamps: Sustainable Strategies and Practices

The target audience comprises scholars and specialists in the field.

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Green Synthesis of Nanoparticles and Their Application in Nanofiltration Membranes for Drinking Water Treatment

Erum Khalid

Abstract

Nanotechnology, one of the fastest evolving fields, focuses on creating nanoparticles (NPs) smaller than 100 nm. The utilization of natural resources to generate nanoparticles, or “green synthesis,” is a scientific advance in nanotechnology that outperforms physical and chemical synthesis procedures. Its sustainability, low toxicity, high yield, and fewer side effects have proven its high-end benefits to humanity. Currently, nanoscience is extensive. An important application of nanotechnology is in water purification, critical for human health as 80% of diseases arise from bacterial contamination of drinking water. Because of their large surface area and adsorption capacity, nanoparticle-enhanced nanofiltration (NF) membranes have revolutionized this field by effectively removing organic pollutants and heavy metals. While photocatalytic nanoparticles like titanium dioxide allow self-cleaning under UV light, antimicrobial nanoparticles like silver and zinc oxide lessen biofouling. Nanoparticles also enhance the chemical and mechanical stability of NF membranes, ensuring durability in challenging conditions. Incorporating green-synthesized nanoparticles further improves the efficiency, selectivity, and long-term performance of NF membranes. This sustainable approach offers a promising solution to global clean water challenges, ensuring safe drinking water by effectively eliminating impurities and reducing environmental impact.

Keywords: drinking water, filtration, green synthesis, nanoparticles, plants

1. Introduction

Nanotechnology is considered to be one of the fastest-emerging fields in creating nanoparticles, which are small particles (less than 100 nm in size). Nanotechnology is also defined as the design, fabrication, and application of material structures, devices, and systems through the manipulation of size and shape at the nanometer scale or dimensions. Chemicals are used as reducing agents in chemically produced

nanoparticles, turning metal ions into nanoparticles. However, green production of the nanoparticles is preferred due to the negative impacts and little biocompatibility of the chemically produced nanoparticles. Eco-friendly reducing agents are made of green synthetic nanoparticles. As a result of its substantial advantages for humanity—energy efficiency, low toxicity, high yields, cost-effectiveness, eco-friendliness, ready availability, and few side effects—the green synthesis of nanoparticles with plants has emerged as a significant topic of nanoscience.

The synthesis of nanomaterials can be broadly classified into three categories: physical, chemical, and biological. Physical techniques that reduce bulk materials mechanically to the nanoscale include ball milling and laser ablation. Chemical techniques, such as hydrothermal synthesis, chemical vapor deposition, and sol-gel processes, provide exact control over the composition, size, and form of nanomaterials. Some distinctive reported forms of nanoparticles (NPs) are core-shell NPs, photochromic polymer NPs, polymer-coated magnetite NPs, inorganic NPs, AgNPs, CuNPs, AuNPs, PtNPs, PdNPs, SiNPs, and NiNPs, while others are metal oxide and metal dioxide NPs, such as ZnONPs, CuO NPs, FeO, MgONPs, TiO₂ NPs, CeO₂ NPs, and ZrO₂ NPs. Each of these has an exclusive set of characteristics and applications and can be synthesized by either conventional or unconventional methods [1]. Physical and chemical processes frequently result in a variety of toxic substances with negative effects when employed for medical applications, necessitating the usage of green synthesis. Green synthesis does not require circumstances like high pressure, energy, temperature, or the avoidance of the formation of harmful compounds, which have an economic cost. The increasing concern over the environmental effects of conventional chemical synthesis methods has led to a significant increase in interest in green synthesis approaches. Green nanotechnology places a strong emphasis on synthesizing nanomaterials using sustainable and eco-friendly methods. The use of non-toxic solvents, renewable resources, and energy-efficient procedures are important tenets of green chemistry. As an environmentally friendly substitute for conventional chemical processes, the use of plant extracts or microorganisms to reduce metal ions into nanoparticles has been thoroughly investigated [2].

Biological synthesis, also called “green synthesis,” is the process of creating nanomaterials using naturally occurring biological processes involving bacteria, fungi, or plants. There are differences among synthesis methods in terms of cost, environmental impact, and scalability [3]. Microorganisms are thought to be nanofactories with great potential as eco-friendly, low-cost tools that can produce nanoparticles without the need for harsh or toxic chemicals. The presence of several reductase enzymes in microorganisms allows them to accumulate and detoxify heavy metals. The reduction of metal salt into nanoparticles is facilitated by these reductase enzymes. Many microorganisms, including bacteria, fungi, and yeast, have been around for a few years. As reducing and capping agents in the synthesis of nanoparticles, proteins, reducing cofactors, metal-resistant genes, enzymes, and organic materials are important components.

Plants can be used to make metal nanoparticles and are readily available. The utilization of natural resources to generate nanoparticles, or “green synthesis,” is a scientific advance in nanotechnology that outperforms physical and chemical synthesis procedures. A type of “green synthesis” involves the creation of nanoparticles using medicinal herbs. Biological substances known as medicinal plants are used to cure ailments on a local or regional level, either directly or after further processing. They have been utilized in China, Greece, Egypt, and India since antiquity. Plants

are used in phytonanotechnology to synthesize nanoparticles. Different plant parts, including the root, fruit, stem, seed, and leaf, are used to create nanoparticles. Uncertainty surrounds the precise process by which plants are used to create nanoparticles. It has been demonstrated that the synthesis of different kinds of nanoparticles is caused by organic acids, proteins, vitamins, and secondary metabolites like alkaloids, flavonoids, terpenoids, polysaccharides, and heterocyclic compounds [4]. Phytonanotechnology has demonstrated a new, easy-to-use, and affordable method for producing nanoparticles. The benefits of phytonanotechnology include scalability, biocompatibility, and the ability to synthesize nanoparticles using water as a universal solvent and reducing agent.

Green synthesis improves biocompatibility and lessens the environmental impact of nanomaterial production, making these materials more appropriate for use in water treatment and other fields [5]. Many green synthesis techniques have been effectively used to create nanomaterials with uses in water management. Heavy metals and organic pollutants can be effectively removed from water by synthesizing silver nanoparticles using plant extracts [6]. Similarly, arsenic and fluoride have been eliminated from contaminated water sources using biosynthesized iron oxide nanoparticles. These studies demonstrate how environmentally friendly synthesis techniques can be used to produce functional nanomaterials that are efficient at treating water while also being environmentally benign.

Global demand for clean drinking water is rising, as is the difficulty in eliminating pollutants like bacteria, heavy metals, and organic pollutants [7]. Wastewater contains 1% of suspended colloidal dissolved particles, according to a 2015 UN-Water report [8]. Public housing produces residential wastewater, which is composed of 10% particles, 99.90% water, and nutrient-rich organic materials that are broken down and decomposed by microbes. Moreover, commercial, industrial, and agricultural operations are the primary sources of wastewater that are not residential or urban, and they also have an impact on the composition of the effluent [9].

It is necessary to halt industrial emissions of hazardous dyes like methylene blue to provide cleaner and non-hazardous water resources. To guarantee that everyone has access to a clean and safe water supply, there is an urgent need for sustainable wastewater management. To eliminate contaminants from various kinds of wastewater, a vast array of conventional and unconventional treatment techniques is available [10]. These approaches have two drawbacks: they require a substantial upfront financial outlay and are not always effective. This challenge is compounded by the need for specialized operating conditions, high energy requirements, and high maintenance costs [11]. On the other hand, nanotechnology holds great potential for the advancement of next-generation wastewater technologies and may even replace existing wastewater treatment methods [12]. Industrial wastewater has been extensively treated through photocatalysis using nanoparticles, specifically chemically produced titanium dioxide. When it comes to delivery, nanoparticles outperform nanotechnology as a whole. Titanium dioxide is classified as an efficient nanomaterial and is used to provide longer-lasting protection from UV light. When highly hazardous, costly, and toxic substances are needed for the chemical synthesis of nanoparticles, the release of these substances into the environment raises significant eco-toxicological concerns [13].

The use of plant extracts, microorganisms, and enzymes offers an upfront environmentally acceptable way to produce nanoparticles from biodegradable materials [14]. Plant extracts are the most effective way to create nanoparticles because they

expedite the reaction process and lessen the chance of associated contamination. They also support the maintenance of the cell's structure [15]. We have primarily concentrated on non-hazardous green chemistry approaches, and we have made an effort to stay up to date on information that summarizes the efficacy of currently used novel techniques and their findings (**Table 1**).

Nanofiltration is a water purification method where particles from water are filtrated through the membrane. Membrane processes may be broadly categorized into four basic classifications: (i) microfiltration, (ii) ultrafiltration, (iii) nanofiltration, and (iv) reverse osmosis membrane filtration. The finest solution for water filtration is nanofiltration membranes [16]. Polyamide membranes vary in cut-off points based on the molecular weight of the species and have a reduced salt rejection. The rejection rate of these membranes is higher than 92%. The nanofiltration membrane is a relatively new technology used in wastewater treatment systems.

Nanofiltration stands out as the most environmentally friendly method of removing a variety of pollutants. It is also used to soften hard water by removing divalent and multivalent ions. The NF membrane contains pores that have an average size of 0.001 μm , or between 1 and 100 nm. With the use of NF membranes, a variety of pesticides can be removed from the environment with an efficiency of up to 99.9%. This is because NF can remove molecules with low molecular weights (as low as 100–200 Da). As of right now, NF is the only filtration technology capable of removing both pesticides and organic pollutants [17].

Nanofiltration was developed in 1970 and became more common in the late twentieth and early twenty-first centuries. Several studies on the particle removal properties and operational costs of nanofiltration have been conducted around the world. The creation of sophisticated filtration systems, adsorbents, and catalysts is the main goal of applying nanotechnology to water management. The application of nanotechnology in water management is primarily focused on the development of advanced filtration systems, adsorbents, and catalysts. Nanomaterials such as carbon nanotubes, metal-organic frameworks (MOFs), and nanocomposites are being explored for their ability to remove pollutants from water with high selectivity and efficiency. Nanofiltration, a membrane-based process that uses nanomaterials, is particularly promising for water treatment. This technology works well for separating ions, organic molecules, and certain viruses and bacteria because it can eliminate particles as small as 1–10 nanometers [18]. To meet the increasing demand for clean water on a worldwide scale, nanofiltration is used in water management to enhance the quality of drinking water as well as to treat wastewater and reuse industrial water [19].

The field of nanofiltration has advanced significantly in recognition of nanotechnology, providing improved water purification performance. Salts, heavy metals, and

Primary	Secondary	Tertiary	Nano based
Coagulating Centrifugation	Aerobic	Evaporation	Photocatalysis Nanofiltration
Flocculation Screening	Anaerobic	Oxidation	Nanocomposites Clay and Zeolites
Centrifugal separation		Ion Exchange	Nanoadsorbents
		Distillation	
		Reverse Osmosis	
		Adsorption	

Table 1.
Different technologies utilized for treating wastewater.

organic molecules can all be effectively removed by using nanofiltration membranes that incorporate nanomaterials like graphene oxide and titanium dioxide. These membranes are especially useful for desalination and the treatment of industrial wastewater, offering a dependable means of generating clean water in areas with a scarcity of freshwater resources [20]. The advancement of nanofiltration technologies is also consistent with the objectives of sustainable water management since these systems can function with less energy and chemicals than those of conventional methods [21]. Because of a variety of unique characteristics, nanoparticles are especially useful in water management applications like nanofiltration. High surface area-to-volume ratios, adjustable surface chemistry, size-dependent optical characteristics, and increased reactivity are some of these attributes. Various studies in the literature support the effectiveness of nanoparticles in removing contaminants from water due to each of these characteristics.

The exceptionally high surface area-to-volume ratio of nanoparticles is one of their most important characteristics. This large surface area makes more active sites available for interactions with impurities, which improves the reactivity and adsorption of nanoparticles. For instance, the large surface area of carbon-based nanomaterials such as carbon nanotubes and graphene oxide makes it easier for organic pollutants and heavy metals to be adsorbed from water. Because of its large surface area, graphene oxide was found to have a substantially higher adsorption capacity for lead (Pb) ions. Nanostructured metal oxides have abundant potential because of their huge comparative areas [22]. Additionally, the surface chemistry of nanoparticles can be significantly adjusted to target particular contaminants. Contaminants such as organic pollutants, heavy metals, and pathogens can be selectively adsorbed and removed from the surfaces of nanoparticles by functionalizing them with specific chemical groups. For example, arsenic from water has been effectively removed using functionalized silica nanoparticles. Their affinity for arsenic species is greatly increased by the surface modification with amino groups [23].

Nanoparticles can be used in a variety of detection and purification technologies due to their highly size-dependent optical and electronic properties. For instance, when exposed to light, silver nanoparticles localized surface Plasmon resonance (LSPR) improves their capacity to identify and break down organic pollutants in water. Silver nanoparticles exhibited superior photocatalytic activity in the degradation of methyl orange under visible light, demonstrating how this property has been used in photocatalytic applications for the degradation of organic pollutants [24].

Regarding water purification applications, nanoparticles frequently show higher catalytic activity than bulk materials. Because of their tiny size and high surface energy, nanoparticles can break down complex organic molecules effectively as catalysts. As an illustration, titanium dioxide (TiO_2) nanoparticles are frequently employed as photocatalysts to break down organic contaminants in water. TiO_2 nanoparticles are highly effective in photocatalytic water treatment processes because of their high reactivity under UV light, which causes contaminants to completely mineralize [25]. The strong antimicrobial characteristics of nanoparticles, especially those of metal and metal oxide, make them useful for water treatment applications involving disinfection. For example, silver nanoparticles have strong antimicrobial properties and are capable of eliminating bacteria, viruses, and other pathogens from water. The release of silver ions, which interact with microbial cell membranes and cause cell death, is the antimicrobial mechanism of silver nanoparticles [26].

The mechanical strength and stability of nanofiltration membranes are frequently enhanced by the use of nanoparticles in the membranes. Adding graphene oxide nanoparticles to polymeric membranes improves their structural integrity and increases their resistance to physical deterioration and fouling. Long-term nanofiltration system operation depends on this improvement. The research conducted by Rana and colleagues (2020) revealed that membranes containing graphene oxide have enhanced mechanical strength and antifouling characteristics, resulting in more effective water filtration procedures [27].

A viable route to environmentally acceptable and long-lasting water treatment solutions is the incorporation of green nanotechnology into water management techniques. Providing access to clean drinking water and reducing the effects of water pollution are two major global challenges that could be addressed by the application of green nanotechnology in water management [28]. Green synthesis techniques use biological sources like algae, bacteria, fungi, and plant extracts to create nanoparticles in an environmentally friendly way. Because of its biocompatibility and lesser toxicity when compared to conventional chemical procedures, this strategy is becoming more and more common. As the field continues to evolve, the collaboration between environmental scientists, chemists, and engineers will be crucial in advancing the development and implementation of green nanotechnologies in water management systems.

2. Methodology

The top-down approach and the bottom-up approach are the two methods most frequently used to create nanoparticles. The top-down approach technique begins with bulk materials that are physically processed (such as milling, grinding, or lithography)

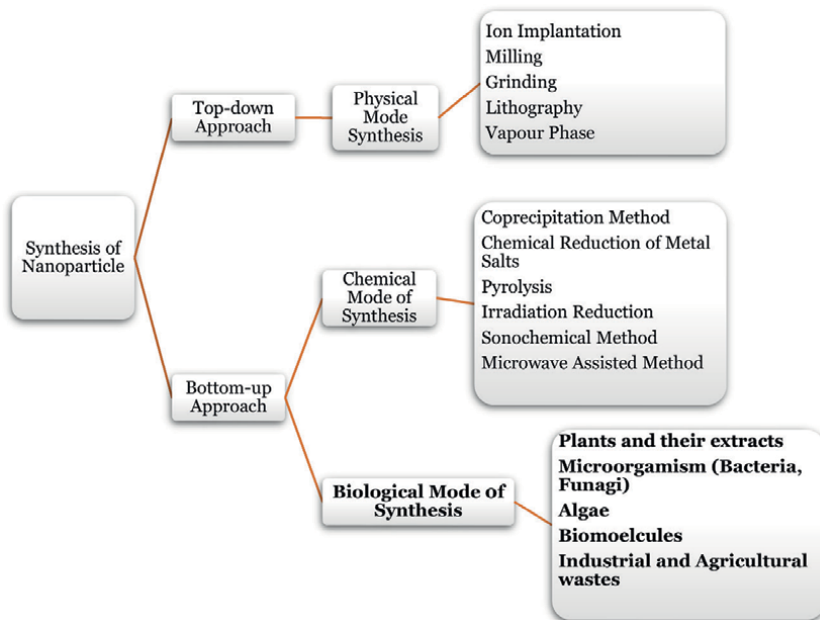


Figure 1.
Flow chart showing different methods of nanoparticle synthesis [29].

into nanoscale particles. Bottom-up approach technique: nanoparticles are created by assembling them molecule by molecule or atom by atom. Metal ions can be reduced into nanoparticles through chemical and biological means in this process. Because bottom-up approaches can produce uniform particles and are precise, they are widely used.

The synthesis of nanoparticles is a quickly developing field with a variety of techniques, including chemical, biological, and physical (green) methods. Because of their efficiency, safety, and sustainability, the development of green synthesis methods that use plant extracts or other biological sources has attracted a lot of attention recently (**Figure 1**) [29].

2.1 Green synthesis

Green synthesis methods generate nanoparticles in an environmentally sustainable way by using biological sources like algae, bacteria, fungi, and plant extracts. Because this method is less toxic than chemical methods and is biocompatible, it is becoming more and more popular. We aimed to focus the environmental sustainability and cost-effectiveness toward the green synthesis of nanoparticles. Furthermore, it offers a comprehensive, thorough summary of green NP synthesis methods, which can be distinguished by their ease of use, financial sustainability, and environmentally favorable utilization of plant extracts. This study highlights how green synthesis methods have the potential to transform the manufacturing of NPs while adhering to environmental stewardship principles and resource efficiency (**Figure 2**) [31].

2.1.1 Microorganism-based synthesis

Microorganism-based synthesis of nanoparticles elucidates a sustainable and adaptable approach to nanomaterial production. Following are the steps to produce nanoparticles by using microorganisms like bacteria and fungi.

2.1.1.1 Selection of microorganisms

The first step in the procedure is to choose a microbe with the capacity to lower metal ions. The ability of various microorganisms, such as yeast, algae, bacteria, and fungi, to synthesize nanoparticles has been investigated. Protozoa like *Pseudomonas aeruginosa* and *Bacillus subtilis* are commonly utilized bacteria, and *Aspergillus niger* is an effective fungal.

2.1.1.2 Cultivation of microorganisms

A suitable growth medium is used to cultivate the chosen microorganism. The culture conditions—temperature, pH, and availability of nutrients—are set up to maximize the microorganism's ability to produce reducing agents. While fungi can be grown in potato dextrose broth, bacteria are usually grown in Luria-Bertani (LB) broth or nutrient broth.

2.1.1.3 Preparing the metal ion solution

A metal precursor solution is made up of salts like gold chloride (AuCl_4), silver nitrate (AgNO_3), or other metal salts. The size and shape of the nanoparticles are largely determined by the concentration of the metal ions.

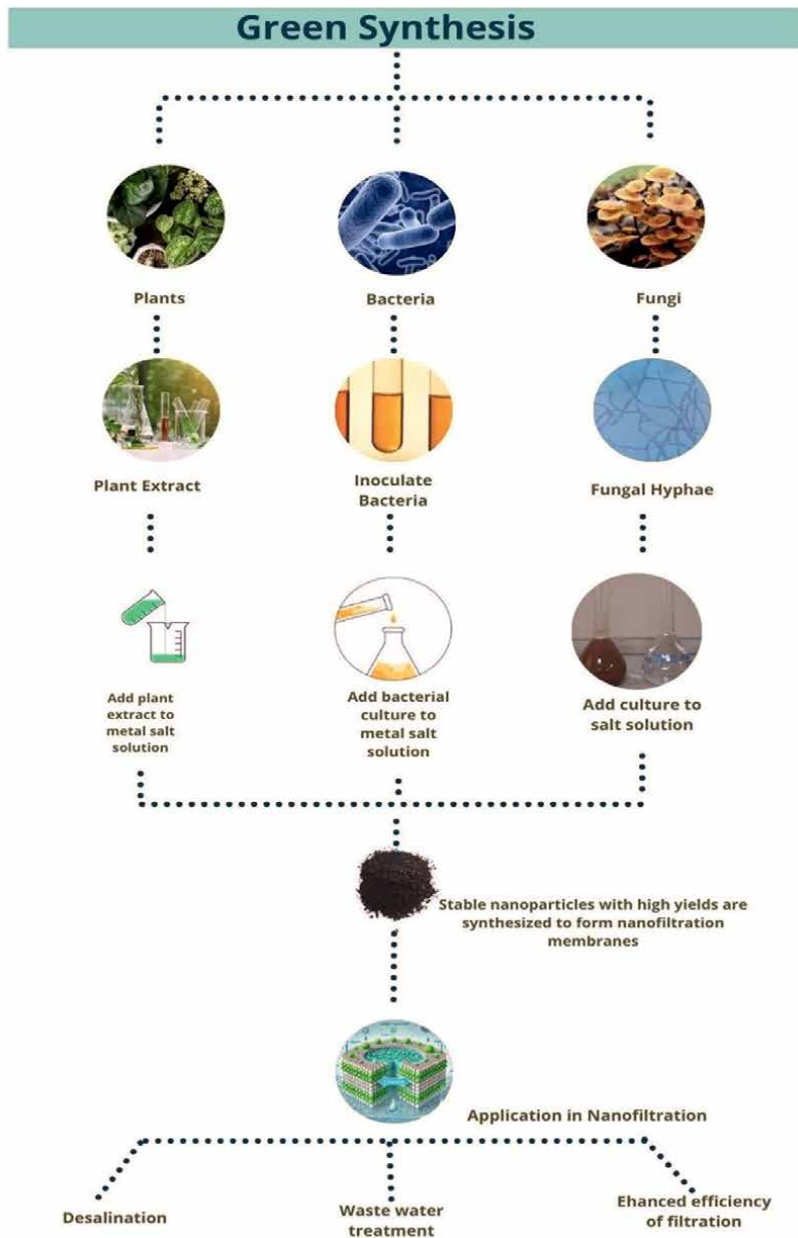


Figure 2. Graphic representation for green synthesis of metallic nanoparticles from plants, bacteria, and fungi and applications in nanofiltration [30].

2.1.1.4 Formation of nanoparticles and bio-reduction

The microorganism culture is supplemented with the metal ion solution. The microbes create proteins, polysaccharides, and other biomolecules, such as nitrate reductase in bacteria, which break down the metal ions into nanoparticles. Usually, this bio-reduction takes place extracellularly (in the surrounding medium) or

intracellularly (within the cell). This reduction process results in the formation of the nanoparticles.

2.1.1.5 Washing nanoparticles

Following their synthesis, nanoparticles are extracted from the biological medium. Numerous methods, including centrifugation, filtration, and precipitation, can be used to accomplish this. The nanoparticles are cleaned of any contaminants or unreacted metal ions using distilled water or ethanol after separation.

2.1.2 Plant-based synthesis

One of the most scalable and sustainable processes for producing nanoparticles is plant-mediated synthesis. Metal ions are reduced to nanoparticle size by phytochemicals like phenolic acids, terpenoids, and flavonoids.

Silver Nanoparticles (AgNPs): Recent research shows that plant extracts such as *Moringa oleifera* and *Azadirachta indica* (neem) can be successfully used to synthesize AgNPs. These nanoparticles are appropriate for biomedical applications and water purification due to their exceptional antimicrobial qualities. AgNPs were created in 2021 using *Moringa oleifera* leaf extract, and the study's findings demonstrated how effective it is at eliminating heavy metals from tainted water [32].

Zinc Oxide (ZnO) Nanoparticles: These nanoparticles, which are made from plant extracts like *Citrus sinensis* (orange peel), can catalyze reactions through photocatalysis, making them useful for treating wastewater. A 2020 study demonstrated how ZnO nanoparticles made from *Citrus sinensis* extract could effectively degrade organic dyes [33].

Following are the steps for the green synthesis of nanoparticles.

2.1.2.1 Extraction of plant material

The preparation of plant extracts, an essential step in this green synthesis approach, is described in detail in the following sections.

Plant materials that have recently been harvested (leaves, stems, and roots) will be held under running water to wash out any contaminants. Following that, the plant parts will be cut into tiny portions, dried out in the shadow, and crushed into a fine powder. Before grinding the sample, the grinder will be rigorously cleaned to remove any residues of previously ground material or any foreign matter that may have been placed on the grinder. Grinding increases surface area, which improves extraction efficiency. The powdered plant sample will be collected in a clean, waterproof plastic bag and stored in a cold, dry area until it is used in another experiment (**Figure 3**) [34].

The formula below will be used to determine the extract's % yield:

Percent Yield = $\frac{\text{Extract Weight}}{\text{Weight of the pot will bed plant sample taken}} \times 100\%$.

2.1.2.2 Synthesis of metallic ion solution

4.25 g of salt will be dissolved in 500 ml of distilled water to form a 0.05 solution. For 25 minutes, magnetic stirring will be done at room temperature. To prevent reduction, the prepared salt solution will be kept in a flask and kept in the refrigerator for later use.

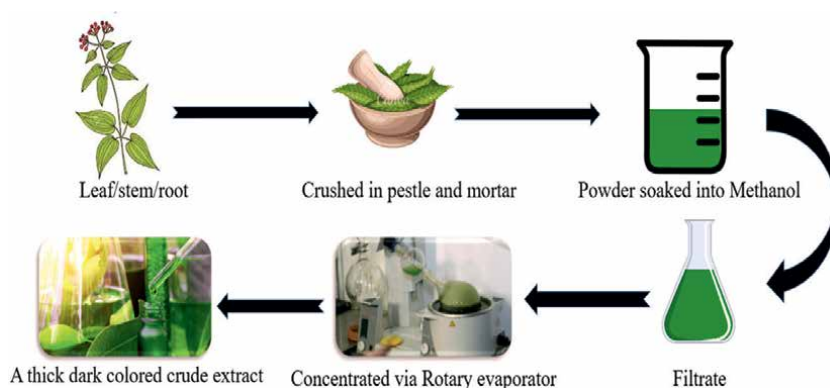


Figure 3.
Flow chart of generating the crude extract [32].

2.1.2.3 Synthesis of nanoparticles

5 ml of plant extract will be added to 45 ml of salt solution in a falcon tube to make a final volume of 50 ml. After that, the solution will be exposed to sunlight for about 30 minutes to allow for reaction. The reaction's completion was confirmed by an appropriate color change. The excess plant extract and unreduced ions will then be removed by centrifuging the suspension at a condition of 6000 rpm for 30 minutes. To remove any impurities and other substances that become adsorbed on the surface of nanoparticles, the supernatant will be discarded, and the pellet thereby produced will be held in distilled water. To obtain pure pellets, this process will be repeated three times. Then, nanoparticle pellets will be dried in an incubator for 24 hours at 60 degrees. After being crushed into a fine powder, dried pellets will be kept in Eppendorf tubes.

2.1.3 Optimization of physio-chemical parameter

See **Table 2**.

2.2 Characterization of nanoparticles

To characterize nanoparticles, the following analysis will be performed in **Figure 4**.

The following are steps to analyze the synthesized nanoparticles [36].

2.2.1 UV-Vis analysis

2.2.1.1 Experimental method

- i. UV-Vis study is performed on silver nanoparticles to assess their optical characteristics using a UV-Vis spectrophotometer.
- ii. The pellets will be collected for sample preparation after centrifugation, with the supernatant being discarded.

Reaction parameters	Effect on nanoparticle synthesis	Properties	Relevance to nanofiltration and water applications
Reaction time	Increased nucleation and growth of NPs	Larger size, potentially lower band gap	Larger nanoparticles may enhance filtration efficiency by increasing surface area and adsorption capacity.
pH	Size, shape, and stability of NPs	Size variation, shape changes, stability	Controlled pH ensures uniform size and stability, improving the performance of nanoparticles in water filtration.
Temperature	Shape: Rod, oblong, spherical	Shape variations: rod, oblong, spherical	Specific shapes can optimize interaction with contaminants, enhancing filtration efficacy.
Concentration of salt	Topological Characteristics	Changes in morphology and surface properties	Morphological characteristics influence the efficiency of contaminants removal during filtration.
Concentration of plant extract	Faster reduction kinetics and better stabilization of NPs	Faster formation, improved stabilization	Rapid and stable nanoparticle formation ensures consistent performance in filtration processes.

Table 2.
Optimization of physio-chemical parameters such as temperature, pH, concentration, and reaction time [35].

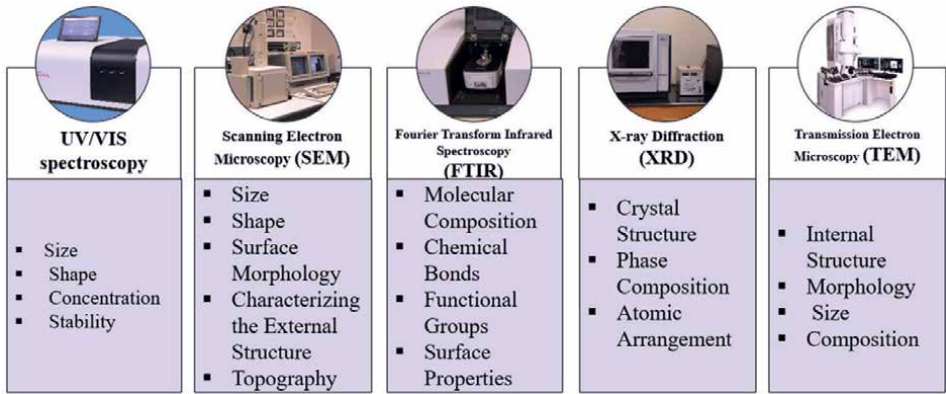


Figure 4.
Characterization techniques of green-synthesized nanoparticles [36].

- iii. To create a homogeneous mixture, the sample will be created by dissolving 20 ml of water in a vial containing pellets.
- iv. A 5 ml sample will be collected from stock and analyzed using water as a blank reference.
- v. This approach is used to validate the manufacture of silver nanoparticles.
- vi. UV-Vis spectra will be detected in the 200–800 nm region.

2.2.2 Scanning electron microscope (SEM)

Using a SEM (scanning electron microscope), the morphological properties of the produced silver nanoparticles will be determined. A sample slide will be made and analyzed at a voltage of 5 kV using a Leo 440i in Cambridge, UK. Well-coating with conductive substance is required for sample preparation.

2.2.2.1 Sample preparation and steps

- i. The sample of dried nanoparticles is carefully put onto an SEM stub, which is a tiny conductive disc made to hold samples for imaging.
- ii. When performing an SEM analysis, make sure the nanoparticle sample is spread evenly across the stub to produce a uniform and clear image.
- iii. There are several ways to distribute the sample onto the stub:
- iv. Applying a thin bristle brush: Apply the powdered dried nanoparticles gently to the stub.
- v. Applying a suspension of nanoparticles: Before imaging, apply a tiny drop of the nanoparticle suspension to the stub and let it air dry.
- vi. Since most nanoparticles and biological materials are non-conductive, a thin layer (5–10 nm) of a conductive metal (e.g., gold or platinum) is sputter-coated onto the sample. This prevents electron charging and enhances image quality.
- vii. The sample is loaded into the SEM chamber, and a vacuum is applied.
- viii. The sample is evaluated at various resolutions to obtain the optimum picture for identifying particle size and shape.

2.2.3 Fourier-transform infrared spectroscopy (FTIR)

It provides insights into the chemical composition and surface functionalization of nanoparticles, such as those modified for drug delivery or environmental applications.

2.2.3.1 Sample preparation and steps

- i. Use a low-temperature oven or a freeze-dryer to dry the nanoparticle sample.
- ii. Form a pellet by combining the dried sample with potassium bromide (KBr).
- iii. Insert the pellet into the holder for FTIR samples.
- iv. Conduct an FTIR scan within the 4000–400 cm^{-1} range to detect functional groups.

2.2.4 X-ray diffraction spectroscopy (XRD)

It is fundamental for determining the crystalline structure and phase of nanoparticles, like TiO_2 and ZnO , essential for applications in photocatalysis and sensors.

2.2.4.1 Experimental method

- i. To form powder, dry the sample at a low temperature after harvesting the nanoparticles.
- ii. Put the powder inside the holder for the XRD sample.
- iii. Utilize a suitable range for the XRD scan, such as $10\text{--}90^\circ 2\theta$.
- iv. To ascertain the crystalline nature, examine the diffraction peaks.

2.2.5 Transmission electron microscopy (TEM)

Morphological features such as internal structure, morphology, size, and composition of prepared silver nanoparticles will be determined by TEM.

2.2.5.1 Experimental method

- i. Centrifugation is used to extract the nanoparticles (e.g., at 10,000 rpm for 15 minutes).
- ii. Drop a pellet into distilled water to re-suspend it, then place the drop on a copper grid coated in carbon.
- iii. By using an infrared lamp, dry the sample.
- iv. Insert the grid into the TEM to image at different magnifications.

2.3 Incorporation of green nanoparticles into NF membranes

Green nanoparticles reduce environmental toxicity while improving water permeability, selectivity, and antifouling properties in nanofiltration (NF) membranes. Phase inversion and LbL (Layer-by-Layer) assembly are two common techniques for adding nanoparticles.

2.3.1 Phase inversion method

Using this technique, layers of materials with opposing charges, such as green nanoparticles, are progressively deposited onto the membrane surface in an alternating fashion [37].

2.3.1.1 Preparing polymer solution

Melt 1 weight percent polyvinylpyrrolidone (PVP) and 18 weight percent polyether sulfone (PES) in dimethylacetamide (DMAc). To guarantee total dissolution, stir the mixture for seven hours.

2.3.1.2 Nanoparticle incorporation

To the polymeric solution, add several concentrations of iron oxide nanoparticles (Fe_3O_4 NPs) at 0, 0.01, 0.03, 0.05, 0.1, 0.3, and 0.5 weight percent. To obtain a homogenous dispersion of nanoparticles, sonicate the mixture for 30 minutes using an ultrasonic bath.

2.3.1.3 Elimination of air bubbles

To help release any trapped air bubbles, let the resulting solution settle at room temperature.

2.3.1.4 Membrane casting

To achieve a consistent 150 μm thickness, cast the polymeric solution onto clean, room-temperature glass plates using a film applicator.

2.3.1.5 Submersion in DI water

Cast films should be submerged in deionized (DI) water right away to cause phase inversion, which will result in the creation of a porous membrane structure.

2.3.1.6 Membrane storage

Before using them again, keep the produced Fe_3O_4 /PES membranes in DI water.

2.3.2 Layer-by-Layer (LbL) nanoparticle assembly in nanofiltration membrane method

This is a common method in which a film of a polymer solution containing green nanoparticles is cast, and the polymer solidifies into a membrane structure by submerging it in a non-solvent bath [38].

2.3.2.1 Getting the solutions ready

Make a dispersion of green-generated nanoparticles in an appropriate solvent, such as graphene oxide or silver. Make a polymer solution by dissolving a biocompatible polymer in a suitable solvent, such as polyether sulfone (PES).

2.3.2.2 First membrane assembly

Start with an already existing nanofiltration membrane that has been treated to improve surface functionality, or start with a clean substrate.

2.3.2.3 Initial cycle of dipping

For a predetermined amount of time, submerge the membrane in the nanoparticle solution, enabling the nanoparticles to attach themselves to the membrane via chemical or electrostatic bonds. To get rid of any unbound nanoparticles, rinse the membrane with a solvent after immersion.

2.3.2.4 Cycle of second dipping

To enclose the attached nanoparticles and form a polymer layer around them, dip the membrane into the polymer solution. To get rid of extra polymer solution, rinse the membrane one more time.

2.3.2.5 Repeating the procedure

To accumulate the required number of layers, dip the membrane alternately in the polymer and nanoparticle solutions. Repeat the procedure many times. Each cycle gradually improves the membrane's characteristics by adding a layer of nanoparticles and then a layer of polymer.

2.3.2.6 Last drying and rinsing

Once the appropriate number of layers has been achieved, rinse everything one last time to make sure any loosely attached ingredients are departed. To firm the structure, let the formed membrane dry at room temperature or by using a controlled drying procedure.

Selectivity, permeability, and antifouling properties of nanofiltration membranes are all improved by this LbL construction method, which also improves their overall functionality and performance.

2.3.2.7 Surface morphology analysis

Using scanning electron microscopy (SEM), the surface morphology of the nanofiltration membranes. By using this technique, one may evaluate the pore structure, thickness, and general shape of the membrane by obtaining detailed photographs of its surface (**Figure 5**) [39].

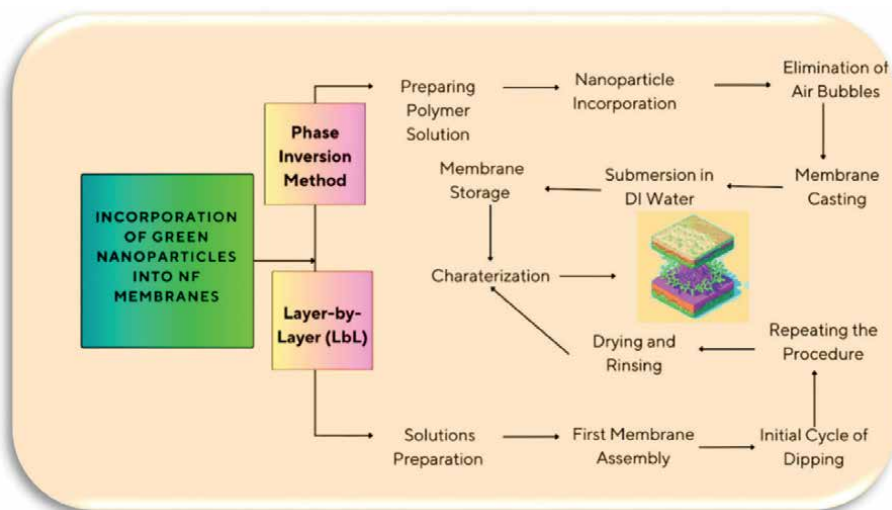


Figure 5.
 Illustrate the incorporation of green nanoparticles into NF membranes via the phase inversion method and LbL method [36–38].

2.4 Application of nanotechnology in water purification and treatment

The world is currently facing significant challenges in meeting the growing demand for drinking water as freshwater supplies are running low due to a lack of rain-fall, population growth, and stricter health-based regulations. Human health depends on clean water, but 80% of diseases in the world are caused by bacterial contamination of drinking water. The most widely utilized methods for treating water are primarily chemical and physical agents like water sediment filters, bromine (Br) and its derivatives, chlorine (fiber and ceramic), reverse osmosis, activated carbon, and so forth, but using halogens has numerous issues because of their high vapor pressure and toxicity. Currently, nanoscience is extensively researched for use in the filtration of water. The most widely utilized methods for treating water are primarily chemical and physical agents like water sediment filters, bromine (Br) and its derivatives, chlorine (fiber and ceramic), reverse osmosis, activated carbon, and so forth, but using halogens has numerous issues because of their high vapor pressure and toxicity [40]. Currently, nanoscience is extensively researched for use in the filtration of water. This brand-new multidisciplinary topic refers to the investigation of changes in chemistry and physics at the nanoscale (1–100 nm). Currently, nanotechnology is being utilized to create novel materials and gadgets, and it is additionally thoroughly studied in water.

Numerous multifunctional green nanomaterials have been created via a range of techniques, and their possible uses have been investigated. Specific compositions, sizes, morphologies, and crystallinities characterize the various materials. Among the primary and secondary metabolites identified are terpenoids, alkaloids, flavonoids, and phenolic acids. These metabolites are essential for the redox processes that result in green, eco-friendly nanomaterials.

Green-synthesized nanoparticles enhance nanofiltration by improving membrane permeability, selectivity, and antifouling properties in water treatment and desalination applications [41].

2.4.1 Water treatment

Organic pollutants, pathogens, and heavy metals can all be effectively eliminated from water by using green-synthesized nanoparticles like titanium dioxide (TiO_2), zinc oxide (ZnO), and silver (Ag). To improve filtration effectiveness, they are added to NF membranes. For instance, plant extracts are used to create Ag nanoparticles, which have antimicrobial qualities that stop biofouling in membranes. This keeps the membranes used in water purification operating longer and at higher filtration rates.

2.4.2 Treatment of wastewater

Membranes enhanced with iron oxide (Fe_3O_4) and other green-synthesized nanoparticles show better selectivity and higher permeation rates in the treatment of industrial wastewater. These nanoparticles, which are frequently made from algae or microorganisms, aid in cleaning wastewater of pollutants, heavy metals, and dyes so that they can be recycled or disposed of safely [42].

2.4.3 Desalination

NF membranes are essential to the desalination process, especially when dealing with saline water. NF membranes selectively reject divalent and multivalent

ions (like calcium and magnesium) while permitting monovalent ions (like sodium and chloride) to pass through, in contrast to reverse osmosis (RO). Freshwater may be affordably provided in arid places because of this selective permeability, which also improves water recovery rates and lowers the energy needs for desalination.

Nanofiltration membranes embedded with green-synthesized nanoparticles, such as ZnO nanoparticles, are used in desalination processes to reject multi-valent ions like magnesium and calcium while allowing water to pass through. ZnO nanoparticles enhance the salt rejection capability while maintaining high water flux. This is especially useful for reducing the energy requirements in desalination [43].

2.4.4 Pollutant removal and dye rejection

NF membranes are employed in industrial settings to purify wastewater that contains pigments and colors. When water is discharged into the environment or used again, the membranes' ability to reject dye molecules efficiently contributes to their quality being restored. In the textile and dye sectors, where wastewater treatment is necessary to comply with environmental requirements, this application is particularly advantageous.

Green synthetic nanoparticle-enhanced nanofiltration (NF) membranes have demonstrated significant potential in wastewater pollution removal and color rejection. The efficiency of the membrane structure is greatly improved by adding ecologically friendly nanoparticles, such as iron, zinc, and silver oxide, by a variety of methods.

High rejection rates for different dyes, including methylene blue and rhodamine B, can be achieved by NF membranes implanted with green manufactured nanoparticles while still retaining adequate water permeability. These NF membranes are an eco-friendly and cutting-edge approach to solving the problems associated with water pollution because of the advantages of employing green synthesis techniques to produce nanoparticles and their efficient water treatment capabilities. The incorporation of these cutting-edge materials into NF technology presents a substantial opportunity for creating water treatment procedures that are more productive, economical, and environmentally sustainable (Figure 6) [44].



Figure 6.
Flowchart illustrating membrane applications enhanced with green nanoparticles [41].

2.5 Performance of nanofiltration enhanced by green-synthesized nanoparticles

Feed water is forced through a membrane during the pressure-driven process of nanofiltration (usually 4–30 bar). Smaller molecules, like water, can pass through the membrane that has been strengthened by nanoparticles, but larger solutes, multivalent ions, and organic molecules are filtered out [45].

2.5.1 Enhanced efficiency of filtration

Because of their special characteristics, nanoparticles greatly increase the filtration efficiency of nanofiltration (NF) membranes. Because of their small size and high surface area-to-volume ratio, nanoparticles offer a greater surface area, which enhances the interaction between the contaminants and the membrane. Higher filtration performance is the result of this improved interaction. Furthermore, additional adsorption sites for pollutants are provided by nanoparticles, which is especially advantageous for the removal of heavy metals and organic pollutants. For instance, compared to conventional materials, activated carbon nanoparticles have better adsorption capacities for a variety of organic contaminants, increasing overall filtration efficiency.

2.5.2 Stability and durability

The incorporation of environmentally friendly synthesized nanoparticles, like ZnO or Fe₃O₄, improves the chemical stability and mechanical strength of NF membranes. For example, it has been demonstrated that ZnO nanoparticles made from algae improve the thermal and chemical resistance of NF membranes, enabling them to function well even under challenging circumstances like industrial effluent treatment.

2.5.3 Improved microbiological qualities

Reducing microbial growth and biofouling is one of the main advantages of adding antimicrobial nanoparticles to NF membranes. Silver, copper, and zinc oxide nanoparticles are well-known for having potent antibacterial qualities. Their inclusion in NF membranes contributes to the membranes' longer lifespan by preventing microbial contamination on the membrane surface. Moreover, organic contaminants are broken down by photocatalytic nanoparticles like titanium dioxide (TiO₂) when exposed to UV light, enhancing the ability of the material to self-clean. The membrane's longevity and performance are further improved by this self-cleaning feature.

Because of their antibacterial qualities, which improve the functionality and durability of the membranes, green-produced nanoparticles have drawn a lot of attention as fillers in nanofiltration (NF) membranes. Green manufactured nanoparticles are safer and more environmentally friendly than conventional nanoparticles since they come from natural sources, reducing the possibility of harm to the environment and human health. The efficacy and variety of uses of plant-based nanoparticles in nanofiltration membranes are demonstrated in **Table 3**. In addition to improving antibacterial capabilities, the application of green synthetic nanoparticles improves membrane performance in a variety of water treatment applications.

According to the literature analysis, nanoparticles made from different plant sources regularly show strong antibacterial activity, which makes them great options

Nanoparticle	Synthesis method	Application	Reference
Silver	Plant extracts	Water purification, antimicrobial agents	[46]
Titanium dioxide	Plant extracts	Photocatalysis for organic pollutant degradation	[47]
Graphene oxide	Plant extracts	Water treatment, antimicrobial agents	[48]
Iron oxide	<i>Lantana camera</i> leaf extract	Antibacterial activity against <i>Pseudomonas</i> sp., <i>Klebsiella</i> sp., <i>Staphylococcus</i> sp., and <i>Salmonella</i> sp. Seed germination of <i>Vigna mungo</i>	[49]
Cobalt oxide	Neem (<i>Azadirachta indica</i>) leaf	Antibacterial activity against <i>S. aureus</i> , <i>B. subtilis</i> , <i>P. aeruginosa</i> , and <i>E. coli</i>	[50]
Silver nanoparticles	<i>Artemisia vulgaris</i> leaf extract	Antimicrobial activity against <i>K. pneumonia</i> , <i>H. influenza</i> , <i>P. aeruginosa</i> , <i>E. coli</i> , and <i>S. aureus</i>	[51]
Copper nanoparticles	<i>Syzygium aromaticum</i> bud extract	Antimicrobial activity against <i>E. coli</i> , <i>A. niger</i> , <i>Penicillium</i> spp., <i>Pseudomonas</i> spp., <i>Bacillus</i> spp., <i>A. flavus</i> , <i>Staphylococcus</i> spp.	[52]
Zinc oxide	Fruit peel extract	Methylene blue	[53]
Gold nanoparticles	Crescentia cujete L	Antibacterial activity against <i>E. Coli</i> , <i>S. Typhi</i> , <i>S. Flexneri</i> , <i>V. Colerae</i> , <i>P. Aurogens</i> , <i>B. Subtilis</i>	[54]

Table 3.
This table summarizes research on plant-based nanoparticles synthesized through green methods, highlighting their antibacterial properties, synthesis techniques, applications in water treatment, and overall effectiveness.

to include in NF membranes. Although the efficiency of silver, zinc oxide, and copper nanoparticles varies depending on the plant source and manufacturing technique, they also have encouraging antibacterial capabilities.

Thus, the following succinctly expresses how nanotechnology is being used to treat industrial wastewater: employing membrane-based nanofiltration methods, metal and metal oxides as nanomaterials, nano adsorbent materials as sorbents, nanoclays, and zeolites; and employing nanoscale semiconductors for using nano-photocatalysis to purify the air. For more than thirty years, membrane technology has been proven to be effective in eliminating a wide range of contaminants from wastewater and water. The secret to comprehending these four membrane filtering methods is the capacity to eliminate various particle sizes from a mixture. The process of nanofiltration stands out as the most environmentally friendly choice for removing different types of pollution. It is also used to make hard water softer by removing divalent and multivalent ions. There are pores in the NF membrane weighing between 1 and 100 nm, or 0.001 μm , on average. Making use of NF membranes, different pesticides could be eliminated from the surroundings with a maximum efficiency of 99.9%. Pesticides were eliminated using NF because low molecular weight molecules (as low as 100–200 Da) are eliminated. NF is currently the only filtration method that can be used to remove pesticides, organic pollutants, and other wastes from water.

3. Conclusion

An extensive review of the environmentally friendly synthesis of nanoparticles and their inventive application in water treatment nanofiltration membranes is

given in this chapter. The field of water treatment, especially for the purification of drinking water, has greatly advanced with the incorporation of nanoparticles into nanofiltration (NF) membranes. Because of their high surface area-to-volume ratio, nanoparticles improve the interactions between contaminants and membranes, giving organic pollutants and heavy metals more places to adsorb. This increases filtration efficiency. While photocatalytic nanoparticles like titanium dioxide contribute to the ability of the membrane to clean itself, the incorporation of antimicrobial nanoparticles like silver and zinc oxide also reduces biofouling, extending the membrane's lifespan. Furthermore, NF membranes' ability to function in challenging environments is enhanced by nanoparticles, which also strengthen their chemical and mechanical stability. Nanoparticles enhance the selectivity and general performance of membranes by controlling pore size and functionalizing their surface, which helps to maintain long-term operational stability.

The utilization of biological sources, such as plants and microorganisms, in the green synthesis of nanoparticles presents a viable and environmentally conscious substitute for traditional chemical methods. When applied to NF membranes, these green-synthesized nanoparticles not only show improved properties but also lessen their impact on the environment. The incorporation of these nanoparticles enhances the efficiency, robustness, and capacity of NF membranes to meet the increasing demand for potable water. Their ability to eliminate pollutants, diseases, and other impurities makes them an important tool in the worldwide effort to supply clean, drinkable water. Nanoparticles derived from various plant sources consistently demonstrate effective activity in water treatment applications, particularly when incorporated into nanofiltration (NF) membranes. The antibacterial qualities of the membranes are strengthened by these plant-based nanoparticles, which also increase the effectiveness of pollutant removal and improve overall performance. These nanoparticles inherent phytochemicals support sustainability in water treatment procedures in addition to their antibacterial properties. Their incorporation onto NF membranes presents a viable way to provide safer and cleaner drinking water. The chapter combines the two, offering a comprehensive picture of how cutting-edge membrane technology and the synthesis of green nanoparticles come together to solve problems in water treatment.

Acronyms and abbreviations

DMAC	Dimethylacetamide
FTIR	Fourier-transform infrared spectroscopy
LB	Luria-Bertani Broth
LbL	Layer-by-layer
LSPR	Localized surface plasmon resonance
NF	Nano filtration
NPs	Nanoparticles
Pb	Lead
PES	Polyether sulfone
PVP	Polyvinylpyrrolidone
RO	Reverse osmosis
SEM	Scanning electron microscope
XRD	X-ray diffraction spectroscopy

Author details

Erum Khalid
Pir Mehr Ali Shah Arid Agriculture University, Rawalpindi, Pakistan

*Address all correspondence to: erumkhalid20@gmail.com

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Perspective Chapter: Desalination as a Strategic Response to Pakistan's Water Scarcity – Analyzing Opportunities, Challenges, and Pathways for Sustainable Solutions

Hifza Rasheed and Muhammad Dilshad Arshad

Abstract

This chapter explores the potential of desalination as a solution to Pakistan's escalating water scarcity challenges, driven by rapid population growth, poor water management, and climate change. With per capita water availability dropping below 1000 cubic meters annually, desalination emerges as a viable option to meet the country's domestic, agricultural, and industrial water demands. However, several barriers to wide-scale desalination implementation exist, including high capital costs, energy-intensive operations, and environmental concerns like brine disposal. The chapter begins by setting the context of Pakistan's water resource challenges, followed by an in-depth analysis of existing desalination models in the country, their success rates, constraints, and the financial implications of scaling up these systems. A review of successful desalination technologies in countries like Israel, Saudi Arabia, and the United Arab Emirates (UAE) highlights best practices that Pakistan can adapt. Key recommendations for Pakistan's desalination future include integrating renewable energy sources to reduce operational costs, improving technical expertise, and adopting environmentally sustainable brine disposal methods. This chapter concludes by outlining policy measures, investment strategies, and technological innovations needed to develop sustainable desalination infrastructure in Pakistan, crucial for enhancing water security in the face of growing demand.

Keywords: desalination, water scarcity, renewable energy, brine disposal, sustainable infrastructure

1. Introduction

1.1 Water scarcity and quality issues in Pakistan

Pakistan is a semi-arid country that depends heavily on the Indus River and its tributaries—Kabul, Jhelum, Chenab, Ravi, and Sutlej—for its water resources.

Together, these rivers contribute over 175 BCM (billion cubic meters) of water annually [1]. The Indus Basin is home to the world's largest contiguous irrigation system, irrigating approximately 18 million hectares of cropland [2]. In the early 1950s, Pakistan was considered a water-abundant country having one of the largest irrigation systems, particularly the Indus River and its tributaries, and the fourth largest groundwater aquifer globally. This abundance supported agricultural development, a backbone of the country's economy, and ensured sufficient water for domestic and industrial use. Later with enhanced agriculture productivity, the country's per capita water availability has plummeted from over 5650 cubic meters per annum in 1951 to below 1000 cubic meters per annum today. The per capita water availability threshold for water scarcity as defined by the United Nations is 1000 cubic meters [3].

Pakistan relies heavily on surface water from its rivers, primarily the Indus River and its tributaries. The Indus River system, which originates in the Himalayas, is the lifeline of Pakistan's water supply. However, upstream water withdrawals and changes in river flow patterns have affected the quantity and timing of water availability. Since 1947, Pakistan, has constructed 3 large dams, 17 barrages, and numerous head works and canals on the Indus River to irrigate its barren lands. The two major reservoirs, Tarbela and Mangla, are challenged by silt accumulation, which has resulted in the loss of 32 and 20% of their storage capacities, respectively [4]. To address the growing population, industry, and electricity demands, the construction of mega dams such as Diamer-Bhasha Dam and Mohmand Dam as well as a number of small dams have been prioritized. However, the country needs to reduce its dependency on a single basin and also harness the potential of floods, hill torrents, and runoff. In Pakistan, dams are the primary focus, but the country has failed to build mega dams to control perennial floods and to store water for scarce periods.

In Pakistan, surface water, particularly as a subnational hydro-political issue, has traditionally been the main focus. However, challenges like groundwater overdraft, salinity, waterlogging, and ecosystem degradation are expected to pose even greater threats to overall water use. Groundwater contributes more than 60% of total water supplies at the farm level, but over-extraction in certain areas has led to the depletion of this vital resource specifically in Punjab and Balochistan provinces. In some regions, excessive use has caused saline (brackish) groundwater to intrude into freshwater aquifers, rendering them unusable.

In addition to surface water quality, groundwater quality in Pakistan presents critical challenges that threaten public health, agriculture, and the environment. Over-reliance on groundwater, particularly in areas with limited surface water, has led to severe depletion, increased pumping costs, and over-exploitation (**Figure 1**). Excessive pumping, especially in coastal and arid regions, has caused saline intrusion, rendering groundwater unsuitable for drinking and irrigation. Groundwater assessment studies undertaken by the Pakistan Council of Research in Water Resources [5–7] highlight severe depletion in parts of Punjab, significant increases in water table depth in the Peshawar Valley due to urban sprawl, and critical declines in the Pishin Lora Basin (**Figure 2**). Over-extraction has also deteriorated groundwater quality, exposing populations to harmful substances, such as arsenic, fluoride, salts, and metals, with serious implications for human health.

Major cities like Karachi and Lahore frequently experience water scarcity, while rural areas struggle to meet the water needs of agriculture, a sector vital to the economy. Water scarcity in Pakistan's desert regions is a significant issue, leading to migration and the deaths of many people and livestock. Conversely, abundant water is available in the Cholistan and Thar deserts but highly saline, with Total Dissolved

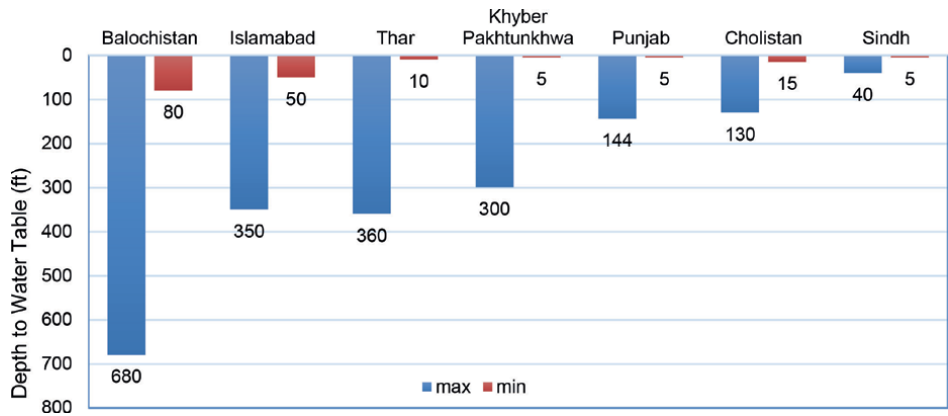


Figure 1.
Depth to water table in different parts of Pakistan.

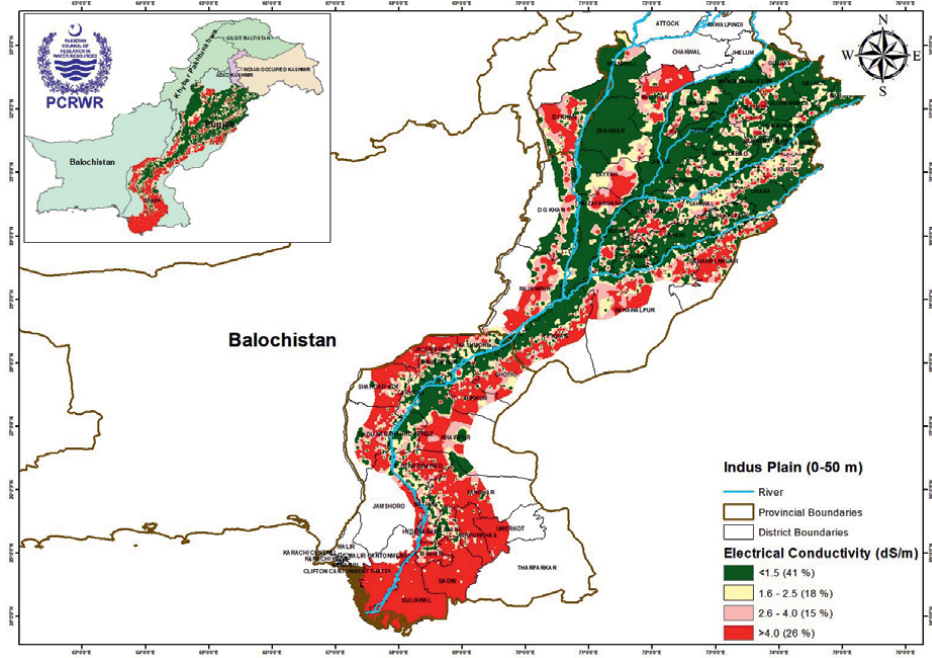


Figure 2.
Groundwater quality in Pakistan [7].

Solids (TDS) levels ranging from 3000 to 19,000 mg/L, making it unfit for both human and animal consumption. Additionally, rapid urbanization and industrialization have led to over-extraction of groundwater and pollution of water bodies, reducing the availability of clean water, as depicted in **Figure 3**.

Agriculture, which consumes most of Pakistan's water, relies on inefficient irrigation methods, while the cultivation of water-intensive crops adds to the strain. Agriculture is the largest consumer of water in Pakistan, accounting for approximately 90% of the total water usage. Traditional flood irrigation methods,

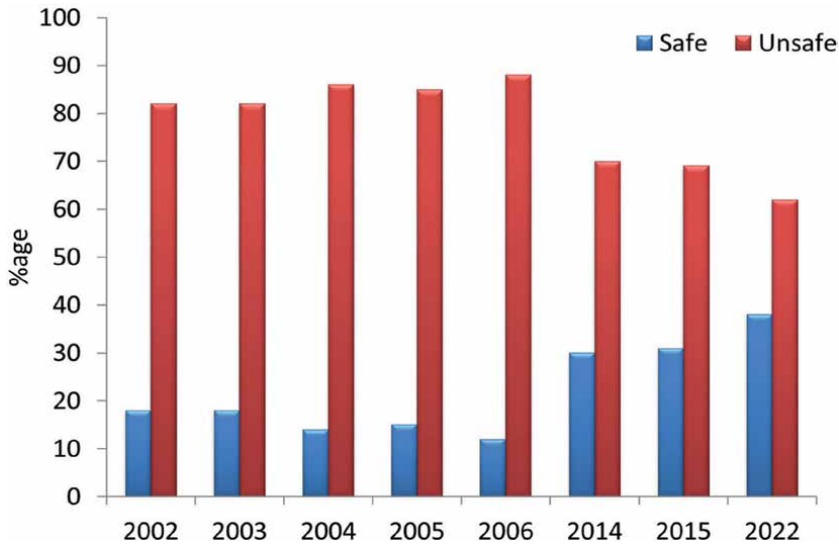


Figure 3.
Improvement in drinking water quality in Pakistan over the years [8, 9].

which are highly inefficient, result in significant water wastage. The cultivation of water-intensive crops like rice and sugarcane further strains the already limited water resources. Traditional irrigation methods result in water losses up to 60%, while poorly maintained infrastructure exacerbates resource depletion. Without adopting modern techniques, the country's water availability will continue to decline.

Pakistan stands in top 10 countries in climate-risk countries despite contributing less than 1% to global greenhouse gas emissions, most probably due to its unique geographical location [10]. Pakistan is surrounded by three high-altitude mountain ranges from east, north, and south, mostly covered with ice caps and glaciers, and the warm Arabian Sea at its south. Due to its geological position and human activities, Pakistan and other South Asian countries are more vulnerable to climate change compared to other regions, as demonstrated over the past two decades. In summary, climate change has exacerbated Pakistan's water crisis, disrupting rainfall patterns, speeding up glacial melt, and intensifying the occurrence of extreme weather events, such as floods and droughts. Between 1998 and 2018, Pakistan experienced nearly 150 extreme weather events, with 14 major floods severely affecting the country since 1990. The most recent floods in 2022 caused an estimated USD 30 billion in damage, with the agriculture sector, a key contributor to Pakistan's Gross Domestic Product (GDP), being the most affected [11]. Moreover, Pakistan is highly vulnerable to Glacial Lake Outburst Floods (GLOFs) due to accelerated glacial melt [12]. Consequently, the combined effects of climate change shocks and shifting land-use patterns have had serious consequences for water resources across various systems and regions. Groundwater, in particular, is impacted both directly through its interaction with surface water bodies, such as lakes and rivers, and indirectly through changes in the recharge process. The direct influence of climate change on groundwater resources is tied to variations in the volume and distribution of groundwater recharge. Pressure exerted by heat waves in addition to rapid population growth and inefficient water management cause a dramatic decline in groundwater table. Pakistan's rapidly growing population, which is expected to surge from 33 million

Year	Population (million)	Water availability (m ³)
1951	34	5300
1961	46	3950
1971	65	2700
1981	84	2100
1991	115	1600
2001	148	1200
2011	170	1050
2025	267	660

Data source: [13].

Table 1.

Per capita water availability in Pakistan.

in 1951 to over 230 million by 2025, is placing immense pressure on its limited water resources (**Table 1**) [14]. The increased demand for water, necessary for drinking, sanitation, agriculture, and industry, is compounded by outdated water management systems. This rapid industrialization, urbanization, fossil fuel use, plastic use, and deforestation have worsened the situation. Industrial discharges, agricultural runoff, and untreated sewage have polluted many water bodies, making the available water unsafe for human consumption and agricultural use. The presence of contaminants like arsenic and fluoride in groundwater further exacerbates the problem. Healthwise, limited access to clean water increases the spread of waterborne diseases, affecting public health and well-being.

According to the International Monetary Fund (IMF), Pakistan ranks third on the list of water-scarce countries (on the water scarcity index that compares national annual water availability with the total annual withdrawals percentage [15]). The ongoing water scarcity and declining water quality highlight the interconnectedness of water quantity and quality, driving up the costs of treatment and distribution. This crisis has wide-ranging consequences. Economically, it threatens the stability of the agricultural sector, which is a major employer and a key contributor to the nation's GDP. Socially and politically, water shortages can spark unrest and conflicts both within the country and with neighboring nations over shared water resources.

Pakistan is increasingly becoming a water-scarce country with limited options for augmenting its water supply. Historically, policymakers have relied on constructing large dams to store and distribute water. While these dams serve to store water, generate power, and control floods, they also have significant ecological impacts. Beyond dams, other water supply options, such as underground water, rainwater harvesting, recycled or reclaimed water, and storm water management, are available. Addressing the water shortage requires exploring ways to utilize these limited resources effectively. In this context, desalination technologies for treating saline or seawater present a promising solution, offering significant potential to help Pakistan meet its growing water needs.

1.2 The National Water Policy and desalination as a potential solution

The Government of Pakistan has initiated various strategies to address water scarcity, including the construction of new dams and reservoirs, the promotion of water conservation practices, and the development of modern irrigation techniques.

However, implementation remains a challenge due to multiple reasons including financial constraints.

The National Water Policy, introduced in 2018, aims to address the country's water challenges by promoting integrated water resource management, enhancing water storage capacity, and improving water use efficiency across all sectors. An important aim of the National Water Policy is to enhance water availability fixing quantifiable targets for the additional water storage through large, medium, and small dams, recycling used waters, desalinization of seawater, and more efficient water use with a timeline and estimated resources required over the next 12 years i.e. by 2030. The policy has also emphasized that desalinization of seawater is a significant source of water and aimed that in a remote area of the country, solar desalination of water will be promoted to provide the communities safe drinking water. However, no effort has been made for desalinization in the light of technology advances and international best practices.

2. How desalination can augment Pakistan's water supply

Desalination is the process of extracting salts and impurities from seawater or brackish water to produce freshwater for drinking, agriculture, or industrial purposes, and it is especially crucial in water-scarce regions like arid or coastal areas. Desalination removes salt through two primary methods: thermal desalination and membrane desalination. In thermal desalination, water is heated to evaporate and leave salts behind, while in membrane desalination, such as reverse osmosis, water is forced through a semi-permeable membrane that blocks salt molecules, producing freshwater. Around 22,000 desalination plants globally are currently supplying clean drinking water to over 300 million people [16]. Following the same, desalination process presents a significant opportunity for addressing Pakistan's escalating water crisis. With its long Arabian Sea coastline and rapidly depleting freshwater resources, desalination could provide a sustainable solution to meet the increasing demand for water across domestic, agricultural, and industrial sectors. To overcome water scarcity challenge, a comprehensive approach is needed, including improved water management practices, strategic investment in infrastructure, and the adoption of alternative water sources like desalination. Sustainable water use and enhanced water governance are essential to safeguarding Pakistan's future water security.

In terms of health, desalination could provide safe drinking water to 61% of the Pakistan's population currently lacking access to clean water [8, 9]. Expanding desalination infrastructure could also bolster economic resilience, creating jobs in construction, operation, and maintenance. For instance, construction of the Carlsbad Desalination Project, San Diego, California, created an estimated 2500 jobs and injected approximately USD 350 million into the local economy [17]. In operational phase, the plant sustains around 36 full-time employees and supports an additional 124 indirect jobs [17]. Desalination can play a key role in supporting agriculture by irrigating arid lands, which are essential for the livelihoods of rural communities dependent on farming. Pakistan's major deserts—Thar, Cholistan, Thal, Kharan, and Chagai—cover 11 million hectares and remain largely barren due to water scarcity and low rainfall [18]. Introducing solar desalination technologies could transform these areas, enabling agricultural irrigation, boosting crop yields, and fostering economic stability in rural regions.

In addition to supporting agriculture, desalination can meet the industrial sector's growing water demands, reducing reliance on over-exploited groundwater. It also enhances public health by providing safe drinking water and improving sanitation, particularly as climate change intensifies water stress. Water disparities across Pakistan's provinces further complicate the issue, with Punjab consuming a significant share of resources for irrigation while Sindh and Balochistan face shortages. Coastal cities like Karachi are increasingly vulnerable as traditional water sources struggle to meet demand. Desalination offers a sustainable solution to address these pressing challenges.

In summary, desalination represents a crucial avenue for addressing Pakistan's water crisis, with significant environmental, economic, and health benefits. Strategic investment in this technology could transform Pakistan's water security landscape and contribute to sustainable development.

3. An overview of desalination technology

Desalination technology refers to the processes used to remove salts and other impurities from seawater or brackish water to produce freshwater suitable for human consumption, agriculture, and industrial use. Desalination technologies can be broadly categorized into two main types: *Thermal* and *Membrane-based* processes. A comparative overview of most prominent desalination technologies under these two categories is given as **Table 2**. This table highlights the process descriptions, energy efficiency, cost ranges, and typical applications for each desalination technology.

Reverse Osmosis (RO) stands out as the most widely used desalination technology, effectively removing up to 99% of dissolved salts by pushing seawater through a semi-permeable membrane. It is cost-effective, with prices ranging from USD 0.60 to USD 1.50 per cubic meter of freshwater produced, and offers good energy efficiency. While there are promising advancements in desalination technologies that are still developing or limited in scale, recent improvements in RO technology have significantly enhanced its efficiency and sustainability. Key innovations, such as energy recovery devices, have notably reduced energy consumption by capturing and reusing energy from the high-pressure brine stream. These advancements not only lower operational costs but also improve the overall performance of RO systems [23]. In addition to energy recovery advancements, the development of advanced membranes has been pivotal in enhancing desalination performance. Researchers are exploring new materials, such as nanotechnology-based membranes and graphene, to improve membrane longevity and efficiency. These innovations address many of the longstanding challenges in desalination, offering the potential for more effective and durable solutions [24].

Thermal Desalination, encompassing methods like Multi-Stage Flash (MSF) and Multi-Effect Distillation (MED), is highly effective but requires significant energy, leading to costs ranging from USD 1.50 to USD 4.00 per cubic meter. This high energy demand is a key factor in its expense. Electrodialysis (ED) and Electrodialysis Reversal (EDR) use electric fields to separate salt ions from brackish water, with costs between USD 1.00 and USD 3.00 per cubic meter. While these methods are less cost-effective for seawater desalination compared to Reverse Osmosis (RO), they are suitable for brackish water applications. Thermal processes, such as MSF, MED, and Vapor Compression (VC), achieve high Total Dissolved Solids (TDS) removal rates of 98–99%, similar to RO, which

Desalination method	Process description	Salts' removal efficiency	Energy efficiency	Cost per cubic meter (USD)	Typical applications	References
Reverse Osmosis (RO)	Seawater is forced through a semi-permeable membrane that allows water to pass while blocking salts and impurities.	95–99%	High	0.6–1.5	Seawater desalination, large-scale water supply	[19]
Thermal Desalination	Seawater is heated to produce vapor, which is then condensed into freshwater. This includes Multi-Stage Flash Distillation (MSF), Multi-Effect Distillation (MED), and Vapor Compression (VC) methods.	98–99%	Low to moderate	1.5–4.0	Areas with access to waste heat or abundant energy	[20, 21]
Electrodialysis (ED) and Electrodialysis Reversal (EDR)	Electric fields drive salt ions through ion-exchange membranes to separate them from water.	80–95% (varies depending on water salinity)	Moderate	1.0–3.0	Brackish water desalination, niche applications	[22]

Table 2.
Comparison of different desalination technologies.

also removes 95–99% of TDS. Electrodialysis is more appropriate for water with lower salinity. Emerging technologies like Forward Osmosis and solar desalination are being explored for their potential to offer sustainable solutions. The integration of renewable energy sources, particularly solar power, is promising for reducing reliance on fossil fuels in desalination. Solar-powered systems, such as solar stills and solar-assisted RO units, are under research for their potential to provide eco-friendly alternatives, especially in regions with ample sunlight [25]. Additionally, hybrid systems that integrate Reverse Osmosis (RO) with thermal desalination methods are emerging as effective strategies to enhance efficiency and adapt to varying water qualities and energy availabilities. These hybrid approaches combine the strengths of both technologies, offering a reduction in overall costs while improving flexibility and adaptability. By leveraging the benefits of RO and thermal processes, these systems can optimize performance across different operational conditions and resource constraints [26, 27].

4. Case studies of successful desalination projects

The global landscape of desalination technology is exemplified by several notable plants, each demonstrating unique strengths. The World Resources Institute (WRI) has scored and ranked future water stress—a measure of competition and depletion of surface water—in 167 countries by 2020, 2030, and 2040 [28]. WRI found that there are 17 countries listed in the category of suffering from extremely high baseline water stress, such as; Qatar, Israel, Lebanon, Iran, Jordan, Libya, Kuwait, Saudi Arabia, Eritrea, United Arab Emirates, San Marino, Bahrain, India, Pakistan, Turkmenistan, Oman, and Botswana [28]. Consequently, some of these countries, such as Saudi Arabia, UAE, Israel, Spain, and Australia, are now global leaders in desalination, having developed advanced infrastructure and technologies to meet their freshwater needs. These countries have invested heavily in desalination plants, and their success is driven by water scarcity, economic resources, and technological expertise. The key features of desalination models developed by these countries are tabulated as **Table 3**.

The Jebel Ali Desalination Plant in the UAE, one of the largest in the world, employs Multi-Stage Flash (MSF) technology to meet Dubai's significant water demand, while Israel's Ashkelon Plant showcases the scalability of Reverse Osmosis (RO) in providing potable water. Likewise, Australia's Perth Seawater Desalination Plant combines RO with renewable energy, reducing environmental impact. Saudi Arabia, reliant on desalination since the 1970s due to limited freshwater resources, has invested heavily in large-scale MSF, Multi-Effect Distillation (MED), and RO plants, establishing itself as a leader through initiatives like Vision 2030. However, desalination remains energy-intensive and contributes to CO₂ emissions, driving Saudi Arabia to explore solar-powered solutions. Globally, RO technology is the most cost-effective and widely adopted method for large-scale desalination, as evidenced by projects in Carlsbad (USA) and Perth (Australia), while thermal processes like MSF are more prevalent in energy-subsidized regions like the UAE. Despite its success, desalination presents environmental challenges, such as brine disposal and high energy consumption. Saudi Arabia, with its vast desalination infrastructure, is focusing on brine concentration and exploring the extraction of valuable minerals like magnesium and lithium, aligning with its Vision 2030 economic goals. In the UAE, plants like Jebel Ali utilize zero-liquid discharge (ZLD) systems and dilution techniques,

Desalination facility	Location	Capacity	Technology	Key feature	Success factors	References
Sorek Desalination Plant	Sorek, Israel	624,000 cubic meters/day	Reverse Osmosis (RO)	State-of-the-art membrane technology and energy recovery	Advanced technology, efficient energy use	[29]
Carlsbad Desalination Plant	Carlsbad, California, USA	189,000 cubic meters/day	Reverse Osmosis (RO)	Largest in the U.S., energy-efficient RO technology	Robust infrastructure, significant energy savings	[30]
Jebel Ali Desalination Plant	Jebel Ali, Dubai, UAE	300,000 cubic meters/day	Multi-Stage Flash (MSF)	Uses waste heat from power generation	Integration with power plants, efficient use of waste heat	[31]
Al-Hidd Desalination Plant	Al-Hidd, Bahrain	200,000 cubic meters/day	Multi-Effect Distillation (MED)	Advanced thermal desalination techniques	Effective use of thermal energy, high production capacity	[32]
Tamaulipas Electrodialysis Plant	Tamaulipas, Mexico	8000 cubic meters/day	Electrodialysis (ED)	Efficient for brackish water treatment	Adaptability to brackish water, lower operational costs	[33]
Gulf Coast Electrodialysis Plant	Gulf Coast, Texas, USA	5000 cubic meters/day	Electrodialysis Reversal (EDR)	Focuses on brackish water treatment	Low energy requirements, cost-effectiveness	[34]
Hadera Desalination Plant	Hadera, Israel	127,000 cubic meters/day	Hybrid (RO and Thermal)	Combines RO and thermal desalination technologies	Synergy of technologies, balanced cost, and efficiency	[35]
Ras Al Khair Desalination Plant	Ras Al Khair, Saudi Arabia	1,025,000 cubic meters/day	Multi-Effect Distillation (MED)	One of the largest desalination plants in the world, integrates MED with RO	Large scale, integration of multiple technologies	[36]
Perth Seawater Desalination Plant	Perth, Australia	140,000 cubic meters/day	Reverse Osmosis (RO)	Significant contribution to Perth's water supply	Consistent supply, integration with local infrastructure	[37]
Tarragona Desalination Plant	Tarragona, Spain	100,000 cubic meters/day	Reverse Osmosis (RO)	Provides a substantial portion of Tarragona's water supply	Efficient operation, significant local impact	[38]
Shuwaikh Desalination Plant	Shuwaikh, Kuwait	200,000 cubic meters/day	Multi-Stage Flash (MSF)	One of the largest MSF plants in the region	High production capacity, effective thermal desalination	[39]

Table 3.
Comparative analysis of global desalination facilities.

repurposing brine for industries, such as agriculture and aquaculture. Israel employs dilution and marine dispersion methods at facilities like Ashkelon, ensuring that brine is discharged far offshore to minimize environmental impact. In Australia, the Perth Desalination Plant uses environmental monitoring systems to manage brine discharge, protecting marine ecosystems, while also exploring renewable energy for brine processing. Although these countries are increasingly committed to sustainable desalination, the ongoing need for innovation remains critical to balance freshwater production with effective brine management and minimize ecological harm.

5. Challenges and opportunities for desalination in Pakistan

Desalination presents a viable solution for Pakistan's water scarcity but faces significant challenges. The high capital costs for building desalination plants, often up to USD 1 billion for large-scale projects, and the energy-intensive nature of desalination processes contribute to substantial operational expenses. Securing financing in a developing country with limited resources and high competition for funds is particularly difficult. Additionally, integrating renewable energy to mitigate costs introduces its own technical and financial complexities. Environmental concerns, such as managing concentrated brine and protecting marine ecosystems, also require innovative solutions and rigorous management practices.

Considering Pakistan's water scarcity forecasting reports, desalination represents a compelling solution. The technology can provide a steady supply of potable water for urban centers like Karachi, reducing the strain on over-exploited freshwater resources and offering a consistent alternative. In rural areas, particularly in coastal regions, desalination can improve access to clean drinking water, which is crucial for enhancing public health and supporting agricultural activities. By ensuring a reliable water supply for irrigation, desalinated water can boost agricultural productivity, especially in arid regions where traditional water sources are scarce. Geographical regions of Pakistan, which highlight the potential for desalination to enhance water security across Pakistan's diverse and water-scarce regions, are as listed below:

1. *Karachi and Coastal Sindh*: Severe water shortages and proximity to the Arabian Sea make desalination vital for domestic and industrial needs.
2. *Gwadar and Coastal Balochistan*: Chronic water shortages in Gwadar and nearby coastal areas could be addressed with desalination to support growth and development.
3. *Makran Coastal Belt*: Arid conditions and water scarcity in southern Balochistan highlight the need for desalination to support agriculture and fisheries.
4. *Thar Desert (Sindh)*: Extreme water scarcity could be mitigated with localized desalination plants using brackish groundwater.
5. *Cholistan Desert (Punjab)*: Frequent droughts and water shortages could benefit from desalination technologies for drinking water and agriculture.
6. *Thal Desert (Punjab)*: Limited freshwater resources, particularly in Layyah and Khushab districts, make desalination a viable option to support the sparse population and agriculture.

7. Salt Range (Punjab): Desalination of brackish groundwater could improve water availability in this region with complex geology and limited resources.

Desalination in Pakistan began in the 1970s with small-scale Reverse Osmosis (RO) plants in pharmaceutical industries and a solar still in Gwadar. The first significant medium-scale plant, a 200,000 GPD (gallons per day) brackish water RO facility, was set up at Saindak Copper mines in 1987. By the 1990s, the industry accelerated with installations in industrial zones like Faisalabad and Dera Ismail Khan, where freshwater sources were scarce. Karachi saw its first beach well intake desalination plants in the 1990s, and the country's first thermal desalination plant was introduced in Lahore. By 1996, Pakistan's first Multi-Effect Distillation (MED) plant was installed at Hub, while an RO plant using open seawater intake was constructed in Gwadar in 2002. A detailed description of past, ongoing, and planned key desalination projects is tabulated as **Table 4**.

The 2000s marked a focus on desalination for Karachi's municipal supply, with several planned projects that never materialized due to financial and logistical issues. One such project was the DHA Cogen Plant in 2008, which, despite many attempts, failed to reach full operational capacity. In the last decade, hundreds of small brackish water RO plants were developed in Sindh, particularly in the Thar Desert region, where a solar-hybrid powered BWRO plant was installed to address acute water shortages and groundwater contamination. Despite limited contributions to municipal supply, desalination remains primarily driven by industrial demand, with the installed capacity exceeding 700,000 m³/day by 2020.

The desalination projects listed in **Table 4** reveal both the potential and hurdles in adopting desalination technology. One of the major barriers is the high operational costs and energy inefficiencies associated with current desalination technology. For instance, the Karachi Coastal Desalination Plant, still in tendering phase, aims to supplement water supply for coastal areas, but its reliance on reverse osmosis (RO)—a process notorious for high energy consumption—raises concerns about its long-term viability in a country where energy costs are already burdensome. Similarly, the Karachi DHA desalination plant, which employed electrodialysis (ED), was shut down due to unsustainable operational costs, underscoring the financial difficulties desalination plants face without a reliable and affordable energy supply. Other projects, such as the Karachi Port Trust (KPT) Manora plant and the Thar Desert desalination initiative, face similar difficulties. The KPT Manora plant, although partially operational, struggles with high costs and technical issues that prevent it from reaching full capacity. Meanwhile, the Thar Desert desalination plants, intended to provide water to rural communities, remain mostly unoperational due to limited funding and technological challenges. Additionally, the Gwadar desalination plants, which aim to support the city's rapid urbanization and industrial needs, are delayed by infrastructure and energy-related challenges. These cases demonstrate a larger issue for Pakistan's desalination efforts: although desalination offers a viable solution to water scarcity, the high costs of capital, energy, and maintenance, combined with weak infrastructure, hinder progress.

In Pakistan, the absence of advanced desalination membrane manufacturing technology significantly impedes efforts to tackle the country's escalating water scarcity issues. Despite the growing demand for desalination to convert saline water into freshwater, Pakistan faces challenges with a lack of local expertise and technology for producing high-quality membranes. In a discussion, the Federal Board of Revenue has informed that Pakistan imports pretreatment and RO membranes worth PKR 8 billion annually, leading to increased costs and vulnerabilities in supply

Case study	Location	Technology	Capacity	Objectives	Key considerations	Year of development	Current status	Reasons for unsuccessful cases
Karachi Coastal Desalination Plant	Karachi, Sindh	Reverse Osmosis (RO)	5 MGD	Supplement water supply for coastal areas	Operational issues and high energy costs	Initiated in 2024	Ongoing bidding process	—
DHA Cogen Desalination plant	Karachi Sindh	Electrodialysis (ED)	3 MGD	Improve local water availability	Limited effectiveness and high energy use	2008	Unoperational	High operational costs
Karachi Port Trust (KPT) Manora Water Desalination plant	Manora island	Membrane filtration technology	200,000 to 250,000 gallons of water per day	Improve local water availability	Operational issues and high energy costs	2012	Partially operational	High operational costs
Gwadar Desalination Plants	Gwadar, Balochistan	Reverse Osmosis (RO)	5 MGD	Support rapid urban growth and industrial needs	Sustainability	2021–2024	Under development	—
		Reverse Osmosis (RO)	1.2 MGD	Support rapid urban growth and industrial needs	High operational costs and energy demands	2020	Operational	Infrastructure delays
Thar Desert Desalination plants (750 No.)	Thar Desert, Sindh	Reverse Osmosis (RO)	800,000 gallons per day	Provide water for rural communities	Adaptation to extreme climate conditions	2015	Most are unoperational	Limited funding and technological challenges
Mithi Plant	Mithi, Sindh	Reverse Osmosis	8 million liters	Provide water for rural communities	Solution to water scarcity	2015	Unoperational	Limited funding and high electricity cost

Table 4.
Case studies of desalination models in Pakistan.

chains and maintenance. The country has struggled to establish RO membrane manufacturing facilities due to high capital investment requirements, a shortage of specialized technical expertise, and difficulties in transferring advanced technology. Additional challenges, such as reliance on imported raw materials, competition with established global manufacturers, and the need for compliance with international standards, further complicate these efforts. This technology gap limits the development of customized solutions for Pakistan's specific water quality issues, such as high salinity and fouling-prone conditions, and hampers the creation of cost-effective, innovative solutions.

Addressing above-mentioned challenges requires investing in research and development, partnering with international technology providers, and establishing local manufacturing facilities to advance membrane technology, reduce import dependency, and enhance the efficiency and sustainability of desalination systems in Pakistan. To effectively address these challenges, Pakistan should focus on investing in advanced, energy-efficient desalination technologies and integrating renewable energy sources to reduce costs and environmental impact. Establishing public-private partnerships and securing robust government support through regulatory frameworks and financial incentives are essential for attracting investment and expertise. Managing environmental impacts, especially brine disposal, is crucial for sustainability. By adopting these strategies and learning from successful international projects, Pakistan can develop a sustainable desalination infrastructure to meet its growing water needs.

Pakistan's unique geographic and socioeconomic context creates both opportunities and challenges for desalination projects. Projections show a steady increase in desalination capacity for industrial and power sectors, with municipal use expected to grow by 2040 (**Table 4**). However, the disposal of brine, a byproduct of desalination, poses significant environmental concerns due to its harmful effects on marine ecosystems. Drawing lessons from successful projects, such as the Perth Seawater Desalination Plant in Australia, which integrates renewable energy sources, offers a way to mitigate the high energy costs of desalination while addressing environmental impacts.

Localized desalination units powered by renewable energy, like solar power, could effectively improve water availability in Pakistan's arid regions, such as Cholistan and Thar. Despite the promise of desalination, significant investment in infrastructure, research, and community engagement is essential to overcome the current challenges. Without such strategic planning and investment, high capital costs, energy inefficiencies, and environmental risks will continue to hinder the viability of desalination projects in Pakistan.

6. Conclusions and recommendations

Pakistan is experiencing fast paced water scarcity as a result of rapid population growth, groundwater depletion, inefficient water use, and the impacts of climate change. Despite the fact that desalination presents a viable solution, present initiatives are constrained by high operating expenses, reliance on imported membranes for technology, insufficient energy efficiency, and technical capacity. The majority of currently operating plants are small-scale, unsustainable and/or partially operational. It is high time to learn and benefit from examples around the world, including Saudi Arabia, UAE, Turkey, and Australia, which has successfully demonstrated that desalination can be successful when combined with cutting-edge technologies, renewable

energy, and efficient brine management. To establish desalination as a practical long-term solution for water security in Pakistan, obstacles like high capital and energy costs, environmental risks, and limited local capacity should be addressed. In this context, the review chapter has enabled to come up with following key strategies:

This is high time when public and private sectors need to engage extensively and work together and look into different ways to fund desalination so that the high initial costs can be spread out over time. Using renewable energy, especially solar and wind, to power desalination plants will lower costs even more and make us less reliant on fossil fuels. Setting up national centres of excellence for membrane manufacturing research will help Pakistan make better membranes and hybrid desalination systems that are better suited to its unique water quality problems. In addition to improving technology, targeted training programs for engineers, scientists, plant operators, and policy planners are also important for improving the technical and managerial skills needed to run a plant effectively. Making and enforcing safe brine should also be a top priority for environmental sustainability. By implementing these recommendations, Pakistan is expected to effectively address its water scarcity issues and ensure the long-term success of desalination systems. A coordinated effort involving government, industry, academia, and international partners will be crucial for achieving sustainable water management.

Acknowledgements

The contribution of Pakistan Council of Research in Water Resources in terms of data provision is highly acknowledged. The authors acknowledge the use of Grammarly Premium (AI tool) for language polishing of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

Author details

Hifza Rasheed* and Muhammad Dilshad Arshad
Pakistan Council of Research in Water Resources, Islamabad, Pakistan

*Address all correspondence to: pcrwr2005@yahoo.com

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Water Allocation Rules in Semi-Arid Zones of Chile

Pablo Álvarez, Sebastián Norambuena, Carlos Villalobos and Pablo Tello

Abstract

The Coquimbo Region, located in the semi-arid zone of Chile, faces significant challenges due to the reduction in water availability, exacerbated by a megadrought since 2010. In this region, precipitation is concentrated in winter, and during the drought, there has been an annual deficit between 25% and 40%. The Chilean Water Code establishes that water rights are granted to private owners, who gather in Water User Organizations (WUOs) to manage and distribute water resources. The water demand in the Elqui River Basin is primarily allocated to agriculture (83%), followed by mining (4%) and human consumption (12.7%). As a result, water distribution is primarily focused on agricultural activity. The implementation of hydrological and water management models has allowed for the evaluation of the impact of different water allocation rules on irrigation demand coverage and water security in climate change scenarios. The results of these models show that flexibility in distribution leads to better outcomes in demand coverage and irrigation security in the region, even under the most severe climate change conditions.

Keywords: water security, climate change, water management, irrigation demand coverage, reliability, water rights

1. Introduction

In the context of arid and semi-arid regions worldwide, the Coquimbo Region (32–29°S) is in the semi-arid zone of Northern Chile (Norte Chico), serving as a transition area between the hyper-arid Atacama Desert and the more mesic Mediterranean climate of central Chile. It borders the Pacific Ocean to the west, while to the east, the topography rises into the Andes Mountains, reaching elevations above 5000 meters above sea level. The region is traversed from east to west by three major hydrographic basins: Elqui, Limarí, and Choapa, which provide water for irrigated agriculture. Its climate is Mediterranean, with precipitation concentrated in winter (May to September), during which 93% of the annual rainfall occurs. One of the region's main challenges is the significant reduction in water availability [1, 2]. Since 2010, the Coquimbo Region, particularly the Elqui River Basin, has experienced a series of dry years, with annual precipitation deficits ranging between 25% and 40% [3]. This phenomenon, known as megadrought, has persistently affected Chile's arid

regions, increasing in both duration and territorial extent [4]. In recent years, the exceptionally prolonged drought has altered expectations regarding climatic variability in the region, drastically reducing reservoir levels and sustainably impacting water supply [5]. Additionally, recent studies indicate a trend toward longer dry periods, which could intensify the magnitude of these extreme events and their economic consequences in the future [6].

Article 1 of the Chilean Water Code (1981, 2005, 2022) regulates continental waters, including both surface and groundwater. In practical terms, water use rights are private, and those allocated for agriculture, human consumption, and industrial or mining activities are classified as permanent consumptive rights [7]. Until 2022, the Water Code did not establish priorities for the distribution of these rights. However, following its latest amendment, in cases of extreme drought, priority must be given to human consumption. Currently, this modification is in the implementation process [8]. Water distribution is carried out proportionally to water use rights, whose owners form non-profit private organizations called Water User Organizations (WUOs). These entities are responsible for managing and distributing water resources among the holders of water use rights [9].

The sustainable management of water resources in arid and semi-arid regions is one of the most critical environmental challenges globally [10]. These regions, with limited water availability, face challenges such as unequal distribution, overexploitation, waste, and the degradation of the water environment [11]. In water-scarce contexts, ensuring an equitable distribution of water is essential. Equity is achieved through mechanisms that ensure a uniform allocation of the resource, whereas prioritizing certain demands may lead to inequalities [12]. To enhance supply security and regional water management, optimal allocation models have been developed to enable a more efficient distribution [13].

In the agricultural sector, integrated approaches promote increased productivity and sustainable development by balancing water resource use with economic and ecological factors [14]. Additionally, cooperation among users and efficient demand management optimize water use, benefiting arid and semi-arid regions [15]. The main challenge lies in the agricultural sector, which holds the largest share of water use rights and represents the highest demand for the resource. Therefore, water distribution must be closely related to the quantity, type, and location of crops, as well as potential evapotranspiration and precipitation [16]. The ability to meet this demand, measured through irrigation coverage, is influenced by two main factors: (i) the water balance, affected by climate change, and (ii) the adaptation of water supply to demand. In this case, resource distribution can be based on two approaches: a fixed value for the entire season (static factor) or a variable value throughout the season (dynamic factor). It is proposed that the water distribution strategy, whether static or dynamic, directly impacts demand coverage and, consequently, the water security of agriculture.

To this end, it is proposed to evaluate the impact of two water allocation rules in an arid zone with strong agricultural influence, considering the context of climate change. The analysis will focus on their effect on irrigation demand coverage and water security.

2. General background of the study area

2.1 Geographical location

The study area corresponds to the Elqui River Basin (**Figure 1**), located in Elqui Province, Coquimbo Region, Chile. It is situated in a semi-arid zone, characterized by

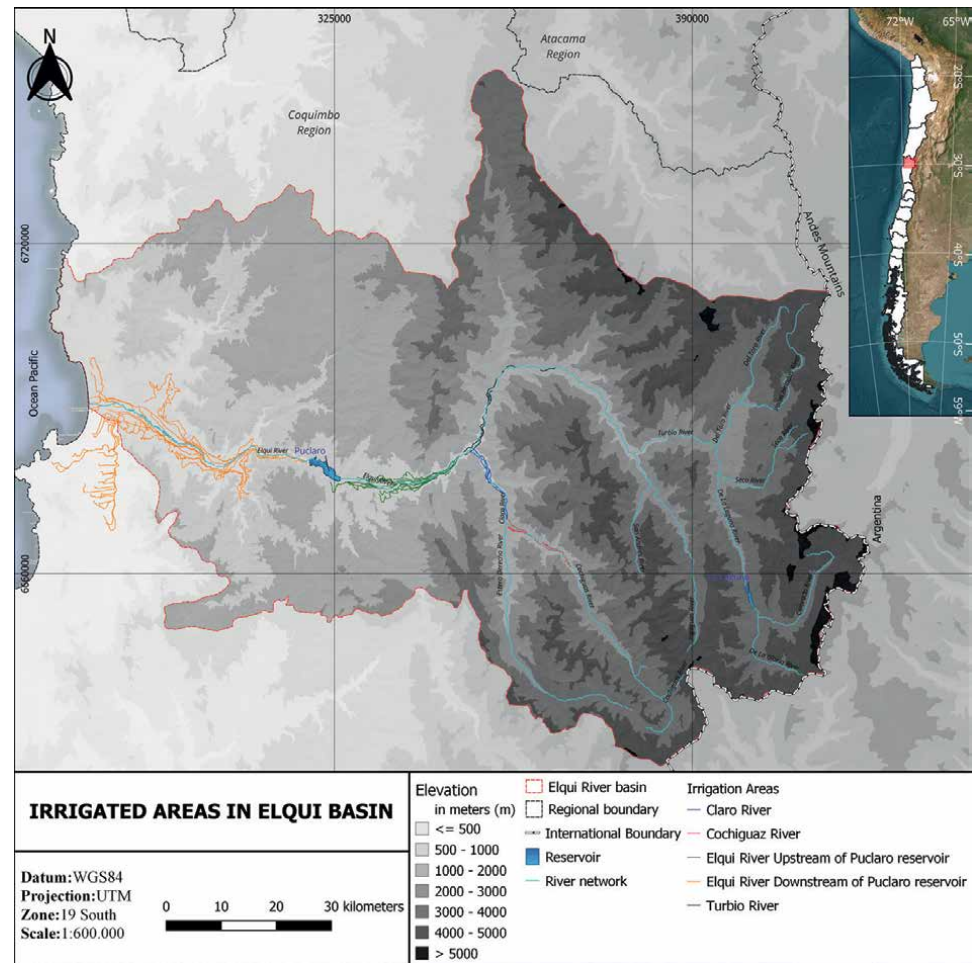


Figure 1.
Study area, Elqui River Basin, and its irrigation areas.

a dry climate and a strong dependence on water for agricultural activities. The basin is regulated by reservoirs, which influence the availability and distribution of water resources. Geographically, it is located between 29°34' and 30°27' south latitude and 71°22' and 69°52' west longitude. It borders the Atacama Desert and the Huasco River Basin, as well as the Los Choros, Honda, and Chacay ravines to the north; the Limarí River Basin and the coastal basins of El Culebrón and Lagunillas ravines to the south; the Andes Mountains and the Republic of Argentina to the east; and the Pacific Ocean to the west [17]. The Elqui River Basin is subdivided into five irrigation sectors: Claro River, Cochiguaz River, Turbio River, Elqui River upstream of Puclaro Reservoir, and Elqui River downstream of Puclaro Reservoir. Each of these sectors has distinct hydrological characteristics that influence the management of the water resource.

2.2 Hydroclimatic characteristics

The Elqui River Basin has a semi-arid climate [16], with seasonal precipitation characteristic of the Mediterranean climate, with 80% of the rainfall occurring

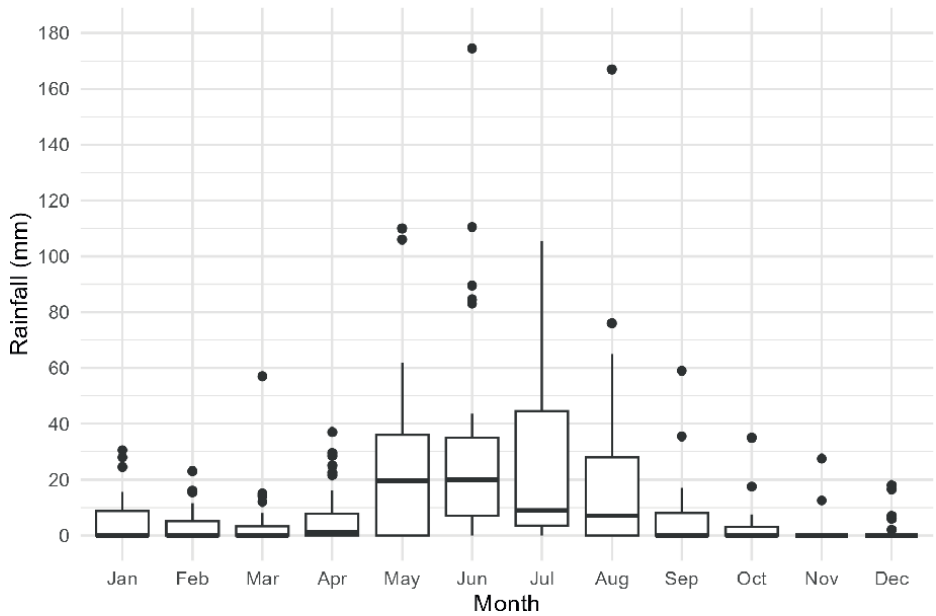


Figure 2. Monthly rainfall at La Laguna reservoir, 1990–2020 (3300 m.a.s.l.). (Source: <https://dga.mop.gob.cl>).

between June and August (Austral winter) (**Figure 2**) [18]. Although the annual precipitation trend (1990–2020) in the upper basin shows a decline, it is not statistically significant ($p \leq 0.05$), consistent with observations in the Coquimbo Region [16].

Figure 3 shows the distribution of average monthly temperatures recorded between 1990 and 2020 at the La Laguna Reservoir meteorological station, located at an altitude of 3300 m.a.s.l. It is observed that the months of June, July, and August have the lowest temperatures of the year ($<5^{\circ}\text{C}$), with July being the coldest month,

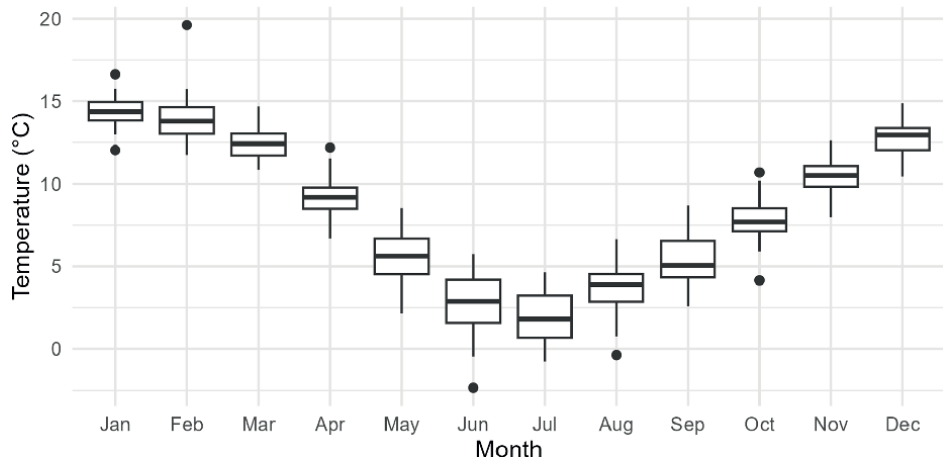


Figure 3. Monthly distribution of average temperatures at the La Laguna Reservoir station, 1990–2020 ($^{\circ}\text{C}$) (3300 m.a.s.l.). (Source: <https://dga.mop.gob.cl>).

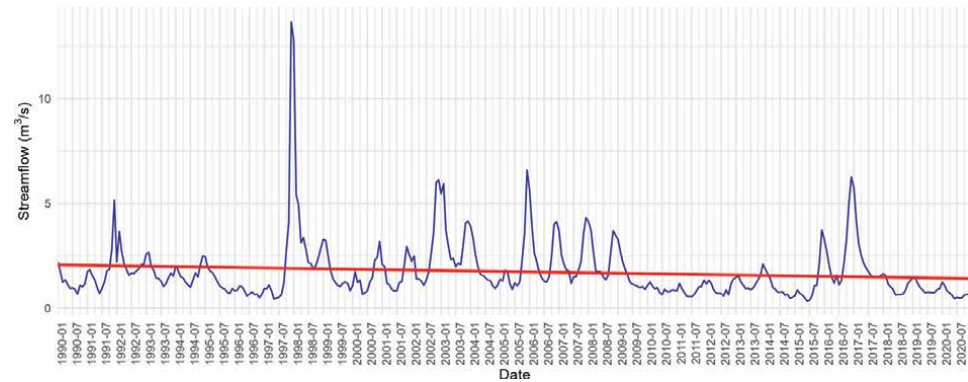


Figure 4.
Streamflow upstream La Laguna Reservoir (3300 m.a.s.l.). (Source: JVRE).

reaching values even below 0°C. In contrast, during January and February, average temperatures range between approximately 12 and 17°C.

The inflow of the La Laguna Reservoir exhibits high seasonal variability [19] and shows a statistically significant decreasing trend, like other gauging stations in the Coquimbo region (**Figure 4**) [16].

2.3 Characterization of water demand

In the Elqui River Basin, 83% of the water is allocated to agriculture, 4% to mining, and 12.7% to human consumption, with urban demand exceeding rural demand (**Figure 5**) [20].

The irrigation demand in the Elqui River Basin consists mainly of deciduous and evergreen fruit trees in the irrigation areas upstream of Puclaro Reservoir, where seasonal demand predominates, with table grapes being the main crop [21, 22].

In the areas downstream of Puclaro Reservoir, short-cycle crops, primarily potatoes, predominate [22], while fruit production is dominated by evergreen species. Irrigation demand varies over time and space, being higher in the irrigation areas upstream of Puclaro Reservoir due to greater atmospheric demand, according to CAMELS-CL data (**Figure 6**) [23].

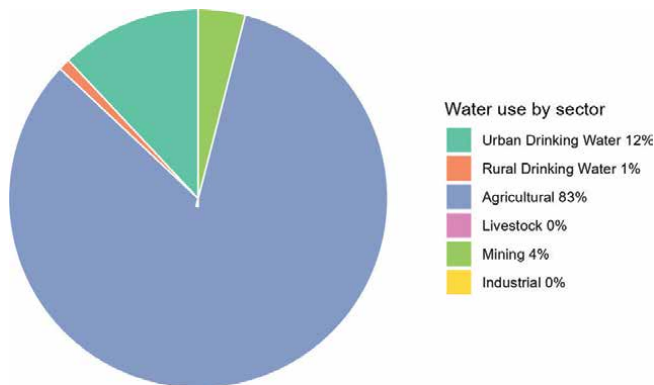


Figure 5.
Water use by sector in the Elqui River basin.

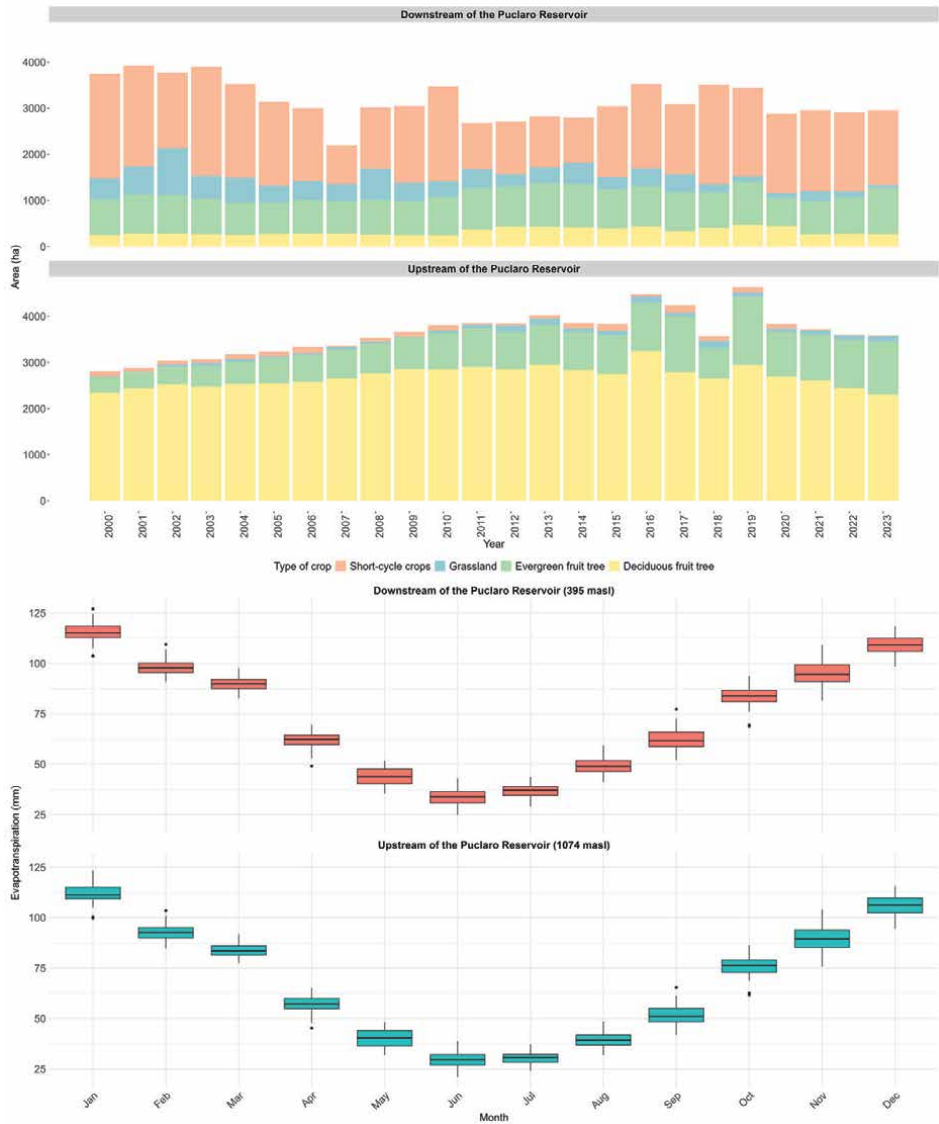


Figure 6. Characteristics of irrigation demand. On the left, the crop composition in the area is shown, while on the bottom, atmospheric demand information is presented.

3. Water allocation rules

The water allocation rules are established by private entities known as Water User Organizations (WUOs), which are regulated by the Water Code [7] and are hierarchically organized according to the surface water source they manage. Within this framework, WUOs are divided into “Juntas de Vigilancia” (Surveillance Boards), responsible for managing natural watercourses, and “Comunidades de Agua” (Water Communities - WCs), in charge of administering artificial watercourses or irrigation canals.

In the study area, the WUO is the Junta de Vigilancia del Río Elqui y sus Afluentes (JVRE). It manages the Elqui River watercourse and distributes water to

118 Water Communities (WCs), each holding water use rights and responsible for managing an irrigation canal within its cultivation zone. In total, the JVRE manages approximately 25,342 water use rights shares. Each share represents a proportional fraction of the available water for the season, with a maximum value of 1 L/s per share.

Each irrigation season, the JVRE determines the flow allocation (L/s) per water use right, following a water distribution rule based on regulations agreed upon by the users themselves. In this process, the Board of Directors, composed of seven elected members within the organization, prepares an allocation proposal, which is then presented to the Assembly of water rights holders. Finally, the assembly determines the water resource distribution for the season.

3.1 Static water allocation rule

Water allocation is determined based on the water availability in the basin, considering the reservoir volume at the beginning of the season and the river flow throughout the period. Based on these factors, the total available volume is established and distributed according to the water use rights managed by the JVRE.

For the hydrological season, a fixed value is assigned, known as “Desmarque,” which corresponds to a proportional fraction of the available water for distribution. The JVRE is responsible for ensuring the delivery of the water at each Water Community (WC) intake point.

3.2 Dynamic water allocation rule

Water allocation is carried out according to the pre-established rule; however, water delivery is adjusted based on the irrigation demand curve for each sector—Claro River, Cochiguaz River, Turbio River, Elqui River upstream of Puclaro Reservoir, and Elqui River downstream of Puclaro Reservoir—allowing for a distribution adapted to the seasonal variability of demand throughout the irrigation season.

4. Hydrological models and water allocation models in Elqui River basin

To achieve the research objectives, three hydrological models were developed at a monthly scale to generate streamflow in the La Laguna River, Cochiguaz River, and Estero Derecho sub-basins. These models provide streamflow inputs for a water allocation model in the Elqui River Basin, considering different climate change scenarios.

The models were implemented using the water evaluation and planning system (WEAP) software, developed by the Stockholm Environment Institute [24]. Calibration was assessed through goodness-of-fit measures, following the classification proposed by Moriasi (**Table 1**) [25].

4.1 Hydrological models

Three hydrological models were developed and calibrated for the generation of surface runoff in the headwater sub-basins of the Elqui River Basin: Estero Derecho at Alcohuez, Cochiguaz River at El Peñón, and La Laguna River at the inflow of La Laguna Reservoir. The modeling was conducted using the Rainfall-Runoff method (Soil Moisture Model).

PBIAS	NSE	RSR	Performance rating
$\text{PBIAS} < \pm 10$	$0,75 < \text{NSE} \leq 1,00$	$0,00 < \text{RSR} \leq 0,50$	Very good
$\pm 10 \leq \text{PBIAS} < \pm 15$	$0,65 < \text{NSE} \leq 0,75$	$0,50 < \text{RSR} \leq 0,60$	Good
$\pm 15 \leq \text{PBIAS} < \pm 25$	$0,50 < \text{NSE} \leq 0,65$	$0,60 < \text{RSR} \leq 0,70$	Satisfactory
$\text{PBIAS} \geq 25$	$\text{NSE} < 0,50$	$\text{RSR} > 0,70$	Unsatisfactory

Table 1.
General performance ratings for recommended statistics for a monthly time step.

For each model, the drainage area was spatially delineated before incorporating the river channel. Subsequently, catchments were added, considering the number of altitudinal zones and the north-south orientation of each area. This process was carried out by reclassifying the Digital Elevation Model (DEM) of the sub-basin into 500-meter altitude intervals.

The catchments were then linked to the river channel through the runoff/infiltration connection, which represents runoff and subsurface water movement leaving each node. Finally, the control streamflow station was incorporated using the Streamflow Gauge element. All these components are schematically represented in **Figure 7**.

Each catchment incorporates climatic and land use information corresponding to the sub-basin of the hydrological model. Subsequently, the model was calibrated using control station data over a 25-year period (1990–2015).

Table 2 presents the goodness-of-fit test results for the hydrological models at the three control points: Estero Derecho at Alcohuaz, Cochiguaz River at El Peñón, and La Laguna River at the inflow of the La Laguna Reservoir. Nash-Sutcliffe Efficiency (NSE): The obtained values range between 0.857 and 0.896, indicating a “Very Good” performance at all monitoring stations. Percentage BIAS (PBIAS): Values ranged between -4.90% and 4.30% , indicating a low deviation between simulated and observed values, with a “Very Good” performance classification in all cases. Root Mean Square Error to Standard Deviation Ratio (RSR): Values varied between 0.323 and 0.377, also corresponding to a “Very Good” performance at all monitoring stations.

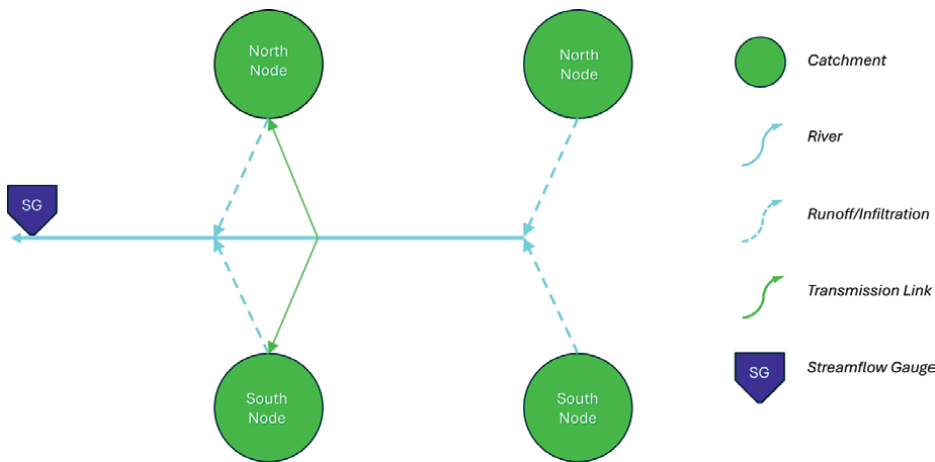


Figure 7.
Schematic representation of the topology of the hydrological model.

Statistics	Estero Derecho at Alcohuz		Cochiguaz River at El Peñón		La Laguna River at the inflow of the La Laguna Reservoir	
	Value	Performance rating	Value	Performance rating	Value	Performance rating
NSE	0.891	Very Good	0.896	Very Good	0.857	Very Good
PBIAS	−3.3%	Very Good	−4.9%	Very Good	4.3%	Very Good
RSR	0.33	Very Good	0.323	Very Good	0.377	Very Good

Table 2.
Statistics applied to hydrological models of Elqui River basin.

Figure 8 compares the observed and simulated monthly average flows of the hydrological models in the sub-basins of the Elqui River between September 1990 and August 2015. The stations are Estero Derecho at Alcohuz (EDA), Cochiguaz River at El Peñón (CREP), and La Laguna River at the inflow of the La Laguna Reservoir (LLR). The observed data are shown as blue lines, while the simulated data are represented by red dots.

It is observed that streamflow increases significantly during snowmelt, reflecting the seasonality of the hydrological regime. The models accurately capture these seasonal variations, which are notable in their calibration, as indicated by the applied statistical measures (**Table 2**).

4.2 Water management model

The modeling period covers a time series from 1991 to 2020, with a monthly time step. The hydrological season begins in September and ends in August of the following year, aiming to accurately represent the water management conducted by the JVRE.

The management model topology was generated based on water demand nodes for each water community under the administration of the JVRE. Additionally, these nodes were linked to the natural watercourse, according to the number of water rights assigned to each water community, with limits established based on the allocation determined by the organization each season.

Each demand node represents the maximum irrigation demand of the 118 Water Communities (WCs) in the study area, corresponding to the 2016 season, calculated according to FAO 56 [26]. The agricultural surface data were obtained from the study Generation and Implementation of a Program for Agricultural Soil Monitoring and Land Use Planning, conducted by the University of La Serena [27]. Meanwhile, the crop coefficients (K_c) by crop group and the potential evapotranspiration of the basin were derived from the hydrological model [28].

The satisfaction of irrigation demand in the model depends on irrigation demand and its monthly distribution, the water rights assigned to each Water Community (WC), and the water supply delivered at each intake point, following the allocation rule established by the JVRE. For the calibration period, the historical allocation implemented by the Surveillance Board between 1990 and 2020 was used.

Table 3 presents the goodness-of-fit statistics for the calibration and validation of the model, using the historical time series (1990–2015). The model demonstrates a “Very Good” performance [25], with a Nash-Sutcliffe Efficiency (NSE) of 0.75 or higher across all evaluated parameters.

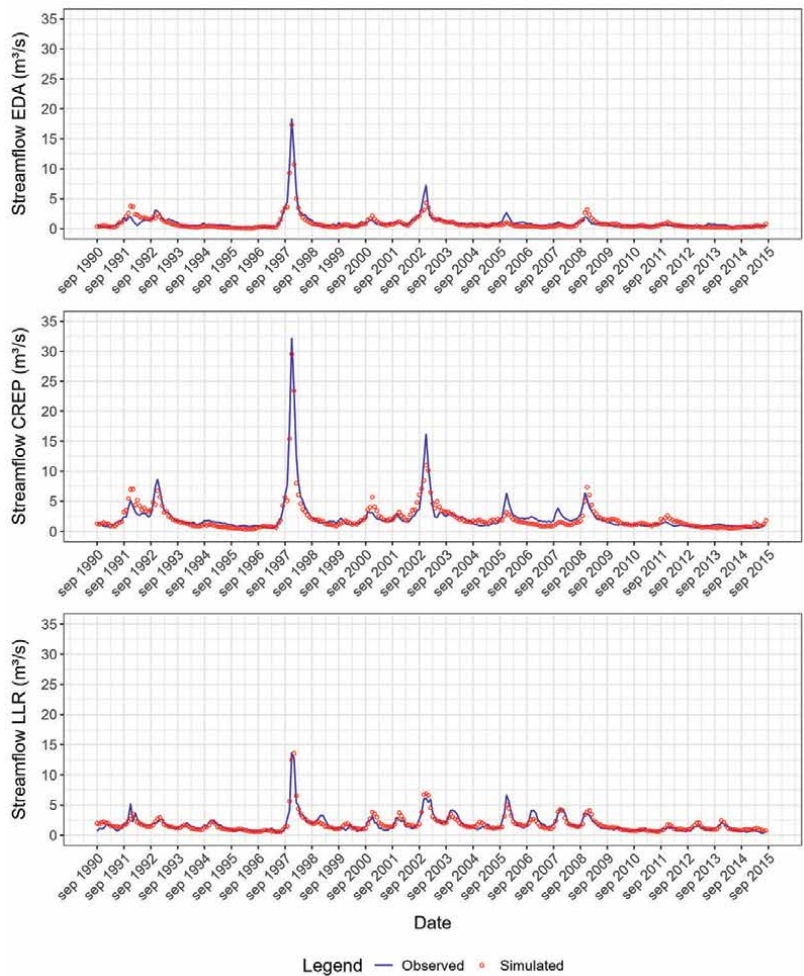


Figure 8. Observed and simulated average monthly streamflow of the Estero Derecho at Alcohuz (EDA), Cochiguaz River at El Peñón (CREP), and La Laguna River at the inflow of the La Laguna Reservoir (LLR) for the period 1990–2015.

Parameters	Statistics						
	NSE	KGE	PBIAS	RSR	RMSE	r	R ²
Claro River at Rivadavia	0.92	0.76	- 15%	0.28	1.3 m ³ /s	0.98	0.96
Turbio River at Varillar	0.92	0.83	-11%	0.28	1.4 m ³ /s	0.97	0.95
Elqui River at Algarrobal	0.86	0.66	-20%	0.37	4.2 m ³ /s	0.97	0.95
Elqui River at Almendral	0.83	0.71	-24%	0.41	3.7 m ³ /s	0.94	0.89
La Laguna Reservoir	0.79	0.68	-3.6%	1.1	9.4 Hm ³	0.82	0.72
Puclaro Reservoir	0.96	0.92	0.8%	0.2	17.0 Hm ³	0.98	0.97

Table 3. Statistics applied to control parameters in water management for the simulated time series between September 1990 and August 2020.

Additionally, the Percentage BIAS (PBIAS) is below 10% for both streamflow and reservoir storage volumes. On the other hand, the Root Mean Square Error to Standard Deviation Ratio (RSR) is 0.5 or lower for all parameters, except for the storage volume in La Laguna Reservoir, where an RSR of 1.1 is recorded.

Figure 9 shows the observed and simulated monthly average flows from the water management model of the Elqui River basin at the gauging stations of the Claro River at Rivadavia (CRR) and the Elqui River at Algarrobal (ERA), as well as the storage of the Puclaro Reservoir (PR) between 1990 and 2020. The observed data are represented by blue lines and the simulated data by red dots.

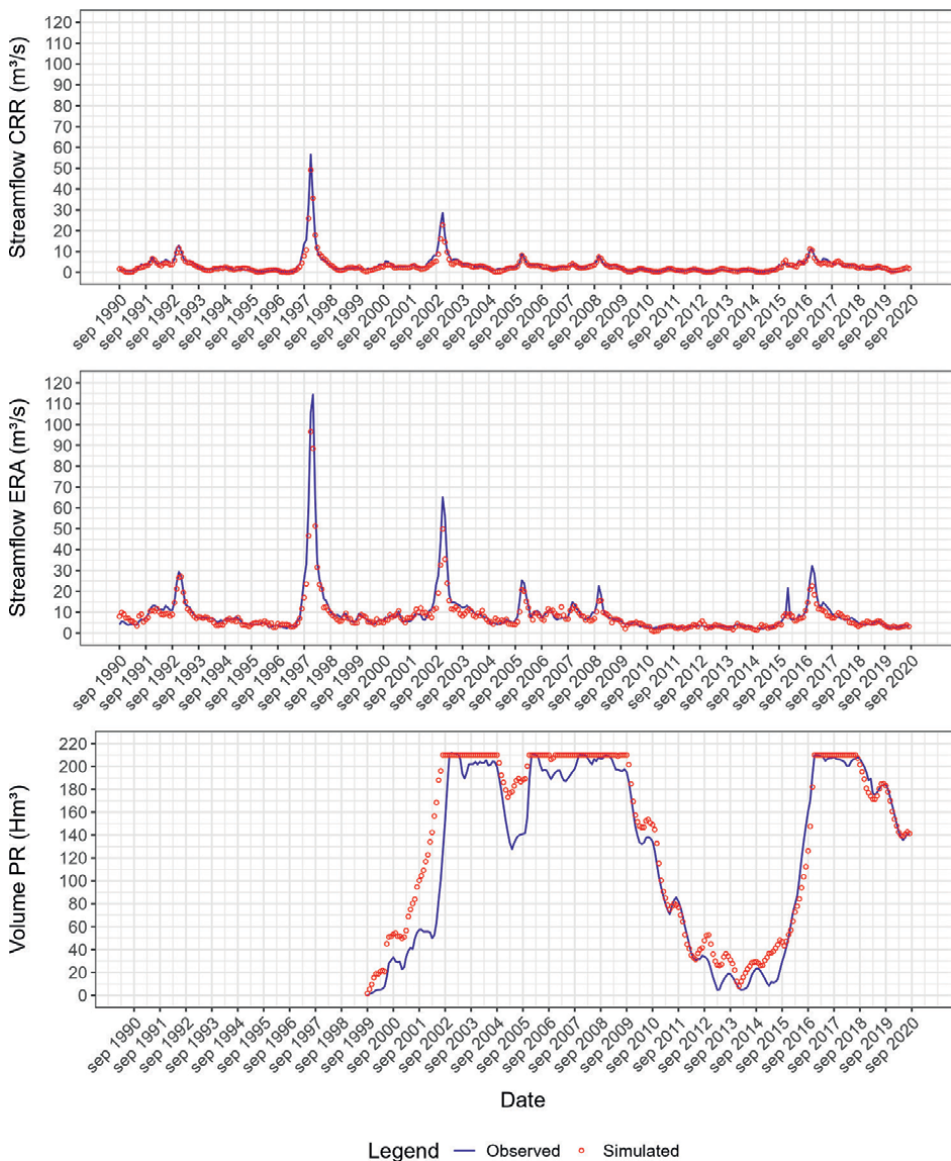


Figure 9.
Observed and simulated average monthly streamflow in Claro River at Rivadavia (CRR), Elqui River at Algarrobal (ERA), and Puclaro Reservoir (PR) for the period 1990–2020.

In CRR and ERA, there is seasonal variability with increases during snowmelt. However, the model performs well in capturing these patterns, although it underestimates some extreme events. In PR, the model accurately represents storage in relation to the observed data, indicating a good representation of its water balance and the incorporation of water allocation rules.

The water management model demonstrates good performance in representing hydroclimatic variability and water allocation rules, reflecting adequate calibration.

4.3 Climate change scenarios

In this study, two medium-term climate change scenarios (2021–2050) were implemented. The first corresponds to the high greenhouse gas emissions scenario (RCP 8.5), while the second represents a lower greenhouse gas emissions scenario (RCP 2.6).

These climate change scenarios were included to evaluate two water allocation rules within the JVRE's water management system, analyzing their impact on water security.

For the generation of climate change scenarios, calibrated hydrological models were used to simulate surface runoff in three headwater sub-basins of the Elqui River Basin: Estero Derecho at Alcohuaz, Cochiguaz River at El Peñón, and La Laguna River at the inflow of La Laguna Reservoir.

The hydroclimatic scenarios were based on temperature and precipitation data simulated by the RegCM4 regional model, available on the (CR)² platform. Data from the stations involved in the hydrological models for water generation were collected.

Based on these climatic variables, two scenarios were generated according to the Representative Concentration Pathways (RCPs) for the period 2021–2050, considering RCP 2.6 and RCP 8.5. The obtained data were incorporated as inputs into the water generation models, allowing for the creation of a flow curve for each scenario, expressed as a monthly mean in m³/s.

These flow scenarios were incorporated to evaluate both static and dynamic water allocation rules, analyzing their impact on agricultural demand coverage and water security across different territories within the Elqui River Basin.

4.4 Water security

To assess the water security of the basin, the indicators coverage and reliability will be analyzed across the five irrigation sectors of the JVRE. The analysis will consider both allocation rules applied to the climate change scenarios RCP 2.6 and RCP 8.5.

4.4.1 Coverage

This indicator represents the percentage of water demand met at each demand site, considering the water balance of each demand node, which in turn represents a water community. Its value ranges from 0% (no supply) to 100% (fully satisfied demand). It is calculated as the average of the time series for the month of peak water demand in each water community within each irrigation area.

In the GHG emission scenarios, RCP 2.6 projects an 18% reduction in basin-generated runoff compared to the historical scenario, while RCP 8.5 estimates an average decrease of 35%.

In both scenarios, the decrease in water availability led to a reduction in demand coverage, as shown in **Tables 4** and **5**. In the RCP 2.6 scenario, the reduction in irrigation coverage is as follows: Claro River: 7.8%; Cochiguaz River: 7.2%; Turbio River: 8.5%; Elqui River upstream of the Puclaro Reservoir: 11.5%; and Elqui River downstream of the Puclaro Reservoir: 11.9%. The greatest reduction is observed in the irrigation zone associated with the Elqui River.

Table 4 presents the percentage of irrigation coverage in different areas under the RCP 2.6 climate scenario, comparing two water allocation approaches: static rules and dynamic rules. The results indicate that irrigation coverage is consistently higher when applying the dynamic rule compared to the static rule. In all evaluated areas, dynamic allocation enhances water availability for irrigation, enabling a more efficient use of the water resource.

Specifically, the highest irrigation coverage is observed in Cochiguaz, where the dynamic rule reaches 87.7%, compared to 81.2% under the static rule. Conversely, the lowest coverage is recorded in Elqui River upstream of the Puclaro Reservoir, with values of 59.1% and 68.0%, respectively. Overall, the implementation of the dynamic rule improves irrigation demand coverage across all areas, with increases ranging from 6% to 9%.

In the RCP 8.5 climate change scenario, irrigation demand coverage shows a reduction compared to the historical period (1991–2021) (**Table 5**), with the following decreases: Claro River: 10.3%; Cochiguaz River: 9.8%; Turbio River: 11.2%; Elqui River upstream of the Puclaro Reservoir: 15.0%; and Elqui River downstream of the Puclaro Reservoir: 15.5%.

Irrigated area	% Coverage – RCP2.6	
	Static water allocation rule	Dynamic water allocation rule
Claro River	78,3	86,3
Cochiguaz River	81,2	87,7
Turbio River	59,3	66,3
Elqui River upstream Puclaro Reservoir	59,1	68,0
Elqui River downstream Puclaro Reservoir	73,7	82,7

Table 4.
Coverage (%) in extended RCP 2.6 scenario underwater allocation rules.

Irrigated area	% Coverage – RCP8.5	
	Static water allocation rule	Dynamic water allocation rule
Claro River	75,8	84,1
Cochiguaz River	78,6	84,9
Turbio River	56,6	62,8
Elqui River upstream Puclaro Reservoir	55,6	64,3
Elqui River downstream Puclaro Reservoir	70,1	79,1

Table 5.
Coverage (%) in extended RCP8.5 scenario underwater allocation rules.

The results indicate that irrigation coverage is higher when applying the dynamic rule compared to the static rule. In all evaluated areas, this strategy optimizes water availability for irrigation, improving demand satisfaction.

Specifically, the highest irrigation coverage is recorded at Cochiguaz, with 84.9% under the dynamic rule, compared to 78.6% obtained with the static rule. On the other hand, the lowest coverage is observed in Elqui River upstream of the Puclaro Reservoir, with values of 55.6% and 64.3%, respectively.

In general, the implementation of the dynamic rule increases irrigation demand coverage across all areas, with improvements ranging from 5–9%. These results highlight the importance of a flexible water allocation strategy to address water challenges in climate change scenarios.

However, in a water deficit scenario, an allocation method based on existing demands could increase coverage by an average of 7.7% across the entire basin. Additionally, the implementation of this strategy, along with the construction of a reservoir in the Cochiguaz area, would allow for an additional 0.6% increase in coverage, compared to the management proposal based solely on a new allocation method.

4.4.2 Reliability

Reliability represents the percentage of time periods in which the demand of a site was fully satisfied, meaning it reached 100% coverage. This indicator is calculated for each water community and is classified according to the established irrigation sectors.

Regarding reliability, the RCP 2.6 climate change scenario shows that areas without regulations present greater security in demand-supply. The Cochiguaz River reaches 79.4% with the static allocation rule, increasing to 82.5% with the dynamic allocation. Similarly, Claro River improves from 76.7% to 82.8% under the same comparison. In contrast, the lowest values are recorded in the Elqui River downstream of the Puclaro Reservoir, with 53.8% and 56.5%, respectively.

The results indicate that the implementation of a dynamic allocation rule improves water availability for irrigation in all evaluated areas. In particular, the increases in reliability are as follows: Claro River: +6.1 percentage points; Cochiguaz River: +3.1 points; Turbio River: +0.9 points; Elqui River upstream of the Puclaro Reservoir: +1.3 points; and Elqui River downstream of the Puclaro Reservoir: +0.3 points.

The dynamic water allocation, based on the agricultural demand curve, optimizes the use of the water resource, especially in areas without storage infrastructure. These results suggest that a more flexible and adaptive management approach is crucial for mitigating the effects of climate change and improving irrigation security (**Table 6**).

In the RCP 8.5 climate change scenario, reliability varies depending on the irrigated area and the water allocation rules. In general, the dynamic allocation rule improves reliability compared to the static rule, suggesting that a more flexible approach to water management can optimize its availability for irrigation.

Cochiguaz and Claro Rivers register the highest reliability values, with 77.3% and 75.2%, respectively, under the static allocation, increasing to 80.6% and 81.8% with the dynamic allocation. In contrast, Turbio River shows intermediate values, with a smaller variation between rules moving from 61.2% to 62.2%.

On the other hand, the lowest reliability values are recorded in Elqui River, particularly in the section downstream of the Puclaro Reservoir, where it varies between 50.4% and 50.7%, depending on the allocation rules. Upstream of the reservoir, the

Irrigated area	% Reliability – RCP2.6	
	Static water allocation rule	Dynamic water allocation rule
Claro River	76,7	82,8
Cochiguaz River	79,4	82,5
Turbio River	63,0	63,9
Elqui River upstream Puclaro Reservoir	56,5	57,8
Elqui River downstream Puclaro Reservoir	53,8	54,1

Table 6.
Reliability (%) in extended RCP2.6 scenario underwater allocation rules.

values are slightly higher (53.6% and 55.2%), although they still reflect a more limited water availability compared to other irrigation areas.

These results indicate that the implementation of a dynamic allocation rule is beneficial in all the sectors analyzed, although its impact varies by location. In areas with less water regulation, such as the Claro and Cochiguaz Rivers, the improvement is more significant, while in the Elqui River sections, the difference is less pronounced, possibly due to limitations in resource availability. Therefore, it is essential to adopt an integrated approach to watershed planning in arid regions, which not only considers interventions on the water supply side but also effective demand management strategies (Table 7) [29].

WUOs must incorporate water allocation rules that maximize the distribution of the resource among their users, optimizing its long-term utilization. However, when the water supply is limited, as in a severe climate scenario (RCP 8.5), the allocation rule alone is not sufficient to improve irrigation security, both in regulated areas and in those without prior regulation infrastructure. This is primarily due to the reduction in streamflow under more extreme climate change scenarios, which directly impacts the functioning of storage structures and the flow of the river downstream [30]. In the arid zone of northern Chile, monthly average flows are the most affected by reservoirs, while in more humid areas, these structures seem to contribute to reducing unsatisfied demand [31]. Reservoir modeling in more humid areas has been shown to improve irrigation resilience during drought periods, enhancing water security in southern Chile.

Irrigated area	% Reliability – RCP8.5	
	Static water allocation rule	Dynamic water allocation rule
Claro River	75,2	81,8
Cochiguaz River	77,3	80,6
Turbio River	61,2	62,2
Elqui River upstream Puclaro Reservoir	53,6	55,2
Elqui River downstream Puclaro Reservoir	50,4	50,7

Table 7.
Reliability (%) in extended RCP8.5 scenario underwater allocation rules.

5. Conclusions

The study demonstrates that the implementation of a dynamic allocation rule significantly improves water security compared to the static rule, increasing irrigation demand coverage by 6–9%. This approach optimizes the distribution of water resources, reducing the impact of water scarcity and adapting better to the variability of demand. In terms of reliability, the dynamic allocation is particularly effective in areas without water regulation, where water availability is more variable. These results highlight the importance of flexible allocation strategies for more efficient and resilient water management in climate change scenarios.

The RCP 8.5 scenario projects a significantly larger reduction in water availability (35%) compared to RCP 2.6 (18%), which negatively impacts irrigation coverage, with decreases of up to 15.5% in the most affected areas. However, the application of a dynamic allocation rule partially mitigates these effects, improving coverage in all irrigation areas. These results emphasize the need for adaptive water management strategies to reduce the impact of climate change on water availability, especially in more extreme scenarios like RCP 8.5.

Acknowledgements

We express our recognition to the “Junta de Vigilancia del río Elqui y sus afluentes” for its support in the research on water allocation rules in the Elqui River basin. Their collaboration has been fundamental to advancing our knowledge and implementing sustainable practices in water resource management.

We also extend our gratitude to the Foundation for Agricultural Innovation (FIA) for their significant financial support for research on water allocation and water management in semi-arid zones.

Author details

Pablo Álvarez^{1,2*}, Sebastián Norambuena², Carlos Villalobos² and Pablo Tello²

1 Departamento de Agronomía, Universidad de La Serena, Coquimbo, Chile

2 Laboratorio de Prospección, Monitoreo y Modelación de Recursos Agrícolas y Ambientales, Universidad de La Serena, Ovalle, Chile

*Address all correspondence to: pabloa@userena.cl

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Endocrine-Disrupting Compound in Mexican Aquatic Environments

*Mario Alfonso Murillo-Tovar, Josefina Vergara-Sánchez,
Hugo Albeiro Saldarriaga-Noreña,
María Luisa García-Betancourt, César Torres-Segundo,
Khirbet López-Velázquez, José Gustavo Ronderos-Lara,
Arquimedez Tolentino-Rojas and Zurisaday Villegas-González*

Abstract

Endocrine-disrupting compounds are compounds of pharmaceutical, lifestyle and industrial origin. The partial remotion of endocrine-disrupting compounds (EDCs) contained in wastewater waste from municipal or industrial origin contributes to their frequent detection in surface water of rivers, lakes and costal zones, as well as they have also been found in groundwater. This chapter contemplates studies of some compounds found in rivers in several environmental compartments in México. The topics that will be included in this chapter involves the detection of traces of EDC in surface and groundwater by chromatographic with mass spectrometric simple and tandem techniques, remotion with nanomaterials, degradation with advanced oxidation processes and risk human exposure and ecological assessment.

Keywords: advanced oxidation, nanomaterials, surface water, pharmaceutical compounds, groundwater

1. Introduction

At a global level, the influence of human activities on the quality and quantity of water resources has grown significantly because of the gradual increase in the world population and the inevitable expansion of sectors such as urban, industrial, mining, livestock and agricultural. The urban sprawl leads to overexploitation of resources and imminent contamination of water bodies, even in areas with low population density; this over time represents a critical problem with serious effects on ecosystems and human health due to the lack of access to quality water [1].

Endocrine-disrupting compounds (EDCs), also known as endocrine-disrupting chemicals, are xenobiotic compounds, such as pharmaceuticals, pesticides, cosmetics, flavoring agents, fragrances, food additives, industrial chemicals and environmental pollutants [2]. EDCs represent a considerable risk in the natural environment,

especially in aquatic ecosystems. For this reason, they have become a key issue within ecotoxicology, making their identification and regulation a priority task [3, 4].

Some of the most frequently mentioned examples of EDCs are: Pesticides (Atrazine, Dichlorodiphenyltrichloroethane (DDT), Methoxychlor (MXC), Vinclozolin and Chlorpyrifos) which are highly soluble in water, toxic and persistent, Detergents and surfactants (Octylphenol, Nonylphenol, Bisphenol A (BPA), triclosan) they are amphiphilic structures featuring a hydrophilic (polar) head and a hydrophobic (non-polar) tail, which regulate their affinity for water and solubility in non-polar substances, respectively, Plasticizers (Phthalates) colorless organic liquids characterized by low volatility and high flexibility, industrial compounds (polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and polycyclic aromatic hydrocarbons (PAHs)) which are highly toxic, pharmaceuticals (cyclophosphamide, vincristine and parabens) they serve as the active component in medications used to treat diseases, natural plant derivatives (coumestrol, genistein, liquiritigenin and phytoestrogens) natural mechanism that plants use to defend themselves against diseases and Heavy metals (arsenic, lead, mercury and cadmium) extremely toxic, widely present in the environment [5].

Water can be contaminated by various human activities; however, one of the main sources of contamination continues to be the direct discharge of wastewater, both treated and untreated, from urban and industrial sectors, as well as leachates from agrochemicals and pesticides used in agricultural production [1, 5]. EDCs enter aquatic ecosystems through a variety of pathways, including wastewater treatment plants (WWTPs) that handle pharmaceutical and medical waste, through the leaching of chemicals from household and industrial products such as detergents and personal hygiene products and pesticide residue from agriculture [6].

Mexico is experiencing a gradual growth in its urban population and industrial areas, which has led to a significant expansion of its agricultural land in recent years, causing serious pollution problems in rivers nationwide. In general, more than 60% of the country's river systems have some type of pollution [7].

An example of contaminated rivers in Mexico is the Atoyac river, located in the state of Guerrero, with an approximate area of 902.70 km² and a length of approximately 76.05 km. According to the CONAGUA publication of January 2025, in the document "Diagnostics based on Water Quality indicators and traffic lights," for the period from 2012 to 2023, of the 5 points monitored in this river, it was determined that 2 have a red light and 3 yellow, which classifies the water quality of this river as contaminated to severely contaminated. This is due, according to the report, to non-compliance with one or more of the parameters established in the Fecal Coliforms, *Escherichia coli* and/or chemical oxygen demand (COD) indicators [8].

In Mexico, there is no adequate legislation or effective sanctions for the discharge of contaminants such as pharmaceutical products, perfluorinated compounds, hormones, personal care and hygiene items, as well as micro and nanomaterials, which have been recognized in recent years as emerging contaminants [9].

Conventional wastewater treatment techniques such as coagulation, flocculation, membrane filtration, adsorption and ion exchange have been shown to be effective in removing the dyes from wastewater at an early stage. However, these methods often involve high investment and maintenance costs, making them economically unviable for many industries [10].

The literature indicates that the use of photochemical processes, especially advanced oxidation processes (AOP), achieves significant degradation of EDCs in a

short period of time. Furthermore, AOP methods generate transformation byproducts with lower toxicity and contribute to decreasing estrogenic activity [11].

To mitigate the harmful effects of EDCs on the environment, research has been conducted using various advanced oxidation processes (AOPs), which seek the *in situ* generation of oxygen-based oxidants for the treatment of contaminants in water. Examples of these are the Fenton process, photo-Fenton, ozonation, TiO₂ photocatalysis and plasma, among others. In contrast to other AOPs, the treatment of contaminated water with plasma is relatively new [12].

2. Measurement and analysis

2.1 Quality of samples, analysis and results

In order to ensure the quality of the results obtained in the analysis of samples, it is advisable to comply with certain criteria that guarantee the cleanliness of both the sample and the treatment and analysis processes. For this, various organizations have established different guidelines and standards describing the correct procedure for sampling, storage, treatment and analysis. Additionally, it is necessary to evaluate and validate parameters in the extraction and analysis that guarantee the results obtained.

2.2 Extraction techniques

The most common extraction techniques used for the determination of emerging contaminants in surface waters are liquid-liquid extraction (LLE), solid-phase extraction (SPE) and solid-phase microextraction (SPME). Extraction techniques are not completely selective, but they help to eliminate compounds with chemical characteristics different from those of the compounds of interest. Additionally, the application of these techniques can improve the performance of the analytical equipment, as well as its operational safety [13].

2.3 Liquid-liquid extraction

The liquid-liquid extraction (LLE) is a purification method that seeks to isolate the compounds of interest contained in the sample. This is a crucial step before the chromatography analysis of emerging contaminants since a good extraction can impact the performance of the analytical instrument. Therefore, it is convenient to determine parameters such as recovery, repeatability and precision. For this, the use of deuterated compounds is useful for this type of procedure [14].

The LLE consists of adding a solvent or a mixture of solvents of low to medium polarity to the sample, then the sample is shaken to allow the solvent-analyte interaction to promote contact between the components of the sample and the solvent, and thus promote the migration of the analytes from the aqueous phase to the organic phase [15]. Then, by allowing the sample to rest, two liquid phases are formed, allowing the organic analytes to remain in the organic phase constituted by the added solvents. Some solvents for the LLE are hexane, acetate, petroleum ether, methylene chloride, tetrahydrofuran, chloroform and acetone. The LLE does not require sophisticated equipment to be carried out, since it can be performed on classic laboratory glassware. The LLE is a technique implemented and validated by the US-EPA [16].

However, LLE is environmentally unfriendly due to the high solvent volumes required [17, 18].

2.4 Solid-phase extraction

Solid-phase extraction (SPE) is perhaps the most frequently used technique for studies of emerging contaminants contained in surface and groundwater in Mexico. Therefore, it is a versatile technique, with adequate and precise recovery percentages. In this technique, water passes through the stationary phase or sorbent packed in a tube where the analytes with affinity to the stationary phase are adsorbed. Depending on the type of stationary phase used in the extraction, the analyte-stationary phase adsorption is carried out through different interaction mechanisms, such as Van der Waals type interactions, hydrogen bond interactions or electron pair interactions [19, 20].

The SPE is an extraction technique with an extensive variety of stationary phases available. The HLB stationary phase have been used in the extraction of drugs [21], including nonsteroidal anti-inflammatory drugs (NSAIDs), analgesics, antibiotics, hormones, bisphenols, alkylphenols, phthalates and pesticides, among others. The affinity of the HLB sorbent toward the wide variety of analytes is due to the sorbent constitution is made from molecularly imprinted polymers. On the other hand, the C18 stationary phase is a good option for the isolation of organic compounds such as drugs, antibiotics, hormones, bisphenols, pesticides and nonylphenols, among others [22–25]. This type of adsorbent is constituted from silica modified with hydrocarbon chains (C18).

The SPE process consists of conditioning the stationary phase, extraction, drying and elution. Conditioning consists of passing organic solvents and water separately through the stationary phase, allowing the solvent to travel by gravity. This is useful to solvate the stationary phase to improve the interaction between the stationary phase and the analyte. For the extraction, vacuum is applied to pass the sample through the stationary phase. The stationary phase is then washed with deionized water and allowed to dry by passing a stream of air through it through the action of the vacuum, which promotes the elimination of the remaining water lodged within the stationary phase. The adsorbed compounds are then eluted with a solvent or mixture of organic solvents.

On the other hand, SPME is an extraction technique similar to SPE, with the difference that in the latter the stationary phase is a polydimethylsiloxane fiber supported on a solid, and it is a solvent-free, simple, sensitive and robust technique [18, 26]. Before the extraction, the stationary phase is introduced into an organic solvent (methanol or acetone) for cleaning and conditioning. It is then directly immersed in the sample and is kept for a certain time so that the analytes are adsorbed on its surface. The fiber is then placed directly into an analysis instrument (liquid chromatograph, gas chromatograph or mass spectrometer). The advantages of SPME are the low solvent consumption (used only for conditioning the stationary phase) as well as the wide variety of presentations for the stationary phase and the wide variety of compounds that can be adsorbed on it. While, among the disadvantages of SPME is the extraction time, which depends on the type of compounds of interest, as well as the equipment required for the desorption of the compounds in the analytical instrument. Despite the advantages of SPME, it has not been fully established in routine analysis in laboratories for the determination of organic compounds in environmental matrices because it is not yet a technique established by the US-EPA [18].

2.5 Identification and determination of emerging contaminants

High-pressure liquid chromatography (HPLC) is a versatile technique that allows the separation of compounds contained in complex samples. The separation of compounds depends mainly on the characteristics of the mobile phase and the stationary phase [27]. One of the advantages of this technique is the willingness to make modifications to the mobile phase, degree of polarity, pH, concentration of the buffer solution and flow rate of the mobile phase. The nature of the stationary phase is essential to obtain a correct separation of the compounds. Currently, there is a wide variety of columns for HPLC, from columns with different degrees of polarity to columns of different lengths or chiral columns. Although it is impossible to manually manipulate the composition of the stationary phase to improve the separation of compounds, actions such as modifying the temperature of the column can be performed. With the correct optimization of analysis parameters, this technique allows the separation of different compounds contained in the sample. However, the liquid chromatograph is insufficient to identify and quantify, so it is necessary to have a sensitivity detector, which identifies the analytes according to the UV spectrum or fragmentation pattern of each compound depending on the type of detector coupled to the HPLC equipment.

Currently, in Mexico, different configurations of HPLC chromatographs coupled to different types of detectors and analyzers have been used; diode array (HPLC-DAD), time-of-flight mass spectrometry analyzer (HPLC-QToF-MS) and triple quadrupole mass spectrometry analyzer (HPLC-MS/MS), among others.

In the HPLC-DAD configuration, after separation in the chromatograph, the compounds are directed to the detector, where they absorb ultraviolet-visible (UV-Vis) light at different wavelengths and in different quantities. The detector analyzes the amount of light that passes through the sample, allowing the obtaining of UV spectra. One of the advantages of this configuration is that it allows the evaluation of the purity of the peak corresponding to the analyte of interest [28]. This configuration is more economical compared to the HPLC-QToF-MS and HPLC-MS/MS configurations, and its low sensitivity can impact difficulties in the detection of compounds, making it necessary to require a larger amount of sample for the detection of the analytes of interest [29].

The HPLC-QTOF-MS configuration is a highly selective analysis technique that improves resolution and accuracy for mass identification, so it can identify hundreds of compounds in a single injection, allowing the identification of isomers when required [30, 31]. In an analysis using HPLC-QTOF-MS, after separation by LC, the sample is ionized and the ions formed pass through a tube (time of flight), where they are separated according to their mass/charge ratio, so the ions with the lowest molecular weight reach the detector first. Due to the physical constitution of HPLC-QTOF-MS equipment, the main disadvantages they present are the high costs and the availability of space for their proper location. Due to sensitivity, it is possible to detect concentrations of up to 0.02 ng/L [32].

The gas chromatography (GC) is a sensitive, robust, reproducible technique with excellent separation capacity. In this technique, the mobile phase is an inert gas (nitrogen, helium) that carries the sample through the chromatographic system. GC consists of vaporizing the sample, which is then directed to the capillary column, where the separation process of the compounds is carried out. Gas chromatography has a greater separation capacity due to the length of the column used (generally 30 m). As in liquid chromatography, the gas chromatograph is coupled to a detector or

mass analyzer. Thus, in addition to the high separation efficiency, it is possible to achieve optimal sensitivity levels to determine trace concentrations.

The gas chromatography coupled with an electron capture detector (GC-ECD) is a selective and sensitive configuration for compounds that have electronegative groups in their chemical structure, such as chlorine, phosphorus and nitrogen. Therefore, this detector is a good alternative for the analysis of organochlorine, phosphorus and nitrogen pesticides [33]. The electron capture detector contains a radioactive source (usually nickel-63) that ionizes the carrier gas, producing an electron current. Thus, when the electronegative groups capture electrons in the carrier gas, a reduction in the current is recorded, proportional to the amount of compound that entered the detector. Among its disadvantages, the ECD is specific for compounds that contain organic groups with electron affinity.

GC-ECD has been used to detect chlorinated, phosphorous and nitrogenous pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, herbicides and pharmaceuticals in water from cenotes, wells, sinkholes, lagoons, rivers and coasts. Masses of up to 1 ng can be detected with this configuration [34], making it a good option for analyzing compounds with electronegative atoms.

Gas chromatography coupled with mass spectrometry (GC-MS) is currently the most widely used technique for low molecular weight compound detection. In the mass spectrometer, the molecule fragmentation is the basis of compound identification according to the fragmentation pattern presented. In this configuration, the quadrupole is essential for separating and filtering the generated ions. Electron impact ionization and chemical ionization are the most commonly used forms of ionization.

Some advantages of GC-MS are the availability of a data library for compound identification analyzed by electron impact ionization, easy use of the analytical equipment, and its ability to achieve higher resolution than in HPLC-MS. Additionally, analysis by electron impact ionization allows for a comparison of the results obtained with those stored in different libraries, among which the NIST stands out [35]. One of the limitations of GC-MS is that for the separation and analysis of compounds, it is necessary that they be volatile and have molecular weights between 50 and 600 Da. However, it is also possible to analyze polar molecules that have been derivatized, to improve their volatility, thermal stability, sensitivity and response to the detector [25, 35]. However, the derivatization process can be laborious and requires more time for sample treatment. Despite the disadvantages, GC-MS is widely used to determine drugs, phthalates, alkylphenols, bisphenols and hormones contained in surface and groundwater, obtaining detection limits of up to 0.001 ng/mL [36].

In gas chromatography-tandem mass spectrometry (GC-MS/MS) configuration, the chromatographic principle is the same as in GC-MS. However, in this configuration, the mass spectrometer has three quadrupoles, so the sensitivity and selectivity are increased compared to GC-MS. In GC-MS/MS, the identification of compounds is favored through the generation of precursor ions and product ions. The correct selection of these ions provides this configuration with improvements in terms of sensitivity and selectivity [37]. In this configuration, the masses of the precursor ions (m/z) are analyzed and filtered in the first quadrupole, while the masses of the product ions are analyzed and filtered in the third quadrupole. The second quadrupole functions as a kind of reaction trap, in which the precursor ions are ionized to produce the product ions [38]. Therefore, the compounds are unequivocally identified when the coelution occurs.

GC-MS/MS has been used to determine alkylphenols, bisphenols and hormones contained in river water samples mainly impacted by direct discharges from urban

drainage systems, obtaining detection limits of up to 0.0002 ng/mL [39]. However, the use of this configuration for the detection and quantification of emerging contaminants dissolved in water has been rarely exploited, which may be due to the high costs of equipment and maintenance, which is perhaps the main disadvantage of this configuration in addition to the disadvantages described for GC-MS.

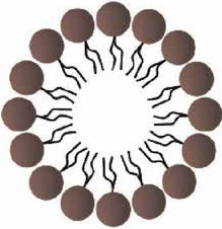
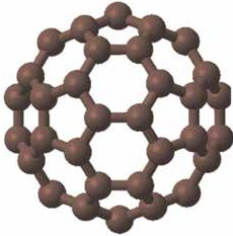
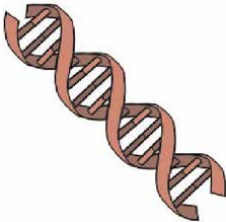
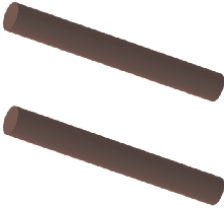
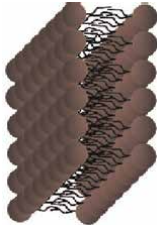
2.6 Nanotechnology for the detection of EDCs

Nowadays, rapid and efficient detection of EDCs becomes crucial because their impact is worrying, with negative effects on human health and aquatic ecosystems and because they present bioaccumulation and persistence [40]. Furthermore, accurate and precise detection is crucial for developing regulations that limit their environmental presence. This allows the effectiveness of elimination methods and designing new mitigation strategies. Since traditional methods, such as chromatography and mass spectrometry, are expensive, laborious and inaccessible, nanotechnology is essential for developing low-cost, fast and sensitive sensors for efficient monitoring [41].

Nanotechnology overcomes these limitations by improving EDC's fast detection, sensitivity and selectivity. Nanomaterials, classified by composition and dimensionality in **Table 1**, have unique physicochemical properties to enhance signal amplification, molecular recognition and miniaturization of detection systems. These materials may be organic, inorganic and carbonaceous, presenting low dimensionality as zero dimension (0D), one dimension and two dimensions (2D). The third dimension consists of self-assembled or intentionally assembled nanomaterials, incorporating 0D, 1D or 2D nanostructures. **Table 1** provides examples of each category. These materials permit the development of electrochemical, optical and biosensor platforms that enable real-time, in-field monitoring of EDCs, making detection more accessible and efficient [42].

2.6.1 Nanotechnology-based detection principles

The enhancement of detection of endocrine-disrupting compounds (EDCs) using nanomaterials is attributed to their high surface area, tunable surface chemistry and unique optical or electrochemical properties, allowing the design of sensitive and selective detection platforms. Nanomaterials enhance the detection of endocrine-disrupting compounds (EDCs) by improving analyte capture, signal amplification and portability. Their high surface area, tunable surface chemistry and unique optical or electrochemical properties make them ideal for developing sensitive and selective detection platforms [43]. The increased analyte capture occurs because nanomaterials possess abundant reactive sites, providing binding sites that enhance the adsorption of EDCs. Additionally, doping and functionalization improve selectivity for specific substances, like bisphenols or other EDCs [44]. The signal amplification for ultra-sensitive biosensors capable of detecting EDCs at trace levels is possible by the fluorescence and colorimetric identification using metallic nanoparticles and quantum dots, while the electrochemical detection sensitivity is enhanced by the conductive nanomaterials such as graphene and carbon nanotubes [45, 46]. The miniaturization and portability of ultra-sensitive sensors using nanostructured materials offer a cost-effective solution for portable, fast, accurate and real-time sensors, serving as an alternative to traditional lab-based techniques [47]. These mechanisms are resumed in

	Organic	Inorganic	Carbonaceous
0D			
	Three dimensions are on the NS.* P-dots, dendrimers, micelles, nanosomes.	Gold and silver nanoparticles, cadmium and silicon quantum dots, quantum dots, zinc and iron oxide nanoparticles.	Carbon Quantum Dots (CQDs), fullerenes, nanodiamonds, nanographite.
1D			
	Two dimensions are on the NS. Polymer nanofibers, perylene-based nanowires, conjugated polymer nanowires, DNA nanowires, organic nanorods.	Zinc oxide nanofibers, copper nanowires, silver nanowires, titanium oxide nanorods, silicon nanotubes.	Carbon nanotubes (CNTs), carbon nanoribbons, carbon nanohorns.
2D			

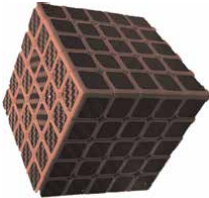
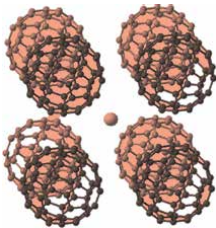
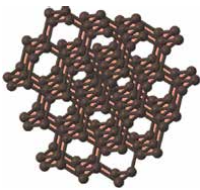
	Organic	Inorganic	Carbonaceous
One dimension is on the NS. Langmuir organic thin films, organic nanoplates, conjugated polymer films.		Metal dichalcogenides (e.g., MoS ₂ and WS ₂), transition metal carbides (MXenes), boron nitride nanosheets, titanium disulfide.	Graphene, graphene oxide, reduced graphene oxide, carbon nanoplates, carbon-based nanosheets.
3D			
All three dimensions are extended beyond the nanoscale (NS).	Tridimensional Arrangements of 0D organic nanostructures.	Bulk metals, bulk ceramics, metal-organic frameworks (MOFs).	Graphite, nanodiamond.
*Nanometer scale (NS) is less than 100 nm.			

Table 1.
Classification of nanomaterials according to composition and dimensionality.

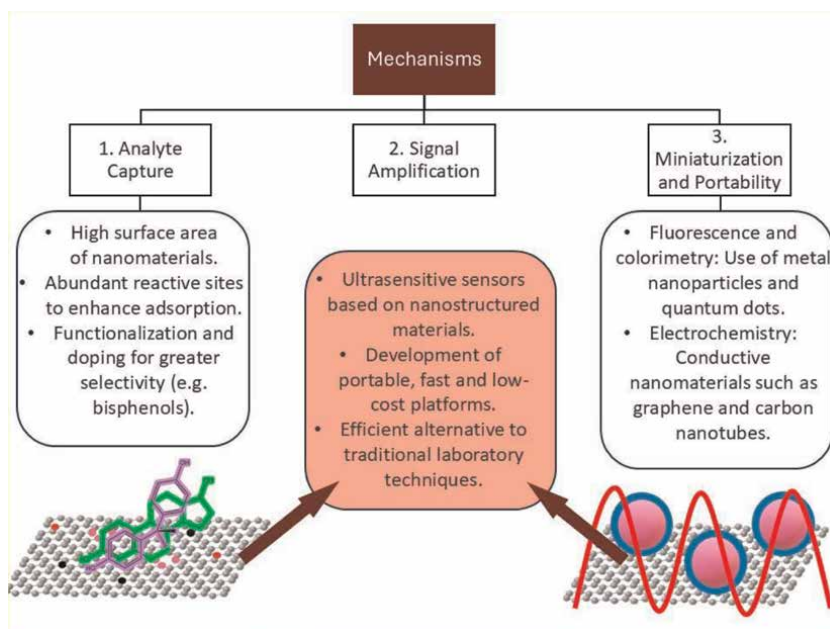


Figure 1.
EDC detection mechanisms based on nanomaterials.

Figure 1 presenting the main interaction for detection of EDCs based on nanomaterials.

2.6.2 Most used nanomaterials for EDCs detection

Diverse sensors have been developed for bisphenols and other endocrine disruptors. For example, the sensors based on membranes of polycaprolactone and graphene oxide exhibited high sensitivity for Bisphenol A, with a low limit detection of 23 nM and good reproducibility was reported [48]. Other examples include gold nanoparticles for the detection of EDCs thanks to their conductivity and capability of signal amplification. The purpose of enhancing their performance is combined with other carbonaceous materials like carbon nanotubes and graphene [49–51]. Bisphenol S detection in water reached the lowest reported detection limit (LOD) and quantification limit (LOQ) of 0.0059 and 0.019 μM , respectively, using an ultra-sensitive detection based on the functionalization of NiO-nanoparticles with supramolecular structures of para-hexanitrocalix[6]arene derivative [52]. However, the platform fabricated using BiOI/ZnO nanoarrays heterojunction and Bis(2-ethylhexyl)phthalate as the recognition element reached a limit of detection of 3.8×10^{-12} mol/L, which was more sensitive than NiO-nanoparticles [53]. This higher sensitivity suggests that the heterojunction of BiOI/ZnO nanoarrays was a strategy more effective for trace detection of environmental pollutants. More recently, studies focused on developing electrochemical sensors from Bisphenol A using boron-doped nanodiamond with iron oxide nanoparticles showing excellent parameters for efficient detection, these results were consistent with those obtained by HPLC. Those results represent a promising and low-cost alternative when compared to conventional analytical techniques [54]. As mentioned, the sensitivity has been improved, mainly using composites and heterojunctions. Research published this year confirmed that combining Cd II,

fluorophenyl-porphyrin and Au nanoparticles (CdTFPP/AuNPs) for a platform with screen-printed electrode increased the sensitivity for detection of bisphenol A, showing a value of 133pM [55]. In conclusion, the sensor CdTFPP/AuNPs is more sensitive than those based on polycaprolactone and GO, but lower than those that employ nanoparticles of NiO and nanoarrays of BiOI/ZnO. However, it is a viable option for BPA detection in environmental systems because of its selectivity, reproducibility and low cost.

2.6.3 Advantages and limitations

The sensors or EDCs nanotechnology bases have important advantages, such as increased sensitivity, the opportunity to detect in real-time and low cost as compared to other traditional techniques. Those benefits are attributed to the physicochemical properties of nanomaterials, which improve signal amplification, miniaturization and molecular recognition. Challenges remain before implementing nanomaterials, such as the stability of nanomaterials under environmental conditions, scalability and interferences in complex samples. Overcoming those limitations results fundamental to implementing nanomaterials to develop EDCs detection with configurability, accessibility and efficiency.

2.6.4 Remarks and prospects

Nanotechnology is under development, demonstrating huge potential for EDC detection, offering important characteristics like low cost, sensitivity, selectivity and real-time detection. Its implementation of environmental studies is fundamental to improving the detection of pollutants, supporting regulation and mitigation for health and care of the environment. The future perspective should include the integration of portable technologies for *in situ* measurements, artificial intelligence for pattern recognition, validation and data processing and normative and regulations development to adapt and implement in environmental monitoring programs. These advances may grant more efficient, accessible and reliable detection, strengthening environmental protection strategies.

3. Emission sources

Water can be contaminated by a diverse number of geogenic processes or anthropogenic activities; however, one of the main sources of water contamination corresponds to direct discharges of treated and untreated wastewater from the urban and industrial sectors onto terrestrial and aquatic ecosystems, as well as leaching of agrochemicals and pesticides from agricultural areas [1].

Mexico has experienced serious contamination of its water resources, with surface waters being one of the most polluted environmental compartments due to industrial and demographic growth in recent years. Rivers and other surface water bodies have been affected by various sources, such as the discharge of urban and industrial wastewater into river systems without adequate treatment, poor solid waste management and the use of untreated wastewater for farmland irrigation, as well as pollution transported by urban runoff along with other non-point sources, have caused more than 60% of Mexican rivers to show signs of pollution, including the presence of

endocrine-disrupting compounds (EDCs), mainly urban and peri-urban rivers draining through the largest cities [1, 56].

Among the most common CDEs detected in aquatic environments are natural estrogens such as 17 β -estradiol (E2) and estriol (E3), synthetic estrogens such as 17 α -ethinylestradiol (EE2), plasticizers such as bisphenol A and bisphenol F (BPF) and alkylphenols such as 4-nonylphenol (4NP) and 4-tert-octylphenol [57, 58]. **Table 2** shows some of the CDEs and their use in everyday life.

Scientific evidence reports the presence of endocrine disruptors (EDs) in the influents and effluents of wastewater treatment plants in Mexico. A recent study determined the dissolved levels of 17 β -estradiol (E2), 17 α -ethinylestradiol (EE2), bisphenol A (BPA), 4-nonylphenol (4NP) and 4-tert-octylphenol (4TOP) in four urban and industrial wastewater treatment plants (WWTPs) in the Monterrey Metropolitan Area, confirming that wastewater discharges in Mexico represent critical sources of endocrine disruptors to aquatic environments [57].

According to CONAGUA, 54% of wastewater is untreated and used in activities such as agricultural irrigation or discharged directly into water bodies. During irrigation with raw sewage (irrigation of farmland using raw wastewater sewage), more hydrophilic and difficult-to-degrade organic contaminants can reach shallow aquifers, leading to the appearance of CDE in groundwater systems. Therefore, irrigation with wastewater incorporates CDE into groundwater in cropland areas due to the infiltration of contaminants into the aquifer [61].

EDCs	Source/use
Triclosan	Personal Care Products
Triclocarban	Personal Care Products
BPA	Plastics
BPB	Plastics
BPC	Plastics
BPF	Plastics
Diclofenac	Pharmaceutical
Diethyl phthalate	Plastics
Caffeine	Pharmaceutical/food industry
Chloroacetonitrile	Disinfection products
Glyphosate	Pesticide
Phenoxycarb	Insecticide
carbendazim	Fungicide
4-nonylphenol	Surfactant
4-tert-octylphenol	Surfactant
17 β -estradiol	Natural Hormone
Striol	Natural hormone/pharmaceutical industry
17 α -etinyIstradiol	Pharmaceutical industry

Table 2.
Sources of CDE [39, 59, 60].

The eastern region of Michoacán (Mexico), known as the end of the Michoacán Avocado Belt, is made up of several municipalities where various economic activities are carried out, including agriculture, livestock, forestry, mining and tourism. In this region, a robust and accurate analytical method based on solid-phase extraction and LC-MS/MS was validated to quantify 21 different pesticides in 16 water samples from rivers, wells and runoff areas. The pesticide analysis revealed the presence of 13 different compounds, including degradation products, in the analyzed water samples. Among the highest concentrations was detected the CDE carbendazim (a degradation product of benomyl), which is a fungicide of the benzimidazole group and is used to stop various types of fungal diseases on herbs, vegetables, fruits, curative and decorative plants and crops such as canola, cereals, etc. This confirms that agriculture is one of the main sources of CDE contamination in Mexico [59, 62].

The complexity of the transport and accumulation pathways of endocrine-disrupting compounds (EDCs) in the environment is closely linked to human activities. The main sources of contamination of aquatic systems with EDCs include industrial effluents, urban effluents and intensive agriculture. These pollutants enter surface and groundwater bodies, as well as soil, initiating a cycle of contamination that poses a significant threat to ecosystems, human health and the sustainability of water resources [60]. It is therefore crucial to identify the specific sources of these compounds and the pathways by which they enter the aquatic environment to implement effective strategies to mitigate their impact and preserve the environmental balance.

4. Technologies for EDCs removal from water

As previously mentioned, EDCs can cause many negative health effects in various aquatic and terrestrial organisms by interfering with their endocrine systems, contributing to a remarked decrease of reproductive capability [63]. One issue of great concern with EDCs is that most of them cannot naturally degrade and tend to accumulate in the ecosystems. Although EDCs are commonly detected at low concentrations in the Mexican aquatic environments, the continuous discharge through wastewater effluents contributes to the occurrence of these persistent pollutants in the environment. To mitigate the presence of EDCs in the aquatic systems, various treatment technologies have been developed, which can be divided in three groups as follows: biological, physical and chemical treatments, even, two or more of these methodologies have been implemented as hybrid treatment for EDCs removal from water [64].

4.1 Biological methods

Aerobic and anaerobic processes are two types of biological methods commonly used for wastewater treatment. Among them, active sludges, membrane bioreactors and sequencing batch reactors are recognized as the most effective aerobic treatments. Anaerobic technologies include anaerobic sludge reactors and anaerobic film reactors, which are considered as environmentally friendly. Nowadays, there are several investigations on the elimination of emerging pollutants such as EDCs utilizing biological treatments; these methods are commonly used in wastewater treatment plants and were primarily designed to eliminate major components from wastewater, including suspended and dissolved solids, biodegradable organic matter, nutrients and pathogens. In several studies conducted in México, it has been estimated that biological

methods in WWTPs can remove various types of emerging pollutants (including EDCs) ranging from 20 to 80% depending on the operating conditions of each [57, 65]. Moreover, also it has been reported that WWTPs can be considered crucial hot spots for the emission of EDCs into the environment. In some cases, levels of the hormones E2 and EE2 in the final effluents of WWTPs were almost five times the initial concentration, while 4TOP was 1.6 times greater in effluents [65]. Therefore, development and implementation of efficient technologies to remove EDCs from water is a crucial study area to contribute with the abatement of the environmental pollution and the adverse effects on the aquatic and terrestrial ecosystems.

4.2 Physical treatment methods

Within the physical processes for water treatment and EDCs removal, the adsorption is one of the most important of them, especially due to the simplicity, flexibility and no production of harmful byproducts. Generally, the adsorption process is divided into two categories: physisorption (weak intermolecular forces such as electrostatic and Van der Waals forces) and chemisorption (involves a chemical reaction, typically for covalent bond formation). However, the efficiency of the adsorption for EDCs removal directly depends on synergetic and complex interactions between the experimental conditions of the process, physicochemical properties of EDCs and characteristics of the adsorbent used [63]. Diverse types of adsorbents have been reported for EDCs removal from water and wastewater, such as zeolites, mineral matter, lignocellulosic materials, activated carbon, biochar, activated hydrochar, carbon nanotubes, graphene's, several hybrid nanocomposites, organic and metal-organic frameworks, among others [50, 66]. For example: It has been reported removal efficiencies up to 90, 99, 99, 96 and 98% for EDCs such as ethyl paraben, diethyl phthalate, BPA, E2 and carbamazepine (respectively) using activated carbon as adsorbent [63]. On the other hand, carbon nanotubes showed 99% efficiency to remove BPF, 89% for BPAF, 98% for EE2 and between 44 and 70% for BPA, while zeolite has shown removal efficiencies of 82% for BPA and 60% for ethoxylates alkylphenols [67, 68].

The membrane and filtration technologies are also considered as another promising physical methods to remove EDCs from water due to several advantages such as wide selectivity, continuous operation, no production of harmful byproducts, adaptability to conventional water treatments and excellent efficiency to remove organic matter including microbes and viruses. In this sense, three main mechanisms have been proposed to explain the removal of EDCs from water: (1) Size exclusion or sieving, considered as the main mechanism, (2) charge repulsion by effect of functional groups, (3) hydrophilic and hydrophobic interactions between membranes and EDCs. The efficiency or EDCs removal by membrane technologies is often related to effect of the physicochemical properties of EDCs, types of membranes and impurities during the process. However, in several studies it has been reported a wide range of efficiencies from 10 to 95%, which can be associated with the physicochemical properties of EDCs; likewise, removal efficiencies of EDCs are related depending on the type of membranes: micro-membranes (0.05–50 μm) < ultra-membrane (1–100 nm) < nano-membrane (0.8–9 nm) < reverse osmosis (0.1–100 nm) [52, 68]. For example, Mexican researchers (in CDMX) reported removal efficiencies of 76% for BPA, 92% for DEHP, 100% for BBP, 100 for E1 and 100 for E2 using a pilot plant of nano-filtration process [69]. Also, efficiencies between 42 and 95 and 53–79% were reported

for EE2 and BPA removal using ultra-filtration method, while efficiencies up to 98–99% were reported for EE2 and BPA removal by a reverse osmosis [68].

4.3 Chemical treatment methods

Chemical treatment methods use chemicals to purify water, reduce pollution, disinfect water or remove hardness. Among them, conventional oxidation processes such as chlorination have been employed to remove EDCs from water. First, chlorination is the most ubiquitous method used for disinfection of potable water and is a critical process for inactivation of viruses and bacteria in the final effluents of wastewater treatment processes. Moreover, according to a study conducted in CDMX (México), the chlorination process has demonstrated remarked effectiveness to remove 81–94% for BPA, 95–97% for 4NP, 92–99% for triclosan [70]. However, some investigations have reported that the use of chlorine for water treatment could promote the chemical transformation of several harmful substances or chlorine residuals [63].

On the other hand, non-conventional removal technologies such as advanced oxidation processes (AOPs) have been considered promising methods for their excellent efficiency in degrading EDCs. AOPs are essentially based on the production of non-selective and highly oxidizing hydroxyl radicals ($\text{HO}\cdot$), which can convert the recalcitrant pollutants into CO_2 , H_2O and other harmless compounds. Among the main AOPs include ozone, H_2O_2 , UV light, heterogeneous photocatalysis, Fenton reaction, anodic oxidation and other combined processes ($\text{H}_2\text{O}_2/\text{O}_3$, O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, UV/Fenton).

Ozone (O_3) is an unstable gas and is produced by irradiating oxygen using a high voltage source (6–20 kV), the dissociated oxygen atoms then associate with other oxygen molecules to form ozone. Moreover, O_3 is a strong oxidizing agent which can produce hydroxy radicals by several decomposition reactions, which can be employed for water treatment and decomposition of pollutants such as EDCs. For example: in CDMX (México) efficiencies of 96, 99 and 96% were achieved for BPA, 4NP and triclosan (respectively) using 3 mgO_3/L [70] and in Jalisco (México), efficiencies between 96 and 99% for E2 and EE2 using 96 mmolO_3/L [71]. For its part, photolysis using UV light is another method employed for the degradation of EDCs, where molecules irradiated with photons can reach excited states and promote chemical reactions to generate free radicals, even, direct interaction between pollutants and UV light may lead to the generation of harmless products; for example, [1] Dos Santos et al., reported 99% of efficiency for an aqueous mixture E1, E2, EE2 and 4NP at UV dose of 186 mJ/cm^2 . Moreover, the efficiency of photolysis can be improved when radicals are generated from intermediates such as O_3 , H_2O_2 or Cl (O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, UV/Cl) [68, 72].

Heterogeneous photocatalysis stands out among the AOPs most studied in México due to the high efficiency to remove EDCs from water. This method involves the generation of hydroxyl radical using a wide variety of metal oxide semiconductors under a light source. TiO_2 and ZnO are the semiconductors most studied, however, in the last years several novel materials, nanomaterials and composites have demonstrated remarked efficiencies for EDCs degradation even under solar light. For example, boron-doped TiO_2 was employed for complete degradation of estriol hormone in water, achieving 71% of mineralization and a nontoxic effluent (Monterrey, México) [73]. Also, the complete elimination of a mixture of BPA, E2, EE2, 4TOP was achieved using the N-doped BiOBr photocatalyst under simulated solar light, while toxicity of the aqueous mixtures was reduced to moderate levels (Monterrey and Tapachula, México) [74–76]. Likewise, $\alpha\text{-Fe}_2\text{O}_3/\text{ZnO}$ composites were employed for 42.2% of

mineralization for a mixture of BPA, 4-t-butylphenol and 4-t-octylphenol under simulated solar light and a nontoxic effluent was obtained after 330 min of irradiation (Monterrey, México) [77].

Fenton reaction also have been evaluated for EDCs removal from water; during this process hydroxyl radicals are generated through the catalytic decomposition of H_2O_2 promoted by Fe ions (Fe^{2+}) at optimal pH between 2 and 4. Moreover, the efficiency of this method can be significantly improved under UV light, which is known as photo-Fenton reaction. The remarkable efficiency of Fenton's reaction has been reported for the complete elimination of EDCs such as triclosan and carbamazepine in a real wastewater sample in Durango, México [78], as well as several mixtures of EDCs detected in sanitary landfill leachates worldwide [79]. On the other hand, Maldonado et al. [64] (Toluca, México) reported the use of boron-doped diamonds electrodes for oxidation of estradiol hormone contained in synthetic urine samples, which reveals that AOPs such as anodic oxidation could be employed for decontamination of hospital wastewater [80].

4.4 Plasma

Plasma technology is classified as an AOPs type, there are different mechanisms to generate plasma; however, for water treatment, the main modalities to generate the discharge are dielectric barrier discharge (DBD), gliding arc discharge (GAD), radio frequency discharge (RFD), corona discharge (CD) and microwave generated plasma (MW). The generation of the plasma discharge can occur above (external) or below (internal) the interface between the air and the treated water [81].

During the plasma treatment process, chemical reactions take place at the interface between the plasma and the liquid, where highly reactive oxidizing species such as $\text{OH}^\bullet$, O , $\text{HO}_2^\bullet$, H_2O_2 , O_2^- , as well as reducing species such as free electrons, H , among others, interact, besides, ozone, UV, high-energy electrons, are present. These species play a crucial role in the degradation of contaminants present in water and can degrade organic compounds [82, 83].

In investigations with various contaminants such as carbamazepine, clofibric acid and iopromide, degradation was achieved using corona discharge: clofibric acid was reduced below the detection limit after 30 min, carbamazepine was degraded by 98% and iopromide by 99%. For carbamazepine, 84% degradation was achieved in solutions including landfill leachate, a more complex medium than wastewater treatment plant effluents or surface waters [84].

Numerous investigations that have used plasma, in its different production mechanisms, for the treatment of effluents, both simulated and real, from the textile industry, demonstrate in a convincing manner the feasibility of implementing this technology before its disposal into bodies of water and thus effectively protecting the environment [85].

4.5 Hybrid systems for EDCs removal

Conventional water and wastewater treatments are not enough to effectively remove a wide variety of EDCs due to their high persistence, low biodegradability, low concentrations, accumulative properties and continuous introduction into the environment through wastewater discharges. Although AOPs are promising methods for removing EDCs from water, their operational effectiveness in water and wastewater treatment processes for the elimination of persistent pollutants is still under

study. For this reason, several hybrid processes have been evaluated and reported in literature which have resulted in notable improvements to remove EDCs from water, contributing to a certain extent to the abatement of water pollution. Hybrid technologies are novel strategies for effective elimination of conventional and emerging contaminants from water and combine two or more biological, physical or chemical treatments; however, selection of the hybrid technique must be subject to the physicochemical characteristics of the effluent to be treated, considering basic parameters such as origin source, pH, organic matter content, suspended and dissolved solids, among many others. The combination of biological treatments and chemical methods are often used and reported in scientific literature for wastewater treatment and elimination of several emerging contaminants, some examples include the implementation of a lab-scale plant for wastewater treatment in Tapachula, México, where an anaerobic reactor UASB was coupled to the Fenton reaction for complete degradation of EE2 and Caffeine, reduction of 80% for chemical oxygen demand and reduction of the toxicity of effluent until moderate levels. Likewise, a system composed of a sequential batch reactor followed for UV/H₂O₂ treatment was employed for total elimination of E2 and EE2 and several nutrients in wastewater samples [86]. Finally, other hybrid methods also have been evaluated for removal EDCs, for example: Fenton reaction was combined with an adsorption process using a column packed with macroporous granular activated carbon and complete removal of BPA, total organic carbon and biological oxygen demand was achieved in Yucatán, México [87].

5. Human and ecological risk assessment

In Mexico, assessing human and ecological risks associated with substances considered endocrine-disrupting compounds (EDCs) in water has gained prominence due to their potential adverse effects on human health and the environment. EDCs can disrupt the endocrine system by mimicking hormones, preventing them from acting or inhibiting their production [88, 89]. Endocrine disruption can occur in both humans and aquatic organisms. However, the level of risk of endocrine disruption depends on the set of EDCs to which the organism has been exposed. Currently, the health risks in humans and aquatic organisms can be measured using official procedures established by the United States Environmental Protection Agency (US-EPA) [25, 56, 90] as well as by the European Union (EU) [91–93]. The potential risk of presenting effects related to EDCs can be evaluated through estrogenic risk, ecological risk and health risk.

5.1 Estrogenic risk assessment

Estrogenic activity is estimated through the concentration of the EDC determined in the environment and its estrogenicity factor or estrogenic equivalent, which is a dimensionless value obtained as the estrogenic equivalent value to 17- β -estradiol (E2) [94, 95]. Thus, the estrogenic equivalent value (EEQ) takes the dimensional units of the determined EDC concentration. Therefore, estrogenic activity is determined as follows:

$$EEQ = C_i E_{2equiv} \quad (1)$$

Where C_i is the concentration of the EDC determined in water, and E_{2equiv} represents its respective estradiol equivalence factor (EEF). Since estrogenic damage

can be caused by different compounds considered EDCs, estrogenic activity is determined as the total estrogenic activity (EEQ_{total}) due to entire of EDCs determined in the analyzed sample [22, 90, 93, 96]. Therefore, total values >1 represent a risk of estrogenic damage to aquatic organisms. EEQ_{total} is determined as:

$$EEQ_{total} = C_i E_{2equiv \dots i} + C_i E_{2equiv \dots ii} \dots C_i E_{2equiv \dots n} \quad (2)$$

In **Table 3**, some EEF values determined for compounds considered EDCs are shown.

Compound	E _{2equiv} (μg L ⁻¹)	Reference
Estradiol (E2)	1.0000	[94]
Estriol (E3)	0.344	
Ethinyl Estradiol (EE)	0.1709	
Diethylstilbestrol (DES)	0.04597	
Estrone (E1)	0.01886	
Nonylphenol (NP)	5.05X10 ⁻⁴	
Octylphenol (OP)	2.13X10 ⁻⁴	
Nonylphenol ethoxylate (NP1EO)	1.336X10 ⁻⁵	
Bisphenol A (BPA)	2.43X10 ⁻⁵	
Di(2-ethylhexyl) phthalate (DEHP)	1.735X10 ⁻⁵	
Dibutyl phthalate (DBP)	1.01X10 ⁻⁵	
Butyl benzyl phthalate (BBP)	7.752X10 ⁻⁶	
Dimethyl phthalate (DMP)	9.804X10 ⁻⁶	
Diethyl phthalate (DEP)	5.747X10 ⁻⁶	
Benzyl butyl phthalate (BZT)	7.286X10 ⁻⁶	
Hydroxybenzyltoluene (HOBT)	6.303X10 ⁻⁶	[95]
Methyl benzyltoluene (MeTBZT)	5.149X10 ⁻⁶	
E1	0.11	
E3	0.11	
EE	1.25	
DES	0.04597	
BPA	3.8X10 ⁻⁴	
NP	2.7X10 ⁻⁴	
NP1EO	4.4X10 ⁻⁶	
Nonylphenol diethoxylate (NP2EO)	4.3X10 ⁻⁶	
OP	2.1X10 ⁻⁴	
Octylphenol monoethoxylate (OP1EO)	4.0X10 ⁻⁶	
Sulfonic acid ethoxylate (SO2EO)	2.0X10 ⁻⁶	

Table 3.
Relative estrogenic factor (EEF) for alkylphenols, alkylphenol ethoxylates, bisphenol A, hormones and phthalates (μg L⁻¹).

Studies conducted in Mexico have found that compounds such as pharmaceuticals, hormones, alkylphenols and bisphenol A exhibit estrogenic activity due to the concentrations detected in aquatic environments, indicating that the bodies of water present a risk of estrogenicity for aquatic organisms [22, 90, 93, 96].

5.2 Ecological risk assessment

The level of ecological risk is determined by the risk quotient (RQ) value. This value is used to evaluate the potential health risk posed by exposure to a specific contaminant and is calculated as the ratio of the measured environmental concentration (MEC) of the compound of interest and the predicted no-effect concentration (PNEC) using the following equation.

$$RQ = \frac{MEC}{PNEC} \quad (3)$$

To determine the ecological risk level:

- $RQ < 1$: Indicates that exposure is considered safe and does not represent a significant risk to human health.
- $RQ = 1$: Suggests that exposure is at the threshold level, which warrants caution.
- $RQ > 1$: Implies a potential health risk, requiring further investigation and possible intervention.

In Mexico, various studies have evaluated ecological risk, determining that compounds such as pharmaceuticals, personal care products, phthalates, caffeine, alkylphenols, bisphenols and hormones may present ecological risk due to the concentrations found in superficial water bodies [22, 56, 89–93, 96].

5.3 Human health risk assessment

The evaluation of human health risk uses the Human Risk Indicator (HRI) from the Quebec Pesticide Risk Indicator (IRPeQ) to calculate the risks that pesticides pose to human health [97]. This indicator was emitted by The Institut national de santé publique du Québec (INSPQ). The HRI considers the main criteria related to the acute and chronic toxicity of active ingredients, as well as their potential for persistence in the environment and bioaccumulation in the human body. Additionally, it considers specific aspects of the final products and application techniques, as well as the quantities used to evaluate the risk of pesticides [59].

The formula for calculating the Human Risk Indicator (HRI) is found in the following equation and is applied to each handled active ingredient.

$$HRI_i = TRI_i \times WF_{f(i)} \times CF_{d(i)} / 10 \quad (4)$$

$$TRI_i = [\Sigma \text{Acute risks} + (\Sigma \text{chronic risks} \times FPer)]^2 \quad (5)$$

where.

TRI represents the toxicological risk index for each pesticide (i).

The calculation is based on the addition of the points assigned to the selected acute and chronic toxicity criteria. *FPer* is a coefficient related to the persistence and bioaccumulation potential in humans. The sum of these variables is squared to broaden the distribution of values and highlight pesticides with the highest risk. *WFf* corresponds to the coefficient assigned to the pesticide formulation, ranging from 1 to 2, depending on the potential contamination *via* the formulation (low risk and high risk, respectively). *CFd* represents the compensation factor for the applied dose of the active substance compared to the recommended reference dose. The total value is divided by 10 to obtain an *HRI* of an acceptable order of magnitude, as the variability can be very high for some active ingredients with a high toxicological risk index. Theoretically, the *HRI* for an active ingredient could range from 1.25 to 17,306 [97]. These ratings are based on proportionality: the higher the rating, the greater the risk.

Studies carried out in Mexico have determined that compounds such as phthalates, pharmaceuticals, hormones, alkylphenols, bisphenol A and metals exhibit a risk to human health due to the concentrations found in aquatic environments, which indicates that the water bodies in which the concentrations of these compounds were determined present a risk to human health [25, 56, 59, 91, 98–100].

Research has identified key sources of EDCs, including agricultural runoff, industrial discharges and untreated wastewater. Understanding these sources is crucial for developing strategies to mitigate risks and protect both aquatic ecosystems and the communities that depend on these water resources. Continuous research and monitoring efforts in Mexico are essential to inform policy decisions and regulatory measures aimed at reducing exposure to EDCs. These initiatives are vital for safeguarding public health and preserving ecological balance, ensuring a healthier environment for future generations.

6. Conclusions

Endocrine-disrupting compounds in aquatic compartments are a current and relevant issue in Mexico. Their presence has been detected in raw and treated wastewater, underground, surface and stagnant waters through techniques that involve their transfer from the aqueous sample to organic solvents by solid-phase extraction, followed by concentration and chemical derivatization and their subsequent analysis by gas chromatography and simple and tandem mass spectrometry and liquid chromatography with diode arrays following quality controls that meet international validation parameters. These have been mainly attributed to the discharge of treated wastewater through conventional processes, which are inefficient for their removal. There are promising advances that seek the development of processes that improve the efficiency of elimination of treated waters, highlighting the exploration of advanced oxidation processes based on ozone and coupled with UV radiation and peroxides and procedures that involve Heterogeneous Photocatalysis, photo-fenton and more recently plasma. Once in the aquatic environment, it has been proven that they represent a serious risk for infants, the adult population, wildlife and flora. There are no regulations governing their presence in treated wastewater, potable water and bodies of water that serve as a source of supply for the population and the food and beverage industry.

Acknowledgements

We would like to thank SECIHTI for scholarships for graduate students.

Conflict of interest

The authors declare no conflicts of interest.

Author details

Mario Alfonso Murillo-Tovar, Josefina Vergara-Sánchez*,
Hugo Albeiro Saldarriaga-Noreña, María Luisa García-Betancourt,
César Torres-Segundo, Khirbet López-Velázquez, José Gustavo Ronderos-Lara,
Arquimedez Tolentino-Rojas and Zurisaday Villegas-González
Faculty of Chemical Sciences and Engineering, Autonomous University of the State of
Cuernavaca, Morelos, México

*Address all correspondence to: vergara@uaem.mx

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Automation in the Water and Wastewater Industry with Artificial Intelligence

Nirmal Kumar Balaraman, Aishvarya Hariharan, Krunal Patel and Arumugam Sonachalam

Abstract

Water treatment plants play a vital role in the supply of drinking water, but management incurs some difficulties. Some of the problems include the achievement of more effluent standards and even the improvement of overall efficiency, bearing in mind the environmental implications. This chapter aims to discuss the possibility of using artificial intelligence (AI) and machine learning (ML) in handling these difficulties. Continuing, we analyze prior studies concerning the automation of water treatment plants using AI/ML and comprehend the issues regarding the interpretation of instrumentation inputs. In this chapter, we intend to make suggestions about applying AI/ML to quantitatively analyze real-time information and manage processes in WTPs. In this chapter, the literature review is conducted to provide an overview of traditional approaches, findings, methods, and issues related to AI/ML applications. We discuss how AI and ML can help solve the problems of interpreting instrumental inputs and describe the choice of algorithms/models for real-time data interpretation and process control. Our findings establish the applicability of AI in reducing the time and cost and enhancing sustainability compliance of water treatment industries. We look at future developments and possibilities of IoT sensors and discuss new trends in AI/ML and their integration for future studies and applications. By applying AI and ML, the water treatment plant can be improved and clean and safe water for communities all over the world can be provided.

Keywords: water and wastewater treatment, PLC, SCADA, artificial intelligence, controls engineering, instrumentation, monitoring, machine learning (ML), process optimization, water treatment plant automation

1. Introduction

Water treatment plants are crucial in the provision of clean and secure water supply to the globe's population [1]. However, increasing such facilities poses a lot of problems, such as achieving high effluent standards, boosting systemic productivity, and conforming to environmental standards, among others. In this introduction, we will discuss the aspects of WTP optimization and the necessity of AI and ML in solving them.

Real-time and autonomous water quality monitoring systems (ROV) play a pivotal role in ensuring the efficiency and effectiveness of water treatment processes. These systems enable continuous monitoring and immediate detection of contaminants, ensuring compliance with strict water quality standards. Water treatment plants (WTPs) are vital for providing clean and safe water to the global population [1]. However, expanding such facilities introduces challenges such as maintaining high effluent quality, improving productivity, and adhering to environmental regulations. This introduction explores the optimization of WTPs and highlights the critical role of AI and machine learning (ML) in addressing these challenges (**Figure 1**).

1.1 Overview of challenges in water treatment plant optimization

Modern water treatment plants encounter numerous and diverse problems in providing consumers with water of high quality and, at the same time, reducing the adverse effects on the environment [3]. There is a challenge in compliance with the generally set regulatory effluent standards. In this feature, there are set limits of different pollutants and characteristics of treated sewage before it is released into the ecosystem. It is necessary to achieve strict control measures by treatment processes and the quality of effluents to follow these standards.

Moreover, the water treatment facilities need to be effective so as to provide purified water in adequate amounts to cater to the increasing needs while also being cost-effective and energy-efficient [4]. Savings do not only relate to costs but also entail environmental benefits concerning the consumption of water and the green impact linked to the treatment phase. Managing between productivity and sustainability is one of the main issues that plant operators and engineers face.

Besides pure compliance and optimization considerations, water treatment plants face challenges due to the variability of water quality and supply. The natural variations in the raw water quality, seasonal changes, and the incidents that may happen, such as spills and contamination, always affect the treatment processes and the quality of drinking water supplies [5]. To address these challenges, flexibility and adaptability are necessary with the aim of continuing service delivery at our facilities.

Addressing these challenges is essential for sustainable water management and safeguarding public health. Access to clean and safe drinking water is a fundamental human right, yet millions of people worldwide lack access to adequate water treatment facilities. By optimizing water treatment plants, we can ensure equitable access

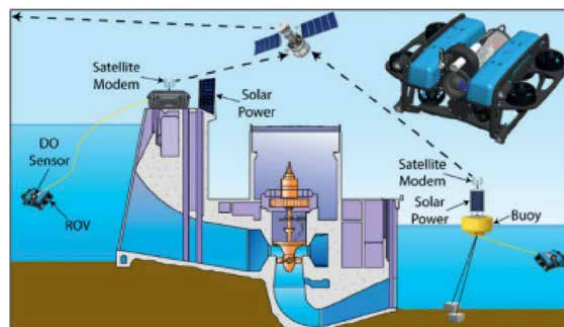


Figure 1.
Real-time and autonomous water quality monitoring system (ROV) in operation [2].

to safe drinking water, protect ecosystems, and support economic development in communities around the globe.

1.2 Introduction to AI and ML technologies for automation

AI and ML are two developing technologies with the potential to solve numerous issues in different fields, and they can be applied to water treatment. AI is the ability of computer systems to mimic human intelligence processes, while ML is about building accurate algorithms on how the computer system is going to improve its capability to learn from data (**Figure 2**) [7].

The figure highlights the role of AI in water and wastewater management through five key applications: control on water treatment, predictive energy optimization, wastewater modeling, timely actions, and optimization of wastewater treatment. These applications showcase how AI enhances efficiency, reduces energy use, and improves sustainability in water resource management.

When it comes to water treatment, there is also a variety of possibilities with the help of AI and ML—for example, process automation or interpretation of big data. These technologies should be in a position to examine big data in real time, recognize patterns and unusual splendor, as well as determine methods of treating procedures that would improve outcomes. Using AI and ML to advanced water treatment plant systems will help increase efficiency and the quality of water and even decrease operating costs.

Additionally, AI and ML help in predictive analysis for presenting a model for maintenance before its failure and scheduling it as per requirements. Such a predictive approach helps to decrease downtimes, increase service life, and maintain the efficiency of treatment processes at the proper level [8].

Altogether, AI and ML can be considered a beacon of light that can help revolutionize the functionality of water treatment plants. Therefore, through these technologies, it will be easier to counter the optimization hurdles, increase efficiency, and provide generations with clean and safe water (**Figure 3**).

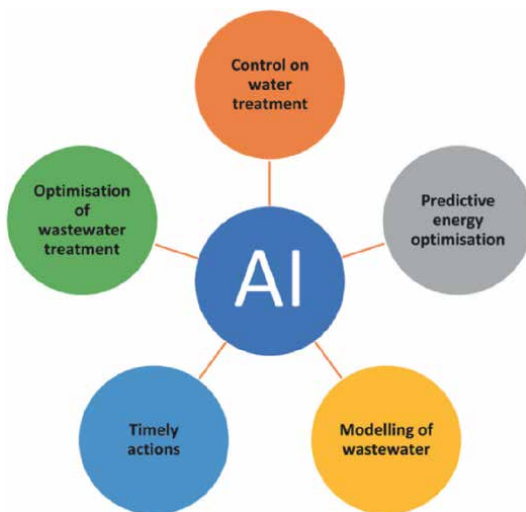


Figure 2.
AI in water and Wastewater Management [6].

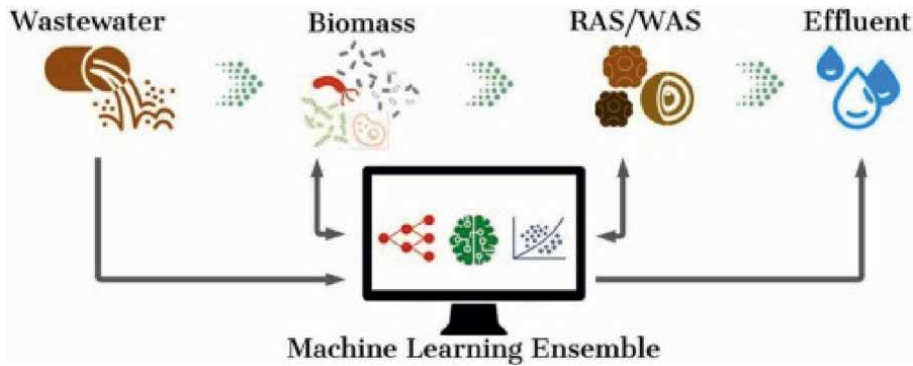


Figure 3.
ML in wastewater [9].

This figure shows a machine learning ensemble applied to wastewater treatment. Wastewater is processed through biomass and RAS/WAS stages, resulting in treated effluent. The machine learning model optimizes each stage, ensuring efficient treatment and high-quality water output.

1.3 Problem statement

The water treatment industry is on the brink of requiring improvement for safety and driving up various feasibility parameters in view of stricter effluent standards. Thus, managing the overwhelming amount of instrumentation input data still remains the major issue of real-time decision-making. AI and ML must be incorporated to understand this data, which translates to the integration of quantitative and qualitative analysis for better process management and control. Thus, the first research question of the study is to use AI and ML to help interpret data in real time, improve and maintain the proper process control, and meet the requirements of regulatory frameworks for water treatment plants.

1.4 Research questions

How can AI and ML technologies be leveraged to optimize water treatment plant operations and improve efficiency?

1.5 Aims and objectives

The aim of this research is to explore how AI and ML can be used in real-time analysis and process improvement of water treatment plants. To achieve this goal, the study is structured around the following specific aims and objectives:

1.5.1 Review existing research on AI/ML applications in water treatment plant automation

This aim concerns the systematic literature review that will be used to establish the analysis of earlier studies, projects, and related initiatives that have applied AI and ML in the automation of water treatment plants. Thus, analyzing the outcomes

of these studies, their strength, and weaknesses, the aim of the work is to uncover the potential of AI/ML in enhancing water treatment and identify its further applications.

1.5.2 Identify challenges related to interpreting instrumentation inputs

This objective aims to capture the issues that relate to the interpretations of instruments' inputs for water treatment plants. Some of these difficulties tend to be the variability of data, noise from the sensor, signal drift, and the treatment procedures, which are usually complicated. Thus, revealing the major real-time data interpretation challenges an organization may face; one can propose robust solutions or coping strategies for each of them.

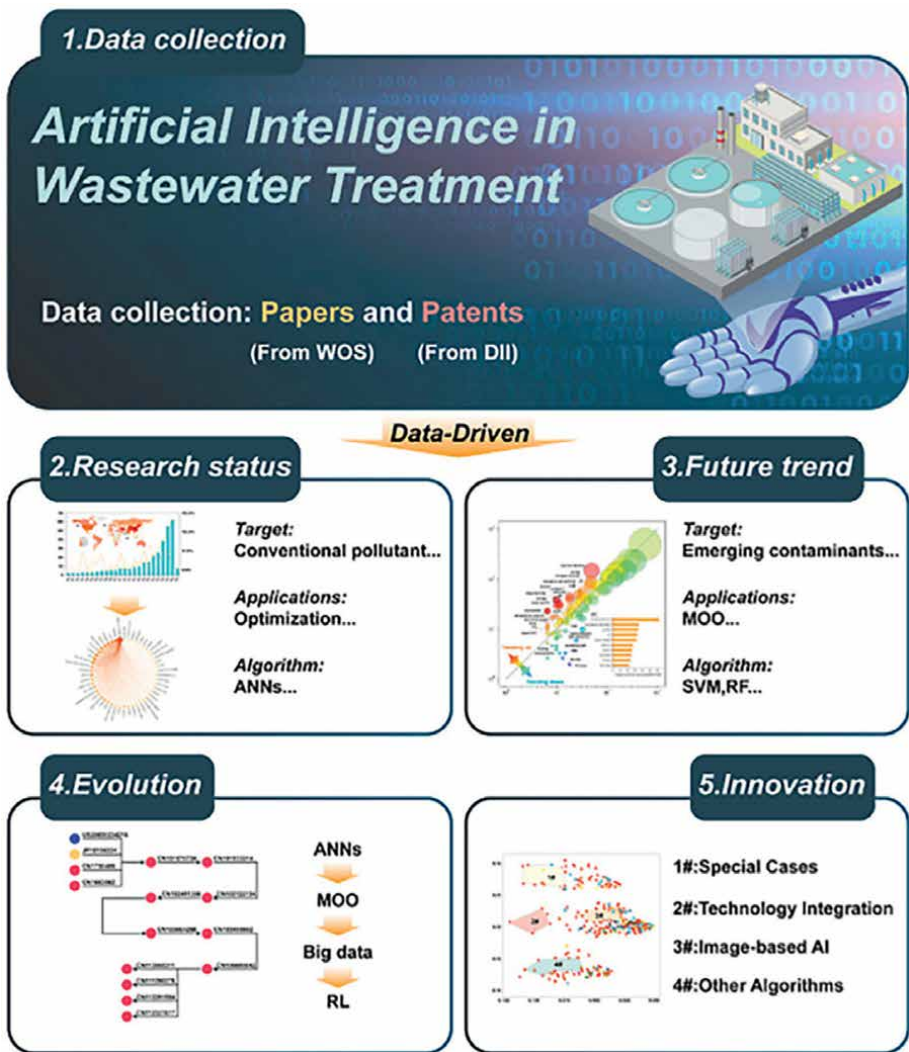


Figure 4.
AI in wastewater treatment [10].

1.5.3 Propose AI/ML techniques for real-time data interpretation and process control in water treatment plants

Expanding on the knowledge from the literature review and the evaluation of the obstacles regarding instrumentation for water treatment plants, this objective seeks to present AI and ML approaches specialized in real-time data analysis and automation of various processes performed in WTPs. Some of these techniques are the approach to supervised learning algorithms when creating an accurate model for predictive modeling, unsupervised learning algorithms for discovering characteristics of abnormal behavior, and reinforcement learning for use in control systems. Through the creation and assessment of these methods, this research study will improve the effectiveness, dependability, and sustainability of water purification procedures (**Figure 4**).

Therefore, the objective and goals of this study stem from the following: Examine studies conducted concerning instrumentation challenges that require the use of AI/ML in the analysis of real-time data interpretation and process control in water treatment plants. Thus, achieving these objectives will serve the goal of enhancing existing and future developments in automation and optimization of the water treatment industry in order to deliver better quality of the final products, enhancing the overall environment.

2. Literature review

2.1 Existing research on AI/ML applications in water treatment plant automation

The use of artificial intelligence (AI) and machine learning (ML) in water treatment plants has gained increasing attention in the last few years [11]. Research done on the available literature yields several studies and projects that have sought to determine the feasibility of AI/ML in the given domain.

2.1.1 Study 1

According to a study [1], a thorough analysis was conducted on the effectiveness of AI in enhancing water treatment operations. They used the machine learning technique to forecast water quality parameters for which treatments can be adjusted beforehand using historical data. Major outcomes revealed that there has been efficiency enhancement of processes and increased capability to forecast changes in water quality (**Figure 5**).

2.1.2 Study 2

In a project by Kulkarni et al. [3], a new applied research area of AI-based predictive maintenance was introduced to a municipal water treatment plant. Thus, the system will be able to analyze the sensor data in real time and identify the possible signs of equipment failure in order to provide a recommendation to perform early maintenance. Such a strategy helped decrease downtime and overall maintenance expenses and increased the reliability of treatment processes.

2.1.3 Study 3

According to the study by I. Taloba [4], neural networks are used to enhance chemical dosing in water treatment plants. In general, through training the neural

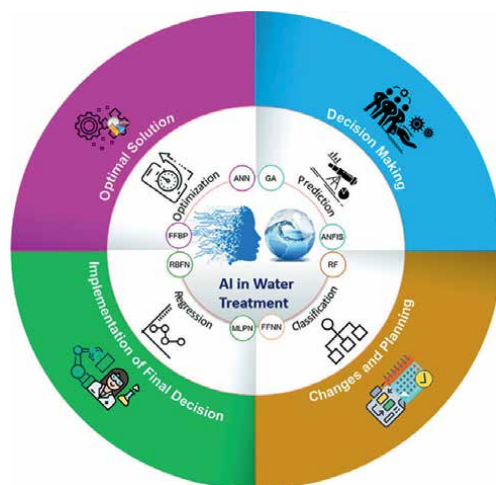


Figure 5.
 AI in water treatment operation [1].

network model, they created the following models of prediction, which forecasted the necessary amount of the chemical reagents depending on the indexes of raw water quality. Such models have been found to help implement concrete measures that cut down tremendously on the use of chemicals and operational costs while still meeting the prescribed water quality norms.

These studies, taken together, clearly establish how AI and ML models are being used to automate different aspects of water treatment plants. These applications include predictive modeling, proactive maintenance, chemical dosing optimization, and many more, and AI/ML technologies provide flexible solutions for efficiency enhancement and minimum operation cost.

2.2 Challenges related to interpreting instrumentation inputs

Despite the great prospects of applying AI/ML in the automation of WTP, several hurdles need to be considered to achieve the full benefits of AI/ML applications [12]. One of the main issues that can be mentioned is related to data interpretation originating from different instrumentation in WTP.

2.2.1 Data variability

The nature of the water quality parameters may fluctuate as a result of various factors like the seasons, changes in the influent, and other environmental factors. Analyzing such changes, as well as differentiating between typical oscillations and actual abnormalities, can be rather problematic for plant operators [10].

2.2.2 Sensor noise and drift

These physical sensors of instrumentation may bring in noise or drift over some time, thereby resulting in measurement errors. It is vital to identify a particular sensor error and develop measures to lessen its impact on data used in decision-making.

2.2.3 The complexity of treatment processes

The treatment process of water is very sophisticated, as it is a multistage process that incorporates different forms of treatment units. Analyzing the data produced by these processes and establishing causal characteristics of the processes might be difficult, especially when the processes are non-linear and dynamic [13].

2.3 How AI and ML can address these challenges?

Some of the important conclusions that can be derived from the developments in AI and ML regarding water treatment plants include:

- *Advanced data analysis:* These technologies have the capability to process huge amounts of data in real time and detect something that a human being will not notice. Using big data analytics thus enables the reduction of operating conditions analysis and provides the operators with an alarm to the existence of certain problems before they reduce or improve the efficiency of certain or all operations.
- *Pattern recognition:* ML algorithms are very powerful in analyzing the data by identifying patterns and relations in the mass of data [7]. These algorithms entail training the ML models for outcomes that have been learned from past data and enabling these to foresee fluctuations in water quality parameters. This feature helps in decision-making and the overall enhancement of treatment processes through the provision of possible future scenarios.
- *Adaptive control strategies:* Intelligent control designs can, therefore, control certain parameters of treatment while being able to change the manner in which they are managed in response to conditions and goals that are currently present. These strategies can help to get the best from the process, reduce energy usage, and meet the requirements of regulating acts and standards by changing the settings of the process depending on the current values of data inputs (**Figure 6**).

Thus, AI and ML represent promising methods of addressing the problems considered in relation to the processes of interpreting the inputs of instrumentation

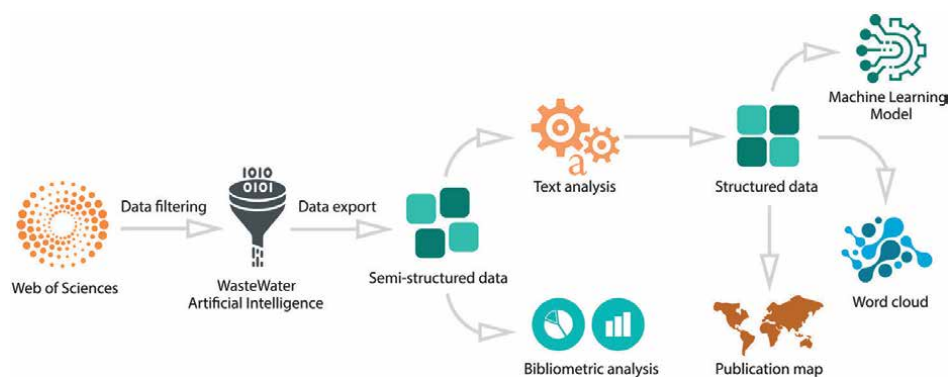


Figure 6. Database processing and analysis methodology for water waste management [13].

in water treatment plants. By using big data analysis, machine learning, and other control strategies, these technologies have the potential to increase the productivity, reliability, and sustainability of water treatment processes and generally help the provision of clean and safe drinking water to communities across the world [13].

3. Methodology

For this research, a case study approach is quite suitable since it facilitates an analysis of vaccination supply chain networks that employ visibility tools. Case studies illustrate specific applications using particular technologies or strategies and the effects of these applications within an overall system.

3.1 AI/ML techniques applicable to water treatment plant automation

AI and/or ML have become useful in automating activities in water treatment plants due to the various applications they present. The last of these techniques uses computer intelligence algorithms for data analysis, prediction, and control techniques optimization. Below is an overview of AI/ML techniques suitable for water treatment plant automation:

- *Supervised learning algorithms*: Supervised learning algorithms are a set of learning methods that follow labeled training data to make some predictions or decisions. In water treatment plants, neural networks, a supervised learning technique of artificial intelligence, are used for predictive modeling. Neural networks use past data on water quality parameters and their treatment, along with other variables like operational history, to forecast probable future results, such as the quality of effluent or a particular equipment breakdown [5].
- *Unsupervised learning algorithms*: Unsupervised learning algorithms find out the structures and/or patterns of the data that do not need classifications. Exploratory techniques in water treatment plants can be done through clustering techniques like k-means clustering. In a way, clustering can be used to classify the data points and look for patterns in water quality data to make anomalous detection or process improvements.
- *Reinforcement learning*: Reinforcement learning is a subfield in machine learning where a system (agent) learns to make decisions through its interactions with the surrounding environment, and the information it gets is in the form of credit, that is, rewards or penalties. In the aspect of water treatment plants, reinforcement learning algorithms can be used to solve the problem of the best control strategy. Control parameters can be adjusted based on sensor feedback and the analysis of their impact on industrial performance, enabling reinforcement learning algorithms to optimize processes in real time [11].

3.2 Algorithms/models for real-time data interpretation and process control

Real-time data interpretation and process control in water treatment plants may not always find applications that require developing or selecting particular algorithms or models. Instead, the emphasis may be placed on assessing the available

off-the-shelf applications or enterprise metasystems containing the necessary functionality. Here are key considerations in this process:

- *Functional requirements assessment:* The first step in selecting appropriate technology for the water treatment plant is thus to evaluate the functional requirements of the plant. Determine what functions and goals the system of automation should meet, in addition to monitoring, prognostics, or feedback.
- *Market research and evaluation:* It is necessary to conduct elaborate market research to determine whether existing software exists to meet the abovementioned functional requirements or whether such systems are integrated into the existing software solutions. Assess the effectiveness and attributes of these solutions for the plant's instrumentation and control systems integration [3].
- *Vendor collaboration and testing:* Approach potential vendors or solution providers with the aim of knowing what the plant needs or needs to be offered in the market. Ask for live or trial runs of the software packages with the aim of observing the efficiency and applicability of real-time data analysis for the water treatment systems and processes.
- *Integration and customization considerations:* Another thing to take into consideration is how easy or difficult it will be to fit into the existing systems of the plant, and another factor is how easily it can be made to support certain preferences or requirements. Consult with selected vendors in a bid to integrate and fine-tune the above-selected solution in the process of serving the plant [5].
- *Validation and verification:* Before the execution of the decision, it is essential to check and confirm the effectiveness of the selected solution through the performance of tests and modeling. Make sure that the solution offers the needed precision, dependability, and speed for the interpretation of real-time data and the control of the processes in the water treatment plant.
- *Training and support:* The selected solution has to be made operational, and training must be conducted for the plant operators and personnel. Also, create sustainable relationships with the vendor after implementation to respond to emerging problems or query the efficiency of the arrangement.

In conclusion, the criteria for choosing real-time data for analysis and process control of water treatment plants may involve reviewing existing software solutions or integrated acquisition systems that conform to the plant's functionality. Thus, the findings of the study, supported by the experiences of vendors and the application of the selected solution, may help automate the process of water treatment, effectively avoiding the development of definite algorithms or models [10].

4. Results and discussions

4.1 Analysis of results obtained through AI-driven automation

The implementation of AI-driven automation in water treatment plant operations has yielded significant results, as evidenced by the following findings:

- *Improved efficiency:* Huge advances through automation have been recorded in water treatment owing to the application of artificial intelligence. When real-time data interpretation and the method of predictive modeling are applied, the treatment operations of the system can be balanced, and the parameters of the system can be adjusted based on the changing conditions.
- *Enhanced process optimization:* Technology has made it easier for the process parameters to be controlled and various treatments to be practiced with more precision and accuracy. Such constant supervision and management enable the system to create awareness of the various optimization prospects and alter the operations in the process.
- *Compliance with effluent criteria:* The use of automated systems facilitated by artificial intelligence has helped in the enhancement of fulfillment of effluent criteria and other regulatory requirements. In this way, the system can predict parameters of water quality and forecast possible complications; thus, it can modify treatment processes to maintain effluent quality at a desirable level or above the standard.

4.2 Impact of automation on efficiency and process optimization

The implications of AI-driven automation for the water treatment industry are far-reaching, with several key benefits and considerations:

- *Improved accuracy and reliability of data interpretation:* Automation makes it possible to produce real-time interpretation of data from not only instrumentation sources but also secure data reliability and quality. This means that through the pattern recognition and analysis of signals beyond the range of human sensorial perception, AI systems are capable of making more prudent decisions and enhancing the treatment processes' efficiency [8].
- *Enhanced operational efficiency and cost savings:* Automation among the plants and the reduction of people's intervention enhance the operation and bring down costs. Through the integration of several aspects of the manufacturing system, it remains possible to cut costs, time, and resources through the automation of recurrent activities and the maintenance schedule.
- *Potential challenges and limitations:* However, the integration of AI solutions in a practical environment can also have some difficulties and limitations. These are the issues related to data quality, trustworthiness, cybersecurity, and the necessity for qualified professionals in creating and sustaining AI. Furthermore, different costs related to the implementation of automation technologies, like the high initial investment costs that some water treatment facilities may face, may pose challenges [12].

To sum up, the use of AI automation in water treatment plants seems to have the ability to significantly improve the work of the organization and make it more efficient, precise, and compliant with all the requirements. As discussed in the previous sections, there are many advantages that can be gained by implementing AI in water treatment plants and industries; however, it is crucial to consider the limitations and potential issues in the process to avoid compromising the probability of achieving a successful outcome from these innovative technologies.

5. Future directions

5.1 Potential advancements and challenges in AI-driven automation

Present-day technologies in artificial intelligence and inducted automation present enormous possibilities in the aspect of productivity increase, reliability in the water treatment plants, and sustainability. Some emerging trends and technologies that could shape the future of AI-driven automation include:

- *Integration of internet of things (IoT) sensors for real-time monitoring:* Some of the parameters are water quality, flow rates, and the conditions or performance of the equipment used, and this information can easily be channeled through IoT sensors. Due to the integration with AI systems, the functionality of these sensors is enhanced, making the monitoring and control of treatment processes broader and more effective.
- *Development of hybrid AI/ML systems for adaptive control and optimization:* Intelligent hybrid systems involve the use of one or more AI techniques, including neural networks, Fuzzy logic, and evolutionary algorithms to allow for adaptable controlling and optimization in similar contexts. Integrated with the featured advantages of different ways, these systems can actively switch between suitable parameters and controlling methodologies in the condition variance [1].
- *Addressing cybersecurity concerns associated with AI-driven automation:* With plants adopting more and more automation with the help of AI, cybersecurity issues are becoming more and more relevant. Protecting such critical physical assets and digital information from networks and cyber threats can be achieved effectively through essential security protocols such as encryption, access control, and anomaly specifications to support the independence and security of complex automation systems powered by AI.

5.2 Potential advancements and challenges in AI-driven automation

Currently, there are several opportunities for future research and advanced research, as well as practical application of automation based on artificial intelligence technologies in water treatment plants. Key areas for future exploration and development include:

- *Advanced data analytics and predictive modeling:* More development into using sophisticated big data analytics and statistically advanced modeling can also help improve the performance of the automation systems that incorporate AI. This includes expanding the use of such approaches as anomaly detection for equipment failures, the approach to predicting equipment maintenance, and the optimization of treatment processes from real-time data.
- *Integration of AI with process control systems:* Studying how best to integrate AI with current process control systems at the water treatment plant could help in the effective acceptance of AI automation. This entails the creation of formalized interfaces and architectural specifications for interconnectivity between AI software and control apparatus.

- *Strategies for overcoming barriers to implementation:* Strategies for Overcoming Barriers to Implementation: Challenges to the use of AI-driven automation and robotics include compliance and regulatory standards and resistance from the workforce to adopt new ways of handling water treatment plants. An understanding of policies, rules, and training methods is one of the approaches that need to be undertaken to tackle these challenges and foster a favorable execution environment for AI-based solutions.

In conclusion, the future of AI-driven automation in water treatment plants is bright, with various prospects where the technology challenges will remain high, but the development prospects will be great. Focusing on new opportunities, evaluating threats, and considering further developments, the application of AI automation in water treatment would enhance the availability of safe drinking water for everyone.

6. Conclusion

In conclusion, the importance of utilizing artificial intelligence and machine learning technologies in the establishment of water treatment plants has been established. In revisiting the study discussions, it is crucial to reemphasize the possibility of optimizing the water treatment sector through intelligent automation in efficiency, sustainability, and compliance.

In this research, it has been established that AI and ML are exceptional tools that can greatly improve the efficiency of water treatment. Using the acquired methods of data analysis, predictive analytics, and closed-loop control, AI automation helps water treatment plants increase their efficiency, reliability, and sustainability levels.

AI and ML's rationale for application lies in the fact that water treatment plant optimization is not devoid of fundamental problems. Whether used for analyzing big data or for making continuous changes to parameters in real time, AI automation provides capabilities for boosting operational performance and achieving compliance objectives.

Also, AI automation is not limited to the potential optimization of existing processes; it also addresses sustainability goals. Through efficient resource management, energy, and the reduction of the negative effects caused to aquatic ecosystems, AI-automated systems support the conservation of water resources.

Prospects for today's water treatment industry are trivial since AI automation is yet to be seen as a trend that will bring change in this water treatment segment. In order to appease the ever-growing necessity of AI automation in water resource management, the following will need to be achieved. Subsequently, it is evident that to achieve the optimum exploitation of AI techniques, further research and implementation will have to be done to achieve the goal of making fresh and safe drinking water available for future generations (**Figure 7**).

In summary, AI and ML have great potential to revolutionize water treatment industries by providing the opportunity to eliminate weaknesses and provide unlimited opportunities by automating the processes in water treatment for the benefit of mankind and the environment. The adoption of AI technology for automation in water treatment sectors makes it possible to create a model for a better future water treatment sector by increasing efficiency to reach its true potential.

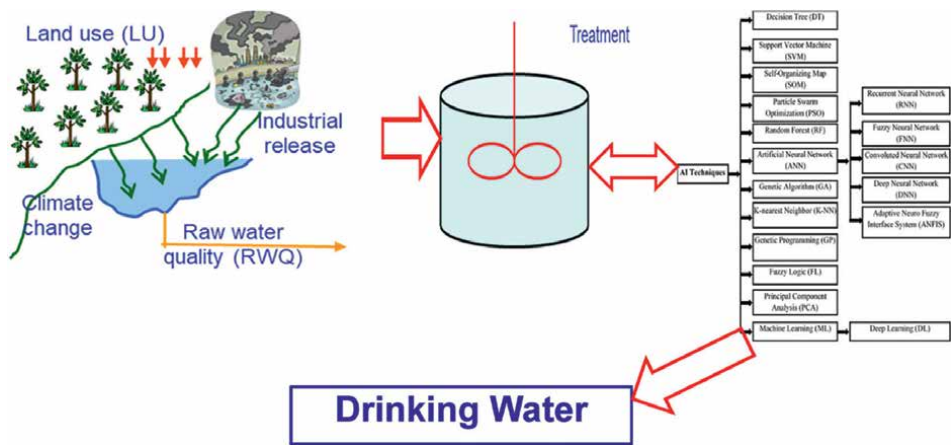


Figure 7.
Artificial intelligence (AI) in drinking water treatment processes [14].

Acronyms

AI	artificial intelligence
ML	machine learning
WTP	water treatment plant
WWTP	wastewater treatment plant
PLC	programmable logic controller
SCADA	supervisory control and data acquisition
HMI	human machine interface

Author details

Nirmal Kumar Balaraman^{1*}, Aishvarya Hariharan², Krunal Patel³ and Arumugam Sonachalam⁴

1 Inframark LLC, Atlanta, USA

2 Dillengr Inc, Dallas, USA

3 Independent Researcher, San Jose, USA

4 Tamil Nadu Open University (TNOU), Chennai, India

*Address all correspondence to: nirmalkumar_b@outlook.com

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Enhancing Water Productivity in Inland Valley Swamps: Sustainable Strategies and Practices

*Mohamed Matthew Blango, Emmanuel Kangoma
and Navo Yambasu*

Abstract

Sierra Leone's tropical climate has high humidity and annual rainfall of 1900–4000 mm, with a dry season from December to March and a wet season contributing over 80% of annual rainfall. Agriculture accounts for 57% of GDP, with 75% of the land classified as arable. Inland Valley Swamps (IVS), covering 690,000 hectares, have the potential for year-round farming, but limited water storage restricts multiple cropping cycles. Sustainable land management and improved Water Productivity (WP) are crucial for food security. Integrating small dams, floating rice, and water-efficient farming enhances Water Productivity. Small earth dams store rainwater for irrigation, enabling double cropping. Rice yields increased from 1.7–3.2 t/ha in the rainy season to 2.5–4.7 t/ha in the dry season. Earth dams also support fish farming, livestock, and groundwater recharge. Cultivating floating rice in reservoir areas optimizes flood-prone land. Water-saving techniques like Alternate Wetting and Drying (AWD) and Aerobic Rice Systems (ARS) reduce water use by 15–30%, allowing crop diversification and triple cropping. Hydrologic models predict declining reservoir storage due to climate change, emphasizing the need for adaptive strategies.

Keywords: Inland Valley swamp, water productivity, earth dam, water-saving techniques, floating rice

1. Introduction

Sierra Leone lies at the northern edge of the equatorial rainforest zone, characterized by a hot and humid tropical climate. With an annual rainfall ranging from 1900 mm to over 4000 mm (averaging 2526 mm), it is one of the most humid countries in Africa. The country experiences two distinct seasons: a dry season from December to March and a wet season, accounting for over 80% of annual rainfall (**Figure 1**). Temperature and solar radiation peak in the dry season at 32°C and 60.9 kcal cm⁻², respectively, while the lowest values occur in the wet season at 20°C and 25.9 kcal cm⁻² [1].

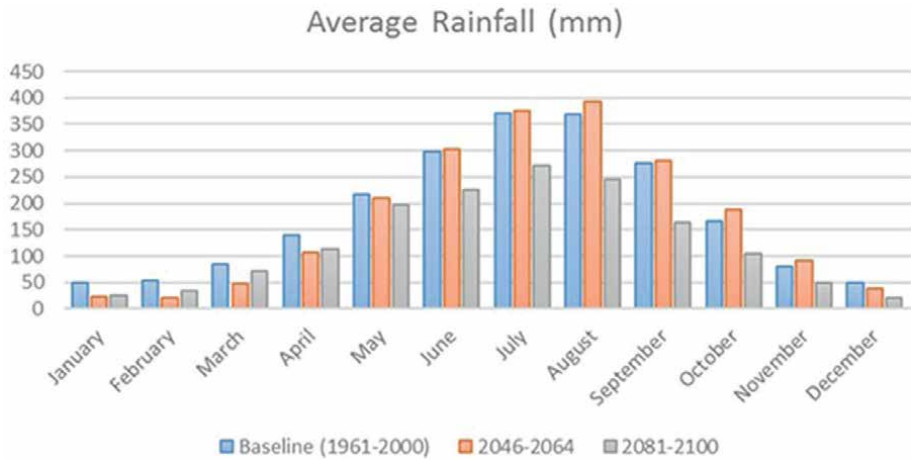


Figure 1.
Baseline (observed) and projected (using GCMs) monthly average rainfall.

Agriculture plays a vital role in Sierra Leone's economy, contributing 57% to the Gross Domestic Product (GDP) and providing livelihoods for approximately 65% of households [2]. The country covers 72,300 km², with nearly 75% of its land (5.4 million hectares) classified as arable. The uplands constitute about 4.3 million hectares of arable land, while the lowlands, estimated at 1.1 million hectares, are subdivided into four major classes: Inland Valley Swamps (IVS), bolilands (drainage depressions), mangroves in coastal tidal zones, and annually flooded riverine grasslands (**Figure 2**). Inland Valley Swamps, covering approximately 690,000 hectares (12.8% of the cultivable area), have significant potential for year-round agriculture due to their rich soils and consistent water availability [3]. These hydromorphic depressions with defined catchment areas are particularly suitable for small dam construction, enhancing water storage and management.

Inland valleys offer considerable potential for sustainable agricultural development across West Africa, with valley bottoms and hydromorphic fringes spanning 20–50 million hectares [4]. These areas benefit from groundwater flow, which improves water availability and enables multiple cropping cycles (**Figure 3**). However, due to limited water storage and the variability of rainfall, many farmers

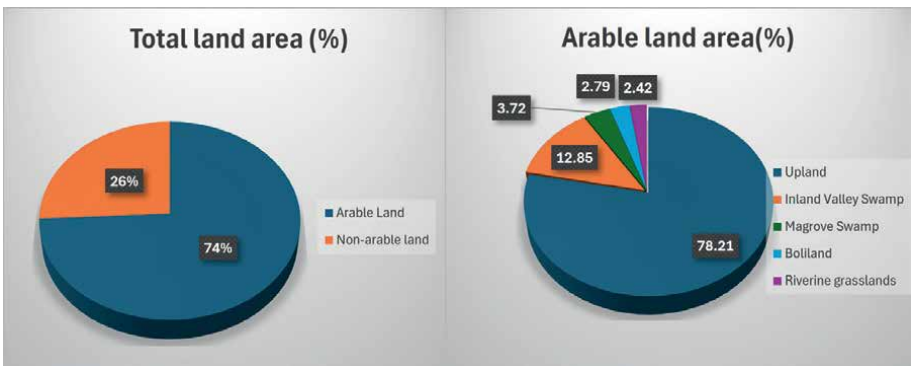


Figure 2.
Total land area and breakdown of arable land area in Sierra Leone.

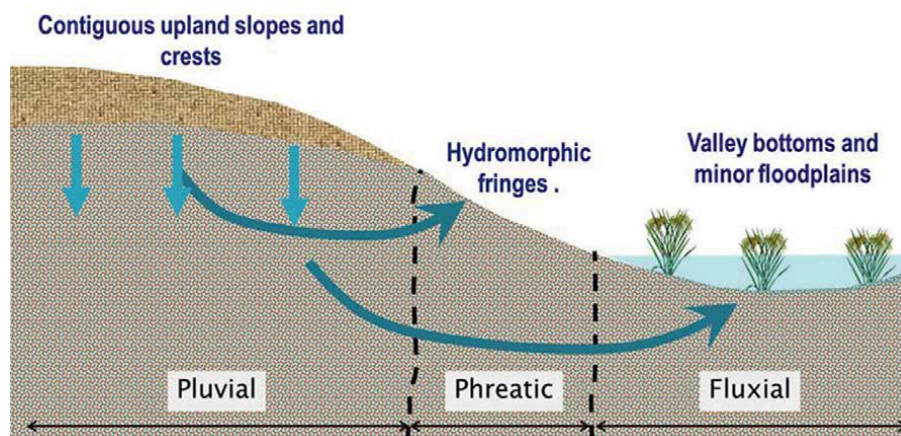


Figure 3.
 Recharge pathways along an IVS toposequence (Adapted from Andriesse et al., [4]).

struggle to cultivate more than one crop per year. Addressing this challenge requires water management solutions, including irrigation technologies and small-scale water storage infrastructure.

Water Productivity is defined as the ratio of agricultural output to the volume of water consumed in the production process. In the context of rice farming, it specifically measures the efficiency of water conversion into rice grain, typically quantified as kilograms of rice produced per cubic meter of water utilized (kg/m^3). Enhancing Water Productivity involves maximizing crop yields while minimizing water use, a critical objective for sustainable water management in both irrigated and rainfed agricultural systems [5, 6]. By optimizing land and water resources, particularly in IVS areas, Sierra Leone can improve food security and ensure resilient agricultural systems in the face of climate variability. This chapter explores the potential of Inland Valley Swamps for improving rice production in Sierra Leone and delves into opportunities for enhancing Water Productivity.

2. Agricultural development potential of Inland Valley swamps

Inland Valley Swamps (IVS) in Sierra Leone are vital for agricultural development, food security, and rural livelihoods. These seasonally flooded lowlands, with high soil moisture retention, are ideal for year-round rice cultivation and other crops like maize, cassava, and vegetables. IVS farming reduces reliance on erratic rainfall, enabling multiple cropping cycles and boosting food production, which is crucial for achieving food self-sufficiency [7, 8].

Maximizing rice production in IVS can reduce Sierra Leone's dependency on rice imports, enhancing food security and saving foreign exchange. Improved irrigation and water management in IVS systems increase yields and incomes for smallholder farmers, many of whom depend on agriculture for their livelihoods. Integrating livestock farming, such as fish and duck rearing, diversifies income sources, enhancing resilience and reducing risks associated with single-crop reliance.

IVS-based farming is more resilient to drought compared to upland farming, ensuring stable food production even during dry spells. Sustainable practices like

controlled water use and agroforestry prevent soil degradation and erosion while reducing deforestation caused by slash-and-burn agriculture. This promotes both food security and environmental conservation [9].

IVS development also offers opportunities for agribusiness and private sector investment. With proper infrastructure, IVS can support mechanized farming, improved irrigation, and agro-processing industries, creating jobs and reducing postharvest losses. Farmer cooperatives and government-led training programs can further enhance productivity and market access, transforming IVS farming into a commercially viable sector [1].

3. Water productivity in different ecosystems

3.1 Upland rice farming

Rainfed upland rice farming in Sierra Leone yields 0.8–1.5 metric tons per hectare due to poor soil fertility, erratic rainfall, and traditional practices like slash-and-burn, which degrade soil health over time [10]. While it requires low initial investment and suits mixed cropping, its vulnerability to climate variability makes it unreliable. Challenges include high erosion rates and minimal use of improved inputs such as fertilizers and high-yield seeds.

Irrigated upland rice farming improves yields to 1.8–2.5 metric tons per hectare by stabilizing water availability and reducing reliance on unpredictable rainfall [2]. However, limited irrigation infrastructure, high development costs, and dependence on external investments hinder its adoption. Despite these barriers, it offers more stable yields and greater food security potential compared to rainfed systems.

Rainfed Inland Valley Swamp (IVS) rice farming achieves Water Productivity, yielding 2.0–3.0 metric tons per hectare, benefiting from natural moisture retention and nutrient-rich soils (**Table 1**). However, seasonal flooding and poor drainage can lead to crop losses. IVS systems are less drought-prone, support multiple cropping cycles, and provide a more sustainable alternative to upland farming.

3.2 Inland Valley swamp (IVS) rice farming

Irrigated IVS rice farming exhibits high Water Productivity, yielding 4.0–5.5 metric tons per hectare through controlled water management, improved fertilizers, and

Ecosystem	Land use system	Yield (metric tons per hectare)	Key characteristics
Upland	Rainfed	0.8–1.5	Low soil fertility, high erosion, dependent on erratic rainfall, minimal input use [10]
	Irrigated	1.8–2.5	More stable yields with irrigation but limited infrastructure and high development costs [2, 11]
IVS	Rainfed	2.0–3.0	Moderate yields due to better moisture retention and soil fertility but prone to seasonal flooding [12]
	Irrigated	4.0–5.5	High productivity with controlled water supply, fertilizer use, and mechanization [12, 13]

Table 1.
Water productivity in different ecosystems.

mechanization [13]. It enables year-round production, ensuring food security and economic benefits. Although it requires significant investment in infrastructure and farmer training, irrigated IVS farming is the most sustainable and resilient system, offering long-term advantages for farmers and national food security. Globally, irrigated lowland systems produce 75% of rice from 93 million hectares [14].

4. Strategies for optimizing water productivity in Inland Valley swamp

Inland Valley Swamps (IVS) in Sierra Leone present significant opportunities for optimizing Water Productivity, enhancing agricultural productivity, and improving food security. These seasonally flooded lowlands, with high soil moisture retention, support year-round rice cultivation and diverse crops like maize, cassava, and vegetables, enabling multiple cropping cycles and boosting food self-sufficiency. Expanding rice production in IVS can reduce reliance on imports, lower foreign exchange costs, and improve food security. Integrated farming systems, such as fish and duck rearing, diversify income and enhance resilience. IVS farming is more drought-resistant than upland farming, offering stability amid climate change. Sustainable practices like controlled water use and agroforestry prevent soil degradation and reduce deforestation, promoting environmental conservation.

Agribusiness investments in IVS can drive mechanized farming, improved irrigation, and agro-processing industries, creating jobs and improving market access. Farmer cooperatives and training programs can equip smallholders with skills to maximize productivity. However, challenges like water management, inadequate infrastructure, limited access to inputs, and land tenure conflicts must be addressed. Strategic investments and sustainable practices can unlock IVS's full potential, fostering agricultural growth, economic development, and long-term food security in Sierra Leone.

4.1 Small earth dams in Inland Valley swamps (IVS)

The construction of small earth dams presents a significant opportunity to enhance Water Productivity in Inland Valley Swamps (IVS). These dams store rainwater during the wet season, ensuring a reliable water supply for irrigation during dry periods. This controlled water management system prevents both flooding and water shortages, creating a stable environment for crop growth. A study by Blango et al. [15] demonstrated that a micro-dam with the capacity of 26,500 m³ (**Figure 4**) enabled the cultivation of a second crop during the dry season, significantly boosting yields. For instance, rice yields increased from 1.7–3.2 t/ha in the rainy season to 2.5–4.7 t/ha in the dry season with supplementary irrigation. This highlights the role of small dams in extending cropping periods and enhancing agricultural productivity.

Beyond crop production, small earth dams support integrated farming systems by providing water for fish farming, livestock, and domestic use, increasing the economic value of IVS areas [16]. They also contribute to soil conservation by reducing erosion and improving groundwater recharge, promoting sustainable land management. For example, Djuma et al. [17] found that a check dam with a storage capacity of 25,000 m³ contributed an average of 3.1 million m³ annually to aquifer recharge, accounting for 30% of total streamflow. This demonstrates the effectiveness of small dams in enhancing groundwater resources, particularly in semiarid regions.

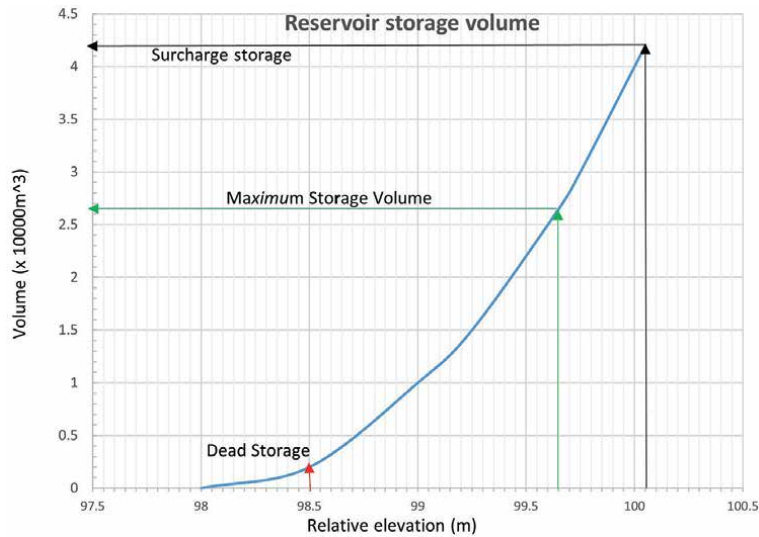


Figure 4.
Depth-storage curve for a reservoir formed by an earth dam.

By implementing small earth dams, farmers can improve resilience to climate variability, optimize water and land resources, and achieve higher agricultural productivity. These structures not only support crop diversification and extended growing seasons but also foster sustainable practices, making them a valuable investment for enhancing food security and rural livelihoods in IVS ecosystems.

4.2 Incorporating floating rice in Inland Valley swamps

Additionally, land productivity under this system could be enhanced through the cultivation of floating rice upstream of earth dams, specifically within the reservoir area. This approach could bring additional land into production, effectively utilizing half the size of the reservoir. Floating rice offers a promising adaptation for farming in Inland Valley Swamps (IVS), particularly in flood-prone areas where water levels fluctuate significantly. Floating rice varieties, characterized by their elongated stems, thrive in deep water, making them ideal for IVS regions affected by seasonal flooding. By incorporating floating rice, farmers can optimize land use in areas that would otherwise be unsuitable for conventional rice cultivation.

Moreover, floating rice requires fewer chemical inputs and can be integrated with fish farming, creating a synergistic system that enhances both food security and economic benefits. This dual-purpose approach not only maximizes resource efficiency but also diversifies income sources for farmers. Integrating floating rice into IVS farming systems can significantly improve resilience against climate change, ensuring sustained rice production even under extreme weather conditions [18]. By adopting this innovative practice, IVS farming systems can become more adaptive, productive, and sustainable, contributing to long-term food security and rural development.

4.3 Water-saving rice farming practices

Water savings from Alternate Wetting and Drying (AWD) and Aerobic Rice Systems (ARS) enhance Water Productivity by enabling additional crops or extended

cropping seasons. AWD reduces water use by 15–30%, while ARS saves even more by growing rice in non-flooded conditions [5]. These savings can irrigate other crops like vegetables, legumes, or maize during dry seasons or in adjacent fields, promoting crop diversification and intensification. For instance, saved water supports double or triple cropping, increasing annual output from the same land. It also enhances integrated farming systems, such as fish farming or livestock rearing, boosting productivity and incomes. By optimizing water use, AWD and ARS improve rice yields and enable sustainable land utilization, supporting food security and rural livelihoods.

Alternate Wetting and Drying (AWD) increased Water Productivity in 92% of cases across 31 field experiments analyzed by Bouman and Tuong [19], despite yield reductions ranging from 0–70%. The reduction in water use was proportionally greater than the yield loss, making AWD valuable for water-scarce regions. Variability in outcomes was linked to irrigation frequency, soil types, and hydrological conditions.

Bouman et al. [20] assessed the tropical aerobic rice variety Apo, finding that aerobic yields were 32% lower than flooded yields in the dry season and 22% lower in the wet season. However, aerobic systems used significantly less water—790–1430 mm compared to 1240–1880 mm in flooded fields. Water savings included reductions in land preparation (190 mm), seepage and percolation (250–300 mm), evaporation (80 mm), and transpiration (25 mm). These findings underscore AWD and aerobic rice's potential to optimize water use while maintaining reasonable yields.

Blango et al. [12] emphasized the importance of water management practices, such as the aerobic rice system and alternate wetting and drying (AWD), in enhancing land use efficiency and rice productivity in tropical Inland Valley Swamps. The study compared these practices with continuous flooding, both with and without biochar soil amendment, highlighting their potential to optimize resource use, improve yields, and promote sustainable farming. Aerobic rice and AWD significantly improved Water Productivity (grain yield per unit of water) compared to continuous flooding.

For example, during the 2015/2016 dry season, continuous flooding used 114% more water than the aerobic system but produced only 15% more rice. Similarly, in the 2016/2017 dry season, continuous flooding used 97% more water but yielded just 11% more rice, demonstrating the superior water efficiency of aerobic rice and AWD, particularly in water-scarce regions. Biochar also enhanced productivity, especially in the dry season, though its interaction with water management had limited effects, suggesting that their benefits could be optimized independently.

The aerobic rice system, irrigated after 50% soil moisture depletion, proved highly water-efficient and well-suited for water-scarce environments, maintaining competitive yields with minimal water input. AWD, which allowed fields to dry before re-flooding, improved Water Productivity, reduced methane emissions, and enhanced soil aeration. In contrast, while continuous flooding produced slightly higher yields, it was less sustainable due to excessive water use.

4.4 Modeling the effects of climate change on land and water resources

Milly et al. [21] argued that the traditional assumption of stationarity in water management was outdated due to climate change, advocating for adaptive strategies using climate models to predict future hydrological conditions. These models provided insights into changes in water availability, precipitation, and extreme weather, enabling optimized land use. For instance, drought-prone areas prioritized

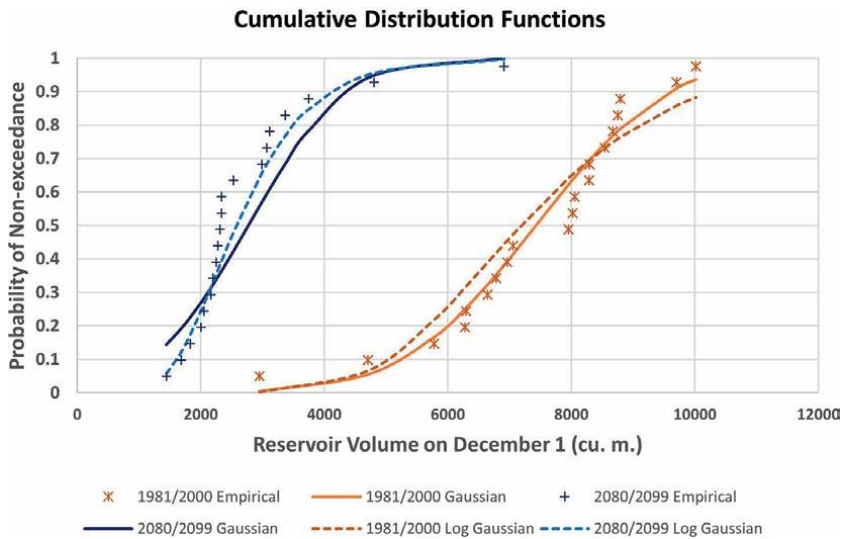


Figure 5.
An indication of reduction in storage volume of water in a reservoir at any probability, in the future (2081–2100) as compared to the baseline period (1981–2000).

drought-resistant crops, while flood-prone regions focused on conservation or flood mitigation. This approach aligned agriculture, urban development, and ecosystem conservation with future climate realities, enhancing resilience and sustainability.

Arnell and Gosling [22] emphasized the role of global climate models (GCMs) in assessing flood risks and guiding land use planning. Hydrologic models identified high-risk areas, enabling targeted measures like reserving flood-prone zones for green infrastructure (e.g., wetlands) and directing development to safer areas. This reduced vulnerability to flooding while improving land use productivity and sustainability. Integrating climate and hydrologic models allowed decision-makers to create resilient, adaptive systems that balanced development and environmental conservation.

Blango et al. [23] highlighted the importance of climate projections in understanding hydrologic processes and the potential of the Soil and Water Assessment Tool (SWAT) for evaluating land use changes, nutrient loading, and water quality, particularly in sub-Saharan Africa. SWAT simulated water storage in reservoirs, accounting for seepage and evaporation, and predicted dam inflows and water management. Using Bias-Corrected and Downscaled WCRP CMIP3 Climate Projections for 2046–2064 and 2081–2100, the study projected a decline in reservoir storage at the onset of the dry season, with 100-year storage volumes decreasing from 10,000 m³ to 6900 m³ (Figure 5). The effective application of SWAT required calibration, as demonstrated using 2014/15 and 2015/16 data, to enhance predictive accuracy and support supplementary irrigation planning. These findings underscored the value of hydrologic models in addressing climate change impacts on water resources.

5. Conclusion

Inland Valley Swamps (IVS) hold immense potential for irrigation, enhancing Water Productivity, and boosting agricultural productivity. Sierra Leone has 690,000 ha of IVS spread across the country. Adopting sustainable water

management practices like Aerobic Rice Systems (ARS) and Alternate Wetting and Drying (AWD) can significantly improve Water Productivity and reduce reliance on erratic rainfall. The water used for Continuous Flooding could irrigate twice the area under ARS, potentially doubling yields.

Micro-dams in IVS support integrated resource management, enabling fish farming and livestock rearing alongside crop production. Additionally, cultivating floating rice in reservoir areas upstream of earth dams optimizes land use, bringing otherwise unproductive land into cultivation. This approach is particularly beneficial in flood-prone regions with fluctuating water levels, increasing food security and resilience.

Improving Water Productivity in IVS is key to sustainable agriculture, economic growth, and climate resilience, ensuring long-term prosperity.

Acknowledgements

We sincerely appreciate all those whose work and data have contributed to guiding the process of achieving food security in Sierra Leone.

The author acknowledges the usage of Chat GPT for language polishing of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

Author details

Mohamed Matthew Blango*, Emmanuel Kangoma and Navo Yambasu
Njala University, Njala, Sierra Leone

*Address all correspondence to: mmblango@njala.edu.sl

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*Edited by Jamila Tarhouni,
Muhammad Akhyar Farrukh and Shaista Ali*

This Edited Volume, *Advances in Water Resources Science*, is a collection of peer-reviewed research chapters that offer a comprehensive overview of recent developments in the field. The book comprises single chapters authored by various researchers and edited by an expert active in the Water Resources research area. All chapters are complete in themselves but united under a common research study topic. This publication aims to provide a thorough overview of the latest research efforts by international authors on Water Resources Science, and open new possible research paths for further novel developments.

J. Kevin Summers, Environmental Sciences Series Editor

Published in London, UK

© 2025 IntechOpen
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ISSN 2754-6713

ISBN 978-1-83634-864-1

