Zero Liquid Discharge in the Dye Intermediate Industry with the Primary Treatment Method

Mamta Saiyad[1]; Nimish Shah[2]; Uchitesh Shettyan[3]; Heli Modi[4]; Milind Joshipura[5]; Ankur Dwivedi[6]; and Shibu Pillai[7]

Abstract: The dye intermediate industry plays a pivotal role in the textile, paper, and chemical sectors, but it is often associated with significant water pollution owing to the release of complex and colored effluents. This paper explores the implementation of zero liquid discharge (ZLD) as a sustainable solution to address the environmental challenges posed by the dye intermediate industry. ZLD is a comprehensive wastewater management approach that aims to eliminate liquid waste discharge, while recovering valuable resources. The paper delves into the specific challenges faced by the dye intermediate industry, such as the presence of recalcitrant organic compounds and intense coloration in wastewater. It examines how ZLD systems, which typically without involving costly membrane processes, evaporation, crystallization, and chemical treatments, can effectively treat these complex effluents to achieve environmental compliance and resource conservation. Furthermore, the paper discusses the benefits of ZLD adoption in the dye intermediate sector. It has been shown that by making alterations to the primary treatment method, ZLD can be achieved. These include the prevention of water pollution, the preservation of water resources, and compliance with stringent environmental regulations. The economic and operational advantages of ZLD are also highlighted. **DOI: 10.1061/JHTRBP.HZENG-1328**. *© 2024 American Society of Civil Engineers.*

Author keywords: Zero liquid discharge; Coagulation; Flocculation; Dye intermediate; Primary treatment method.

Introduction

In the world of industry, the widespread use of dyes, from small-scale enterprises to colossal factories, spanning tanneries, food production, cosmetics, textiles, and pharmaceuticals, has left a significant mark. With a staggering annual global production of 1 million t, the textile sector stands out as a major contributor to dye emissions into our ecosystem. Alarming figures reveal that dye industries alone discharge approximately 7,500 metric t of pollutants annually (Maheshwari et al. 2021). The complex molecular structures of dyes, characterized by aromatic rings intertwined with various functional groups and π-electron systems, enable them to absorb light within the 380–700 nm spectra, creating the vivid colors that we love. However, these same properties also give rise to the presence of chromogens and chromophores, which can have far-reaching implications (Kumar et al. 2021; Rápó and Tonk 2021). Among the multitude of natural and synthetic dyes, those containing azo groups have garnered particular attention for their high carcinogenic potential, stemming from the release of amines and benzidines. Additionally, the nonbiodegradability of dye molecules allows them to persist in the environment, posing continuing hazards (Al-Tohamy et al. 2022; Alsukaibi 2022).

In light of these concerns, the importance of removing dye molecules from wastewater before its release into the environment is essential and plausible. The repercussions for aquatic life, following direct contact with dyed waters, have been severe. Moreover, observations in human health range from skin irritations to diseases akin to cancer. While numerous approaches have been proposed for treating dye-laden effluents, the search for the most effective technique continues (Bal and Thakur 2021; Alsukaibi 2022). In this study, we strive to consolidate comprehensive insights into dyes, their deleterious effects, and treatment methodologies on a global scale, while also offering an Indian perspective. Furthermore, a comparative analysis of available techniques and recent advances in purifying dye-containing wastewater is carried out, shedding light on potential solutions to this pressing environmental and health issue. To adopt affordable alternatives to costly methods for treatment is crucial (Maheshwari et al. 2021; Castillo-Suárez et al. 2023; Islam et al. 2023; Khan et al. 2023; Sudarshan et al. 2023).

Methods for Treatment of Liquid Effluents

Numerous methods are developed for the treatment of liquid effluents generated by chemical industries. These methods can be classified as conventional methods [such as coagulation/flocculation, precipitation, biodegradation, filtration (sand), adsorption using activated charcoal (AC), etc.] and advanced methods (Maheshwari

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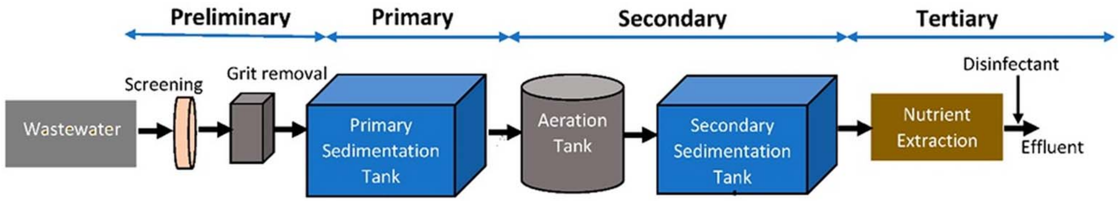

Fig. 1. Wastewater treatment steps.

et al. 2021). Wastewater treatment for dyes and intermediates from the textile and chemical industries is essential to minimize environmental pollution and ensure compliance with environmental regulations. These effluents often contain a variety of organic and inorganic compounds that can be harmful to aquatic ecosystems and human health (Sharma et al. 2021; Al-Tohamy et al. 2022; Alsukaibi 2022). Fig. 1 shows a general overview of wastewater treatment processes for dyes and intermediates: preliminary treatment followed by primary, secondary, and tertiary treatment (Enebe et al. 2023).

Preliminary Treatment

This includes screening and grit removal, in which large debris and objects are removed using screens or grates to prevent damage to downstream equipment (Maheshwari et al. 2021; Akbar et al. 2023; Nishat et al. 2023).

Primary Treatment

After preliminary treatment, water goes for a primary treatment, in which wastewater is allowed to settle in a tank, and solids, including large dye particles and some intermediates, settle to the bottom as sludge. This is also called sedimentation. This is followed by equalization, in which wastewater flow and composition are evened out to reduce shock loads to downstream treatment processes (Maheshwari et al. 2021; Akbar et al. 2023; Nishat et al. 2023).

Secondary Treatment

Many dyes and intermediates are organic compounds that can be biodegraded by microorganisms. Common biological treatment methods include activated sludge processes, aerobic and anaerobic digestion, and sequencing batch reactors (SBRs). These are followed by aeration (Enebe et al. 2023). In activated sludge processes, aeration provides oxygen to microorganisms, promoting the breakdown of organic compounds. As a part of the next step, nutrient addition is done. Nutrients like nitrogen and phosphorus may be added to enhance microbial activity in the treatment process (Maheshwari et al. 2021; Akbar et al. 2023; Nishat et al. 2023).

These methods are very simple to apply and very cost-effective. These methods consume large quantities of chemicals such as lime and alum. At the end, these methods generate a large amount of sludge, which is difficult to handle. Some metal particles cannot be possibly treated with these methods, and decoloration is sometimes difficult to achieve, requiring some advanced processes (Grégorio and Lichtfouse 2018).

Tertiary Treatment (Advanced Treatment)

Chemical coagulation and flocculation: Chemicals such as alum or ferric chloride are added to facilitate the removal of residual color and fine particles. After coagulation and flocculation, wastewater is filtered through sand, anthracite, or other media to further remove fine particles (Enebe et al. 2023; Vymazal 2023; Yaqoob et al. 2023). Some of the advanced oxidation techniques such as ozonation, UV irradiation, or hydrogen peroxide treatment can be used to oxidize and break down persistent organic compounds. Technologies like ultrafiltration or nanofiltration can be employed to realize high-quality effluent by removing remaining impurities and dyes (Ma et al. 2021; Akbar et al. 2023; Nishat et al. 2023; Yaqoob et al. 2023). The sludge generated in the primary and secondary treatment processes is often dewatered to reduce its volume before disposal or further treatment. According to the characteristics, sludge can be disposed of. It can be incinerated, landfilled, or sometimes can be used for energy recovery or agricultural purposes in accordance with regulatory requirements. Effluent from the tertiary treatment stage may be suitable for reuse within the industrial process if its quality meets specific standards (Maheshwari et al. 2021; Akbar et al. 2023; Nishat et al. 2023).

Regular monitoring and testing ensure that the effluent quality complies with local environmental regulations and discharge permits. It is essential to tailor wastewater treatment processes to the specific characteristics of the dyes and intermediates present in the effluent, because different compounds may require different treatment approaches. Additionally, industries should work closely with environmental consultants and regulatory agencies to ensure compliance and minimize the environmental impact of their wastewater discharges (Maheshwari et al. 2021; Akbar et al. 2023; Nishat et al. 2023).

Advanced Wastewater Treatment Methods: A Comparative Overview

Wastewater treatment is a critical process to ensure the removal of pollutants before effluents are discharged into the environment. As environmental regulations become more stringent and water scarcity concerns rise, there is an increasing need for advanced wastewater treatment methods that go beyond conventional processes (Jagmohan et al. 2021; Akbar et al. 2023; Gürtekin 2023; Nishat et al. 2023; Rashid et al. 2023; Ronda et al. 2023; Tarpani and Azapagic 2023; Varol et al. 2024). Many advanced treatment methods are being explored and a comparative analysis of their effectiveness is being reported.

Membrane Bioreactors

Membrane bioreactors (MBRs) combine biological treatment with membrane filtration, offering superior effluent quality and reduced footprint compared with conventional activated sludge processes. MBRs produce high-quality effluent and leave a smaller footprint compared with conventional activated sludge systems. However, they are energy-intensive and require frequent membrane cleaning and maintenance (Mishra et al. 2022; Qrenawi and Rabah 2023; Rahman et al. 2023; Zahmatkesh et al. 2023).

Reverse Osmosis

Reverse osmosis (RO) involves forcing water through a semipermeable membrane to remove contaminants. It is particularly effective in desalination and removing dissolved ions. RO is highly effective in removing dissolved contaminants, achieving up to 99% removal rates. Nano filtration (NF) offers selective removal of certain ions, while allowing others to pass through. However, both processes require high-energy inputs and produce concentrated brine waste (McIlvaine 2008; Criscuoli et al. 2023; Hu et al. 2023; Mendoza et al. 2023; Alonso et al. 2024; Mangalgiri et al. 2024).

Advanced Oxidation Processes

Advanced oxidation process (AOPs) involve the generation of highly reactive hydroxyl radicals to break down organic and inorganic pollutants. AOPs are effective in treating recalcitrant organic compounds and emerging contaminants. However, they can be expensive to implement and require a careful control of operating conditions to optimize performance (Ma et al. 2021; Prado de Nicolás et al. 2022; Ponnusami et al. 2023; Feijoo et al. 2023; Liu et al. 2023; Mahbub and Duke 2023; Mukherjee et al. 2023; Yaqoob et al. 2023).

Constructed Wetlands

Natural or engineered wetlands use plants, microorganisms, and substrate to treat wastewater through physical, chemical, and biological processes. Constructed wetlands are cost-effective, require low maintenance, and are environmentally sustainable. They provide habitat for wildlife and can enhance landscape aesthetics. However, their performance may vary depending on site-specific conditions and require larger land areas compared with other treatment methods (Alnaser et al. 2023; Madeira et al. 2023; Tang et al. 2023; Vymazal 2023; Waly et al. 2023; Ali et al. 2024).

Electrocoagulation

Electrocoagulation (EC) involves the use of electric current to destabilize and aggregate contaminants for easy removal. EC is effective in removing suspended solids, heavy metals, and organic pollutants. They offer a chemical-free alternative to traditional coagulation processes but may require higher operating costs for electricity, electrode maintenance, limited applicability for certain contaminants such as dissolved inorganic compounds, highly soluble organic compounds, nonaqueous phase liquids (napls), and so on (Magnisali et al. 2022; Javed and Mushtaq 2023; Faraj et al. 2024). EC is less effective for removal of dissolved inorganic compounds such as nitrates, phosphates, and sulfates, which may require other treatment methods like ion exchange or membrane filtration. Some highly soluble organic compounds, especially those with complex molecular structures or low molecular weights, may not be effectively removed by electrocoagulation alone. This method may have limited effectiveness in removing trace contaminants present in very low concentrations, such as certain heavy metals or persistent organic pollutants. It may not be suitable for treating nonaqueous phase liquids, such as oils and greases, which require specialized separation techniques like gravity separation or dissolved air flotation. While EC can effectively remove pathogens and bacteria through electrochemical disinfection, certain biological contaminants, such as spores or resistant microorganisms, may be more challenging to eliminate completely. It is important to note that the effectiveness of electrocoagulation can vary depending on factors such as the specific contaminants present, their concentrations, and the operating conditions of the EC system. In some cases, EC may be used as part of a multistage treatment process or in combination with other treatment technologies to achieve desired water-quality goals (Magnisali et al. 2022; Javed and Mushtaq 2023; Mao et al. 2023; Faraj et al. 2024).

UV-C and Advanced Oxidation UV

UV-C irradiation and AOP-UV utilize ultraviolet light to disinfect and degrade organic pollutants. Both of these method offers effective disinfection. There is no chemical addition in UV-C irradiation, versatile for AOP-UV. However, there is a limited penetration during disinfection for UV-C, whereas, method AOP-UV can penetrate more but it is an energy-intensive method (Gonçalves et al. 2023; Ramos et al. 2023).

Membrane Distillation and Forward Osmosis

Membrane distillation (MD) and forward osmosis (FO) are emerging membrane-based processes for wastewater treatment, utilizing differences in vapor pressure or osmotic pressure to separate water from contaminants. These methods offer potential advantages in treating high-salinity or brackish wastewater streams, achieving high water recovery rates and producing low-volume concentrated brine. However, these technologies are still under development and may require further optimization for commercial-scale applications.

Each method has varying efficiencies for different contaminants. RO excels in removing dissolved solids, while AOPs are effective for complex organic pollutants. Initial and operational costs differ significantly. MBRs may have higher upfront costs, while EC and constructed wetlands may offer more economical solutions. Consideration of energy consumption, chemical use, and the generation of byproducts is essential for evaluating the environmental impact. The suitability of each method depends on factors such as the type of contaminants, the scale of operation, and regulatory requirements. In short, the choice of an advanced wastewater treatment method should be tailored to the specific needs and constraints of the wastewater stream. A holistic approach, considering treatment efficiency, costs, and environmental impact, is crucial for implementing sustainable and effective wastewater management strategies (Jagmohan et al. 2021; Akbar et al. 2023; Ponnusami et al. 2023; Gürtekin 2023; Krishnan et al. 2023; Nishat et al. 2023; Yaqoob et al. 2023).

Out of these various wastewater treatment methods, all are undeniably effective. The financial implications associated with their implementation are considerable. In response to the challenges posed by the cost-intensive nature of traditional wastewater treatment approaches, the concept of minimum liquid discharge (MLD) emerged as a strategic paradigm shift. MLD is not merely a modification of existing methodologies; rather, it represents a forward-thinking approach to wastewater management by specifically addressing the economic concerns associated with liquid discharge. The essence of MLD lies in the development and implementation of methods designed to minimize the generation of liquid waste, aligning with the broader goal of achieving sustainable and cost-effective wastewater treatment. Unlike conventional methods that focus predominantly on treatment efficacy, MLD places a premium on reducing the volume of liquid effluent discharged into the environment, thereby optimizing the overall cost-efficiency of the treatment process.

Within the framework of MLD, a spectrum of innovative and advanced technologies has been harnessed. These technologies, ranging from membrane filtration and advanced oxidation processes to closed-loop systems, are strategically employed to not only elevate the quality of treated water but, crucially, to curtail the quantity of liquid discharge. This shift toward minimizing liquid generation brings forth a dual benefit: it not only meets stringent environmental regulations but also addresses economic concerns by mitigating disposal costs. Furthermore, MLD emphasizes the integration of water reuse and resource recovery into wastewater treatment processes. By facilitating the recycling of treated water for various nonpotable purposes and the reclamation of valuable resources from wastewater streams, MLD contributes to the circular economy model. This holistic approach aligns with sustainable practices and enhances the economic viability of wastewater treatment initiatives over the long term.

While MLD undeniably presents a promising avenue for optimizing wastewater treatment, it is essential to acknowledge that the adoption of such advanced approaches is not without its challenges. The implementation of MLD technologies may require initial investments, and considerations must be made regarding factors such as energy consumption, brine disposal, and the regulatory landscape. The evolution from traditional wastewater treatment to the minimum liquid discharge concept underscores a commitment to both environmental sustainability and economic prudence. By championing strategies that minimize liquid waste generation, MLD stands as a beacon for the future of wastewater treatment—driving innovation, efficiency, and responsible resource management.

MLD Concept in Wastewater Treatment

The MLD concept represents an advanced approach to wastewater treatment that aims to minimize the volume of liquid effluent released into the environment, moving closer to the goal of zero liquid discharge. MLD involves the reduction of liquid waste generation through efficient treatment processes, recycling, and resource recovery. Fig. 2 shows the key principles and benefits associated with the MLD concept.

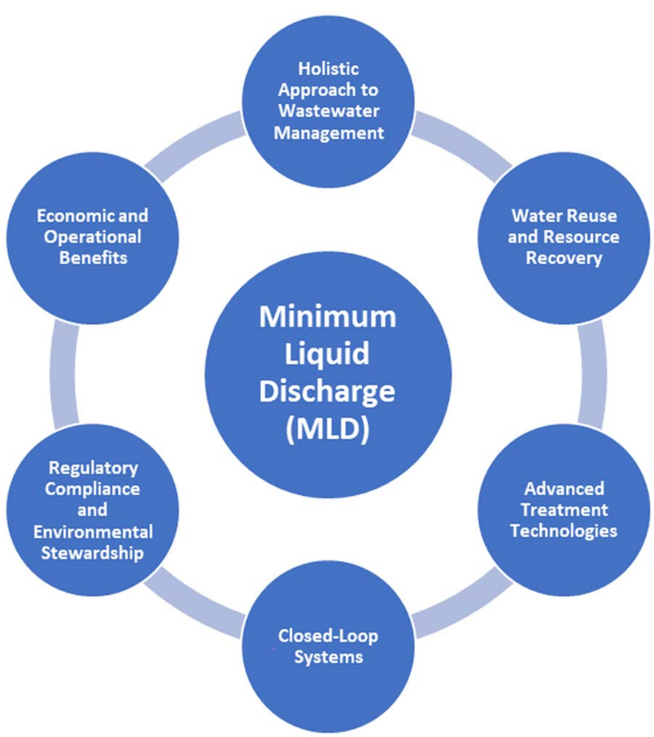

Fig. 2. Key principles and benefits associated with the MLD concept.

MLD integrates various advanced treatment technologies to not only realize high-quality effluent but also achieve a significant reduction in the volume of liquid discharge. The focus is on comprehensive wastewater management that considers both environmental impact and resource recovery. The concept of MLD emphasizes the recovery and reuse of treated water and valuable resources from wastewater. This includes recovering water for nonpotable uses such as industrial processes, agricultural irrigation, and potable reuse in some cases. Additionally, MLD promotes the recovery of nutrients, energy, and other valuable by-products from wastewater. To achieve these goals, wastewater treatment plants often incorporate advanced treatment technologies such as membrane filtration (including reverse osmosis), advanced oxidation processes, and biological treatment methods like MBRs. These technologies ensure a higher degree of pollutant removal and produce a cleaner, more reusable effluent. These systems aim to establish closed-loop water cycles within industrial or municipal facilities. This involves treating wastewater on-site, recycling a significant portion of the treated water for internal processes, and minimizing external discharge. Closed-loop systems contribute to water conservation and reduce the environmental impact of wastewater discharges. The MLD concept aligns with increasingly stringent environmental regulations and a growing emphasis on sustainable practices. By reducing the volume of liquid discharge, industries and municipalities can demonstrate their commitment to environmental stewardship and meet regulatory requirements effectively. While the initial implementation of MLD technologies may involve higher upfront costs, the long-term economic and operational benefits are significant. Reduced water consumption, lower disposal costs, and potential revenue generation from resource recovery contribute to the economic viability of MLD systems.

Implementing MLD requires careful consideration of the specific characteristics of the wastewater stream, the technological infrastructure, and the regulatory landscape. Challenges may include high-energy requirements for certain treatment processes, the potential for brine disposal in desalination-based MLD systems, and ensuring the quality and safety of reused water (Panagopoulos 2021, 2023; Panagopoulos and Giannika 2022, 2023; Panagopoulos and Haralambous 2020; Avramidi et al. 2023).

The MLD concept represents a paradigm shift in wastewater treatment toward sustainable and responsible practices. By focusing on water reuse, resource recovery, and advanced treatment technologies, MLD contributes to environmental conservation, regulatory compliance, and the long-term resilience of water management systems.

In the event that the liquid component within industrial effluent can be either reused or effectively removed, the risk of resource pollution is significantly mitigated. Hence, the pivotal concept of zero liquid discharge (ZLD) is designed to enable the comprehensive reuse of all water contained in the liquid effluent, ensuring that solely solid residues are discharged as waste. This innovative approach not only minimizes the environmental impact by preventing liquid pollutants from entering water resources but also maximizes the conservation and sustainable utilization of water within industrial processes. By adhering to the principles of ZLD, industries can significantly enhance their environmental stewardship, optimize resource efficiency, and contribute to a more sustainable and circular approach to water management.

Zero Liquid Discharge

ZLD is an advanced wastewater management process that aims to minimize or completely eliminate the discharge of liquid waste from industrial processes. It is particularly important in industries that generate large volumes of wastewater containing pollutants, salts, and other contaminants that can have negative environmental impacts if released into water bodies or the environment.

The ZLD process involves several stages and technologies to achieve its goal, such as pretreatment, concentration, crystallization, evaporation, membrane processes, chemical treatment, recycling and reuse, and residuals management. After removal of larger solids and initial separation of liquids from the wastewater stream, various methods are employed to concentrate the wastewater by removing water content. This can be done through techniques such as evaporation and crystallization or membrane processes such as reverse osmosis. Crystallization is a critical step for removing dissolved solids. It involves cooling the concentrated wastewater to encourage the formation of crystals, which can then be separated from the liquid phase. Evaporation involves heating the concentrated wastewater to cause water to evaporate, leaving behind solid salts and other pollutants that can be collected and disposed of properly. Techniques such as reverse osmosis and ultrafiltration use membranes with specific pore sizes to selectively separate water and contaminants, allowing clean water to pass through, while retaining pollutants. Chemical processes can be employed to precipitate and remove specific contaminants from the wastewater. After implementing the various treatment steps, the remaining water can often be treated to a quality suitable for reuse within the industrial process, reducing the overall demand for fresh water. The solid waste and concentrated by-products generated during the ZLD process need to be managed and disposed of in an environmentally responsible manner, which might involve methods such as landfilling or repurposing them in other industries (An et al. 2022; Patil et al. 2023).

ZLD is an environmentally responsible approach because it significantly reduces the impact of industrial processes on water resources and aquatic ecosystems. It is often used in industries such as power generation, chemicals manufacturing, textiles, pulp and paper, and more, in which large amounts of complex wastewater are generated. While ZLD offers many benefits, it can also be energy-intensive and expensive to implement, and therefore, it is often adopted by industries that have a strong commitment to sustainability and responsible resource management (Prado de Nicolás et al. 2022; Vignesh Kumar et al. 2022; Kodialbail and Sophia 2023; Panagopoulos 2023; Panagopoulos and Giannika 2023).

Coagulation–Flocculation Method

Coagulation–flocculation is a widely used treatment method for the removal of suspended solids, colloids, and other impurities from wastewater. The process involves the addition of coagulants to destabilize particles in the water, allowing them to come together and form larger, settleable flocs. There are many factors that affect the efficiency of the coagulation–flocculation process, such as the nature of the contaminants, wastewater characteristics, pH, temperature, and the type and also the dosage of coagulants and flocculants used. Laboratory-scale tests are often conducted to optimize the coagulation–flocculation process for specific wastewater characteristics. Regular monitoring and adjustments are necessary to ensure consistent and effective treatment. Coagulation–flocculation is effective for the removal of suspended solids, turbidity, and certain dissolved substances from wastewater. This method has been explored to obtain zero liquid discharge from the dye intermediate plant. It is an innovative idea that has never been used.

Chemical Oxygen Demand

Chemical oxygen demand (COD) is a critical parameter in the assessment and treatment of wastewater. It measures the amount of oxygen required to chemically oxidize organic and inorganic substances in the water. COD provides a quantitative measure of the pollution load in wastewater. Higher COD values indicate a higher concentration of oxidizable pollutants, reflecting the extent of contamination. COD helps assess the potential impact of wastewater discharge on aquatic ecosystems. High COD levels can deplete dissolved oxygen in receiving waters, adversely affecting aquatic life and leading to issues like eutrophication. Monitoring COD levels before and after treatment helps evaluate the effectiveness of wastewater treatment processes. Effective treatment should significantly reduce COD levels, indicating the removal of pollutants.

Experiments

Laboratory-grade alum, lime, ferric chloride ($FeCl_3$), and $FeSO_4$, were purchased from Sisco Research Laboratories Pvt. (SRL)—India. The flocculants anionic polymer (A), cationic polymer (B), and nonionic polymer (C) were purchased from local suppliers. All the reagents for COD were prepared in our laboratory in accordance with American Public Health Association (APHA) methods (Lipps et al. 2023).

For this research work, the wastewater was collected from M/s Varahi Intermediates, G.I.D.C. Naroda, Gujarat. The company produces metaphenylene diamine 4-sulphonic acid (MPDSA), which is one of the major raw material intermediates to produce mordant dyes, reactive dyes, etc. chemical structure of MPDSA is shown in Fig. 3. The effluent emerging from the plant had a COD of 32,000 and total dissolved solids (TDS) of 566.

Experiments on coagulation and flocculation were performed using a jar test apparatus, followed by the standard APHA method, as shown in Fig. 4 (Lipps et al. 2023). The coagulant and flocculant solution was prepared in water. A 10-mL coagulant solution was added into 100 mL of wastewater. After sufficient mixing for 60–70 s, 1 mL of flocculent solution was added for achieving 30–40 rpm agitation speed and allowed for settling. The supernatant was collected by filtration. The water was finally treated with 10 g of activated carbon per 100 mL. The slurry formed was kept for 10 min for stirring at 50–60 rpm speed to ensure efficient adsorbent action. After that, the solution was filtered. The resultant filtrate was colorless and turbid-free.

Initially, experiments were carried out with the conventional method. Coagulants were used with individual flocculants such as alum—A/B/C, lime—A/B/C, and so on. The concentration of the prepared coagulant and flocculant solution is given in Table 1. An attempt was made to combine the coagulants with the individual flocculants. The two combinations that were selected were alum with lime—A/B/C and $FeCl_3$ with lime—

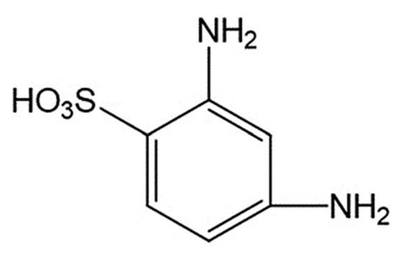

Fig. 3. Structure of MPDSA.

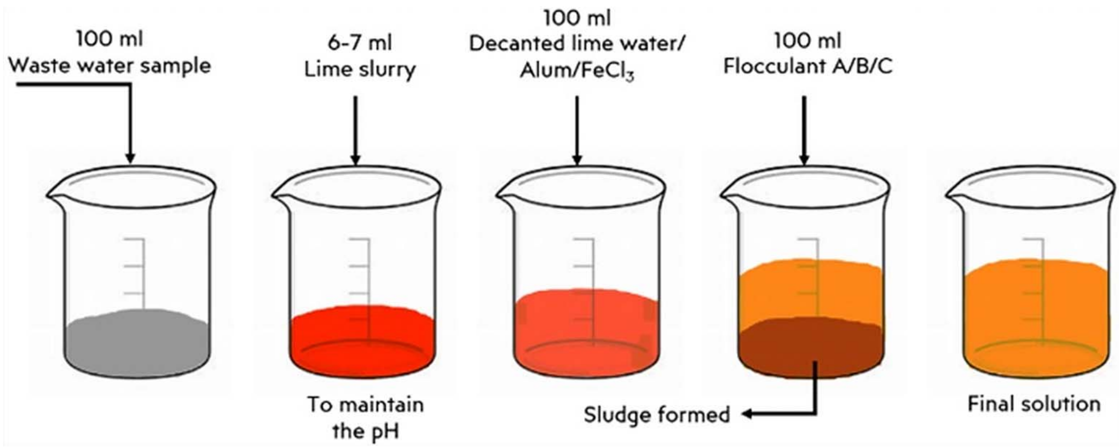

Fig. 4. Experimental setup for single-stage coagulation–flocculation.

Table 1. Concentration of Coagulants and Flocculants used

Role of chemical	Name of chemical	Concentration (%)
Coagulants	Alum	12.5
	Lime	12.5
	$FeCl_3$	5
Flocculants	A (anionic)	1
	B (cationic)	1
	C (nonionic)	1

A/B/C; 10% coagulant solution and 1% flocculent solution were prepared in distilled water.

Results and Discussion

All parameters are measured following the standard APHA method (Lipps et al. 2023). COD and TDS were measured at each stage and the obtained results are shown in Figs. 5–8. It was found that the COD level calculated at each stage was reducing.

During the experiments using the conventional method of a single coagulant in a single stage, no significant reduction in TDS was observed. While there was some reduction in COD and sludge generation, the overall results were unsatisfactory. To address this, a novel two-stage approach was employed, leading to significant reductions in both TDS and COD. The experiments were further enhanced by using combinations of two coagulants, also conducted in two stages, which showed a substantial reduction in COD, as illustrated in Fig. 8. Both stages demonstrated considerable effectiveness in achieving the desired results. Although the color of the liquid became lighter, it was not completely removed, necessitating treatment with activated charcoal.

The wastewater treatment experiments revealed varying levels of effectiveness among different coagulant–flocculant combinations. Untreated wastewater, containing 545 ppm TDS, posed

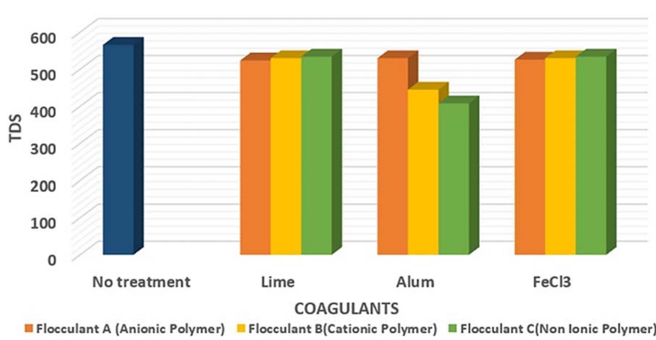

Fig. 5. TDS results for single coagulants with different flocculants in single stage.

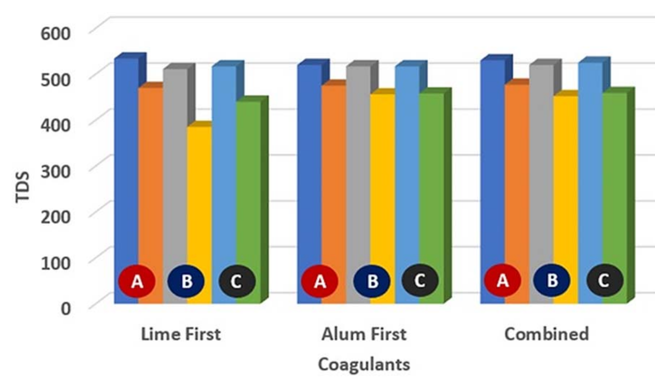

Fig. 6. TDS results for lime–alum combination carried out in two stages.

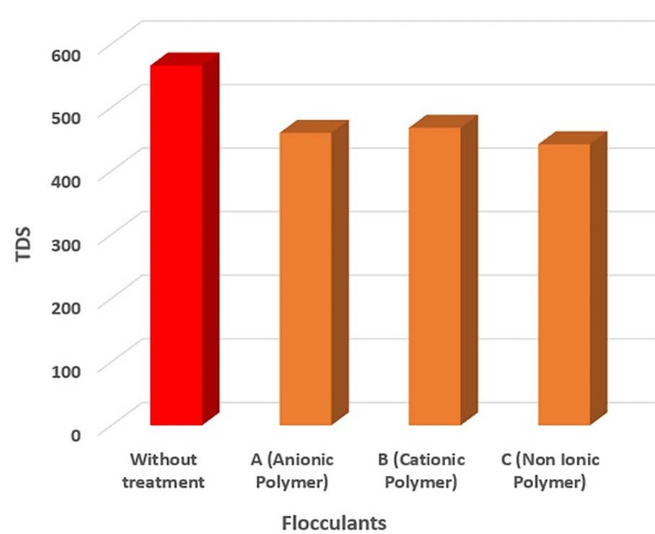

Fig. 7. TDS results for $FeCl_3$–lime combination carried out in two stages.

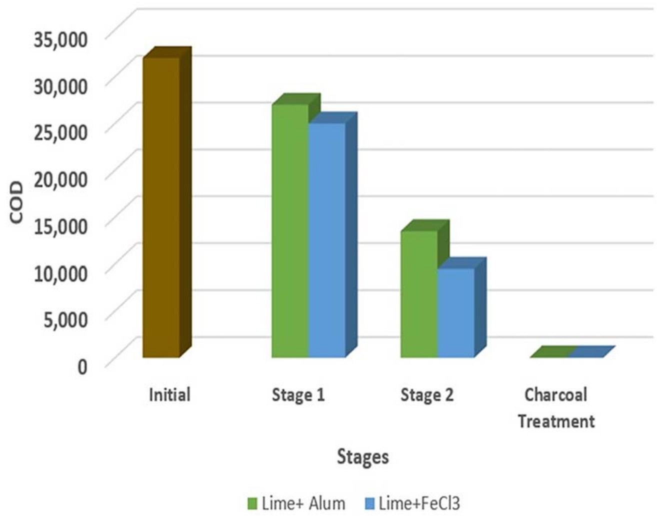

Fig. 8. COD results after each treatment stage.

challenges to conventional methods. When lime was used as a coagulant, only minor TDS reductions were achieved with different flocculants: 510 ppm with anionic, 520 ppm with cationic, and 526 ppm with nonionic flocculants. Alum as a coagulant showed limited effectiveness, reducing TDS to 525 ppm with anionic, 410 with cationic, and 390 ppm with nonionic flocculants. $FeCl_3$ showed no notable TDS reduction with any flocculant.

The breakthrough concept of combining coagulants was explored to enhance treatment efficiency. Lime followed by alum resulted in TDS reductions to 450 ppm with anionic and 370 ppm with cationic, while nonionic flocculants failed to achieve levels below 450 ppm. The lime-$FeCl_3$ combination did not yield significant improvements.

Additionally, the study evaluated the effects on COD, a critical parameter for wastewater quality. Both lime-alum and lime-$FeCl_3$ combinations showed promising results in reducing COD levels. In Stage 1, COD decreased from 32,000 to 25,000, with further reductions to 10,000 in Stage 2. Interestingly, lime-$FeCl_3$ proved more effective than lime–alum in COD reduction. Charcoal treatment further reduced COD levels to below 50 ppm, demonstrating its efficacy in meeting stringent wastewater quality standards.

Overall, the study highlights the importance of selecting appropriate coagulant–flocculant combinations and considering innovative strategies for optimizing wastewater treatment processes. The potential of the lime–$FeCl_3$ combination and charcoal treatment in achieving significant reductions in TDS and COD levels is evident, which is crucial for environmental compliance and public health protection. The final treated solution, after activated carbon treatment, achieved COD levels below 50 and TDS levels below 150, well within government norms of 200 COD and 500 TDS. The treated water became clear and reusable. No other parameters were measured.

Conclusion

Achieving ZLD traditionally relied on energy-intensive technologies such as RO, membrane filtration (MF), and multiple effect evaporator (MEE), resulting in significant operational costs. This study challenges the conventional approach by demonstrating the efficacy of coagulation–flocculation methods, traditionally regarded as primary treatment methods. Employing pairs of coagulants and implementing a two-stage operation, the treatment process achieves remarkable effectiveness in water reclamation. As the COD can be reduced below government norms, the industry may release it. But as the water becomes very clean after the treatment process, it can be reused in industry, resulting in zero discharge at very low cost. Recovered freshwater from this process finds diverse applications, including gardening, utility purposes, and industrial operations within the plant. This not only mitigates the risk of water pollution but also plays a pivotal role in combating water scarcity challenges faced by industries. With such repurposing wastewater and minimizing discharge, industries can contribute to sustainable water management practices and reduce their environmental footprint. This novel approach underscores the importance of exploring alternative methods for ZLD, offering a cost-effective and environmentally sustainable solution for water management in industrial settings.

Data Availability Statement

Some or all data, models, or codes that support the findings of this study are available from the corresponding author upon reasonable request.

References

Akbar, M., A. Yaqoob, I. Ahmad, and A. Ahmad. 2023. "Wastewater treatment: An overview." Chap. 2 in *Sodium alginate-based nanomaterials for wastewater treatment micro and nano technologies*, edited by A. Ahmad, I. Ahmad, T. Kamal, A. M. Asiri, and S. Tabassum, 19–34. Amsterdam, The Netherlands: Elsevier.

Ali, M., et al. 2024. "Domestic wastewater treatment by Pistia stratiotes in constructed wetland." *Sci. Rep.* 14 (1): 7553. https://doi.org/10.1038/s41598-024-57329-y.

Alnaser, Z. H. A., S. R. Chowdhury, and S. A. Razzak. 2023. "Constructed wetlands for wastewater treatment in Saudi Arabia: Opportunities and sustainability." *Arabian J. Sci. Eng.* 48 (7): 8801–8817. https://doi.org/10.1007/s13369-022-07411-2.

Alonso, E., C. Sanchez-Huerta, Z. Ali, Y. Wang, L. Fortunato, and I. Pinnau. 2024. "Evaluation of nanofiltration and reverse osmosis membranes for efficient rejection of organic micropollutants." *J. Membr. Sci.* 693: 122357. https://doi.org/10.1016/j.memsci.2023.122357.

Alsukaibi, A. K. D. 2022. "Various approaches for the detoxification of toxic dyes in wastewater." *Processes* 10 (10): 1968. https://doi.org/10.3390/pr10101968.

Al-Tohamy, R., S. S. Ali, F. Li, K. M. Okasha, Y. A.-G. Mahmoud, T. Elsamahy, H. Jiao, Y. Fu, and J. Sun. 2022. "A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety." *Ecotoxicol. Environ. Saf.* 231: 113160. https://doi.org/10.1016/j.ecoenv.2021.113160.

An, W., J. Zhao, J. Lu, Y. Han, and D. Li. 2022. "Zero-liquid discharge technologies for desulfurization wastewater: A review." *J. Environ. Manage.* 321: 115953. https://doi.org/10.1016/j.jenvman.2022.115953.

Avramidi, M., C. Spyropoulou, C. Loizou, M. Kyriazi, J. Novakovic, K. Moustakas, D. Malamis, and M. Loizidou. 2023. "Adding value to reclaimed water from wastewater treatment plants: The environmental feasibility of a minimal liquid discharge system for the case study of Larnaca." *Sustainability* 15 (19): 14305. https://doi.org/10.3390/su151914305.

Bal, G., and A. Thakur. 2021. "Distinct approaches of removal of dyes from wastewater: A review." *Mater. Today:. Proc.* 50: 1575–1579. https://doi.org/10.1016/j.matpr.2021.09.119.

Castillo-Suárez, L. A., A. G. Sierra-Sánchez, I. Linares-Hernández, V. Martínez-Miranda, and E. A. Teutli-Sequeira. 2023. "A critical review of textile industry wastewater: Green technologies for the removal of indigo dyes." *Int. J. Environ. Sci. Technol.* 20 (9): 10553–10590. https://doi.org/10.1007/s13762-023-04810-2.

Criscuoli, A., O. Bamaga, Q. Wang, Z. Cui, A. Nahri, M. Albeirutty, W. Jin, and E. Drioli. 2023. "Integration of membrane bioreactors with reverse osmosis and membrane distillation units for wastewater treatment: Recent developments and future perspectives." *Sep. Purif. Rev.* 52 (4): 400–412. https://doi.org/10.1080/15422119.2022.2119867.

Enebe, N. L., C. B. Chigor, K. Obileke, M. S. Lawal, and M. C. Enebe. 2023. "Biogas and syngas production from sewage sludge: A sustainable source of energy generation." *Methane* 2: 192–217. https://doi.org/10.3390/methane2020014.

Faraj, H., A. Jamrah, S. Al-Omari, and T. M. Al-Zghoul. 2024. "Optimization of an electrocoagulation-assisted adsorption treatment system for dairy wastewater." *Case Stud. Chem. Environ. Eng.* 9: 100574. https://doi.org/10.1016/j.cscee.2023.100574.

Feijoo, S., X. Yu, M. Kamali, L. Appels, and R. Dewil. 2023. "Generation of oxidative radicals by advanced oxidation processes (AOPs) in wastewater treatment: A mechanistic, environmental and economic review." *Rev. Environ. Sci. Bio/Technol.* 22 (1): 205–248. https://doi.org/10.1007/s11157-023-09645-4.

Gonçalves, B. R., A. Della-Flora, C. Sirtori, R. M. F. Sousa, M. C. V. M. Starling, J. A. Sánchez Pérez, E. M. Saggioro, S. F. Sales Junior, and A. G. Trovó. 2023. "Influence of water matrix components and peroxide sources on the transformation products and toxicity of tebuthiuron under UVC-based advanced oxidation processes." *Sci. Total Environ.* 859: 160120. https://doi.org/10.1016/j.scitotenv.2022.160120.

Grégorio, C., and E. Lichtfouse. 2018. "Wastewater treatment: An overview." In *Green adsorbents for pollutant removal fundamentals and design*, edited by G. Crini and E. Lichtfouse, 1–21. Cham, Switzerland: Springer.

Gürtekin, E. 2023. "Optimization of synthetic domestic wastewater treatment performance in anoxic/aerobic sequencing batch reactor with zeolite addition." *J. Environ. Sci. Health., Part A* 58 (6): 525–537. https://doi.org/10.1080/10934529.2023.2199655.

Hu, Z., D. Guan, Z. Sun, Z. Zhang, Y. Shan, Y. Wu, C. Gong, and X. Ren. 2023. "Osmotic cleaning of typical inorganic and organic foulants on reverse osmosis membrane for textile printing and dyeing wastewater treatment." *Chemosphere* 336: 139162. https://doi.org/10.1016/j.chemosphere.2023.139162.

Islam, T., M. R. Repon, T. Islam, Z. Sarwar, and M. M. Rahman. 2023. "Impact of textile dyes on health and ecosystem: A review of structure, causes, and potential solutions." *Environ. Sci. Pollut. Res.* 30 (4): 9207–9242. https://doi.org/10.1007/s11356-022-24398-3.

Jagmohan, S., A. Mwasha, and W. Mellowes. 2021. "Potential use of tropical landfill leachate in manufacturing Portland cement concrete." In *Proc., Conf. Theme: 'Science, Technology and Innovation: Vehicles for a Knowledge Based Economy'*, edited by K. F. Pun and_R. Lancashire. Jamaica, Kingston: The Caribbean Academy Sciences (CAS).

Javed, A., and A. Mushtaq. 2023. "A critical review of electrocoagulation and other electrochemical methods." *Int. J. Chem. Biochem. Sci.* 23: 98–110.

Khan, W. U., S. Ahmed, Y. Dhoble, and S. Madhav. 2023. "A critical review of hazardous waste generation from textile industries and associated ecological impacts." *J. Indian Chem. Soc.* 100 (1): 100829. https://doi.org/10.1016/j.jics.2022.100829.

Kodialbail, V. S., and S. Sophia. 2023. "Concept of zero liquid dischare—Present scenario and new opportunities for economically viable solution." Chap. 1 in *Concept of zero liquid discharge innovations and advances for sustainable wastewater management*, edited by C. M. Hussain and V. S. Kodialbail, 3–31. Amsterdam, The Netherlands: Elsevier.

Krishnan, R. Y., S. Manikandan, R. Subbaiya, N. Karmegam, W. Kim, and M. Govarthanan. 2023. "Recent approaches and advanced wastewater treatment technologies for mitigating emerging microplastics contamination—A critical review." *Sci. Total Environ.* 858: 159681. https://doi.org/10.1016/j.scitotenv.2022.159681.

Kumar, A., U. Dixit, K. Singh, S. P. Gupta, and M. S. Jamal Beg. 2021. "Structure and properties of dyes and pigments." Chap. 8 in *Dyes and pigments—Novel applications and waste treatment*, edited by R. Papadakis, 131–149. Rijeka, Croatia: IntechOpen.

Lipps, W. C., E. B. Braun-Howland, and T. E. Baxter. 2023. *Standard methods for the examination of water and wastewater*. Washington, DC: American Public Health Association.

Liu, W., Y. Lu, Y. Dong, Q. Jin, and H. Lin. 2023. "A critical review on reliability of quenching experiment in advanced oxidation processes." *Chem. Eng. J.* 466: 143161. https://doi.org/10.1016/j.cej.2023.143161.

Ma, D., et al. 2021. "Critical review of advanced oxidation processes in organic wastewater treatment." *Chemosphere* 275: 130104. https://doi.org/10.1016/j.chemosphere.2021.130104.

Madeira, L., F. Carvalho, A. Almeida, and M. Ribau Teixeira. 2023. "Integrated process of immediate one-step lime precipitation, atmospheric carbonation, constructed wetlands, or adsorption for industrial wastewater treatment: A review." *Water* 15: 3929. https://doi.org/10.3390/w15223929.

Magnisali, E., Q. Yan, and D. V. Vayenas. 2022. "Electrocoagulation as a revived wastewater treatment method-practical approaches: A review." *J. Chem. Technol. Biotechnol.* 97 (1): 9–25. https://doi.org/10.1002/jctb.6880.

Mahbub, P., and M. Duke. 2023. "Scalability of advanced oxidation processes (AOPs) in industrial applications: A review." *J. Environ. Manage.* 345: 118861. https://doi.org/10.1016/j.jenvman.2023.118861.

Maheshwari, K., M. Agrawal, and A. B. Gupta. 2021. "Dye pollution in water and wastewater." In *Novel materials for dye-containing wastewater treatment*, edited by S. S. Muthu and A. Khadir, 1–25. Singapore: Springer.

Mangalgiri, K., Z. Cheng, and H. Liu. 2024. "Development of dissolved organic matter-based indicators to understand the degradation of organic contaminants in reverse osmosis concentrate from potable reuse systems." *J. Hazard. Mater.* 470: 134060. https://doi.org/10.1016/j.jhazmat.2024.134060.

Mao, Y., Y. Zhao, and S. Cotterill. 2023. "Examining current and future applications of electrocoagulation in wastewater treatment." *Water* 15: 1455. https://doi.org/10.3390/w15081455.

McIlvaine, R. 2008. In Vol. 115 of *Reverse osmosis*. 3rd ed., edited by J. Kucera. Hoboken, NJ: John Wiley & Sons.

Mendoza, E., G. Blandin, M. Castaño-Trias, L. L. Alonso, J. Comas, and G. Buttiglieri. 2023. "Rejection of organic micropollutants from greywater with forward osmosis: A matter of time." *J. Environ. Chem. Eng.* 11 (5): 110931. https://doi.org/10.1016/j.jece.2023.110931.

Mishra, S., R. Priyadarshini Singh, P. K. Rout, and A. P. Das. 2022. "Membrane bioreactor (MBR) as an advanced wastewater treatment technology for removal of synthetic microplastics." Chap. 3 in *Development in wastewater treatment research and processes removal of emerging contaminants from wastewater through bio-nanotechnology*, edited by M. Shah, S. Rodriguez-Couto, and J. Biswas, 45–60. Amsterdam, The Netherlands: Elsevier.

Mukherjee, J., B. K. Lodh, R. Sharma, N. Mahata, M. P. Shah, S. Mandal, S. Ghanta, and B. Bhunia. 2023. "Advanced oxidation process for the treatment of industrial wastewater: A review on strategies, mechanisms, bottlenecks and prospects." *Chemosphere* 345: 140473. https://doi.org/10.1016/j.chemosphere.2023.140473.

Nishat, A., et al. 2023. "Wastewater treatment: A short assessment on available techniques." *Alexandria Eng. J.* 76: 505–516. https://doi.org/10.1016/j.aej.2023.06.054.

Panagopoulos, A. 2021. "Techno-economic assessment of minimal liquid discharge (MLD) treatment systems for saline wastewater (brine) management and treatment." *Process Saf. Environ. Prot.* 146: 656–669. https://doi.org/10.1016/j.psep.2020.12.007.

Panagopoulos, A. 2023. "Zero liquid discharge and minimal liquid discharge strategies for sustainable saline wastewater (brine) management and valorization." Chap. 16 in *Resource recovery in industrial waste waters*, edited by M. Sillanpää, A. Khadir, and K. Gurung, 337–351. Amsterdam, The Netherlands: Elsevier.

Panagopoulos, A., and V. Giannika. 2022. "Comparative techno-economic and environmental analysis of minimal liquid discharge (MLD) and zero liquid discharge (ZLD) desalination systems for seawater brine treatment and valorization." *Sustainable Energy Technol. Assess.* 53: 102477. https://doi.org/10.1016/j.seta.2022.102477.

Panagopoulos, A., and V. Giannika. 2023. "Study on the water resources and the opportunities for sustainable desalination & minimal/zero liquid discharge (MLD/ZLD) practices in Greece (Eastern Mediterranean)." *Sustainable Water Resour. Manage.* 9 (4): 106. https://doi.org/10.1007/s40899-023-00884-5.

Panagopoulos, A., and K.-J. Haralambous. 2020. "Minimal Liquid Discharge (MLD) and Zero Liquid Discharge (ZLD) strategies for wastewater management and resource recovery—Analysis, challenges and prospects." *J. Environ. Chem. Eng.* 8 (5): 104418. https://doi.org/10.1016/j.jece.2020.104418.

Patil, Y., S. T. Malkapuram, V. Hakke, P. Dilipkumar, P. Narsimha, M. P. Rayaroth, T. Joseph, S. Sonawane, and G. Boczkaj. 2023. "Zero liquid discharge strategies for industrial wastewater reuse and resource recovery." Chap. 3 in *Resource recovery in industrial waste waters*, edited by M. Sillanpää, A. Khadir, and K. Gurung, 45–65. Amsterdam, The Netherlands: Elsevier.

Ponnusami, A. B., S. Sinha, H. Ashokan, M. V. Paul, S. P. Hariharan, J. Arun, K. P. Gopinath, Q. H. Le, and A. Pugazhendhi. 2023. "Advanced oxidation process (AOP) combined biological process for wastewater treatment: A review on advancements, feasibility and practicability of combined techniques." *Environ. Res.* 237: 116944. https://doi.org/10.1016/j.envres.2023.116944.

Prado de Nicolás, A., A. Molina-García, J. T. García-Bermejo, and F. Vera-García. 2022. "Reject brine management: Denitrification and zero liquid discharge (ZLD)—Current status, challenges and future prospects." *J. Cleaner Prod.* 381: 135124. https://doi.org/10.1016/j.jclepro.2022.135124.

Qrenawi, L. I., and F. K. J. Rabah. 2023. "Membrane bioreactor (MBR) as a reliable technology for wastewater treatment: Review." *J. Membr. Sci. Res.* 9 (1): 1–19. https://doi.org/10.22079/jmsr.2022.548826.1532.

Rahman, T. U., et al. 2023. "The advancement in membrane bioreactor (MBR) technology toward sustainable industrial wastewater management." *Membranes* 13 (2): 181. https://doi.org/10.3390/membranes13020181.

Ramos, R. O., W. S. Lopes, Y. H. D. M. Luna, M. V. da C. Albuquerque, V. D. Leite, J. T. de Sousa, M. C. U. Araújo, and W. S. Lopes. 2023. "Treatment of wastewater for reuse using advanced oxidation process: A bacterial inactivation mechanism approach." *Int. J. Environ. Sci. Technol.* 20 (10): 11275–11286. https://doi.org/10.1007/s13762-022-04732-5.

Rápó, E., and S. Tonk. 2021. "Factors affecting synthetic dye adsorption; desorption studies: A review of results from the last five years (2017–2021)." *Molecules* 26 (17): 5419. https://doi.org/10.3390/molecules26175419.

Rashid, S. S., S. N. Harun, M. M. Hanafiah, K. K. Razman, Y. Q. Liu, and D. A. Tholibon. 2023. "Life cycle assessment and its application in wastewater treatment: A brief overview." *Processes* 11: 208. https://doi.org/10.3390/pr11010208.

Ronda, A., P. Haro, and A. Gómez-Barea. 2023. "Sustainability assessment of alternative waste-to-energy technologies for the management of sewage sludge." *Waste Manage. (Oxford)* 159: 52–62. https://doi.org/10.1016/j.wasman.2023.01.025.

Sharma, J., S. Sharma, and V. Soni. 2021. "Classification and impact of synthetic textile dyes on Aquatic Flora: A review." *Reg. Stud. Mar. Sci.* 45: 101802. https://doi.org/10.1016/j.rsma.2021.101802.

Sudarshan, S., S. Harikrishnan, G. RathiBhuvaneswari, V. Alamelu, S. Aanand, A. Rajasekar, and M. Govarthanan. 2023. "Impact of textile dyes on human health and bioremediation of textile industry effluent using microorganisms: Current status and future prospects." *J. Appl. Microbiol.* 134 (2): lxac064. https://doi.org/10.1093/jambio/lxac064.

Tang, J. K., M. N. H. Jusoh, and H. Jusoh. 2023. "Nitrogen and phosphorus removal of wastewater via constructed wetlands approach." *Trop. Aquat. Soil Pollut.* 3 (1): 76–87. https://doi.org/10.53623/tasp.v3i1.214.

Tarpani, R. R. Z., and A. Azapagic. 2023. "Life cycle sustainability assessment of advanced treatment techniques for urban wastewater reuse and sewage sludge resource recovery." *Sci. Total Environ.* 869: 161771. https://doi.org/10.1016/j.scitotenv.2023.161771.

Varol, S., A. Alver, and L. Altaş. 2024. "The water footprint assessment for advanced biological wastewater treatment plant." *Int. J. Environ. Sci. Technol.* 21 (2): 2035–2048. https://doi.org/10.1007/s13762-023-05242-8.

Vignesh Kumar, N., R. A. Mozumder, and N. Laskar. 2022. "Sustainable concept of zero-liquid discharge and its impact on climate change: Detail case studies." *J. Clim. Change* 8 (4): 63–71. https://doi.org/10.3233/JCC220031.

Vymazal, J. 2023. "Wastewater treatment and control through wetlands." In *Water sustainability*, edited by H. X. Zhang, 49–70. New York: Springer.

Waly, M. M., S. B. Mickovski, and C. Thomson. 2023. "Application of circular economy in oil and gas produced water treatment." *Sustainability* 15 (3): 2132. https://doi.org/10.3390/su15032132.

Yaqoob, A. A., C. Guerrero-Barajas, A. Ahmad, M. N. M. Ibrahim, and M. B. Alshammari. 2023. "Advanced technologies for wastewater treatment." Chap. 8 in *Green chemistry for sustainable water purification*, edited by A. Shahid-ul-Islam, H. Shalla, and M. Shahadat, 179–202. Austin, TX: Scrivener Publishing.

Zahmatkesh, S., M. Karimian, R. Pourhanasa, I. Ghodrati, M. Hajiaghaei-Keshteli, and M. A. Ismail. 2023. "Wastewater treatment with algal based membrane bioreactor for the future: Removing emerging contaminants." *Chemosphere* 335: 139134. https://doi.org/10.1016/j.chemosphere.2023.139134.