

Thematic ASSET Bulletin on

Waste water Remediation Strategies: Current Status and Future Perspective

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**Editor
A. Bhattacharyya**



**Association of Separation Scientists and
Technologists (ASSET)**



Contents

Editor's Note

Dear ASSET Members,

ASSET regularly publishes bulletins covering different aspects of separation science and technology emphasizing its applications for societal be. Application of separation science and technology in various fields are widening due to the development of the state of the art technologies in this area.

In the previous issues we have brought out bulletins on various topics, viz. perspectives in Separation Science, chromatographic separations, separations in liquid phase, uranium harvesting for application in nuclear industries, separations technology in the development of radiopharmaceuticals etc.

Water is indispensable for the survival of the civilization. Increasing population and industrial development significantly contributes to the pollution of the surface water. Treatment of the water to make it pollutant free is very much essential for the sustainability of the eco system. In one of our previous issue we covered some of the techniques followed for the water treatment. However, the demand of potable water is increasing enormously. We, therefore, made an attempt to bring out this issue on "Waste water Remediation Strategies: Current Status and Future Perspective", which is being released during the ASSET one day theme meeting on the same topic.

I would like to thank all the distinguished authors for their contribution in bringing out this thematic bulletin.

I want to specially thank Dr. Virendra Kumar and Nilanjal Mishra of RTDD for collecting the articles.

I am thankful to Dr. P.K. Mohapatra, President ASSET and Dr. S. Jeyakumar and Dr. S.C. Tripathi, Vice-Presidents, ASSET for their support in bringing out this bulletin.

Finally, thank you all for your cooperation.

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From President's desk



Dear ASSET members,

With growing industrialization, necessary for a developed society, comes the risk of environmental pollution. One of the major consequence of this is the generation of large inventory of industrial wastewater emanating from dye, petroleum, leather industries etc. With a view to protect our Environment, strict wastewater processing norms are the need of the hour. In this connection, a one day Theme meeting entitled "Wastewater Remediation Strategies: Current Status and Future Perspectives (WRS-2024)" is being organized by ASSET with partial financial support from Board of Research in Nuclear Sciences (BRNS) on April 6, 2024. The WRS-2024 meeting will host 9 lectures by eminent researchers working on very important topics, mainly on i) treatment strategies using chemical / physical and biological methods; ii) regulatory aspects and iii) integrating scientific and engineering methods including scale-up studies. The lectures are from research institutes as well as from industries with a perfect blend of basic science and technology. Overall, the lectures have separation science and technology as the theme and will be highly beneficial to the above mentioned industries looking for wastewater remediation methodologies for a sustainable process with long-term applicability. You will be happy to know that some of these technologies developed at BARC have found takers at textile industries and the collaborations are at a very advanced stage.

I am pleased inform you that the special issue of Bulletin entitled "Wastewater Remediation Strategies: Current Status and Future Perspectives (WRS-2024)", brought out on the occasion of the Theme Meeting includes 9 articles from the speakers who are well-known experts in their respective fields and gives an insight to the role of separation science & technology in the area of wastewater treatment. This will go a long way in saving our Environment with the long term goal of a 'Vikshit Bharat'.

I am highly obliged to Shri Vivek Bhasin, Director, BARC for his support in conducting the Theme Meeting and also for his constant encouragement. The help rendered by Dr. Virendra Kumar and Dr. Arunasis Bhattacharyya bringing out this Bulletin is highly appreciated.

Similar to the past events, we are expecting overwhelming response to this Theme Meeting. I thank all the contributors to the Bulletin and ASSET members for their efforts in organizing this important event.

P.K. Mohapatra

Guest Editorial



With steep population and industrial growth, large scale generation of wastewater has emerged as a serious environmental and health concern. Industrial wastewater contains a number of pollutants, such as dyes, heavy metals, oil, pharmaceuticals etc. The complexity and diversity of pollutants in wastewater make it imperative to explore innovative solutions for effective treatment. In this context, the role of radiation technology is crucial considering its ability to spawn innovations that can be employed judiciously for wastewater remediation while also highlighting the peaceful use of nuclear technologies.

The Department of Atomic Energy, under its societal initiative mandate, has taken the lead in developing novel technologies and disseminating information about sustainable processes for tackling various elements of environmental pollution. The DAE-BRNS one day theme meeting on "*Wastewater Remediation Strategies: Current Status and Future Perspectives (WRS-2024)*" organized by ASSEET is one such step in this direction. The 'WRS 2024' serves as a pivotal platform for experts, researchers, and industrialists to converge, exchange knowledge, delve into technological advancements, and advocate for the practical implementation of sustainable wastewater treatment solutions. We acknowledge the support extended by BRNS in facilitating this endeavour.

The present thematic bulletin encompasses a wide array of topics, including ground-breaking applications developed by the Department of Atomic Energy (DAE) to address water pollutants originating from various industries. For instance, BARC has recently developed a novel radiation grafted biodegradable adsorbent based technology (RAD-TED) for treating textile dye wastewater. The efficacy of electron beam irradiation in tannery effluent treatment has also been demonstrated. Similarly, ozone-based advanced oxidation processes and innovative technologies like the indigenous hybrid granular Sequencing Batch Reactor (SBR) technology for wastewater treatment are equally noteworthy. We recognize the significance of non-nuclear technologies developed at IITB and NCL Pune, including advanced oxidative treatment and Hydrodynamic Cavitation-based processes. A brief case study focusing on the optimization and performance improvement of a Common Effluent Treatment Plant (CETP) and mitigation of challenges faced has also been presented in this bulletin from industrial perspective. One of the articles on Environmental Regulatory and Policy Aspects Related to Disposal and Management of Industrial Wastewater will certainly help us to understand the importance of robust infrastructure, operational efficiency, and clear policy frameworks for effective wastewater management in India.

We are confident that this theme Meeting WRS 2024 organized by ASSET will foster awareness about diverse technologies, including ionizing radiation-based solutions, for sustainable wastewater management. The present thematic ASSET bulletin presents a collaborative efforts and innovative research from different partners that will certainly help us in better understanding on diverse wastewater remediation technologies that not only meet the stringent requirements of government policies but also resonate with the larger goals of sustainability and environmental stewardship.

Virendra Kumar
(Convenor WRS 2024 & Guest Editor)

Environmental Regulatory and Policy Aspects Related to Disposal and Management of Industrial Wastewater

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Abstract: The surge in global wastewater production due to the industrial revolution and rapid urbanization has led to significant environmental and health threats. The industrial sector contributes 22% to global water consumption, with a concerning 80% of generated wastewater discharged into water channels. This paper explores the complexities of wastewater management in India, addressing challenges from insufficient treatment infrastructure to policy ambiguities, requiring private sector involvement. Despite exceeding the global average, India's current wastewater treatment capacity is at 27%, falling short. Major urban centres operate treatment plants below required capacity, emphasizing the urgent need for additional facilities. Policy gaps and jurisdictional ambiguities hinder cohesive implementation, urging immediate and comprehensive interventions. The paper stresses on the importance of robust infrastructure, operational efficiency, and clear policy frameworks for effective wastewater management in India.

Keywords: Industrial wastewater, policy, industrial wastewater, environmental challenges.

Introduction

In the field of environmental engineering, wastewater is a complex and multifaceted term with various definitions. This report adopts a comprehensive perspective in line with the definition provided in the United Nations Environment Programme/United Nations Human Settlements Programme document 'Sick Water' [1]. Wastewater, according to this definition, encompasses domestic effluent (blackwater and greywater), water from commercial establishments and institutions, industrial effluent, stormwater, urban run-off, and agricultural, horticultural, and aquaculture effluent, whether in a dissolved or suspended state.

The industrial revolution and swift urbanization have led to a substantial increase in global wastewater production. The industrial sector alone utilizes an average of 22% of the world water consumption. Shockingly, around 80% of the total wastewater generated is discharged into water channels, posing significant threats to environmental integrity, human health, and aquatic life[2]. In developed regions such as North America and Europe, industrial water consumption significantly surpasses that of developing countries, standing at 50% and 4–12%, respectively[3]. The United States, leveraging advanced technologies and technical expertise, has achieved notable success in wastewater treatment (WWT). According to a 2019 study by Acumen research and consulting, the global industrial WWT market is projected to reach \$16.5 billion by 2026, with an average Compound annual growth rate of 4.5% [4].

In 2017, a United Nations Water and United Nations Educational, Scientific and Cultural Organization report emphasized that high-income countries treat about 70% of both municipal and industrial wastewater. In contrast, upper-middle-income countries treat 38%, lower-middle-income countries treat 28%, and lower-income countries are limited to only 8%[3,5]. Alarming, based on current trends, it is anticipated that approximately 80% of global wastewater is discharged without any treatment[3]. As outlined in the Central Pollution

Control Board (CPCB) latest report published in March 2021, India currently possesses a WWT capacity of about 27% and a sewage treatment capacity of 18.6%, with an additional 5.2% capacity in the process of being added[6]. Despite surpassing the global average of approximately 20% for waste and sewage treatment capacity, the scale of the challenge within India remains substantial. Given the magnitude of the issue, the existing capacity falls short of adequacy. Without expeditious interventions, there is a looming threat of serious complications that necessitate an immediate and effective response. Analyzing the statistics, the report reveals that India's water treatment infrastructure is grappling with the demand, with a capacity utilization of 27%. The sewage treatment sector is also under strain, operating at a capacity of 18.6%, with an expansion effort to enhance this capacity by an additional 5.2%[6].

Despite surpassing the global average, India's current WWT capacity stands at 27%, creating a substantial shortfall. Major urban centres like Delhi and Mumbai operate WWTPs at less than half of their required capacity, highlighting the urgent need for additional facilities. The paper underscores policy gaps and federal jurisdictional ambiguity within India's constitutional framework, leading to power imbalances and hindering cohesive policy implementation. As India grapples with the intricate landscape of wastewater management, urgent interventions are imperative to address these challenges. This paper advocates for a comprehensive and immediate response, emphasizing the importance of robust treatment infrastructure, operational efficiency, and clear policy frameworks to navigate the complexities of wastewater management in the country.

Wastewater

Wastewater can be categorized into four main types: stormwater runoff, domestic, agricultural, and industrial [7], as illustrated in Figure 1. The brief description of the different type of wastewater is presented in following sections.

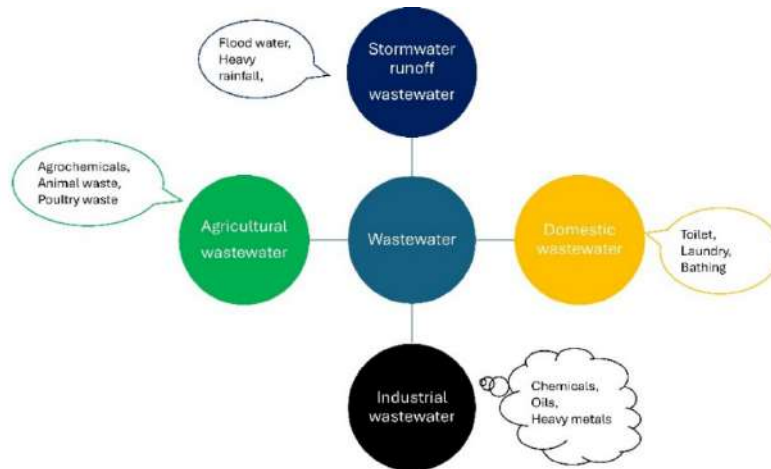


Figure 1 Types of wastewater

Industrial wastewater: The CPCB has identified 17 industrial categories, ranging from iron and steel plants to pharmaceutical complexes, as significant sources of pollution. State Pollution Control Boards (SPCBs) and Pollution Control Committees (PCCs) play a crucial role in overseeing and ensuring compliance with CPCB standards for emissions or pollutant discharges within their respective jurisdictions[8]. Specifically, coal-fired thermal power plants, the largest contributors to industrial air pollution, face dual regulation by both the CPCB and the Ministry of Power, emphasizing the need for comprehensive regulatory oversight. Industrial wastewater contains a range of pollutants, adversely affecting human,

aquatic, and agricultural ecosystems. Paint and dye manufacturing, textile, pharmaceutical, paper, and petrochemical industries release heavy metals like chromium, zinc, lead, and others (Table 1). Phenol and phenolic compounds, common in oil refineries and drug manufacturing, pose environmental challenges. Petrochemical industries discharge refractory pollutants, hindering biological treatment [9]. Paper and pulp industry wastewater varies in composition based on production methods, containing suspended solids and organic materials. Textile industries release urea, nitrogen, phosphorus, heavy metals, surfactants, and bleaching agents. Perfluoroalkyl acids (PFAAs), associated with health risks, are released by textile treatment and fluoropolymer production [10–12]. High-salinity wastewater, impacting diverse life forms, originates from petroleum, leather, food processing, and agro-based industries [13]. Table 1 summarizes the pollutants from major industrial sectors.

Table 1: Primary waste generated from different industries

Industry	Primary pollutants	References
Dye	Cu, sulfides, salt, formaldehydes and colour	[13,14]
Paper and pulp	Organic and chlorophenol compounds, Adsorbable lignin,suspended solids, tannins, sterols, colors, biocides, Organic Halogens (AOX), etc.	[15,16]
Textile	Fe, Cr, chlorinated compounds, urea, salts, H ₂ O ₂ , high pH, surfactants	[14]
Petrochemical	Petroleum hydrocarbons, phenolic compounds, nitrobenzene, alkanes, chloro alkanes, high salt, etc.	[9,13,17]
Pharmaceutical	Cd, Ni and phenolic compounds	[18,19]
Metal processing	Heavy metals, Perfluorooctane sulfonate (PFOS),oiland grease, cyanide, phenol, and NH ₄ -N	[13,20]
Paint Manufacturing	Volatile Organic Compounds (VOCs), Cr, Zn, Pb etc.	[21,22]

Existing Methods of Industrial Wastewater Treatment

Based on the type and amount of pollutant present different methods are employed for the wastewater treatment. Figure 2 depicts the various methods used for the wastewater treatment.

Membrane filtration: Membrane filtration is crucial for removing metals from mixed metal wastewater through porous or non-porous membranes, with factors like material selection and membrane pore size influencing performance [23]. This technology includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF, as a pre-treatment, effectively separates particles in low-pressure conditions (10–150 µm)[24]. UF operates similarly, eliminating bacteria and organics at low pressure (150–250 µm). NF, with a 0.001 µm pore size, requires high pressure, efficiently separating low molecular weight compounds in an eco-friendly process. Despite its heavy metal removal efficacy, NF faces limitations like high installation costs, increased operational costs due to fouling, and reduced efficiency in the presence of other metals[25].

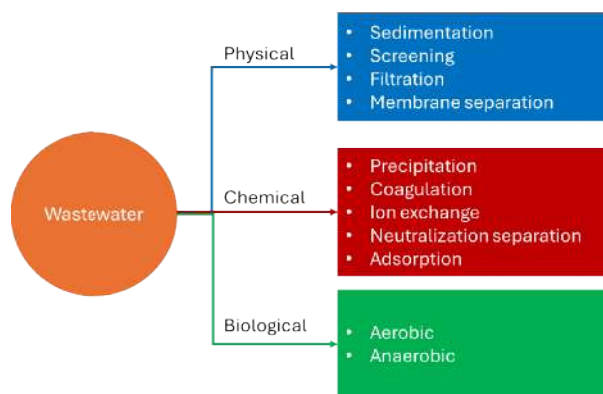


Figure 2 Different methods of wastewater treatment

Chemical precipitation: Chemical precipitation is a conventional method involving the addition of specific chemicals to extract metals from wastewater. This process includes hydroxide precipitation, sulphide precipitation, and chelating precipitation, primarily relying on pH adjustments. However, this method generates a substantial amount of sludge, incurring additional costs for its management and disposal[23]. The efficiency of the process is influenced by factors such as metal concentration, wastewater type, reaction conditions, and the presence of compounds that may inhibit reactions[26].

Ion exchange: Ion exchange involves the interchange of ions between liquid and solid phases, influenced by factors like pH, temperature, anions, initial concentrations of adsorbent and sorbate, and contact time[13,26]. Typically employing natural or synthetic resins, this method is commonly used for metal removal from wastewater. Despite its effectiveness, ion exchange has drawbacks. The process can be uneconomical due to the high cost and sensitivity of the resins used, leading to lower metal extraction efficiency[27]. Additionally, resins require frequent replacement as reused ones degrade quickly, emitting foul odour.

Bio-sorption: Biosorption, a physicochemical process, involves microorganisms, plant parts, agro-industrial wastes, and biopolymers that act as biosorbents. Metabolically passive metals adhere to the surface of these biologically derived materials, binding based on functional groups such as hydroxyl, carboxyl, amino, ester, sulfhydryl, carbonyl, and phosphate groups[28,29]. Recognized as an advantageous method for metal recovery from wastewater, biosorption offers a simple operational process with low costs, no additional nutrient requirements, high uptake capacity, easy availability, and the ability to regenerate biosorbents[29,30]. Unlike conventional methods, biosorption does not increase the COD of wastewater. Fungi, with unique cell wall features, exhibit excellent binding properties, making them suitable for biosorption. Fungi's ease of growth, high biomass yield, and modifiability enhance their industrial applicability. Yeast, particularly *Saccharomyces cerevisiae*, shows robust biosorption capacity[31]. Discarded plant materials like roots, leaf powder, bark, and pods also serve as effective agricultural waste for metal recovery.

Government Initiatives in Water Pollution Control and Conservation

Over the years, the Indian government has taken significant legislative and programmatic steps to address the critical issues of water pollution and conservation. Figure shows the year-by-year policies and framework implemented by Government of India.

Figure 3 shows the timeline of the policies and regulation for the wastewater management. Below is an in-depth exploration of key government policies/initiatives:

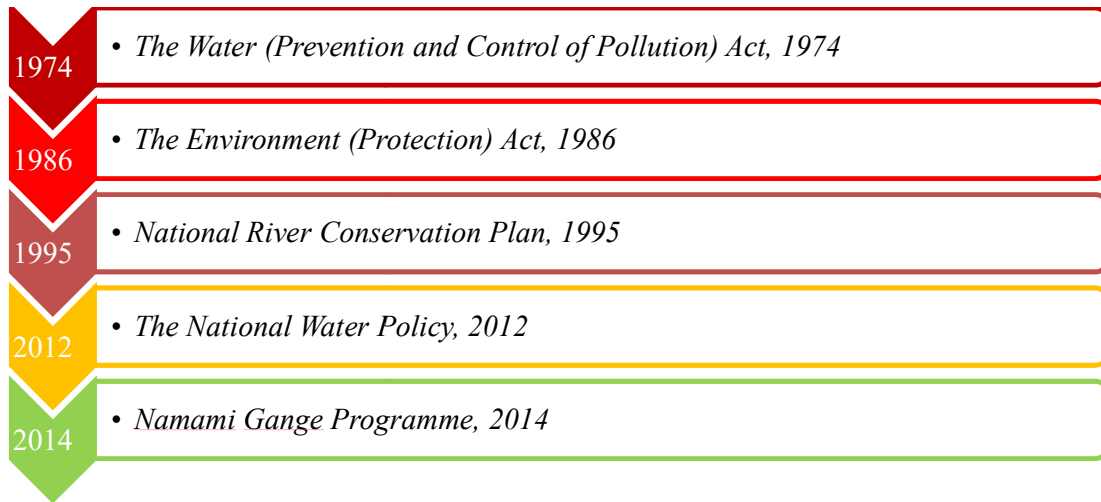


Figure 3 Timeline of the policies and initiatives for the wastewater management

The Water (Prevention and Control of Pollution) Act, 1974: Enacted in 1974, this landmark legislation was the first direct response to the escalating problem of water pollution and the need for conservation in India. The Act specifically addresses wastewater discharge as a form of pollution and establishes both Central and SPCBs (SPCBs). These boards play a pivotal role in the prevention and control of water pollution. Their responsibilities include the inspection of sewage and trade effluents, WTPs, and the formulation and enforcement of standards for the same.

Environment (Protection) Act, 1986: The combined impact of the Environment (Protection) Act, 1986, and the Water (Prevention & Control of Pollution) Act, 1974, has significant implications for industrial units. According to the provisions of these acts, industrial entities are mandated to install effluent treatment plants (ETPs). These plants are crucial for treating effluents to comply with predetermined environmental standards before discharging into rivers and other water bodies. This integrated approach aims to regulate industrial pollution and ensure adherence to environmental norms.

National River Conservation Plan 1995: The National River Conservation Plan (NRCP) focuses on pollution abatement measures. One of its key initiatives involves the installation of sewerage systems to capture raw sewage flowing into rivers through open drains. This diverted sewage is then treated in STPs to prevent its direct discharge into water bodies[32]. The NRCP's comprehensive strategy includes the implementation of various pollution control mechanisms to safeguard the quality of river water. The Central and SPCBs/Committees actively tackle industrial pollution prevention and control. The primary focus of the NRCP was to enhance the water quality of major rivers, crucial water sources in the country, by executing pollution abatement initiatives.

The National Water Policy, 2012: The National Water Policy of 2012 sets forth a compelling directive for the recycling and reuse of water, establishing it as a fundamental norm[33]. The policy advocates for the treatment of wastewater to specified standards before endorsing its reuse, emphasizing the importance of a meticulously planned tariff system. This system is designed to incentivize the utilization of treated water across diverse sectors, such as

industries and agriculture. Furthermore, the policy underscores the need for encouraging the reuse of urban wastewater derived from kitchen and bathroom sources.

NamamiGange Programme 2014-2023: The NamamiGange Programme is a holistic initiative by the Union Government with two objectives: the effective abatement of pollution and the conservation and rejuvenation of the National River Ganga. According to data from the National Mission for Clean Ganga, 68 STPs have been completed across several states under this program. These states include Haryana, Uttar Pradesh, Uttarakhand, Bihar, Jharkhand, West Bengal, Delhi, Rajasthan, and Himachal Pradesh. Additionally, 48 sewage treatment management projects are actively under implementation, further contributing to the ambitious goals of the NamamiGange Programme[34].

In essence, these government initiatives underscore a commitment to addressing the multifaceted challenges of water pollution and conservation. Through legislative frameworks and strategic programs, India is actively working towards sustainable and comprehensive solutions to safeguard its water resources.

Wastewater Management Challenges in India:

Wastewater management in India presents a multifaceted challenge, encompassing issues ranging from insufficient treatment infrastructure to policy ambiguities and the imperative need for private sector involvement. A detailed examination of these challenges sheds light on the intricacies of India's wastewater management landscape.

Inadequate wastewater treatment (WWT) infrastructure: The foundation of effective wastewater management lies in a robust treatment infrastructure. Regrettably, India faces a glaring deficit in such facilities. A recent report by the CPCB (March 2021) underscores the national water treatment capacity at a mere 27.3%. This deficiency is acutely felt in major urban centers like Delhi and Mumbai, where the available WTPs operate at less than half of the required capacity. The dire need for additional treatment facilities is evident, especially considering the escalating volumes of wastewater generated by these densely populated regions.

Dysfunctional treatment plants: Compounding the challenge is the operational status of existing WTPs. Many of these crucial facilities are either in a state of disrepair or have never commenced operations. A 2019 research report reveals a disheartening state of affairs with respect to STPs initiated under flagship programs like the Ganga Action Plan and Yamuna Action Plan. Out of the colossal 33,000 MLD of wastewater generated, only a fraction, 7,000 MLD, is effectively collected and treated. This not only signifies a colossal waste of resources but also exacerbates the environmental impact of untreated wastewater.

Policy gaps and federal jurisdictional ambiguity: India's constitutional framework adds layers of complexity to wastewater management. While water is identified as a State matter in Schedule 7 of the constitution, the Union List provisions grant the Parliament authority to legislate on inter-state water regulation. This dichotomy creates a jurisdictional ambiguity, fostering power imbalances between central and state authorities. The result is a lack of clarity in delineating roles and responsibilities among stakeholders, contributing to challenges in cohesive policy implementation.

Disintegrated state-level approach: The fragmentation in wastewater governance extends beyond federal structures and manifests within states. The governance of water resources is fragmented at local levels, both rural and urban, as outlined in the 73rd and 74th Constitutional Amendment Acts. While decentralization is integral for addressing local nuances in

wastewater management, the disintegrated approach impedes the efficient execution of policies and hampers the overall development of water bodies. A more cohesive strategy, recognizing water governance at all levels, is imperative for sustainable and effective wastewater management.

Lack of public private partnership: Recognizing the monumental scale of the wastewater challenge, relying solely on government resources is untenable. A potential solution lies in fostering private-public partnerships (PPP). However, the current efforts in this direction fall short of the required capacity. Given the financial constraints faced by the government, strategic collaborations with the private sector are imperative. These partnerships can bring innovation, efficiency, and additional resources to the table, ensuring a more sustainable and effective approach to wastewater management in India.

In conclusion, addressing the challenges in wastewater management in India requires a multifaceted and integrated strategy. From enhancing treatment infrastructure and revisiting policy frameworks to fostering collaborative public-private initiatives, a comprehensive approach is essential to ensure the sustainable management of wastewater resources and the preservation of environmental health.

Sustainable Wastewater Management Approaches

Zero liquid discharge (ZLD): ZLD is a wastewater management strategy focused on the comprehensive treatment and reuse of industrial wastewater within its source facility [35]. Mandated by the CPCB in 2015, ZLD targets industries like textiles, pulp and paper, distilleries, and tanneries. The textile industry in Tirupur stands out as a pioneering adopter of ZLD, utilizing RO technology to recycle treated wastewater and recover valuable salts. Despite aligning with environmental sustainability goals, challenges, such as costs and operational complexities tied to RO technology, hinder optimal ZLD scheme performance. Economic challenges also arise from the expenses associated with thermal treatment units, increasing capital costs [7]. Successfully implementing ZLD requires a delicate balance between environmental benefits and economic feasibility, with the subsequent section exploring case studies that highlight instances of overcoming challenges, offering valuable lessons for the broader industry landscape.

Transforming wastewater: A circular approach for sustainability Currently, a significant 80% of water supply transforms into wastewater, presenting environmental and health risks. The current practices, encompassing physical, chemical, and biological methods, signify substantial progress in WTP. However, mere treatment is insufficient, given the persisting impurities and associated drawbacks.

Optimizing the entire WWT process is crucial, embracing a cradle-to-cradle approach. A shift from a linear "use and throw" to a circular "use, treat, and reuse" paradigm is essential for effective wastewater management. This holistic approach ensures resource efficiency and sustainability.

Pricing of treated water: Since the establishment of WWTPs incurs significant capital investment, the pricing of treated water must be strategically determined to encourage widespread acceptance. It is advisable that the cost of treated water remains below that of potable and drinking water, fostering affordability and accessibility. Leveraging the value generated from nutrients such as phosphorus and nitrogen, along with biogas energy, provides a viable financial model to offset the setup and operational costs of treatment plants. Technologies harnessing biogas from organic compounds in sewage, as successfully

implemented in cities like Gresham and Oakland in the United States, showcase financially sound and energy-efficient models for consideration.

Decentralized wastewater treatment: A paradigm shift towards decentralized WWTPs offers a versatile solution adaptable to varying operational scales. Deployable in small industries, industrial parks, small townships, urban and rural clusters, factories, and gated societies decentralized plants have the advantage of on-site installation. This approach enables the direct treatment of wastewater at its source, enhancing efficiency and minimizing the need for extensive transportation networks.

Public private partnership in wastewater management: Encouraging private partnerships in wastewater and sewage management introduces opportunities for leveraging advanced technologies, implementing localized systems, and enhancing overall efficiency. Private investments can play a pivotal role in providing smaller towns and villages with the necessary resources to establish competent wastewater management plants. Additionally, private entrepreneurs can contribute significantly to the effective management and maintenance of existing STPs, addressing the performance gaps that currently hinder optimal functionality.

Uniform Laws Across States: To address the fragmented landscape of wastewater management policies, there is a pressing need for uniform laws across states in India i.e at the central level. Presently, only a handful of states, including Haryana, Madhya Pradesh, Gujarat, Maharashtra, Chhattisgarh, Rajasthan, and Karnataka have adopted comprehensive wastewater management policies. To optimize efforts in combating water pollution, a centralized mandate and consistent laws across states are essential to ensure a cohesive and coordinated approach.

In conclusion, the way forward in wastewater management demands a holistic and adaptive approach that embraces technological innovation, strategic partnerships, and legislative coherence. These multifaceted strategies collectively pave the way for sustainable and efficient wastewater management practices in India.

Case studies

Chemplast Sanmar Limited: Chemplast Sanmar Limited, a leading manufacturer specializing in silicon wafers, PVC resins, caustic soda, chlorinated solvents, and chloro chemicals, grappled with a wastewater challenge marked by elevated levels of oil, grease, VOCs, COD, and total dissolved solids (TDS) reaching up to 10,000 mg/L. To tackle this issue comprehensively, Aquatech introduced a high efficiency reverse osmosis (HERO™) ZLD system (Figure 4). This innovative system maintains a high pH>10 (Figure 4) environment within the RO section. After the successful installation of the HERO™ ZLD system, Chemplast achieved an impressive 88–90% water recovery, specifically for RO, resulting in a cumulative water recovery exceeding 97%. The treated water is repurposed as cooling water within the facility. Additionally, the sludge generated is responsibly disposed of in landfills, while the recovered salt undergoes recycling, contributing to a circular economy by reintegrating into manufacturing processes. This integrated approach not only addresses Chemplast's WTP needs but also highlights the potential for effective water recovery and resource reuse in industrial settings.

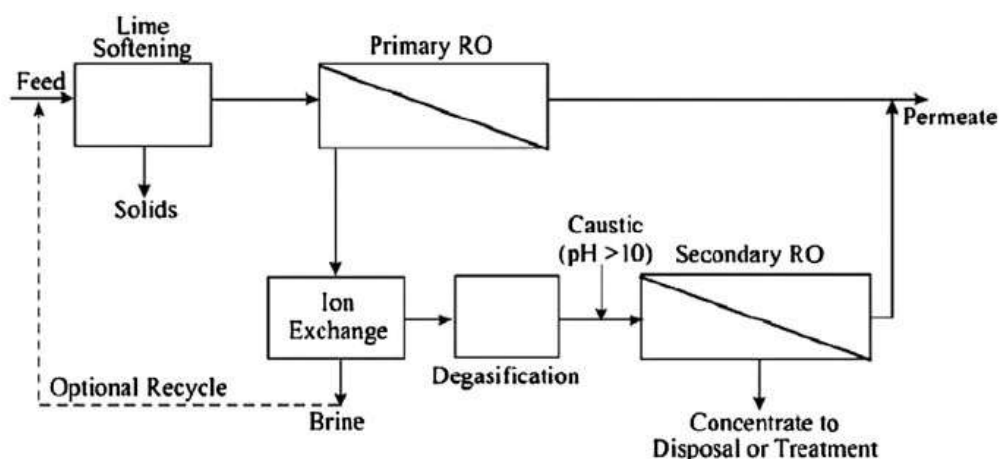


Figure4 High efficiency reverse osmosis

Pharmez Special Economic Zone (SEZ) Ahmedabad: Located in proximity to Ahmedabad, the Pharmez SEZ is under the management of Zydus Infrastructure. This facility hosts a common effluent treatment plant meticulously crafted to address the industrial wastewater emanating from 12 distinct pharmaceutical sites. The treatment process primarily involves a clarification unit complemented by a membrane bioreactor boasting a capacity of 750 KLD. Notably, recognizing the evolving environmental needs, the plant underwent subsequent upgrades to align with ZLD standards.

Conclusions

In conclusion, industrial wastewater management in India confronts a myriad of challenges, encompassing deficient treatment infrastructure, policy ambiguities, and the crucial necessity for private sector involvement. The inadequate wastewater treatment infrastructure, dysfunctional treatment plants, policy gaps, and jurisdictional ambiguities within the constitutional framework highlight the complexities. A disintegrated state-level approach further hampers efficient policy execution, emphasizing the need for a cohesive strategy. The lack of robust public-private partnerships and the potential of zero liquid discharge underscore the importance of innovative approaches. Transitioning to a circular paradigm, optimizing the entire wastewater treatment process, and encouraging decentralized wastewater treatment can enhance sustainability. Pricing treated water strategically, leveraging valuable by-products, and fostering uniform laws across states are crucial steps toward effective wastewater management in India.

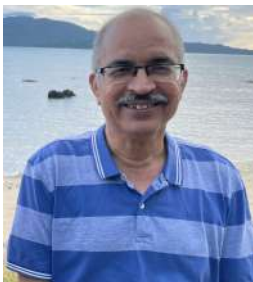
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Integrating Science & Engineering for Sustainable Developments in Industrial Wastewater Treatment for Chemical and Allied Industries

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Abstract

Water and safe environment is essential to life. It is a common observation that many rivers and surface water sources are highly polluted mainly due to industrial effluents and therefore providing safe water and also cleaner environment is an important agenda for developing countries like India. Further, water scarcity is another challenge in many parts which demands effective treatment of the wastewaters and recycle and reuse. Deriving sustainable solutions through innovations that are not just limited to laboratory developments but can be techno-economically exploited in real life applications is a huge challenge, especially in Indian context where the common trend is to rely on imported technologies than focusing on indigenous technology developments through advanced research. Make in India and assimilation of the developed technologies is therefore essential. We, at CSIR-NCL, have developed a new device based on vortex flow, named as vortex diode for hydrodynamic cavitation that can offer significant benefits in terms of improved economics and profitability due to high efficiency for the degradation of various organic pollutants. The technology has the benefits such as ease of operation, mild operating conditions, easy maintenance and low space requirement compared to many existing treatment technologies. The technology with TRL 9, is proved to be useful for treating different industry wastewaters such as pharmaceutical industry, distillery industry, fertilizer industry, dyes and textile wastewater treatment.

Keywords: *Degradation, Effluent treatment, Oxidation, Pollution control, Sustainability*

Introduction

Removal of various contaminants from wastewaters has been a challenging task and industries are required to meet the pollution control norms pertaining to the various pollutants. Refractory organic pollutants, that are difficult to degrade biologically and similarly, a new class of emerging pollutants pose specific problems in this regard for which the practical solutions are not easily available or are highly cost intensive. The conventional effluent treatment plants (ETP) typically employ primary treatment to reduce part pollutant load followed by secondary treatment where up to 95% pollutant load is eliminated and finally tertiary treatment or polishing step to meet the desired pollution control norms. In these three steps, a large number of physical, chemical, physico-chemical and biological methods can be used depending upon the nature of the pollutants, concentration and the desired extent of removal. The most common industrial wastewater treatment technologies include, coagulation, adsorption, ion exchange, advanced oxidation, biological treatment,

membrane technologies etc. In wastewater treatment, generally no one technology is suitable to meet the desired norms and therefore apt integration of various methodologies is essential. The final decision in this regard is largely dictated by the techno-economic feasibility of the combined operations and among the operations, it is instructive to continuously evaluate the newer developments in terms of materials and methods, processing and technologies; the final selection also depends on the possible/ futuristic changes in the chemical processing or variations in the effluent- quantity and quality. Hydrodynamic cavitation is one specific form of advanced oxidation process, highly promising alternative for the removal of organic pollutants, a destructive technology that generates no secondary waste. It is possible to employ the hydrodynamic cavitation technology in isolation or in combination with other established treatment methodologies for increased cost effectiveness. The selection of cavitation reactor and process intensification is crucial.

CSIR NCL's Technology for Water and Wastewater Treatment-Lab to Commercialization

Our work focuses on the challenges pertaining to the integration of science and engineering for sustainable developments in industrial wastewater treatment for chemical and allied industries. It is felt that the approach of “going back to nature” needs to be followed in the search of sustainable solutions as most of the present day “synthetic” solutions tend to create secondary problems thereby entering in the “do loop” of problem solving. The development of innovative technologies for water and wastewater treatment is critical to clearly bring out the utility of using fresh approach in the form of newer reactor developments in hydrodynamic cavitation technology and also for effective process intensifications. In this context, our research has focused on the concepts of Indian knowledgebase combined with modern science and engineering to revisit the environmental problems to develop practical solutions. The existing methodologies can also be further modified with newer developments based on natural materials and for new technology development apart from applications. The development of biocoagulants using naturally available cheaper resources and formulations can offer attractive improvements to the existing coagulation process in terms of reduced sludge formation and improved efficiencies. The development of bio-nanocomposites also highlights utility of this approach for improved performance not just for removal of pollutants, but also for the elimination of harmful bacteria in drinking water treatment. Apart from the use of natural biomass for developing bio-nanocomposites, the use of cow-ghee for enhancing the properties of the adsorbents also appears to be highly promising in the development of new adsorbents. The newer materials and methods can be highly useful in a wide range of water and wastewater treatment applications.

Hydrodynamic Cavitation Technology and Innovation- Vortex Diode

We have developed an advanced oxidation processes and new devices-Vortex diodes(Fig.1).The devices have simple design and can be employed easily for effluent treatment (US9422952B2, IN397769, EP2766314, PCT/IN2012/000676, US9725338B2, IN338553, PCT/IN2020/051007, WO 2021/111476 A1, US2021111476). The technology can be easily integrated with the existing ETP operation for increased effectiveness and for reduced cost of treatment. The CSIR-NCL's design of Vortex diode has been scaled-up for flow rates up to 40 m³/h. The technology has been licensed to M/s VIVIRA Technologies, Pune and ~ 30 units of CSIR-NCL designs were sold till 2020.We have been working with different industries to demonstrate effectiveness of the technology at a pilot plant scale of 1 m³/h at NCL(Fig. 2).

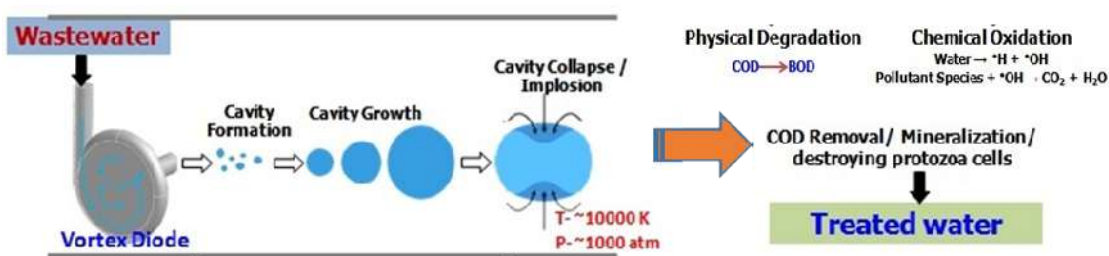


Fig. 1. Vortex Diode Cavitation Reactor and Hydrodynamic Cavitation Mechanism



Fig. 2. Pilot Plant Facility at CSIR-National Chemical Laboratory (Capacity: 1 m³/h)

CSIR-NCL's Cavitation technology using vortex diode is useful for degradation and removal of variety of dyes/ organic pollutants/ ammoniacal nitrogen (Bhandari et al., 2021, <https://doi.org/10.1016/j.ultsonch.2020.105306>). Vortex diode is a cavitating device that employs rotational flow, has no moving elements, and has many advantages over most conventional devices in terms of high energy efficiency due to low-pressure requirement, less clogging/ choking due to the larger opening area, and easy scale-up. The technology also has advantages such as no secondary waste, significant ease of operation and is believed to be cost effective as compared to other advanced processes. The cavitation process can be effectively combined with existing treatment methodologies such as biological treatment (e.g. Distillery industry), coagulation, adsorption (e.g. dyes, textile, fertilizer industry) for improving techno-economic feasibility apart from reducing environmental pollution.

Our inventions in the form of newer cavitation device- vortex diode, dual activity devices, surface coated cavitation reactors and intensified hydrodynamic cavitation provide promising new alternatives in water and wastewater treatment for the removal of various organic pollutants/contaminants. The hydrodynamic cavitation technology is successfully

demonstrated specifically for the removal of API pollutants for pharmaceutical wastewater treatment, for distillery wastewater treatment for the removal of COD and ammoniacal nitrogen and also for increasing gas yield by converting part COD to BOD by combining cavitation with biological treatment, for the removal of refractory pollutants from dyes and textile industry effluents, for fertilizer industry effluents treatment and so on.

Real Life Application of Hydrodynamic Cavitation and Vortex Diode Reactor

Pharmaceutical Industry Wastewater Treatment

Pharmaceutical wastewaters contain many emerging contaminants in the form of active pharmaceutical ingredient (API) pollutants; high concentrations in industrial effluents and in extremely small concentrations in the contaminated surface waters. CSIR-NCL's hydrodynamic cavitation technology and advanced oxidation processes offer solutions to real life implementations for the effective degradation of API pollutants, such as Naproxen, (common nonsteroidal anti-inflammatory drug), Metformin (antidiabetic drug), antibiotics such as Ciprofloxacin, Cephalexin etc. CSIR-NCL's vortex flow-based device, vortex diode requires significantly lower pressure drop (~ 0.5 to 1 bar) compared to the conventional device, orifice (~ 5 to 10 bar). A significantly high removal of Naproxen was obtained using vortex diode and process intensification. Similarly, high degradations to an extent of 100% were achieved for Ciprofloxacin, Metformin and Cephalexin. Intensifications of the type of hydrogen peroxide addition, pH manipulations were highly effective in enhancing the rate and extent of degradation. The typical cost of treatment for hydrodynamic cavitation was ~ 40 -70Rs./m³, though it can vary with the nature of the compound and nature of the process intensification. A new development in the form of dual activity cavitation enhances the rates significantly due to the catalytic effects and the dual function cavitation reactors can provide further attractive alternative to the existing technologies in real-life applications. Advanced oxidation processes and hybrid processes viz. ozonation, Fenton, photo-Fenton, UV+H₂O₂, cavitation+H₂O₂ can also effect complete degradation depending upon the nature and concentration of the pollutant. The results clearly highlight utility of intensified advanced oxidation processes and hydrodynamic cavitation in wastewater treatment, in general and degradation of API pollutants, in particular. The developed strategy was successfully used for treating real industrial wastewater from pharma sector where close to 40% TOC removal using only vortex diode cavitation can be increased to over 90% removal using intensified cavitation with hydrogen peroxide/ ozone and subsequently to 100% removal using the process integration of cavitation and adsorption. Thus, the advanced oxidation processes can be effectively combined with existing treatment methodologies for improving techno-economic feasibility apart from reducing environmental pollution contributing to 'sustainable technologies for water and wastewater treatment' – indigenous newer developments in "Water & Environment", "Swachh Bharat" and "Make in India" programs.

The hydrodynamic cavitation is effective in the degradation of the API pollutants and vortex flow based device, vortex diode requires significantly lower pressure drop (≤ 1 bar) compared to the orifice (≥ 5 bar), indicating lowered energy consumption- by an order of magnitude. The degradation of various types of API pollutants was practically complete using vortex flow-based hydrodynamic cavitation (HC) and appropriate process intensification even for high initial concentrations, 10 ppm or higher. Process intensifications in the form of aeration/ hydrogen peroxide combination, pH modifications, reactor type etc. are crucial to ensure 100% degradation and the cavitation yields in such intensified processes were found to be

order of magnitude higher than that for conventional hydrodynamic cavitation or for conventional devices such as orifice. Fig. 3 depicts the typical degradation results using conventional cavitation and advanced oxidation processes (AOP) and the possible extent of degradation enhancements using different forms of process intensifications. It is evident that naproxen degradation of ~20% using conventional HC or AOP could be successfully increased to ~85% using apt process intensification strategy of hydrogen peroxide addition/aeration of pH modifications (Dixit et al., 2022, <https://doi.org/10.1016/j.cep.2022.108799>). The extent of degradation of various API pollutants can be similarly degraded to an extent of 100%, otherwise not possible using conventional technologies. A new form of cavitation processes was developed using reactors of dual activity for increased efficiency (Dixit et al., 2023, <https://doi.org/10.1016/j.cherd.2023.02.03>; <https://doi.org/10.1016/j.cherd.2023.10.002>). It is evident that Ciprofloxacin degradation can be enhanced from ~20% to ~100% using the newer development of dual activity vortex diode and process intensification (Patil et al., 2022, <https://doi.org/10.1016/j.cherd.2022.09.027>). Huge enhancements in per pass degradation and cavitation yields for Cephalexin were observed, ~3000% and 1450% respectively. The high enhancements substantiate the dual activity due to catalytic effect and highlight the potential of the dual function cavitation reactors in real-life applications, not just for increased efficiencies but also for significantly reduced costs in industrial wastewater treatment. The destructive removal of harmful refractory pollutants consequently provides sustainable processes for environmental pollution control (Bhandari et al. 2023, <https://doi.org/10.1016/j.cherd.2023.10.002>). The strategy was successfully employed for demonstrating treatment of real pharmaceutical industry wastewater. Also, the process integration strategy by combination of cavitation and adsorption can ensure 100% removal. In such cases, the overall cost of operation dictates the selection of the process. In conclusion, Advanced oxidation processes and CSIR-NCL's hydrodynamic cavitation technology, in particular vortex diode are highly useful for the degradation of various API pollutants such as nonsteroidal anti-inflammatory drug, antidiabetic drug and antibiotics. The results clearly highlight utility of intensified hydrodynamic cavitation in industrial applications.

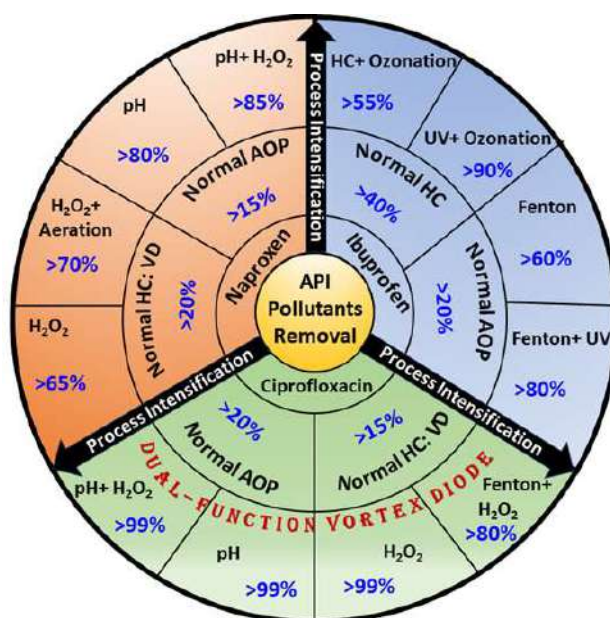


Fig. 3. Effectiveness of advanced oxidation processes and process intensifications.

Dyes and Textile Industry Wastewater Treatment

Dyes and textiles industry is one of the largest polluting industry sectors in India. Dyes also find applications in many other industries such as paints, ink, leather, polymer and plastics. The removal of dyes, especially refractory dyes is quite challenging as apart from creating pollution, presence of dyes also imparts colour even in small concentrations. Close to 70% of dyestuff gets consumed in textiles alone and hundreds of dye industries, corresponding to ~70 to 80% of the total capacity are located in western India. Most of the units are small scale industries having difficulty in effectively treating the effluents *insitu* and also in technology assimilation.

The effluents generated in these industries is highly complex containing organics such as benzene, xylene, toluene, aniline and such organics and the effluents have typically COD in the range of 2000 to 35000 ppm and also ammoniacal nitrogen as high as 3000 ppm. There are no general solutions available and hydrodynamic cavitation technology using vortex diode can be highly useful in the removal of not just COD but also for effective removal of ammoniacal nitrogen below 30 ppm as required. The strategy that can be considered for treating such effluents is shown in Fig. 4.

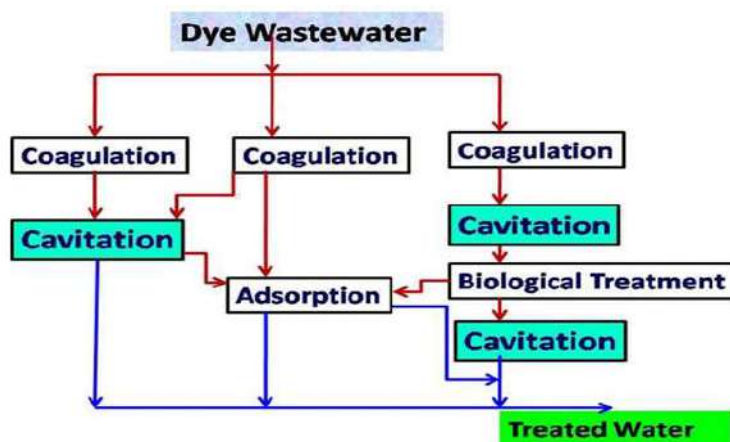


Fig. 4. Dye Wastewater Treatment Strategy

Fertilizer Industry Wastewater Treatment

Fertilizer industry represents a huge complex with many plants, each generating different type of wastewater containing variety of pollutants such as organics, alcohols, ammonia, nitrates, phosphorous compounds and heavy metals. The removal of organic pollutants and ammoniacal nitrogen are the two important objective in the wastewater treatments. We have studied the real effluents from 6 different sources with streams containing extremely different concentration of ammoniacal nitrogen and COD (Bhandari et al., 2016, <https://doi.org/10.1080/19443994.2016.1186399>). The stream containing the high COD concentration of the order of 1,25,000 ppm could be successfully treated with the conventional hydrodynamic cavitation using vortex diode and 85% reduction in the COD could be achieved, reflecting applicability of the vortex diode. For the effluent streams

containing high ammoniacal nitrogen content in the range of 300 to 1700 ppm, close to 40-87% removal could be achieved using hydrodynamic cavitation. The importance and success of cavitation compared other existing processes here clearly implies practical application with significant ease of operation and techno-economic feasibility without generating secondary waste.

Distillery Wastewater Treatment

Distillery wastewater typically have very high COD above 1,00,000 ppm and BOD above 45000 ppm. In view of the high BOD content, the biological treatment of the type anaerobic treatment is well established in the existing industrial set-up. In distillery wastewater treatment plant, the hydrodynamic cavitation process can find applications in different locations for meeting different objectives. The technology is found to convert part COD into BOD which is reflected in the increase in the gas yield. As per the data from real industry installations, up to 20% increase in the gas yield could be obtained by integrating the hydrodynamic cavitation using vortex diode prior to sending the wastewater to bio-digester. A typical installation in the distillery is shown in Fig.5. The increased gas yield offers value addition to the existing plant, which otherwise is not possible with other wastewater treatment technologies and therefore attractive. The technology is also useful to reduce ammoniacal nitrogen and COD.



Fig.5. Distillery wastewater treatment

Newer Developments

Drinking water treatment

Providing safe drinking water is a major challenge as is evident from the increasing human population and increased environmental pollution. Safe drinking water is necessary to prevent occurrence of large number of waterborne diseases and to save millions of lives. Since many of the conventional physical methods (e.g. heating, radiation, microwave, filtration, UV

irradiation, plasma) have difficulties such as scalability, high cost and prolonged treatment times and the existing chlorine based methods have problems in the form of carcinogenic disinfection byproducts, it is essential to develop a methodology which provides safe and healthy drinking water at low cost with substantial ease of operation, scale-up and without harmful disinfection by-products. CSIR-NCL's water disinfection technology, SWASTIHK (Safe Water and Sustainable Technology Initiative from Indian Knowledgebase), a hybrid hydrodynamic cavitation technology, has the potential to provide alternative to existing disinfection processes including chlorination (Bhandari et al., 2019, <https://doi.org/10.1016/j.ultsonch.2019.104820>). The technology can completely eliminate the harmful bacteria such as gram-negative (*Escherichia coli*), gram-positive (*Staphylococcus aureus*) and also antimicrobial resistant (AMR) bacteria apart from relatively less researched, and difficult to remove opportunistic pathogen (<https://doi.org/10.1016/j.ultsonch.2020.105272>). The SWASTIHK technology, for the first time, successfully demonstrates the use of different natural oils such as eucalyptus oil, clove oil, peppermint oil, ajwain oil etc. in conjunction with hydrodynamic cavitation so as to effect cell destruction through the rupture of cell wall, oxidative damage and possible DNA denaturation. The technology reveals exceptionally high rates of disinfection and complete removal of all types of bacteria, within minutes, using very small concentration of oil, 0.1%. The oil after the treatment can be easily separated and recycled. The consequent reduction in the time of operation results in drastic lowering the cost of disinfection to an extent of ~Rs. 2.5/m³ or 0.25 Paise/L. The developed methodology, SWASTIHK, has the potential to provide viable alternative to chemical disinfection methods, provide ease of scale-up and also possible health benefits (Bhandari et al., 2022, <https://doi.org/10.1016/j.bej.2022.108631>; Bhandari and Balapure, 2024, <https://doi.org/10.59143/isas.jisas.2.3.BSVG2322>).

Newer Reactors and Cavitation Processes

The vortex diode is one invention of CSIR-NCL that is being used in different industries, for reducing COD, ammoniacal nitrogen and also for industries where increase in gas yield from the existing biological treatment plant is applicable. Recently, we have also improvised the vortex diode device by adding catalytic activity to the cavitation activity and the new reactors with this dual function are termed as Dual Activity Cavitation Reactors that have potential to significantly enhance the performance in the wastewater treatment. The proof of the concept was established for pharmaceutical industry wastewater treatment. Further research is still required to evaluate the enhancements in the efficiency for wastewater treatments of different industry sectors. In continuation of the idea of the dual function reactors, new form of cavitation reactors are developed with internal surface coating by different catalytic metals such as nickel, copper etc. The newer surface coated cavitation reactors not only would reduce the cost of equipment by order of magnitude, but at the same time would enhance the degradation of specific pollutants using specified catalytic metal coating. This again needs to be investigated further for various types of effluents and specific pollutants. The newer developments in the cavitation reactors are shown in Fig. 6. We, at CSIR-NCL, have been working closely with industry in this regard. However, it is essential that effective hand-holding is realized in the form of academia-research-industry interactions, collaborations and technology developments for not just developing but also successfully translating/implementing the new research for industrial as well as societal benefits.

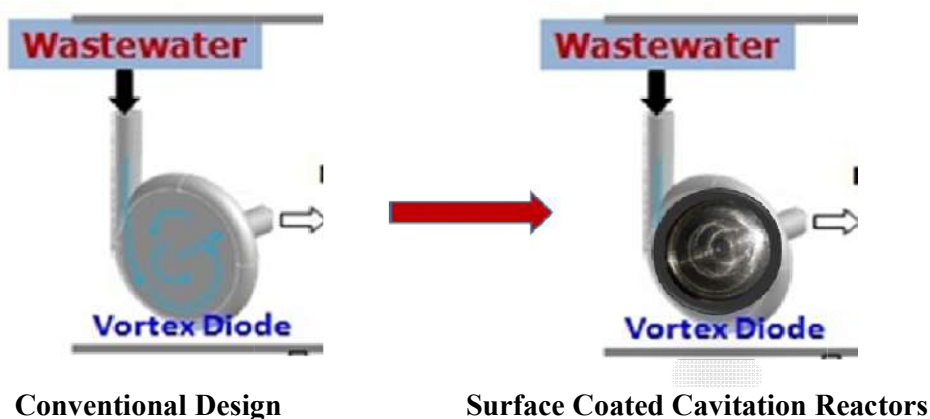


Fig.6. Newer developments: Transformation of Conventional Reactors into Dual Activity Cavitation Reactors

It is instructive to note that the new developments in the form of surface coated cavitation reactors can possibly have many applications in the catalytic reactions, unexplored so far since hydrodynamic cavitation was envisaged to be only a process based on the generation of oxidising species and consequent advanced oxidation of organics apart from physical effects such as shock waves. The addition of catalytic activity in the process without the external addition of the catalyst, homogeneous or heterogeneous, implies many more applications of the hydrodynamic cavitation technology over and above the wastewater treatment.

Our research in the area of water and wastewater treatment, improved processes, new equipment, new materials, new processes, process improvisations and also for education are summarized in Fig. 7 depicting Technology, Research and Education.

Deliverables ✓Prototype- Newer Materials ✓Implementation at Industry ✓Installations at different levels		Industry/ Societal Benefits ✓ Reduced Pollution ✓ Recyclable Water ✓ Preserving Ecology	> Cavitation + Adsorption/ ion-exchange + Coagulation + Oxidation + Biological treatment + Membrane separation
		Bhandari et al., IN397769 US9422952B2 EP2766314 PCT/IN2012/000676 US9725338B2 IN338553 PCT/IN2020/051007 WO 2021/111476 A1 US2021111476.	

Fig. 7. Improved Efficiency, Economics and Sustainability through Newer Developments

Conclusions

In the existing wastewater treatment scenario, it is evident that the ready solutions are available only in few cases. Since each effluent is different, it is necessary that industry specific methodologies be developed, at times by integrating the conventional and new technologies for effective removal of the pollutants and for increased cost-effectiveness. It is also necessary to appreciate the fact that wastewater as a source of energy be considered where applicable. CSIR-NCL's hydrodynamic cavitation technology and vortex diode offers one indigenous technology, a highly promising alternative to many existing technologies and can be used for the degradation of pollutants; in isolation or the technology can be integrated in the existing ETP set-up for reduced operational costs. It can be concluded that hybrid processes combining newer coagulants, adsorbents and hydrodynamic cavitation with newer devices can offer techno-economically feasible solution to industrial wastewater treatment.



Dr. Vinay M. Bhandari is presently working as a Chief Scientist and Professor-AcSIR, in the Chemical Engineering & Process Development Division of the CSIR-National Chemical Laboratory, Pune, India. He obtained his B. Chem. Engg. from UDCT, Bombay (1985; now ICT Mumbai) and Ph. D. (Chem. Eng) from IIT Bombay (1993). He has more than 32 years of research experience apart from 2 years of industrial experience. He worked as a visiting faculty at Tohoku University, Sendai, Japan in 1998-99 and also as visiting scientist at Korea Institute of Energy Research, Daejeon, South Korea during 2004-05. Dr. Bhandari guided several graduate and post-graduate students and has worked as a consultant to many industries. He has more than 250 publications/presentations and has filed 26 Patents (12 Patents granted, including US/WO Patents). He recently co-authored 2 books- "*Industrial wastewater treatment, recycling and reuse*" (Elsevier, 2014) and "*Hydrodynamic Cavitation: Devices, Design and Applications*" (John Wiley & Sons Inc., 2022). He has developed 4 technologies based on hydrodynamic cavitation- for Disinfection of water (SWASTIHK); for Industrial wastewater treatment (commercialized in India) and for Desulfurization of fuels. He is recipient of several prestigious awards including Green & Sustainable Chemistry award, SERB-IGCW-2017 and IGCW-2023. His desulfurization work received GYTI award for Technological Innovation, conferred by the Hon. Vice President of India in 2019. His research interests include Chemical and Environmental Engineering, Advanced Separation Processes and Industrial wastewater treatment, recycle and reuse.

Radiation functionalized adsorbents: A viable solution for textile dye wastewater remediation

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1. Introduction

Textile printing and dyeing are crucial processes in the textile industry involving the use of various chemicals and dyes to color textile fibers and print fabrics, which generates a significant amount of wastewater, termed as textile dye effluent. The large amount of effluent generated from cotton textile industries contains a range of toxic and recalcitrant dyes and other auxiliary chemicals (salts, surfactants, gum, silicates, metal ions etc.) that can have harmful effects on aquatic life and human health, if discharged in to water bodies without proper treatment [1]. Colored wastewater discharged from these industries is not only an aesthetic pollutant but also contaminates ground water and sabotages aquatic ecosystems by modifying the aquatic environment, both physically and chemically. Moreover, the intense color of dyes reduces transmission of sunlight into water and decreases the dissolved oxygen content [2]. This impairs the photosynthesis activity of aquatic plants and algae, depreciating their proliferation and affecting other aquatic life forms as well. The effluent can also contaminate the soil, causing soil pollution and affecting the whole ecosystem. The severity of the situation can be gauged by the fact that annually, the textile industry discharges around 280,000 tons of refractory textile dyes worldwide, with 10-15% of these dyes entering the environment through wastewater[3]. With growing alarm over despoiling of our environment, government agencies worldwide are enforcing stringent laws and regulations to mitigate pollution, making it mandatory for industries generating effluents to resort to effective treatment measures prior to discharge.

In view of this, the textile dye effluent is a serious environmental issue that demands our immediate attention. It is essential to adopt proper treatment methods to reduce the amount of effluent discharged into the environment and minimize its adverse effects on human health and the ecosystem. To address these issues, there has been a growing interest in developing sustainable and environmentally-friendly dyeing and printing processes for the textile industry. These strategies can include the use of natural dyes, recycling of waste water, awareness and demand for sustainable products and development of more efficient treatment methods.

Some of our recent developments in the field of radiation processing of polymeric materials for environmental pollutant remediation are being presented in this article. This includes different types of polymeric adsorbents developed by radiation grafting process for the treatment of industrial wastewater [4-7]. A radiation grafted cotton cellulose adsorbent based process has been up scaled to industrial scale and successfully translated to a viable technology (Rad-TED) for treatment of cotton textile dye wastewater. It is a concerted effort towards developing eco-friendly and sustainable treatment processes for textile dye wastewater in order to safeguard the environment and promote sustainable industrial practices and growth.

2. Dye wastewater remediation methods

The various dye wastewater treatment methods developed over the years can be broadly classified in to two categories (Fig. 1):

(i) **Physico-chemical methods:** This method works on principle of separation of dye molecules from waste water using different processes, such as adsorption, ion-exchange, filtration (micro, ultra and RO filtration membranes) and flocculation/coagulation using inorganic or organic flocculants)

(ii) **Degradation/Oxidation methods:** In this method, dye molecules are degraded or decomposed with the help of different degradation and oxidation processes. These include biodegradation, chemical oxidation (ozone, Fenton's reagent, photo catalysis), radiation degradation and electrochemical oxidation which includes both electro-oxidation and electro-coagulation.

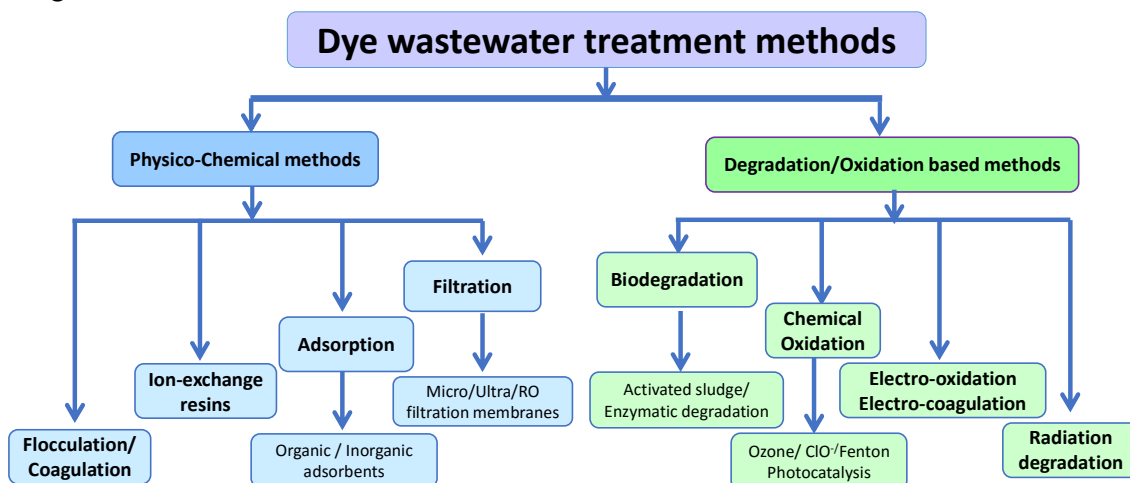


Figure 1: Schematic of reported dye wastewater treatment strategies

Due to the complexity of textile dye wastewater, no single universal treatment process is adequate to solve this problem. Therefore, combinations of different processes have been proposed and are being used for this purpose. The most popular combination method currently prevalent in the industry is coagulation, biodegradation followed by filtration via reverse osmosis. But these methods are severely restricted in their utility by numerous limitations. For instance, coagulants, which, more often than not, are used in excess in industries without prior optimization, lead to generation of large volumes of colored sludge as a secondary waste. Activated sludge treatment process is constrained by its long treatment duration along with solid sludge generation. The use of ultra-filtration and RO membranes for dye wastewater as a tertiary treatment step, on the other hand, is restricted by high initial and operational costs and the stringent feed quality parameters required to be met to avoid fouling of the membranes. Such quality control involves significant financial burden and skilled manpower for plant operation. The use of oxidation/degradation methods, such as ozonation, Fenton's reagent, hydrogen peroxide etc. have also occasionally been attempted at industrial scale but the primary demerits of these methods is the incomplete degradation of pollutant leading to generation of toxic degraded by-products which continue to inhabit the wastewater even after the treatment process. Unless mineralized, these by-products can pose serious health risks owing to their toxic nature [8].

Although every approach has its own merits and shortcomings, the adsorption being a physico-chemical separation approach, seems to be the most appropriate choice since it is not only comparatively simple but cost effective and efficient. Moreover, the complex aromatic configuration in these dye structures make them resistant to degradation, thereby making the adsorption process an ideal candidate for remediation of these pollutants. Using easily upscalable functional adsorbents, the pollutant moieties are entirely sequestered from water, which eliminates the chances of generating toxic secondary degradation by-products in the

treated water. In this regard, radiation technology can play an important role in developing efficient high performance low-cost functional polymeric adsorbents [4,5,9].

3. Radiation processing of polymers

Polymers constitute one of the most versatile class of materials in our day-to-day lives with applications in various important fields, including environment, industry, healthcare, sensors, agriculture, etc. [10-12]. Most of the polymers possess desired thermo-mechanical properties, but fall short in chemical properties that may be essential for certain target applications. Radiation processing of polymers is an efficient process to achieve desired functionality as well as for incorporation of unique or superior characteristics. The novelty of these processes arises from the fact that radiation technology is a green, ambient reaction process that does not necessitate the use of harmful chemicals (initiators, chemical reductants and organic solvents), is easily upscalable and offers better control over process parameters [4]. Although radiation processing of polymers encompasses three different processes viz. radiation degradation, cross linking and grafting, the scope of the current article shall be restricted to a discussion on radiation grafting process alone.

Radiation induced graft polymerization (RIGP) is a surface modification approach, wherein the surface properties of the material are tailored using suitable functional monomers, as per requirement [5-7]. In RIGP, new polymer chains of desired functional monomers are grown over an existing polymer backbone chain using ionizing radiation as a source of initiation. The mechanism of RIGP involves formation of free radicals on an existing polymer backbone due to radiation induced cleavage of bonds. These free radicals initiate graft copolymerization chain reaction from the monomers, leading to the growth of functional grafted chains anchored to the base polymer. The RIGP reaction can be performed by four different approaches (Fig. 2):

i) Simultaneous irradiation grafting (SIG): This approach is also called as direct or mutual grafting, wherein a polymer substrate is first dipped in the monomer solution and the whole mixture, comprising of the polymer substrate and monomer solution, is simultaneously exposed to ionizing radiation. Radicals are generated both on the polymer backbone as well as in monomer solution. While radicals generated on polymer backbone initiate graft copolymerization reaction, those in the monomer solution can result in the formation of homopolymers. This method is simple and typically yields high degree of grafting. Moreover, it is more suitable for radiation sensitive polymer backbones. On the downside, the formation of homopolymer along with the graft copolymer leads to significant monomer loss.

ii) Post-irradiation grafting (PIG): In this grafting method, the polymer backbone is first exposed to ionizing radiation to generate free radicals on it. It is subsequently dipped in the monomer solution, to initiate the graft copolymerization reaction under elevated temperature. Though yielding lower grafting yields, the primary advantage of this method is that there is a much lower probability of homopolymer formation. This method is more suitable for radiation resistant polymer backbones.

iii) Peroxidation grafting (PeG): This involves the use of peroxide compounds to initiate the grafting process [13]. Here the polymer is first irradiated in the presence of air to produce hydroperoxides and peroxides. The polymer peroxides, which are often stable at ambient temperature can be decomposed in contact with monomer by heating to produce peroxy radicals that initiate graft polymerization reaction.

iv) Multi-step simultaneous grafting (MSSG): This approach is adopted to increase the grafting yield for a grafting system where limited grafting yield is obtained via the conventional simultaneous grafting method. The process involves multiple iterations of

the mutual irradiation grafting process, with the base matrix in each step containing a progressively increasing grafted chain content by virtue of the previous grafting step, until achieving the desired grafting yield [14].

Radiation grafting is characterized by grafting yield (G.Y.), determined gravimetrically using relation (1)

$$GY (\%) = \frac{W_F - W_I}{W_I} \times 100 \quad (1)$$

Where, W_F and W_I are the weights of the polymer backbone before and after RIGP, respectively.

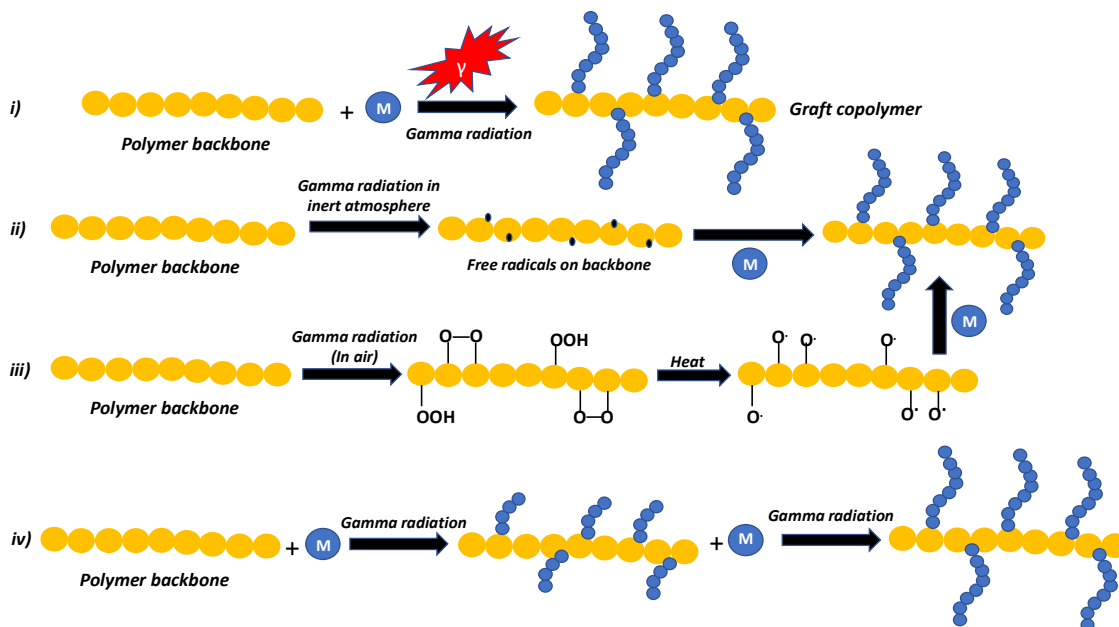


Figure 2. Schematic of various methods of RIGP

4. Radiation grafted functional polymeric matrices

A range of functional polymers have been synthesized in our laboratory via RIGP process for remediation of different types of water pollutants. Monomers with varying functional groups, e.g., anionic, cationic, chelating, etc., have been grafted onto different polymeric matrices, such as Cotton cellulose, Polyurethane foam (PUF), PTFE, PP, PE, etc., of different shapes and geometries (sheet, fabric, foam, beads, scrap, woven/non-woven cloth, etc.). These functional polymeric matrices were used to remove/separate water pollutants such as dyes [4,5,15,16], metal ions [6,7] and pharmaceuticals from water.

4.1. PUF based adsorbent

RIGP has been successfully used for converting PUF waste into a value-added product in the form of a functional adsorbent containing grafted Polyacrylic acid (PAA) chains (PAA-g-PUF). This adsorbent has been validated in laboratory scale for removal of basic dyes from water. The complete process from fabrication of PAA-g-PUF to dye adsorption and desorption in batch and continuous flow operation is presented in Fig. 3. To investigate the adsorption capacities and characteristics of the PAA-g-PUF adsorbent, batch and column mode studies were conducted using model dyes, such as Basic Red 29 (BR29) and Methylene Blue (MB). The results showed that the PAA-g-PUF adsorbent,

with a grafting yield of 90%, had room temperature adsorption capacities of 310 mg.g^{-1} and 242 mg.g^{-1} for BR29 and MB, respectively[15]. It is important to understand the adsorption phenomenon and establish its equilibrium and kinetic characteristics, which can be achieved by using different equilibrium and kinetic models with linear and nonlinear fitting analysis of the adsorption data. Furthermore, the PAA-g-PUF adsorbent can be regenerated using an optimized eluent system and reused for more than 10 adsorption-desorption cycles, making it a practical and sustainable solution for wastewater treatment.

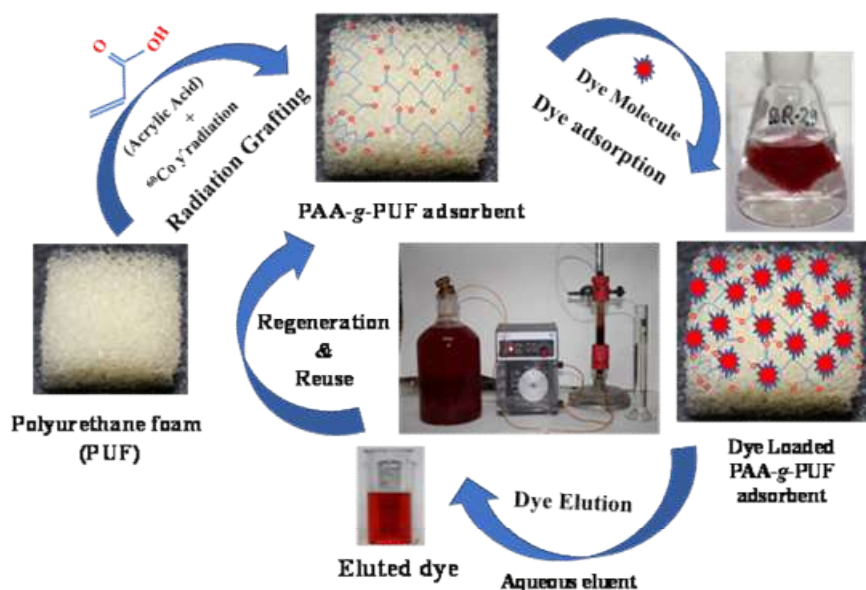


Figure 3: Transformation of waste PU foam to a valuable adsorbent via radiation grafting process

Continuous flow mode studies were also conducted using a fixed bed packed column, which allowed for the establishment of breakthrough curves. These curves were analysed using different models to obtain breakthrough adsorption parameters. Overall, the radiation-induced grafting process is a promising method for converting PUF waste into a value-added product, such as a functional adsorbent for effective remediation of dye wastewater.

4.2. PTFE based adsorbent

On similar lines, Teflon scrap has also been successfully valorized by grafting polyacrylic acid to develop a unique anionic adsorbent (PAA-g-Teflon) for remediation of basic dyes [16]. Studies carried out on the adsorption of two model dyes, Basic Red 29 (BR29) and Basic Yellow 11 (BY11) revealed the system to be efficient in removing both dyes with excellent uptake capacities and fast kinetics. The adsorption of the basic dyes was observed to follow different adsorption isotherm models depending on structure and size of the dye molecule, while the adsorption capacity was also observed to increase with temperature. Moreover, the dye laden PAA-g-Teflon adsorbent could be regenerated using an optimized eluent system. The radiation functionalized PAA-g-Teflon adsorbent thus can offer an alternative for treatment of effluent containing dyes.

4.3. Cotton cellulose-based adsorbents for textile dye effluent treatment

Due to various merits of ubiquitous and abundant biopolymer, cellulose was chosen as a suitable natural polymer backbone and employed for large scale application of radiation grafted adsorbents for wastewater treatment. Distinctive properties, such as renewability, biodegradability, ease of modification and processibility, widespread abundance, non-toxicity, etc. legitimizes its claim as a sustainable, low-cost alternative to synthetic polymer-based materials. India, as a global leader in cellulose production, generates vast amounts of cellulose fabric waste from cotton cellulose processing industries, most of which is either discarded or incinerated as a means of disposal. Therefore, efforts are being made to instead utilize this cellulosic waste for production of value-added products. Reusing functionalized cellulose in its various forms is an integral step towards ensuring a “cradle-to-cradle” circular economy where “trash becomes cash” and the raw materials and final products undergo minimum loss in value by adhering to a closed loop economic system. As a renewable resource, adsorbents synthesized using cotton cellulose thus provide a sustainable alternative to traditional synthetic polymer based non-biodegradable adsorbents.

Gamma radiation grafted cotton cellulose-based adsorbents have shown promising results for textile dye effluent treatment. Research has demonstrated the effectiveness of these adsorbents in capturing dyes from wastewater. For example, a single step-RIGP was used to graft Poly(vinylbenzyltrimethyl ammonium)chloride (PVBT) onto cellulosic cotton textile waste to transform it in to a valuable cationic adsorbent (PVBT-g-Cellulose) and reported for effective removal of dyes from water, exhibiting equilibrium adsorption capacities of ~ 540 mg/g, ~ 474 mg/g and ~ 122 mg/g for acid blue 25(AB25), acid yellow 99(AY99) and acid blue 74(AB74), respectively[9]. Similarly, an anionic cotton fabric-based adsorbent was synthesized by radiation grafting it with 4-vinylbenzenesulfonic acid sodium salt with an adsorption capacity of 320 mg.g^{-1} for cationic dye basic red 29 (BR29) [5]. Furthermore, functionalized cotton fibres were used to capture Methylene Blue and Neutral Red effectively [17]. These studies highlight the potential of utilizing modified materials for efficient removal of dyes from textile effluents.

We have prepared both anionic and cationic group containing cellulose based adsorbents via gamma radiation induced mutual irradiation grafting method. While Quaternary ammonium group containing monomers (MAETC, VBT, MPTAC) were grafted to impart cationic functionality [4,5,9], anionic functionality was achieved through the use of sulphonic with cotton cellulose fabric as the base polymer matrix [5]. These adsorbents were initially employed for removal of ionic dyes from textile waste waters at the laboratory scale, with experiments conducted in both batch and column adsorption modes to standardize various adsorption parameters. Among these, PMAETC-g-Cellulose adsorbent has been selected and upscaled up to industrial scale textile dye wastewater treatment. The schematic of the fabrication and working principle of treatment process is depicted in Fig. 4.

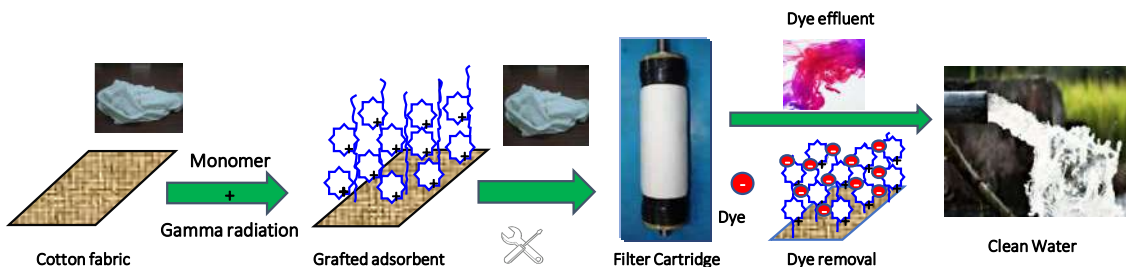


Figure 4: Radiation grafting based fabrication and working principle of treatment process

4.4. Radiation assisted Adsorbent technology for Textile Effluent Decolouration (*Rad-TED*): A lab to land success story

With the knowing fact that almost 90 % of dyes used in cotton and viscose textile industries are anionic in nature, the MAETC grafted cotton cellulose fabric adsorbent, by virtue of its established adsorption characteristics, was shortlisted for validation as a viable dye effluent treatment technology.

4.4.1. Laboratory scale studies and validation in relevant environment

Initial laboratory scale studies were carried out on simulated as well as actual dye wastewater samples collected from affected sites to achieve process intensification in relevant environment. Atypical schematic of remediation of textile wastewater using radiation grafted cellulose adsorbents and validation of the technology in laboratory (Fixed bed packed column setup) and operational environments (portable upscaled setup) is presented in Fig.5a.

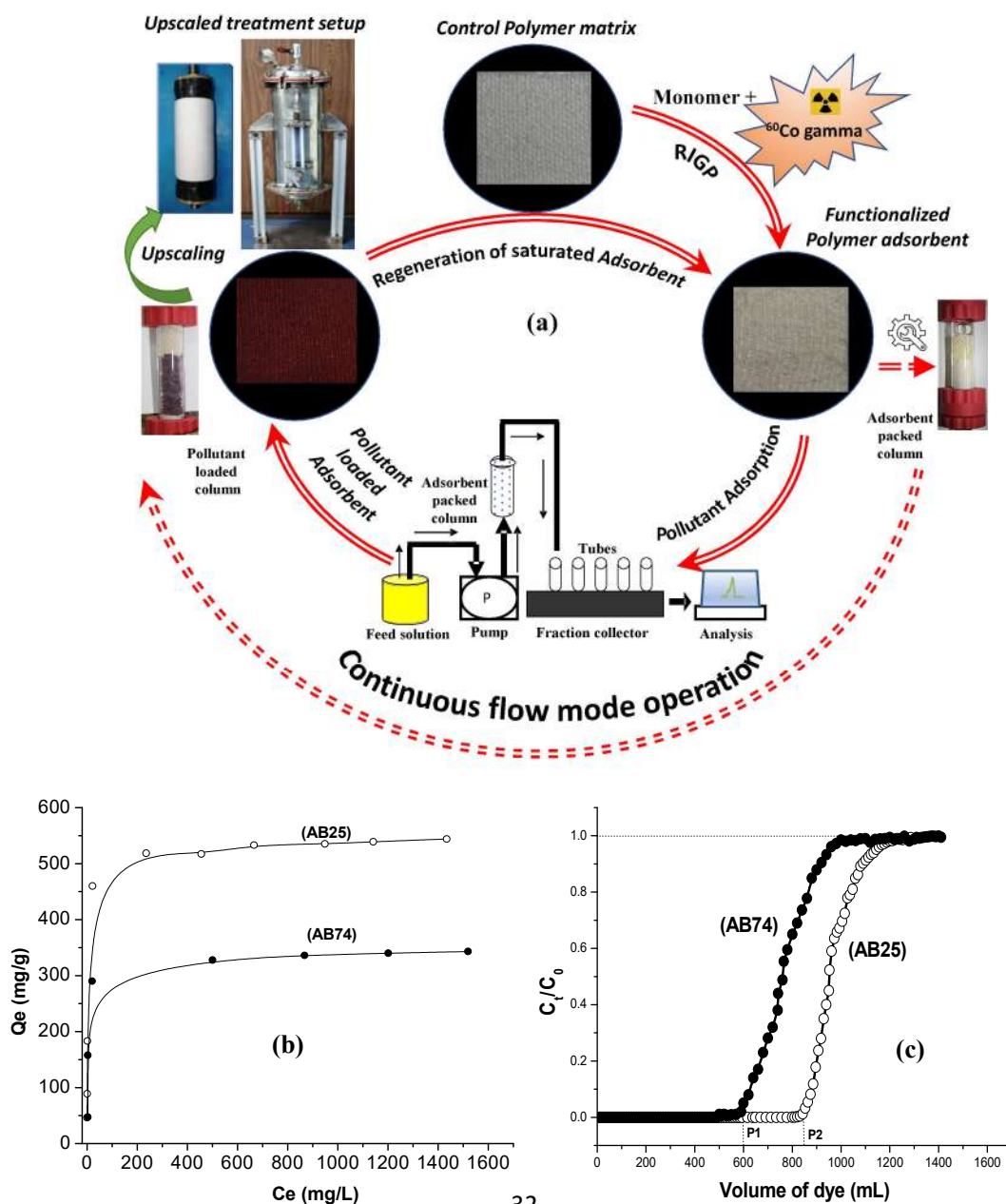


Figure 5: (a) Schematic of remediation of textile wastewater using radiation grafted cellulose adsorbents and validation of the technology in laboratory (Fixed bed packed column setup) and operational environments (portable upscaled setup). (b) equilibrium adsorption isotherm and (c) breakthrough curves for column adsorption of two textile dyes AB25 and AB 74).

The kinetic and equilibrium adsorption parameters, which are vital for predicting the performance and commercial deployability of any adsorbent system, were determined using Acid Blue 25 (AB25) and Acid Blue 74 (AB74) as model textile dyes for investigating the adsorption process. It was observed that in the batch adsorption process, the grafted adsorbent showed excellent uptake towards both dyes, with fast uptake kinetics and adsorption capacities in excess of 300 mg.g^{-1} for AB74 and over 500 mg.g^{-1} for AB25 (Fig 5b). Adsorption studies conducted in the column adsorption mode revealed the adsorbent to be successful in removal of both dyes, with the adsorption of AB25 proving to be more efficient with a delayed breakthrough (Fig. 5c).

On the basis of the data gathered from successful experiments, the adsorbent based process was upscaled for initiating field trials to validate the process in operational environments.

4.4.2. Feasibility field trials, large-scale on-site demonstration and technology transfer

A portable treatment setup was initially conceptualized, designed and fabricated for testing the efficacy of the treatment protocol in operational environments. The indigenously designed set up is equipped with an adsorbent cartridge bearing up to $\sim 1 \text{ kg}$ of adsorbent material, which, in the form of grafted cotton fabric, is wound in multiple layers over a perforated cylindrical rod to ensure maximum contact time and dye adsorption efficiency. When coloured wastewater is passed through this cartridge, the functional groups present on it remove the dye molecules and decolourize the wastewater, as shown in Fig. 4. The portable treatment setup was used for validation of the technology in operational environments through feasibility field trials carried out on a range of dye effluents at various cotton textile industry sites in Rajasthan (Fig. 6a)

The design success was followed by replication and further upscaling to pilot scale prototype modular setups capable of housing multiple cartridges that could be operated in series or parallel modes for enhanced throughput and efficiency. The prototype pilot treatment setups were subjected to long term field trials at various industrial sites (Fig. 6b).





(c)

Figure 6:(a) Portable setup for feasibility field trials (b) 30 KLD pilot plant (c) 75-100 KLD modular industrial scale plant

After successful feasibility field trials, A 30 KLD demonstration plant has been designed and installed in a cotton textile industry at Jodhpur, Rajasthan, which was run for almost one year for pilot scale trials and demonstrations (fig. 6b). During this period, the plant has successfully treated over 10,00,000L of the textile dye wastewater, which was reused by the same industry, leading to saving on fresh water consumption and associated costs. An industrial scale 75 KLD plant has been fabricated in-house at BARC and installed at the cotton industry to meet the daily requirements of individual cotton industries in Jodhpur (fig. 6c).

Finally, Bhabha Atomic Research Centre (BARC), under the aegis of DAE's societal initiative mandate to promote the Swachh Bharat Mission, has refined and matured this indigenous process to develop a technology named "*Radiation assisted Adsorbent technology for Textile Effluent Decoloration (Rad-TED)*" for removal of dyes from cotton textile wastewater streams. The '*Rad-TED*' technology (WT26RTDD) is available on BARC portal for transfer to interested parties.

The salient features of the '*Rad-TED*' include:

- i. *Use of Low cost, renewable, biodegradable and naturally abundant cellulose as a base material*
- ii. *Single step-green-radiation technology based adsorbent fabrication process*
- iii. *Small footprint, energy efficient and easily up-scalable process.*
- iv. *Ensuring recyclability of treated water to minimise the daily fresh water requirement of the industry and the associated costs.*

The radiation technology based novel treatment process '*Rad-TED*' can play an important role in assisting small scale industries to comply with environmental norms through effective water recycling in water scarce zones.

4. Conclusion

Radiation processing is a clean, green and highly versatile technology that has proved successful in the designing of new advanced functional materials for a broad spectrum of environmental applications. This includes development of radiation grafted functional adsorbents for water remediation applications. In particular, an indigenously developed cellulose based green adsorbent for treatment of textile dye wastewater, codenamed '*Rad-TED*', has been remarkably successful and is a glowing example of efficient lab to land transition of applied research. The technology offers a promising solution for the sustainable treatment of textile dye effluents, in line with the United Nations' Sustainable Development Goal number 6 (SDG6), which advocates clean water

and sanitation for all. Moreover, as a part of DAE's societal initiative mandate, it also highlights the crucial role that radiation technology can play in contributing towards the Government of India's 'Swachh Bharat and Swasth Bhaarat' missions. Therefore, radiation functionalized green and efficient adsorbents can pave the way towards a cleaner and more sustainable future for the textile industry and mankind.

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chapter, 21 technical reports, 42 invited talks and 02 technology transfers in his credit. He has been actively involved in Board of Research in Nuclear Sciences (BRNS) and served as an International Atomic Energy Agency (IAEA) expert lecturer for workshops and meeting in the field of radiation processing of polymers for societal applications.



Dr. Nilanjali Misra joined the Bhabha Atomic Research Centre, Department of Atomic Energy as a Scientist in 2009 after completing his Masters in Chemistry from IIT Delhi. He completed his Ph.D. from the Homi Bhabha National Institute, Mumbai in 2015. He is a recipient of the prestigious Marie Curie Postdoctoral Fellowship (2018-2020) in addition to numerous other awards, including the Department of Atomic Energy Young Scientist Award-2016, Society for Radiation Research Young Scientist Award-2017, Indo-Scandic Honor Diploma, Sweden for promotion of Science-2019 and Prof. Harimohan Memorial Award-2021. He has authored over 27 articles in peer reviewed international journals, 03 book chapters and 07 IAEA/BARC technical reports. He is a life member of the Indian Nuclear Society, the Indian Society for Radiation and Photochemical Sciences, the Asian Polymer Association and several other bodies of repute. His research activities include significant work in the field of radiation processed polymers, nanomaterials and composites for applications in the field of catalysis, healthcare and environmental pollutants remediation. Some of his recent work also focusses on the development of plasma deposited coatings for novel applications in healthcare and industry. He has contributed significantly towards the promotion of radiation and plasma processed polymer technologies and has 02 Technology Transfers to his credit in the field of wastewater treatment.

Case Study Gujarat Eco Textile Park, Surat, Gujarat: Optimization and Performance Improvement of CETP for Textile Industries Engaged in Dyeing and Printing of Synthetic Fabric using Disperse Dyes

Ashish Mehta

Abstract:

This case paper presents a brief case study focusing on the optimization and performance improvement of a Common Effluent Treatment Plant (CETP) at Gujarat Eco Textile Park Ltd, catering to textile industries in Surat, Gujarat, engaged treatment of wastewater generated from dyeing and printing synthetic fabrics using dispersed dyes. Highlighting the challenges faced by the CETP, such as mixed influent quality, high-temperature influent, and elevated pollutant loads, the study outlines a range of strategic interventions including production, water conservation projects, lab studies, CETP upgradation, advanced treatment technologies for recycling, and waste minimization techniques for waste. Through real-life examples and best practices, the paper demonstrates the successful implementation of optimization strategies resulting in improved effluent quality, reduced energy consumption, and enhanced environmental compliance. Lessons learned and recommendations underscore the importance of proactive measures and continuous innovation in achieving sustainable wastewater management in textile industries and water stewardship.

1. Introduction

1.1 Overview of CETP for Textile Industries in Surat, Gujarat

Surat, a prominent textile hub in India, houses numerous textile industries engaged in dyeing and printing synthetic fabrics using dispersed dyes. These industries collectively discharge a significant amount of wastewater, necessitating the operation of a Common Effluent Treatment Plant (CETP). The CETP serves as a centralized facility to treat wastewater from multiple textile units, ensuring compliance with environmental regulations. Gujarat Eco Textile Park is located at Palsana, Dist. Surat was established in the years 2009 under the SITP scheme of the Ministry of Textile, Govt. of India.

The Gujarat Eco Textile Park has 40 Nos. of member industries engaged in textile processing. CETP encompasses around 70 Nos. of member industries engaged in textile processing for their environmental compliances. CETP is having capacity of 60 MLD with a treatment scheme as Primary treatment with a collection, screening, and equalization system, followed by Physico chemical treatment using reactive clarified. Primary treatment wastewater is handled at an aeration system equipped with a Cyclic activated sludge system (CASS) using a SCADA–PLC system. Sludge dewatering is handled through a filter press and belt press.

CETP has built a recycling and reuse plant of 25 MLD capacity with ultrafiltration, reverse osmosis and MVR system for salt management.

1.2 Importance of Optimization and Performance Improvement for CETP

Textile processes are water intensive and there is a trend of shortage in the last decade for natural availability of good water quantity & quality for industrial needs. To have sustainable development of the region and ensuring conservation of water resources, it had become of

prime important point. It was felt that the industry needs to optimize water usage and achieve new benchmarks for effective usage, cost-saving, and environmental compliance. The required technical and financial support was provided by GETP for the cluster for this water conservation initiatives.

Textile industries connected with GETP – CETP are mostly MSME units engaged in the processing of synthetic dyeing and printing of cloth at Palsana Cluster. They lack essential know-how, resources, and experience for cleaner production and water conservation. CETP provided them with technical support by establishing a clean production cell for conducting water audits, energy audits, and effective implementation of cleaner production (CP) at the end of member units so that wastewater quantity is reduced, and the new benchmark is developed and maintained.

During the last 10 years, there has been a trend of processing mixed fabric which includes cotton cloth. Apart from this, there had been the addition of a few denim units engaged in cotton processing. This has led to changes in wastewater characteristics. As the CETP was planning to go with recycling of wastewater, it was also very important to maintain high efficiency of treatment at each stage of CETP to meet the UF and RO plant feed criteria for an effective recycling system. To achieve this it is very important to maintain CETP inlet criteria.

Optimization and performance improvement of the CETP are paramount for several reasons:

- Compliance with stringent environmental regulations regarding effluent discharge.
- Conservation of water resources by recycling and reusing treated effluent.
- Minimization of environmental impact caused by untreated or poorly treated wastewater.
- Reduction of operational costs through energy efficiency measures and waste minimization techniques.

1.3 Cleaner Production (CP) Drive for Water Conservation in Member Textile Units

Gujarat Cleaner Production Centre (GCPC) was engaged through MOU for CP assessment and water audit at selected 10 Nos of member units. FICCI was also involved separately through CP cell in carrying out a study on water and utility consumption and its optimization through energy audits. The study was carried out for two years and several implementation measures were adapted as per the standardised CP checklist. Due to CP implementation, GETP members were able to reduce around 25% of water consumption and around 14% of waste water generation quantity reduction coming to CETP inlet.

The increasing emphasis on water conservation within textile units has led to higher concentrations of effluent at the CETP inlet. This heightened concentration poses challenges to the treatment process and necessitates advanced treatment technologies.

1.4 Critical Point to Improve CETP Effluent Quality for Recycling and Reuse

To facilitate the recycling and reuse of treated effluent, it is essential to enhance the quality of effluent discharged from the CETP. This involves the implementation of advanced treatment processes such as Ultrafiltration (UF) and Reverse Osmosis (RO) to achieve the desired water

quality standards. It was desirable to have < 5 mg/L TSS (ideally Nil), < 70 mg/L COD, and < 5 mg/L BOD for the effective operation of the recycling plant having UF & RO system.

2. Challenges in CETP for Textile Industries

2.1 Mixed Influent Quality with Cotton and Synthetic Fabric Processes

The CETP receives wastewater with varying compositions due to the mixed processes involving cotton and synthetic fabric. This heterogeneity complicates the treatment process and requires tailored solutions. Due to mixed dispersed and reactive dye imparts a challenge for higher TSS, BOD and COD levels.

2.2 High Temperature of Influent at CETP Impacting Biological Process

Textile units operate in batch process and need several utilities in the form of hot water or steam. Due to this effluent generated and received at the CETP inlet is in the temperature range of 40 -45 Deg C. The high temperature of influent wastewater at the CETP adversely affects the efficiency of biological treatment processes, necessitating measures to mitigate temperature impacts.

2.3 High TSS and Color Load Imparting Higher BOD & COD Load

The presence of high Total Suspended Solids (TSS) and color load in the mixed influent contributes to elevated levels of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), posing challenges to biological treatment processes.

2.4 Refractory COD from Textile Chemicals and Auxiliaries

Certain textile chemicals and auxiliaries used in cotton and denim processing contribute to refractory COD, which is challenging to degrade through conventional biological treatment methods.

2.5 High Energy Consumption in Aeration Process

The aeration process, essential for biological treatment, consumes a significant amount of energy with usage of conventional root blower. High energy consumption adds to operational costs and carbon footprint.

2.6 Inefficient Treatment Processes & Its Environmental Impact

Inefficient treatment processes lead to incomplete removal of pollutants, resulting in environmental pollution and non-compliance with regulatory standards. It was not challenging to meet statutory norms prescribed by GPCB i.e. < 250 mg/L of COD and 30 mg/L of BOD but achieve even higher norms to meet inlet criteria for ultra filtration and reverse osmosis.

3. Strategies for Optimization and Performance Improvement

3.1 Lab Study and Pilot Trials Using Different Processes for Above Challenges

Conducting lab studies and pilot trials helps identify effective treatment processes and technologies tailored to address specific challenges encountered in the CETP. Multiple consultants and experts were involved for these types of studies. BARC, Mumbai was one of the expert supports for conducting such studies through Electrochemical treatment. Ozonation treatment was studied with Ozone Research, Nagpur. During lab trials various studies were carried out at the lab scale and pilot scale to know the effect of temperature, electrochemical treatment, usage of bio enzyme and brochure, and studies related to UF and RO applications.

3.2 Flow Metering System, Pre-ETP Treatment at Textile Unit Source – Segregation at Source, Electrochemical & Ozone Treatment at Textile Unit Source**

It was imperative to strictly maintain the quality and quantity of effluent from source. Installation of a flow metering system facilitates accurate measurement of wastewater flow rates from member unit sources, enabling better process control. Implementing pre-ETP treatment at textile unit sources, such as segregation at source and electrochemical/Ozone treatment, helped reduce the pollutant load entering the CETP and meet the CETP inlet criteria. Despite the increase in new industry load and change in product quality the influent quality had been stable since last 5 years.

3.3 New Cascade Cooling System at CETP for Temperature Reduction of Effluent

Introducing a cascade cooling system at the CETP effectively reduces the temperature of influent waste water to around 2-3 degrees C, mitigating and restricting adverse impacts on biological treatment processes.



Fig. 3.3 New Cascade Cooling System at CETP

3.4 New Pre-Sedimentation Tank for TSS Removal and Reduction of BOD/COD Load

Incorporating a pre-sedimentation tank aids in the removal of TSS from the influent, subsequently reducing the BOD/COD load on the treatment system. It helps to have higher residence time for better equalization and homogenization of effluent. It contributed to around 10% of BOD & COD load reduction and around 12- 15% of TSS reduction.



Figure 3.4 New Pre-Sedimentation Tank

3.5 Efficient Coagulation with PAC for Color, Turbidity, and TSS Reduction up to 90% with Decreased Sludge Generation Quantity

Utilizing Poly Aluminium Chloride (PAC) for coagulation achieves significant reductions in color, turbidity, and TSS levels in the effluent, accompanied by decreased sludge generation, leading to operational and environmental benefits. Usage of PAC, and CETP could consistently achieve 75-80 % of TSS reduction and around 35 – 40% of COD and BOD reduction in the primary clarification.



Figure 3.5 Stage wise effluent quality – Colour, TSS and Turbidity, a) Raw influent b) O/L Primary Treatment c) Outlet Secondary d) RO permeate – Recycle water

3.6 Use of Hypochlorite and Ozone at Source for Refractory COD Treatment

The application of hypochlorite and ozone at the source effectively targets refractory COD, enhancing the overall efficiency of wastewater treatment. Units with high COD and color

stream were monitored directly by the CETP team for effective pre-ETP operation. Effective primary treatment ensures source segregation and its treatment separately using physical chemical and ozonation treatment. Effective scale-up for individual large units and CETP level is being evaluated currently for future improvements.

3.7 Use of Turbo Blowers for Energy Efficiency Measures at Aeration Process

Integration of centrifugal turbo blowers in the aeration process improves energy efficiency, reducing operational costs and environmental impact. Root blowers were dismantled which led to energy savings of around 35% in electricity bills.



Fig 3.7 a) Centrifugal Turbo Blower and b) SCADA- PLC control Room

3.8 Advanced Treatment Technologies for CETP, Automation, and SCADA PLC Optimization

Adopting advanced treatment technologies including fibre disc filter, ultrafiltration, and reverse osmosis, coupled with automation and SCADA PLC optimization, enhances process control, efficiency, and reliability of the CETP for recycling and reuse of treated wastewater. CETP is successfully recycled textile-treated wastewater of around ~ 6.0 MLD daily since November – 2022 and its current capacity has increased to ~ 10 MLD (Jan -2024 onwards). This is quite a big initiative for recycling textile effluent on such a large scale effectively and consistently supporting the initiatives to reduce the water footprints of the textile industry, promote water stewardship, and achievement of SDG goals compliance.



Figure 3.8 a) New Fibre Disc Filter System b) Ultrafiltration Plant C) Reverse Osmosis Plant

3.9 Sludge Dryer, Moisture Reduction, Landfill Quantity Elimination with Co-processing as Waste Minimization Techniques

Implementing sludge dryers and moisture reduction techniques minimizes sludge volume while opting for co-processing offers an environmentally sustainable solution for managing residual waste. A successful trial run was conducted, and dryer was commissioned, An updated CCA is awaited from SPCB. It will help in sludge volume reduction and increase in calorific value of mix sludge making it useful for cement co-processing. It will help to avoid penalties imparted by landfill facilities in case of higher moisture content in the sludge and support environmental compliances as per CPCB guidelines.

4. Case Studies and Best Practices of CETP Covering Above Points

4.1 Successful Implementation of Optimization Strategies

Gujarat Eco Textile Park, CETP, Surat has successfully implemented the optimization strategies, resulting in improved effluent quality, reduced operational costs, and enhanced environmental compliance.

4.2 CETP Examples of Performance Improvement

GETP implemented a comprehensive optimization plan at their CETP, leading to an average 30% reduction in energy consumption, an average 40% decrease in sludge generation, an ~

80% reduction in color, TSS, Turbidity, and an average ~ 65- 85 % BOD & COD levels in the effluent.

4.3 Recommendations

Lessons learned from these case studies emphasize the importance of proactive measures, continuous monitoring, and technological innovation in achieving sustainable wastewater management in textile industries. Recommendations include ongoing research and development to further enhance treatment efficiency, as well as knowledge sharing among industry stakeholders and member unit support to promote & implement best practices.

In conclusion, the optimization and performance improvement of CETPs for textile industries at GEPT is crucial for achieving environmental sustainability, regulatory compliance, and resource conservation. Through strategic planning, innovative technologies, and collaborative efforts, other textile manufacturers & CETP in India can effectively address wastewater challenges while contributing to a cleaner and greener future.

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Mr. Ashish Mehta: As a professional with over two decades of experience in the field of Environmental Engineering, Mr. Ashish Mehta is a distinguished expert known for his extensive knowledge and profound insights into Hazardous Waste Management, Waste Water treatment, Energy audit, Cleaner Production, EHS, sustainability, integrated management systems, circular economy, and ESG (Environmental, Social, and Governance) practices. His academic background, coupled with hands-on experience, positions him as a sought-after speaker and thought leader in the industry.

Advancements in Biological Wastewater Treatment for Sustainable Development

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Abstract

Water, food and energy security are interlinked and central to sustainable development. Wastewater is an important component of water-food-energy nexus and recovery of resources can link water, nutrient and energy cycles. Thus, effective treatment of wastewater is essential for public health and sanitation, water reclamation, preventing environmental pollution and protecting water resources as well as reuse applications. Several mainline treatment technologies including activated sludge process, moving bed bioreactor, sequencing batch reactor and membrane bioreactor are used in wastewater treatment plants. The granular sludge sequencing batch reactor is an emerging treatment choice for providing effective treatment and improving sustainability. The granular sequencing batch reactor is preferred because of effective contaminant removals, superior settling properties, lower land footprint and costs.

Keywords: activated sludge; aerobic granulation; aerobic granules; sequencing batch reactor; sewage.

1. Introduction

Water, food and energy security are interlinked and efficient management of these resources is central to sustainable development. Wastewater (liquid waste) is an important part in the water-food-energy nexus as it creates a link between the water and element cycles for recovering resources. The liquid wastes are often categorized based on their source of generation, includes domestic wastewater, industrial wastewater, urban runoff, agricultural runoff and wastewater from commercial farming like livestock and aquaculture. The liquid waste arising from homes (domestic wastewater or sewage) is rich in organic matter, reactive nitrogen (ammonium and nitrate), phosphate, pathogens and suspended matter. Apart from these pollutants, liquid waste arising from the industries, hospitals and live-stock farms contain toxic and recalcitrant contaminants like antibiotics, surfactants, hormones and endocrine disrupting chemicals. Therefore, apart from causing sanitation issues and spreading infectious diseases, the release of inadequately treated sewage is greatly connected to the ecosystem biodiversity and functioning of water bodies. Eutrophication and other ecosystem changes caused by pollution are major events for impacting biodiversity of aquatic ecosystems. The pollution problems of sewage are compounded by population growth, rapid urbanization, insufficient wastewater infrastructure as well as non-functioning of installed treatment systems. About 80% of sewage produced by global population finds its way to oceans in untreated or inadequately treated form. This untreated human waste is responsible for causing infectious diseases in humans, creating algal blooms, eutrophic-conditions, environmental degradation and elimination of sea-grass in certain regions.

Biological treatment (secondary treatment) is an integral part of wastewater treatment plants (WWTPs) installed for removing soluble and particulate pollutants from domestic and

industrial wastewaters (Fig. 1). By convention, biological wastewater treatment is achieved using activated sludge process which requires huge land footprint for aeration and settling tanks. Activated sludge based WWTPs have become much more complex because of multiple process units and requirement of re-circulation flows when modified for achieving biological nutrient (E.g., nitrogen and phosphate) removal. Conventional activated sludge process is now more than century old biological process, yet it is widely used in WWTPs across the world. In activated sludge process, microbial growth is maintained in the form flocs for wastewater treatment (Nanchaiah and Sarvajith 2019). Activated sludge is a mixed microbial community that feed on the biodegradable organic substrates present in the wastewater. Due to the loose structure and poor settling properties of activated sludge, secondary clarifiers are employed for achieving activated sludge and treated wastewater separation. In addition, aeration tanks are partitioned for maintaining anaerobic, anoxic and aerobic conditions which are required for achieving biological nutrient removal (Nanchaiah et al., 2019). Requirement of large land footprint, associated capital costs, complex process design and energy for re-circulation of biomass and wastewater are the major drawbacks of activated sludge technology. These drawbacks are related to compactness and settling properties of activated sludge.

Membrane based biological treatment (i.e. membrane bioreactors) methods have been developed to address the drawbacks of activated sludge process. These systems have improved sludge-treated wastewater separation, treatment efficiency and provided compact WWTPs. However, they are not widely implemented due to high capital costs, high energy costs and membrane biofouling problems. To improve treatment and sludge-treated wastewater separation, aerobic granular sludge was developed. Granular sludge represents a distinct microbial community as compared to AS and emerged as the promising option for biological treatment in WWTPs.

The aim of this article was to present sewage treatment status in India, to provide an overview of different biological treatment systems. The uniqueness of granular sludge for providing advanced wastewater treatment was discussed. The AGS technology was compared with the other mainline technologies such as moving bed bioreactors (MBBRs) and membrane bioreactors (MBRs) in terms of treatment efficiency, land footprint and costs.

1. Sewage treatment status in India

About 80% of the water supplied for domestic uses will get converted to sewage. In this process of sewage generation, several organic and inorganic pollutants in both soluble and particulate form are introduced. Table 1 describes type and concentration of common pollutants in the sewage. Although pollutants are lower than 2% (%w/w), a suitable treatment method is essential to avoid pollution of natural waters, to provide sanitation, to recover water and nutrients. Available WWTPs can treat only about 20-30% of the sewage generated in Class I and II cities (source: report on “sewage treatment market in India 2018”). About 70-80% of sewage generated in Class I and II cities of India are not receiving any kind of treatment. The large gap between sewage generation and available treatment capacity is considered the main reason for continued pollution of water bodies.

Existing sewage treatment plants are equipped with different biological treatment technologies such as oxidation ponds, activated sludge process, sequencing batch reactor, biofilm reactor or membrane bioreactor. Conventional activated sludge process is the widely used mainline treatment method and catering to more than 50% of the WWTPs in India. However, sequencing batch reactor technology is increasingly considered especially in urban

India due to advantages like lower land footprint, more control on process and nutrient removal capabilities.

2. Microbial communities: Flocs, Biofilms and Granules

In 1904, Arden and Lockett have for the first time described the use of activated sludge for aerobic wastewater treatment. Activated sludge refers to a microbial community which removes the pollutants from the wastewater and gets separated out from the treated wastewater by flocculation process under non-mixing conditions. Typically, activated sludge is characterized with irregularly shaped flocs with about 100 μm in size (Fig. 2). In conventional activated sludge process, the biomass concentrations are maintained at about 2 to 4 g/l. The low biomass concentrations are attributed to less dense microbial structure and poor settling properties. However, advanced treatment systems such as membrane bioreactors and sequencing batch reactors allows higher biomass retention and higher levels of activated sludge in bioreactor tanks.

Biofilm and granular sludge-based treatment systems have been developed to improve the treatment and to reduce the land footprint of WWTPs. Biofilms are mixed microbial communities immobilized in a self-produced heterogeneous biopolymer matrix (Fig. 2). It is well established that microbes resident in the biofilms can tolerate pollutants and exhibit efficient biodegradation/biotransformation of pollutants. The biofilm reactors are suitable for enrichment of slow-growing microbes such as nitrifying bacteria, important for removing ammonium-nitrogen. Some of examples of conventional biofilm systems include trickling filters, rotating biological contactors, and constructed wetlands are used for wastewater treatment. Some of the biofilm-based systems such as moving bed biofilm reactor and membrane aerated biofilm reactor are suitable for large scale WWTPs. Sloughing of biomass from the biofilms is a concern in biofilm-based treatment systems.

Granules are mixed microbial communities in the form of macro-scale particles with definite shape as compared to activated sludge flocs (Fig. 2). The granules can rapidly separate out from the treated wastewater water by sedimentation under idle condition (Morgenroth et al., 1997). Due to compactness and high densities, granules exhibit much higher settling properties as compared to activated sludge flocs. Due to this, separation of sludge from the treated wastewater is carried out in the treatment tank itself without requiring a secondary clarifier tank. Figure 4 shows the differences between activated sludge and granular sludge. Due to above mentioned biomass properties, it is possible maintain 2 to 4-fold higher biomass levels in granular sludge reactors as compared to conventional activated sludge process.

3. Biological treatment options

The different process units of WWTPs are grouped under primary, secondary and tertiary treatment systems (Fig. 1). Primary and tertiary treatment are often achieved using physical and chemical methods. While, the secondary treatment is achieved using a biological treatment involving microbial communities either in the form of activated sludge, biofilms or granules. Overall, biological treatment is critical to WWTPs as it removes most of the pollutants such as organic carbon, reactive nitrogen (ammonium, nitrate and nitrite), phosphate and other pollutants from the waste water. In fact, the WTTPs are categorized in to different types based on the type of biological treatment. The land footprint, cost, treatment efficacy, knowhow availability, process reliability and amenability for large scale applications are used for selecting an appropriate treatment technology.

Removal of contaminants from wastewater and separation of microbial sludge-treated wastewater are the two important tasks in any biological treatment. Although activated sludge process was originally designed for removing organic matter (biochemical oxygen demand) by heterotrophic microorganisms, it has been suitably modified to remove nitrogen and phosphate. However, this requires addition of multiple process units and introduction of wastewater re-circulation flows (Fig. 3). Unlike removing organic carbon, removal of nitrogen and phosphate requires different redox conditions including aerobic, anoxic and anaerobic conditions. Subsequent to treatment, activated sludge is separated out from the treated wastewater via flocculation in a clarifier tank. Due to these reasons, activated sludge process requires large land footprint and costs. Biofilms have been primarily developed to improve biological treatment especially nitrification and to reduce the land footprint of plants. Granules are developed as replacement for activated sludge to improve treatment, reduce land footprint and to minimize process complexity. Formation of granules is a developmental process (Fig. 4) and dependent on reactor operating conditions, wastewater characteristics and environmental parameters.

Other mainline technologies such as moving bed bioreactors, membrane bioreactors and sequencing batch reactors (SBR) are utilized for designing compact WWTPs. In case of MBBR, microbial growth is mostly as biofilms on moving carriers. Secondary clarifier tanks are still used in MBBR for separating the suspended growth (activated sludge) and detached biofilm-biomass from the treated wastewater. Since membranes are used for separating activated sludge and treated wastewater, secondary clarifier tanks are not required for MBR operation. SBR technology is extensively considered for building centralized and decentralized WWTPs. Although SBR is a batch process, the continuity in treatment is achieved by operating multiple tanks simultaneously in different phase (Fig. 5). Moreover, both the treatment and separation of activated sludge from the treated wastewater are achieved in the single treatment tank without requiring secondary clarifier tanks.

4. Granular sludge technology for aerobic wastewater treatment

Anaerobic granular sludge reactors are widely used for treating high strength wastewaters like dairy, brewery and food industry effluents. Although these bioreactors are economical, they cannot efficiently remove ammonium and phosphate, hence, not suitable for treating domestic wastewater. The formation of granules from activated sludge flocs and their use for aerobic wastewater treatment in lab-scale sequencing batch reactor was reported in 1997. During the last two decades, the granules-based treatment has emerged as the most promising for aerobic wastewater treatment. Granule formation is a developmental process and it is influenced by reactor operating conditions, wastewater characteristics and environmental conditions (Fig. 4). Sequencing batch reactor is ideal for reliable cultivation of granules and for their stability (Fig. 5). It has been thoroughly investigated for prospective applications in domestic and industrial wastewater treatment. Several studies showed that granules perform much better than activated sludge in performing biological treatment as well as tolerating and removing toxic/recalcitrant contaminants. Previous research showed that granules can be fine-tuned for degrading a variety of toxic and recalcitrant organic compounds including dyes, phenols, metal chelating agents, organo phosphorus compounds, nitroaromatic compounds, anilines and pharmaceuticals. Effective removal of heavy metals and metal(loid) oxyanions by granules was also demonstrated.

Formation of granules was investigated for removing various organic and inorganic pollutants of interest to industrial wastewater including those of nuclear fuel cycle operations. This research showed that bacterial granules can be developed for removing different organic (i.e. tributyl phosphate, *n*-butanol, dibutyl hydrogen phosphate, 2,4-dinitrotoluene,

nitrilotriacetic acid, *p*-nitrophenol, textile dye and acetonitrile) and inorganic contaminants (i.e. ammonia, nitrate and phosphate) (Nancharaiah and Reddy 2018; Nancharaiah et al., 2006a, 2006b, 2015, 2018; Reddy et al., 2017; Sarvajith et al., 2018). It is also evident that granules are a better choice for biodegradation / biotransformation of recalcitrant or toxic pollutants present in the industrial wastewater including effluents of nuclear fuel cycle operations. Many of these studies on cultivation of granules under different process conditions, effect of reactor operating parameters and removal of contaminants were performed in lab-scale bioreactors under defined conditions. These studies have identified optimum parameters for granulation and potential applications of granules in treatment of domestic and industrial wastewaters. Additionally, formation of granules from seawater-borne microorganisms was demonstrated for applications in saline wastewater treatment. This method avoids the long acclimation periods involved in adopting activated sludge for treating saline wastewater. Moreover, this approach can be offering effective treatment as it relies selection and enrichment of indigenous halophilic bacteria instead of using halotolerant organisms.

Because of potential use in WWTPs, formation of granules and biological treatment were studied in pilot-scale and full-scale bioreactors (Pronk et al., 2015; Li et al., 2014; Nancharaiah et al., 2023). Currently, granules are considered a perfect replacement for activated sludge flocs for providing sustainable wastewater treatment. Due to advantages such as effective treatment, reduction of land footprint and costs, granular process has been applied in WWTPs for the treatment of municipal and industrial wastewater. The granular process has been already applied in about 100 full scale WWTPs (Giesen et al., 2013; Pronk et al., 2017). Plants with treatment capacities of ranging from 100 to 600,000 m³/d have been reported for treating domestic wastewater. Many of these plants installed in the Netherlands and China are treating mixed wastewater comprising of domestic and industrial wastewaters.

Application of granules-based treatment was evaluated for treating real domestic wastewater under tropical conditions. Although treatment was effective, phosphate removal was found to be not efficient. To improve biological nitrogen and phosphate removal, addition of granular activated carbon particles to granular reactors was studied. This new method aimed at formation of biofilms and better retention of microorganisms during the start-up phase. The higher inter-particle interactions among the biofilm particles and initial aggregates would also contribute to faster granulation process (Fig. 6). To demonstrate the use of this new method in sewage treatment, pilot-scale plants have been setup for treating real-sewage under tropical climate conditions (<https://www.ndtv.com/india-news/nuclear-engineers-fighting-water-pollution-with-sewage-treatment-plant-1768223>). The lab-scale and pilot-scale studies showed that the new strategy helps achieving efficient treatment of wastewater including removal of nitrogen, phosphate and coli form bacteria. The technology is referred to as hybrid granular sequencing batch reactor (hgSBR) and made available for deployment in WWTPs (<https://www.barc.gov.in/technologies/sbr/index.html>). Several private companies have signed technology transfer agreement with BARC for deployment of hgSBR technology WWTPs. Efforts have been already made in this direction and the technology has been implemented for in several full-scale sewage treatment plants. The treatment capacities of these plants are ranging from 10 KLD to 1.5 MLD. The plants in operation for treating domestic wastewater at different places including Kalpakkam, New Delhi, Shirdi and Surat. Several plants are under construction phase in Mumbai, Shirdi and Ghaziabad.

5. Comparison of treatment efficiency, land footprint and costs

Granules are capable of removing of simultaneously organic carbon, ammonium nitrogen and phosphate from the wastewater in a single bioreactor tank without requiring partitions. Subsequent to treatment, separation of granules from the treated wastewater is done in the same treatment tank. Thus, no separate aerobic and anoxic compartments and secondary clarifiers are needed for achieving wastewater treatment. This would get translated to lesser land footprint for granules-based process as compared to activated sludge process. In comparison to the conventional activated sludge process, the reduction in land footprint is huge and up to 70%. However, the land footprint reduction is about 20% when the granular process is compared to the existing activated sludge-based sequencing batch reactor. The land footprint of granular systems is comparable to membrane bioreactor. Due to high membrane costs, high energy and biofouling issues, membrane bioreactors are not widely considered as compared to sequencing batch reactor.

The number of tanks, tank sizes, decanters and mechanical equipment required for the secondary treatment will vary among conventional activated sludge process, activated sludge sequencing batch reactor, membrane bioreactor and granular sequencing batch reactor (Fig. 7). Overall, the reduction in the number of tanks, tank sizes and lesser equipment would make granular sequencing batch reactors more attractive for their consideration in WWTPs (Bengtsson et al., 2018; Nancharaiyah et al., 2019). Moreover, lower sludge generation and sludge management practices are also contributing to lower costs. Pronk et al. (2015) reported energy savings of up to 48% in full scale granular process than AS process. The conservative estimates show up to 30% energy savings with granules-based treatment as compared to other activated sludge technologies³. The reduction in energy costs is mainly attributed to no return sludge pumping and re-circulation of wastewater for nutrient removal. While, membrane bioreactors are energy intensive due to (i) high rate of sludge return pumping and (ii) high aeration rate at the membranes to minimizing fouling. The overall energy requirement of MBR is 50 to 70% higher as compared to granules based system.

6. Future directions and conclusions

Granular sludge is a compact microbial community and distinct from that of activated sludge with respect to particle size, microstructure, functional microbes, biopolymer type and content and settling velocities. The granular sludge sequencing batch reactors are more sustainable and offer reduction in land footprint and costs as compared to activated sludge sequencing batch reactors and other mainline wastewater treatment technologies including moving bed bioreactors and membrane bioreactors. The granular sludge is more robust and can tolerate and perform biological treatment in the presence of toxic contaminants as well as under fluctuating loading conditions. Research also suggest that the operating conditions generate lower sludge as compared to other systems. Overall, granular sludge process appears to be the most sustainable technology considering advanced wastewater treatment along with lower land footprint and costs. This technology can be considered for both green field projects and capacity extension of existing plants to increase wastewater treatment infrastructure in India.

The applicability of the technology under diverse climate conditions needs to be studied in future. Additionally, the applicability of the granules-based treatment to be explored for various industrial effluents including those generated in aquaculture industry. Apart from effective wastewater treatment and environmental sustainability, granules offer potential resource recovery options like biopolymer, alginate-like polymer, phosphate-enriched sludge etc. (Fig. 8). Although it is optimized for implementation in WWTPs, the mechanism of granule development and factors affecting the stability of these granules are not yet understood well. Further research is necessary for understanding molecular mechanisms involved in granule formation, identifying factors of granule stability, developing new

cultivation strategies, and excess sludge management practices for wide-spread implementation of granular sludge technology.

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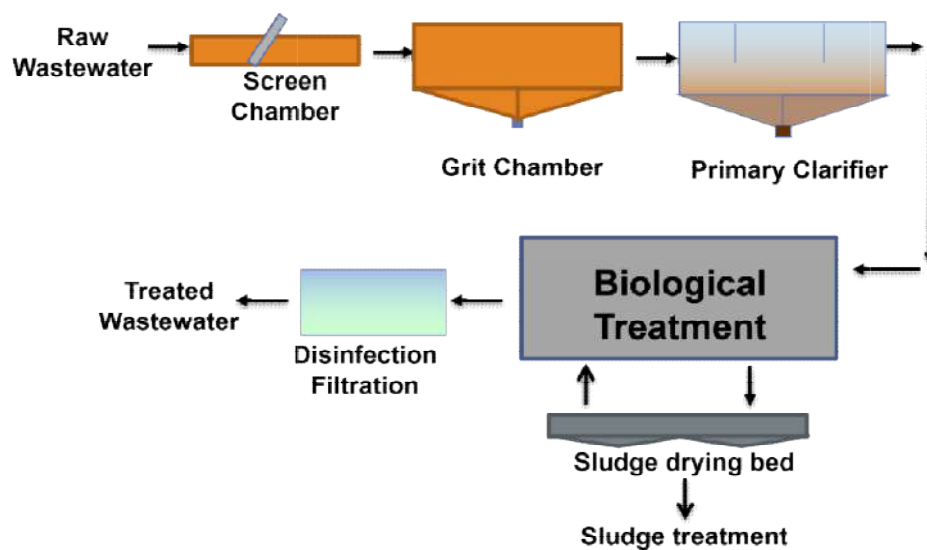


Figure 1. An overview of treatment process units in a wastewater treatment plant.

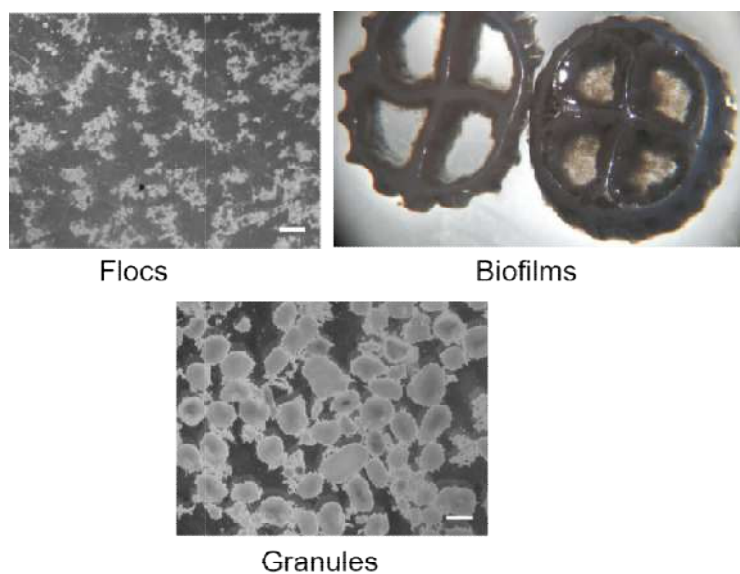


Figure 2. Different microbial communities used in the biological treatment (secondary treatment) of wastewater treatment plants.

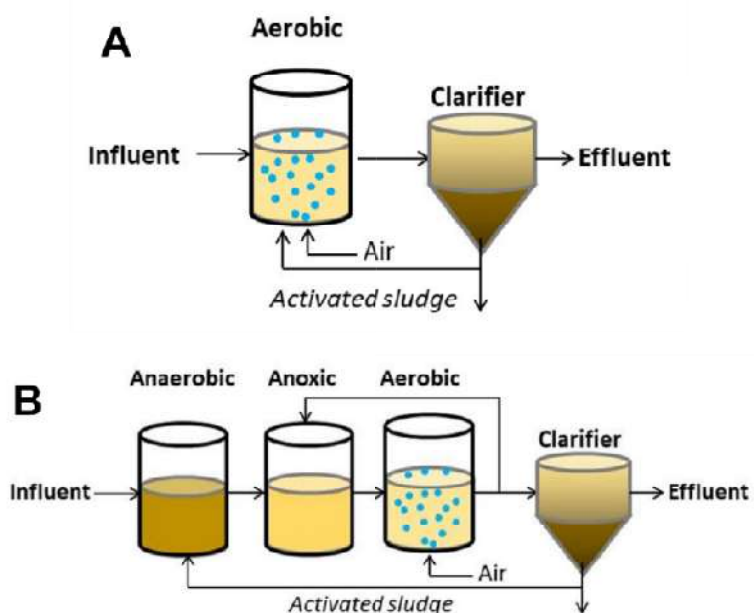


Figure 3. Activated sludge process configurations used for treating domestic wastewater. A) two-tank configuration. B) four-tank configuration used for achieving nitrogen and phosphate removal from the wastewater.

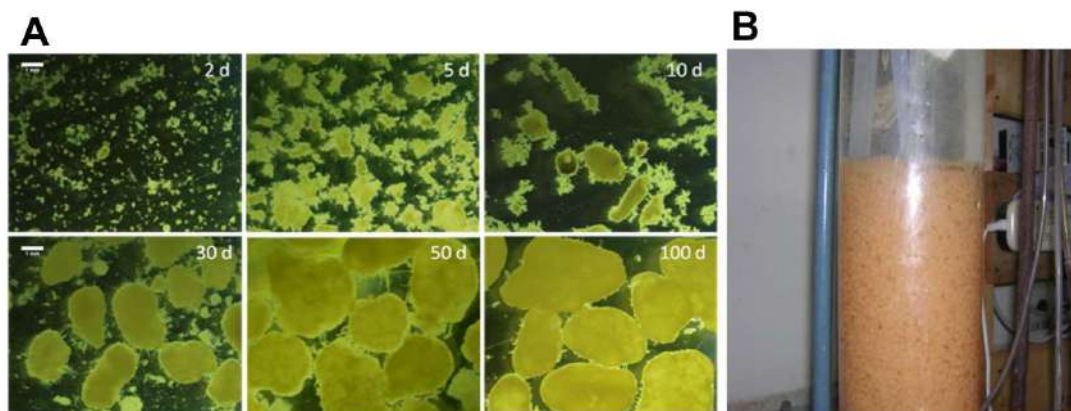


Figure 4. Time course formation of millimetre-sized granules (A) and granular bed (B) in a lab-scale sequencing batch reactor.

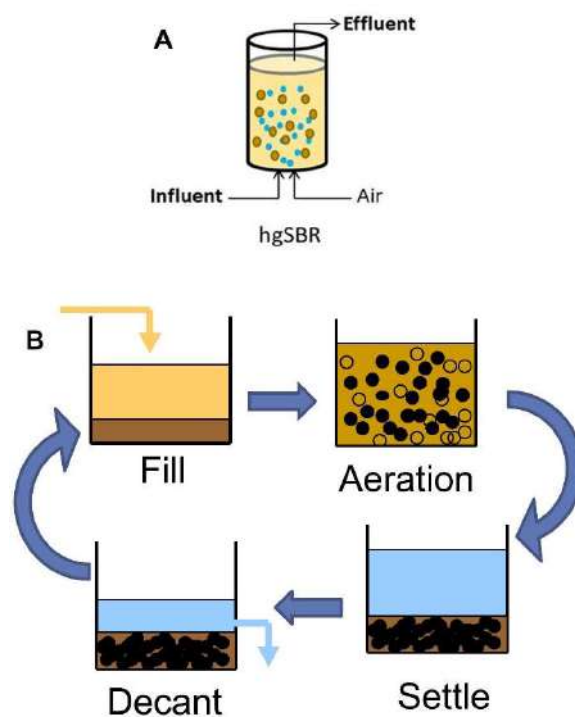


Figure 5. hgSBR process configuration (A) and different phases of cycle (B).

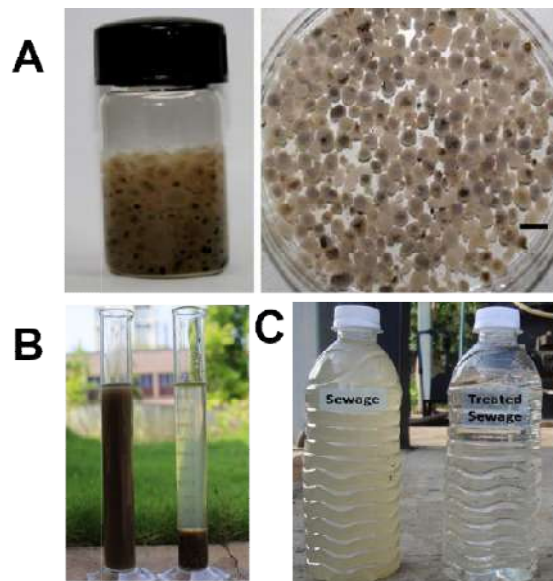


Figure 6. Morphology (A) and (B) settling properties of hybrid biofilm granular sludge (HBGS). C) sewage before and after biological treatment in a hybrid granular sequencing batch reactor.

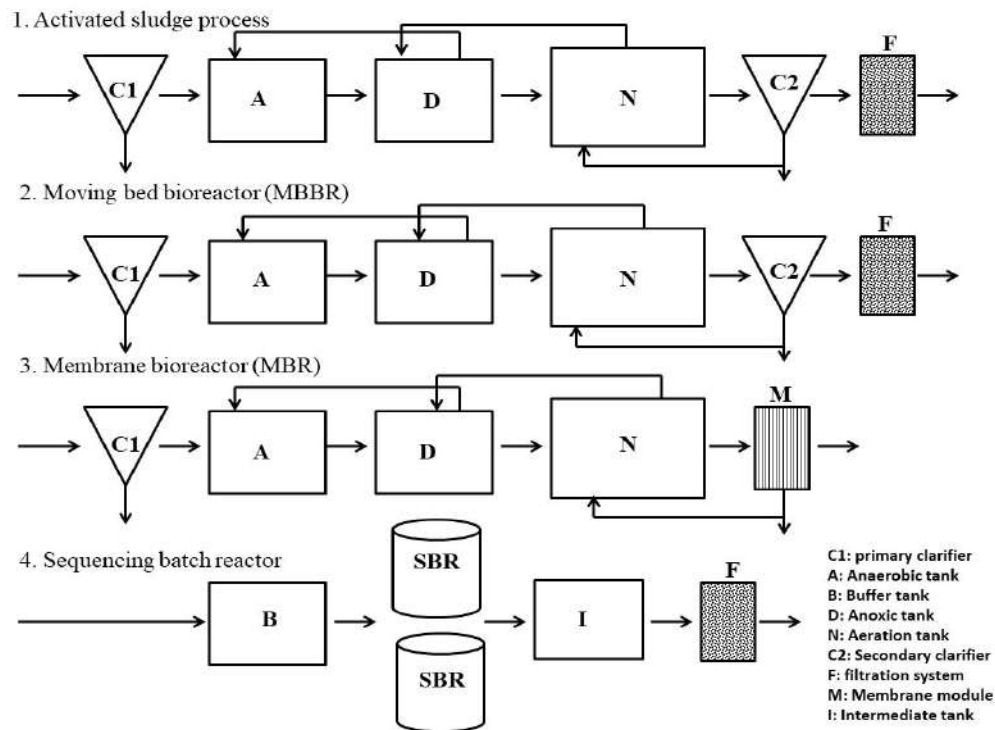


Figure 7. An overview of different biological treatment technologies (reproduced from Nanchaiah et al., 2019)

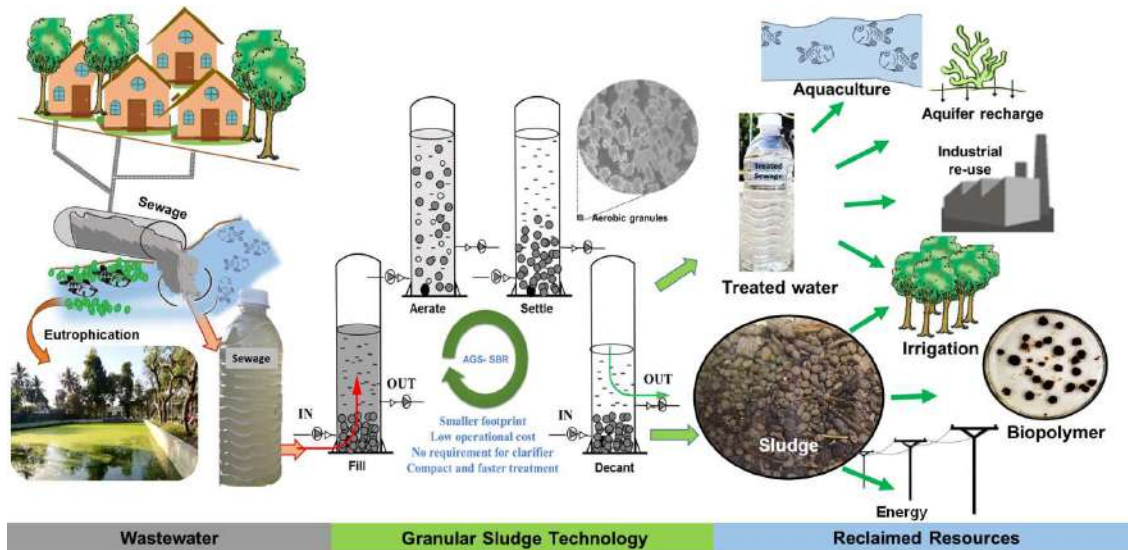


Figure 8. Futuristic wastewater treatment plants with granular SBR technology and resource recovery.



Dr. Y.V. Nancharaiah obtained Master of Science in Biochemistry from Andhra University, Visakhapatnam in 1993 and Ph.D. in Biochemistry from University of Madras in 2009. He joined Water & Steam Chemistry Division (WSCD), BARC in 1995 after completing 38th BARC Training School in Biology & Radiobiology discipline. He carried out post-doctoral work at Arizona State University, USA (Dec 2010 to Feb 2011) and UNESCO IHE, the Netherlands (Feb 2014 to Aug 2015) through IUSSTF and Marine Curie Fellowship programs. He worked as guest-scientist (2021 to 2022) on biofilm-reactors at Technical University of Munich (Germany) under Indo-German Collaboration. He was selected for prestigious American Society for Microbiology (ASM) research professorship and worked as guest-scientist (2009 to 2010) on *Clostridium* sp.

metabolism at Brookhaven National Laboratory, USA. Presently, he is a Scientific Officer H and Head, Biofouling and Biofilm Processes Section. He is a recipient of coveted DAE Homi Bhabha Science & Technology Award (2017), Fellow of the Biotech Research Society (FBRS), India (2022) and Fellow of the Academy of Sciences Chennai (FASCh) (2023). He owns a patent on bacterial granules based biological wastewater treatment and authored over 120 articles in high impact peer reviewed journals. He is the key person for developing patented BARC's hybrid granular SBR (hgSBR) technology which has been transferred to 27 private companies for deployment in wastewater treatment plants. The technology has entered into commercialization phase with several full-scale hgSBR plants with various capacities of up to 1.5 MLD have been installed for treating domestic wastewater. He also identified novel compounds for prospective biofilm and biofouling control applications. His major research interests include biofilms and biofouling control, bioremediation, wastewater treatment and microbial biotechnologies.

Experimental verification of waste water treatment using SBR technology

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Introduction

About 80% of the water used by the community comes out of the houses in the form of waste water which unless properly collected, conveyed, treated and safely disposed of, may pollute our precious water resources and cause environmental degradation. Hence, the need of the day is to re-use and re-cycling of waste water after necessary treatment for various beneficial uses so as to reduce the ever-increasing demand of the fresh water. In order to do so, an experimental facility was built in house for treating domestic sewage using philosophy of sequencing batch reactor.

Requirement of Sewage treatment

Any type of waste, whether it is solid waste or liquid waste is the product of our day-to-day activities which includes domestic and industrial as well. Improper disposal of these waste in the environment may become a threat not only to human life but also our eco system. Some of them are air pollution soil contamination and water pollution. Hence, it is very important to put efforts for effective waste management which mitigates adverse health and environmental impacts, conserves resources, and improves the liveability.

The most potent of these pollutants is the sewage. When untreated sewage accumulates and is allowed to become septic, the decomposition of its organic matter leads to nuisance conditions including the production of malodorous gases. In addition, untreated sewage contains numerous pathogens that dwell in the human intestine tract. Sewage also contains nutrients, which can stimulate the growth of aquatic plants and may contain toxic compounds or compounds that are potentially mutagenic or carcinogenic. For these reasons, the immediate and nuisance-free removal of sewage from its sources of generation followed by treatment, reuse or dispersal into the environment in an eco-friendly manner is necessary to protect public health and environment.

Technologies available

The present available technologies for waste water treatments includes mainly Physical, Chemical & Biological treatment. The details of technologies are briefed below-

- 1) **Physical Treatment** – It is basically primary treatment of waste water. Examples of physical treatment are screening, filtration, sedimentation, coagulation, floatation, ultra-filtration, micro-filtration, reverse osmosis etc. removal of floating materials like dead animals, tree branches, papers, pieces of rags, woods etc., heavy settleable inorganic solids and fat & grease, large suspended organic solids such as human faeces, animal waste, oil, urea (urine), pesticides, herbicides, fruit and vegetable waste.
- 2) **Chemical Treatment** –Chemical treatment of wastewater are usually carried out for industrial wastewater as they contain chemical pollutants and toxic substances in a large proportion, such as the wastewaters from chemical or pharmaceutical manufacturing, pulp and paper mills, laboratories and textile manufacturers. Chemical treatment is often necessary before the biological treatment. The treatment involves

neutralisation, sedimentation, chemical oxidation, chemical coagulation, adsorption, de-ionisation etc.

- 3) **Biological Treatment** – It is the treatment of wastewater in which biological decomposition of organic material is carried out using microorganism. It is generally carried out under aerobic or anaerobic conditions.

Our effort to mitigate the problem –In the year 2016, Technical Services Division of BARC undertook the work of development of sewage treatment based on SBR technology in co-ordination with Water & Steam Chemistry Division, Chemistry Group, Kalpakkam, who has also done similar work in this field. The work was taken up by TSD in the following stages –

- 1) Stage-1: Treatment of sewage in lab scale capacity, i.e., 12 Litre
- 2) Stage-2: Enhancing the capacity to 550 Litre
- 3) Stage-3: Further enhancement of the capacity by 3000 Litre
- 4) Stage-4: Construction of a pilot plant in BARC campus, Trombay having a capacity of 10 KL per day

Basic Treatment Processes and their effect on Sewage treatment – Treatment processes are mainly classified as –

- 1) **Preliminary treatment**– It is basically the removal of –
 - a) Floating materials like dead animals, tree branches, papers, pieces of rags, woods etc,
 - b) Heavy settleable inorganic solids,
 - c) Fat & grease.

Process used –

- (i) Coarse & fine Screening – Removal of Removal of floating paper, rags, clothes etc.
- (ii) Grit Chamber – Removal of grit and Sand
- (iii) Skimming Tanks – Removal of oil & grease

BOD Removal – 5 to 30%

Removal of suspended & dissolved Solids – 2 to 40%

Removal of Bacterial Load – 10 to 20%

- 2) **Primary treatment** – Removal of large suspended organic solids such as human feces, Animal waste, Oil, Urea (urine), Pesticides, Herbicides, Fruit and vegetable waste.

Process used – This usually accomplished by sedimentation in Settling basin or septic tanks (for small colonies or in rural areas)

BOD Removal – 30 to 35%

Removal of suspended & dissolved Solids – 60 to 65%

Removal of Bacterial Load – 25 to 75%

*** Preliminary and Primary treatment are often known as Primary Treatment also.

- 3) **Secondary OR Biological treatment** – It involves further treatment of the effluent coming from the primary sedimentation tank. Removal of fine suspended non settleable solids including biological decomposition of organic matter. In these biological units, bacteria decompose the fine organic matter to produce clearer effluent.

Process used–

- i) Activated Sludge Process (ASP)
- ii) Sequencing Batch Reactor (SBR)
- iii) Moving Bed Bio Reactor (MBBR) / Fluidized Aerobic Bioreactor (FAB)
- iv) Membrane Bio Reactor (MBR)

BOD Removal – 50 to 90%

Removal of suspended & dissolved Solids – 70 to 90%

Removal of Bacterial Load – 40 to 98%

- 4) **Tertiary treatment** – It consists of removal of organic load left after secondary treatment and involves series of additional steps after secondary treatment to further reduce organics, turbidity, nitrogen, phosphorus, metals, and pathogens.

Process used– Coagulation, filtration, activated carbon adsorption of organics, reverse osmosis, and additional disinfection.

BOD Removal – 100%

Removal of suspended & dissolved Solids – 100%

Removal of Bacterial Load – 100%

*** Tertiary treatment of wastewater is practiced for additional protection of wildlife after discharge into rivers or lakes. Even more commonly, it is performed when the wastewater is to be reused for irrigation.

Fig.1 as shown below shows the flow diagram of sewage from start to end –

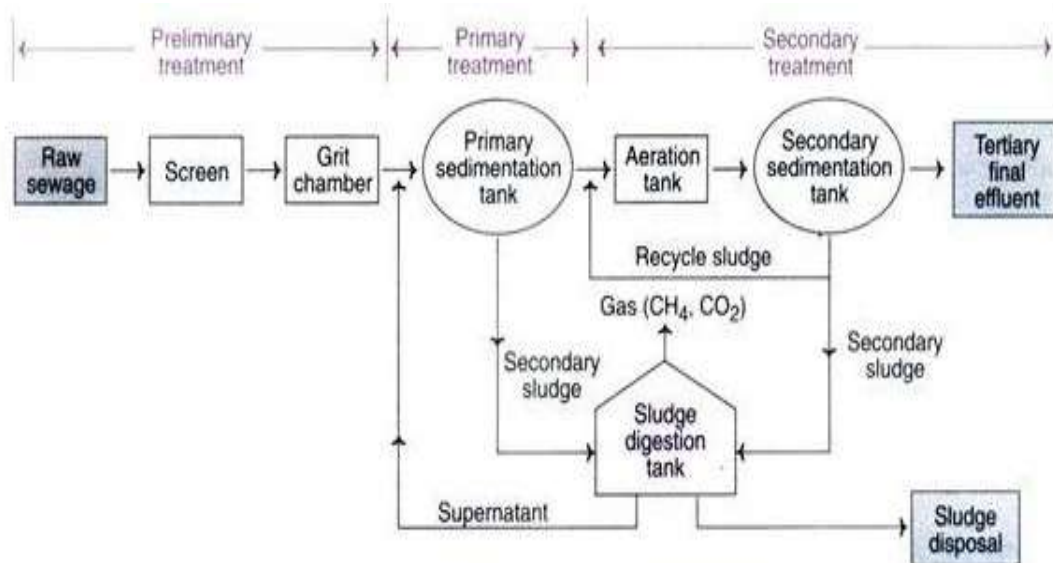


Fig.1 Flow diagram of sewage treatment

We, in our Trombay campus experimented on secondary treatment of waste water using Sequencing Batch Reactor (SBR) technology. SBR technology of waste water treatment is basically a fill and draw activated sludge process in which the waste water is added to a single “batch” reactor, treated to remove undesirable components and discharged. The treatment of waste water has five phases, i.e., Fill, React, Settle, Draw & Idle as shown in fig.2

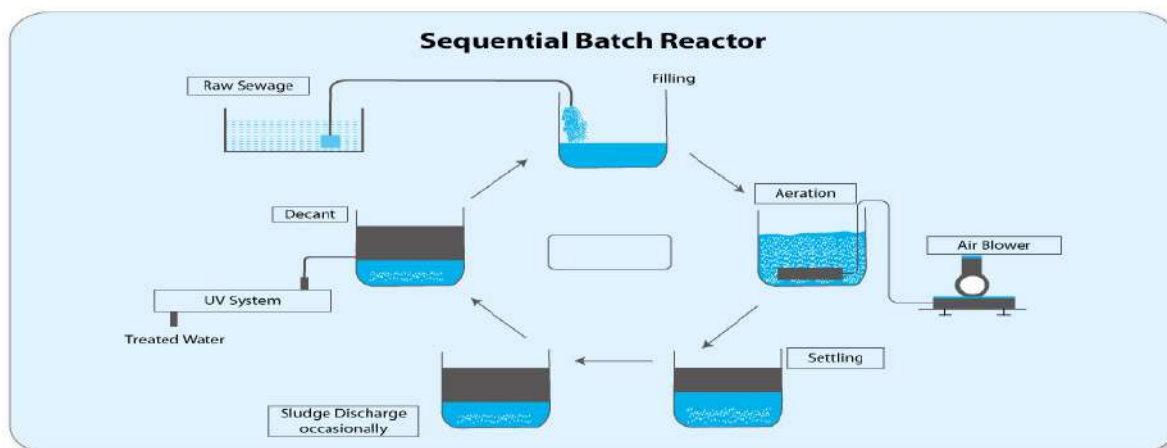


Fig.2 Stages of SBR process

Brief description of process involved in each phase are as follows –

- (A) **FILL PHASE**–During the fill phase, raw wastewater enters the facility and mixed with naturally occurring microorganism. The influent brings food to the microbes in the activated sludge creating an environment for biochemical reaction to take place.
- (B) **REACT PHASE** – During this phase, no wastewater enters the basin. Air is introduced periodically to allow the microorganism to breath & consume waste product. This phase allows for further reduction of wastewater parameters.
- (C) **SETTLE PHASE** – During this phase, activated sludge is allowed to settle under quiescent condition, no flow enters the basin and no aeration and mixing takes place. The activated sludge tends to settle as a flocculent mass, forming a distinctive interface with the clear supernatant. This phase is a critical part of the cycle, because if the solids do not settle rapidly, some sludge can be drawn off during the subsequent decant phase and thereby degrade effluent quality.
- (D) **DECANT PHASE** – This is the withdrawal phase to discharge the clarified effluent from the reactor. There are several withdrawal mechanisms available. It may be as simple as a pipe fixed at some predetermined depth with the flow regulated by an automatic valve or a pump.
- (E) **IDLE PHASE** – This phase occurs between Decant and Fill phase. This is the time between cycles which is used to prepare the SBR for next cycle. It is also used to adjust the cycle time between the SBR reactors. Sludge wasting is also performed during this phase.

The focus of construction setup of our stage wise experiments, above five phases and their working principle was kept in mind as all the process are carried out in a single tank.

STAGE-1

Treatment of sewage in lab scale capacity, i.e., 12 L capacity:

We started developing SBR setup by using a small 12 Litres Jar used for collecting purified water from water purifier and other in-house material available in TSD's AC workshop as described below –

Set up description –

Waste Water Source– Sewage well near Green House

Aeration Tank– Water collecting jar of 12 Litre capacity used in water purifiers (Fig.3)

Supply of Air– Air Compressor with throttling valve

Fine bubble diffuser – Ceramic filter (Fig.3) used in pre-filtration in water purifiers having porosity of approx. 5 microns

Piping – Copper tubes used in Air Conditioning



Fig.3 Water collection jar & Ceramic filter

Description of work –

Stage -1 of our experiment has been started using sewage available in BARC campus, i.e., sewage well near Green House. Sewage was kept in a 12L jar which is fitted with a ceramic filter and connected with controlled supply of compressed air passing through the ceramic filter creating fine bubbles in the water in order to achieve uniform mixing of oxygenated air in the sewage (Fig.4).



Fig.4 Set up with 12L jar

After several days & hours of aeration of various samples of sewage, some samples of treated water were sent to NABL accredited lab (Mumbai Waste Management Ltd., Panvel) for testing of raw & treated sample. The results were shown in the following tables 1 & 2 –

Date of Sample: 19/10/2016 (Table-1)

Sr. NO.	Sample Name	Parameters				
		pH	TSS (mg/L)	DO (mg/L)	COD (mg/L)	BOD (mg/L)
1	Raw Sewage from Well	7.42	98.0	4.61	96.0	33.1
2	Treated Water (Tank-1)	7.50	84.0	4.32	76.8	28.44
3	Treated Water (Tank-2)	7.67	72.0	3.84	48.0	17.14

Date of Sample: 04/11/2016 (Table-2)

Sr. NO.	Sample Name	Parameters				
		pH	TSS (mg/L)	DO (mg/L)	COD (mg/L)	BOD (mg/L)

1	Raw Sewage from Well	7.58	94.0	4.53	82.8	25.87
2	Treated Water (Tank-2)	7.71	82.0	4.87	55.2	19.71

The results were good and after transferring the sludge in 1000 ml measuring jar, the following were observed –

- a) Very fast settling of flocks/sludge (7-10 mins)
- b) Water transparency after settling was excellent
- c) The quantity of sludge did not increase after many batches
- d) Bad smell reduced drastically
- e) For better treatment supply of nutrients from outside to sewage is required

STAGE-2

Enhancing the capacity to 550 L capacity

The outcome of stage-1 was encouraging and it was decided to enhance the capacity of reactor for 12 Litre to 550 Litres and use the sewage from a nearby community, i.e., Anushakti Nagar colony. More detailed setup was prepared and incorporation of fine bubble diffusers, supply of air through air blower instead of air compressor, air flow measuring device, GI piping, valves & other required fittings were carried out. The tank has been fabricated in combination of Acrylic Sheet (Two sides) and Stainless-Steel sheet (Two sides) to have transparency to observe the aeration and settling process. In this stage, more uniform mixing of oxygenated air was achieved due to use of fine bubble diffusers and controlled supply of air. Also, sufficient quantity of bio mass, various nutrients etc. had been added from time to time which resulted in faster settling of sludge and clearer supernatant water with better transparency and reduced odour in two weeks' time.

For getting regular supply of domestic sewage, a contract was awarded to a firm to transport sewage on daily basis from sewage pumping station tank of Anushakti Nagar colony to BARC.



Fig.5 SBR-550 Litre capacity

Samples of raw & treated sewage from these experimental set ups were sent for testing in NABL & MoEF accredited laboratories on regular basis to ascertain the results obtained with respect to various parameters like COD, BOD, pH etc. as per CPCB guidelines. Results of one of few samples are shown in table-3 below.

Date of Sample: 27/04/2017 (Table-3)

Sr. NO.	Sample Name	Parameters				
		pH	TSS (mg/L)	DO (mg/L)	COD (mg/L)	BOD (mg/L)
1	Raw Sewage from Anushakti Nagar	8.08	48.0	BDL	113.39	37.79
2	Treated Water	7.72	12.3	5.36	20.62	6.87

	(550 L Tank)					
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STAGE-3

Further enhancement of the capacity by 3000 Litre

Subsequently, an upgraded set up of 3000 L capacity SBR tank was fabricated in TSD and this time samples of sewage from BARC hospital were taken for treatment and analysis.



Fig.6 SBR-3000 Litre capacity (BARC Hospital)

Results of one of the samples tested is reproduced in the table -4 below –

Date of Sample: 02/06/2017 (Table-4)

Sr. NO.	Sample Name	Parameters				
		pH	TSS (mg/L)	DO (mg/L)	COD (mg/L)	BOD (mg/L)
1	Raw Sewage from BARC Hospital	6.88	548.0	0.53	370.0	123.33
2	Treated Water (3000 L Tank)	6.73	76.0	2.05	70.0	23.34

The outcome of treatment shown above were very interesting and considerable reduction of parameters like TSS, COD & BOD were observed. The quantity of dissolved oxygen was also improved.

Owing to the results so obtained, it was decided to put this 3000 L SBR tank for field trial by shifting it to BARC hospital along with all its associated accessories for operation in 24X7 basis and the whole setup was transported to site and put in operation on regular basis. The plant was initially run on 4 (four) cycles per day (24-hour operation) which had been subsequently increased to 6 (six) cycles and 8 (eight) cycles per day. Both influent and effluent samples were sent for testing to outside NABL/MoEF accredited labs as well as in house testing was carried out in Analytical Chemistry Division of BARC. Some of the date wise test results so obtained are tabulated below –

Sr. NO.	Date	Sample Name	Parameters				
			pH	TSS (mg/L)	BDO (mg/L)	COD (mg/L)	Total N2 (mg/L)
1	10/08/2017 (Tested by Mumbai Waste Mgmt. Ltd. (NABL Accredited Lab))	BARC Hospital	7.17	936.0	27.27	90.0	4.59
		Treated Water (4-Cycles)	6.97	188.0	2.74	8.0	23.34
2	12/10/2017 (Tested by ACD, BARC)	BARC Hospital	6.90	---	76.8	96.0	---
		Treated Water (6-Cycles)	7.20	---	4.8	48.0	---
3	24/10/2017 (Tested by ACD, BARC)	BARC Hospital	7.0	---	166.0	192.0	---
		Treated Water (8-Cycles)	7.10	---	14.0	64.0	---

Bio-Sciences Group had carried out Microbiological testing of sewage generated from BARC Hospital and commented as –

“There is a decrease in the bacterial count by ~10 fold after primary treatment. However, the coliform MPN which is greater than 100 indicated that this water is not adequate for direct use and needs further treatment to kill microbes. The high presence of faecal streptococci also makes it unsafe for use in present form. The variations among the different samples from same source could be accounted to the dynamic nature of hospital sewage and waste generated on daily basis”

The set up at BARC hospital was visited by W&SCD officials. Dr. Y V Nancharaiah, WSCD had carried out some analysis on Hospital sewage and suggested for implementation of a cycle regime for promoting granule formation. Microscopic images of biomass collected from bioreactor at BARC Hospital by Dr. Nancharaiah showed formation of micro-granules.

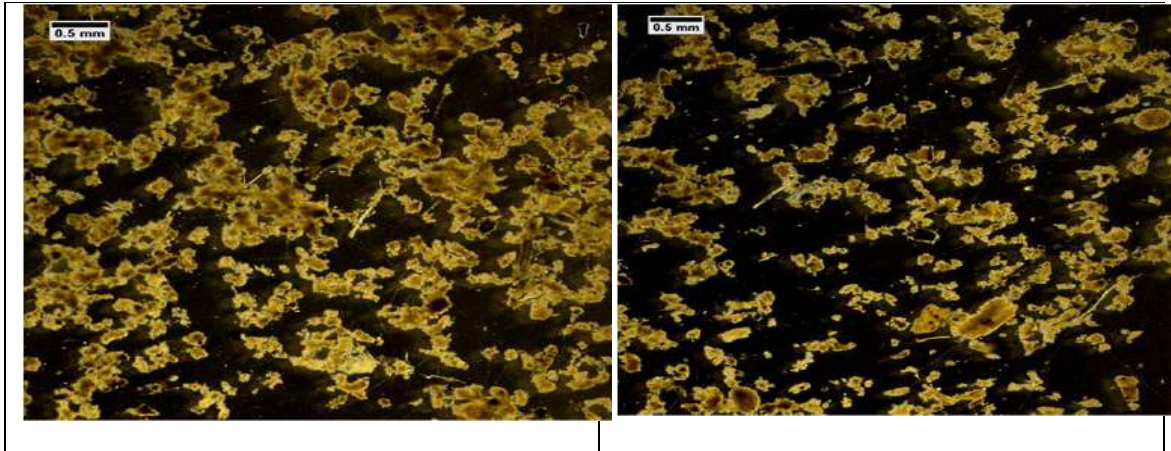


Fig.7 Microscopic images of biomass

Dr. Y. V. Nancharaiah, WSCD recommended to implement automatic operation of cycles [on/off of filling pumps, aeration and withdrawal of treated water].

STAGE-4

Construction of a pilot plant inside BARC campus having a capacity of 10KL

A fully automatic sewage treatment plant based on SBR technology has been constructed in the integrated sewage treatment facility near Green house, BARC, Trombay in which all processes of sewage treatment, viz. Primary, Secondary (SBR) and Tertiary are implemented. Piping and Instrumentation Diagram (P&ID) of the newly constructed plant is shown below –

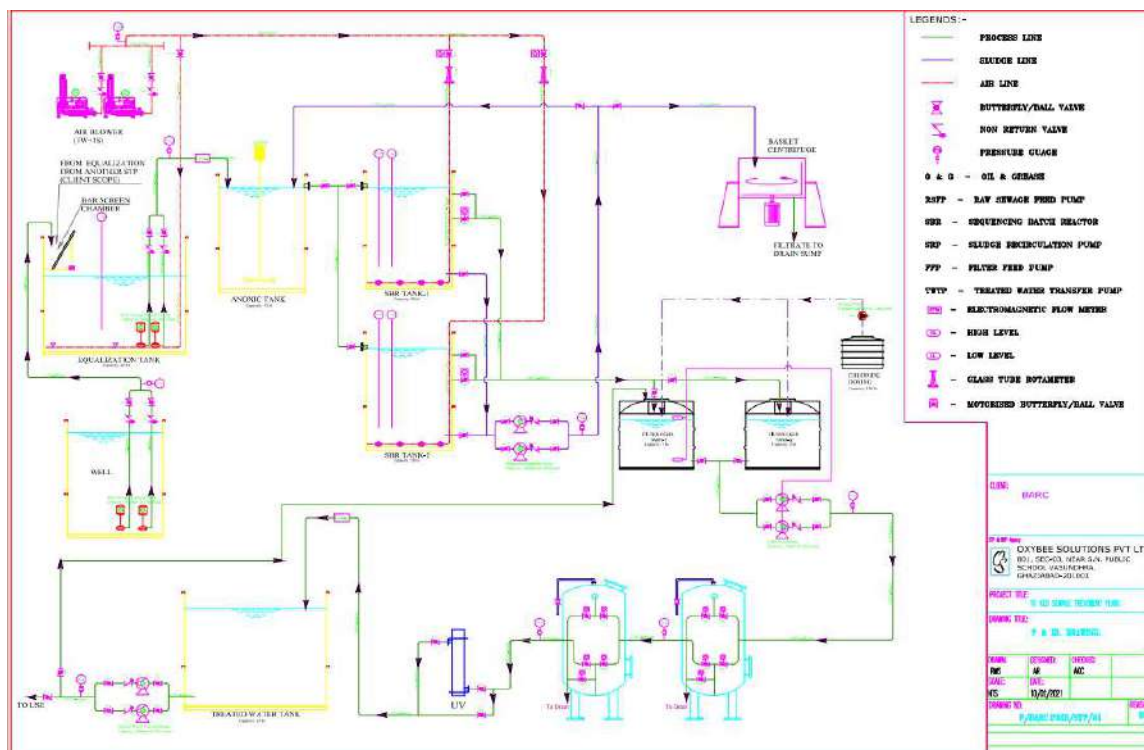


Fig.8 P&ID of 10KL Pilot Plant

Brief construction details of the plant are –

Sr. No.	Tank	Size in M	MOC
1	Equalisation	2.5 x 2.5 x 3.71	MSEP
2	Anoxic	1.25 x 2.5 x 3.71	MSEP
3	SBR (2 Nos.)	2.5 x 2.5 x 3.71	MSEP
4	Treated water	2.5 x 2.5 x 3.71	MSEP
5	Twin Lobe Roots Blowers (VFD motors)	Q = 100 m ³ /hr, H = 0.5 Kg/Cm ²	1W+1SB
6	Various sewage pumps	Various capacities	Total 10 Nos.

7	Chlorine Dosing Pump	1.5/3/6 LPH at 4 Kg/Cm ²	1 No.
8	Basket Centrifuge	25 Kg/Batch	1 No.
9	Dissolve Oxygen Meter	Required capacity	2 Nos.
10	Ultra-Level Transmitter	Measuring Range of 0.3 to 10 M	3 Nos.
11	UV System	Disinfection capacity of 10Cu.M/hr @ 600 J/Sq. M.	1 No.
12	Fine & Coarse Bubble Diffuser	Required capacity	10 Nos.
13	Piping, Manual & Motorised Valves, NRVs etc.	Required size	Required quantity
14	Pressure Sand Filter	Required size & capacity	1 No.
15	Activated Carbon Filter	Required size & capacity	1 No.
16	HMI system	--	For automation

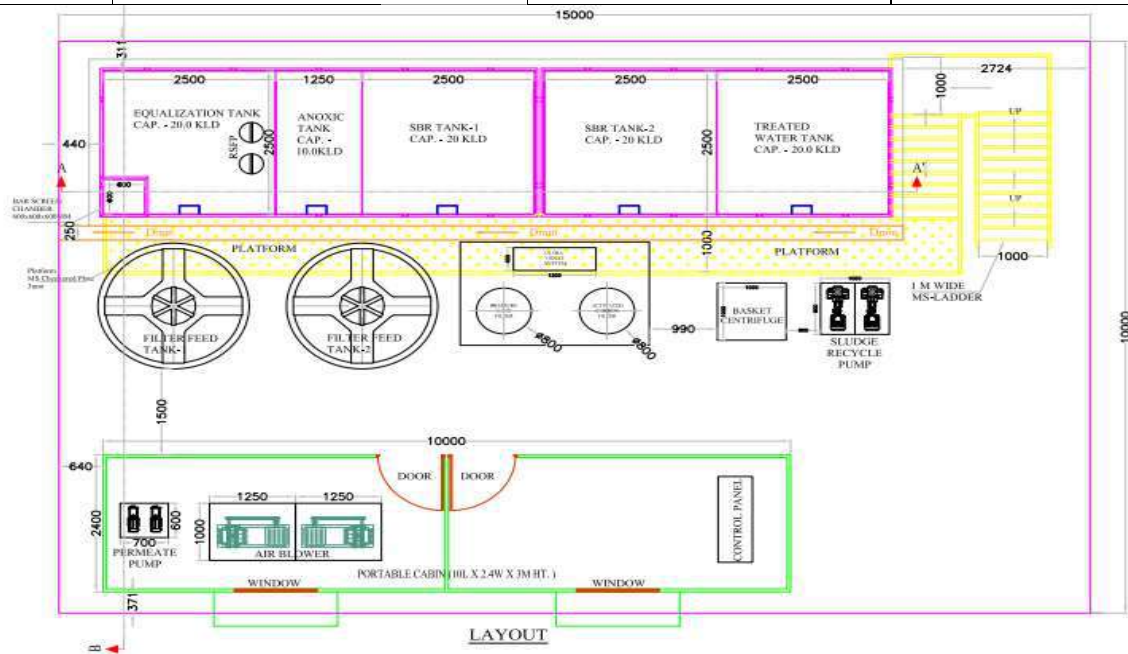


Fig.9 Lay out of 10 KL Pilot Plant



Cycle of operation proposed –

TIME	PROCESS (SBR TANK-1)	PROCESS (SBR TANK-2)
t = 0 hr.	Filling Start Aeration starts Recirculation starts	---
t = 1 hr.	Filling Stop Aeration Continuous & Recirculation continuous for 30 mins more	Filling Start, Aeration starts, Recirculation starts
t = 2 hr.	Aeration Continuous	Filling Stop, Aeration Continuous & Recirculation continuous for 30 mins more
t = 3 hr.	Aeration Stopped Settling Starts	Aeration Continuous
t = 4 hr.	Decantation Starts	Aeration Stopped, Settling Starts
t = 5 hr.	Filtration Starts	Decantation Starts
t = 6 hr.	Filtration Continuous	Filtration Starts
t = 7 hr.	---	Filtration Continuous
t = 8 hr.	Backwash of filter	Backwash of filter

End use of treated water in BARC– Treated water shall be used in BARC gardens developed by L&CM.

Conclusion – Wastewater treatment using sequencing batch technology has been experimentally verified and found it as an efficient & effective method to treat sewage using very less footprint. The compactness of the plant gives a way to utilize it in smaller clusters of housing societies. The treated water can be successfully used for gardening and flushing and help in reducing the dependency on municipalities.

Reference

- 1) CPHEEO Manual, Ministry of Urban Development, New Delhi
- 2) Sewage Disposal and Air Pollution Engineering by Santosh Kumar Garg



Shri Abhinandan Sharma has joined BARC after completing Diploma in Mechanical Engineering (Specialization in Production) in the year 1998 and completed Bachelor of Engineering (Mechanical) from Sardar Pate College of Engineering, Mumbai in the year 2003. He is having experience of more than 25 years in the field of Air Conditioning & Refrigeration Systems and is responsible for Maintenance and Projects in this field in the department. Shri Sharma was involved in various HVAC projects such as construction of Controlled Atmosphere Cold Storage Facility at KRUSHAK Irradiation plant at Lasalgaon, Designing of HVAC system for upcoming DAE Exhibition Centre in Trombay, Air Conditioning of LWRD shed, CMPD building, Food Technology Building, Cold rooms & Deep Freezers of departmental canteens etc. He is also responsible for maintaining various air conditioning equipment in BARC. He is the recipient of the DAE Group achievement award in the year 2017 for Excellence in Science, Engineering and Technology for commissioning of Apsara-U facility.

A Novel Way of Waste Water Treatment using Advanced Oxidation Processes

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Abstract

The waste water coming from various industries especially textile and tannery is highly polluted. It is mixed with several organic dyes that are difficult to remove using conventional chemical and biological methods. Advanced oxidation processes (AOPs), including high energy ionizing irradiation, involving the reaction of hydroxyl radicals ($\cdot\text{OH}$), are emerging as an efficient technique for complete degradation of organic compounds with minimized generation of sludge. Gamma radiation, UV and e-beam can be used as ionizing radiation. Among all high energy e-beam is more effective.

A 1 MeV, DC accelerator is under development at EBC, Kharghar; it will be exclusively used for waste water treatment. Experiments are carried out on several effluents collected from Textile and Tannery industry to study the efficacy of e-beam in reducing the colour, COD, BOD of waste water. Effect of combined processes like e-beam with ozonation or induced flocculation is explored. The present paper gives overview of the electron accelerator technology, its use for waste water treatment and way forward. It highlights the experimental results achieved at EBC, Kharghar. Experiments are carried out on simulated and real effluents using electron accelerator commissioned at EBC, Kharghar. Effect of electron beam is studied on the simulated water prepared with 50 ppm 'Blue' colour Azo dye; it turned colourless at a dose of about 16 kGy. Tannery water received from Inlet of Kanpur tannery is treated with e-beam, effect of electron beam on the Chromium content is studied; it reduced by ~90% at 20 kGy dose. Effluents collected from different stages of CETP plant of Unnao Tannery are treated by electron beam; COD reduction of ~53 % is observed in the water collected from Equalization tank. Effect of e-beam with combination of Ozone treatment is also studied. A Textile effluent collected from Jodhpur industrial area, upon treatment with e-beam showed ~80% reduction in COD with addition of $\text{K}_2\text{S}_2\text{O}_8$ at 5kGy dose. Wash cycle effluent is collected from Technocraft Textile industry, Murbad, Maharashtra, India. It is treated with e-beam in combination with Ozone. About 46% COD reduction is observed with addition of $\text{K}_2\text{S}_2\text{O}_8$ and e-beam irradiation at 10 kGy dose and Ozonation. Effect of Induced Flocculation using radiation grafted cotton cloth as a pre-treatment is studied. It has shown promising results where flocculation followed by electron beam treatment has shown COD reduction of 86% at e-beam dose of 20 kGy in Jodhpur textile water.

Waste water treatment using plasma is an emerging technique. A 'Magenta colour Azo dye' solution when treated by plasma turned colourless in ~ 45 min. The measured % decolouration of dye solution is ~97%. Pulsed electrical discharges, produced using high voltage pulse power supply, are also used for wastewater treatment. It significantly reduces the organic compound, and also decolours the wastewater.

1. Introduction

Environmental pollution is a major concern in the world. It not only affects human life but is harmful to the aquatic animals, flora and fauna thus leading to imbalance in the eco-system. Quality of drinking water is decreasing in distinct part of the globe due to environmental pollution. Major contribution to the aquatic pollution is from Tannery, Textile and Pharmaceutical industry that release toxic, harmful chemical and organic material including dyes in the water body or river. Every year ~7793 ktons textile waste is generated in India. India has more than 2000 tanneries that produce more than 2 billion sq. feet leather annually.

These industries are becoming point source for water pollution and a decisive, inescapable, threat to disturb the ecosystem and homeostasis of the environment [1]. Textile and tannery industries consume huge amount of water. There has been an increase in concern in terms of release of recalcitrant pollutants to environment. From decades physico-chemical techniques like screening, grease and fat skimming, coagulation- cum-flocculation followed by settling are being used either individually and in combinations to make the effluent amenable for biological treatment. Figure 1 shows the conventional waste water treatment process in the Tannery industry [2]. Limitations of conventional method are huge amount of secondary waste generation that is disposed of as land filling and long retention time. The emerging technologies such as ‘Advanced Oxidation Process’ can overcome these issues and are helpful to destroy toxic and biologically refractory organic contaminants [3]. Tannery industry produces huge amount of wastewater which will be characterised by some of the parameters such as COD, BOD, TDS, TSS, pH, chromium, chlorides, sulphates, nitrates, colour, oil and grease. Biological treatment of tannery effluent is not effective since it contains high salinity and xenobiotic compounds. Treating effluent conventionally does not meet the desired parameters to discharge water to water bodies. Recently AOPs are gaining importance which produces powerful and non-selective oxidant hydroxyl radicals which can degrade recalcitrant organic pollutants.

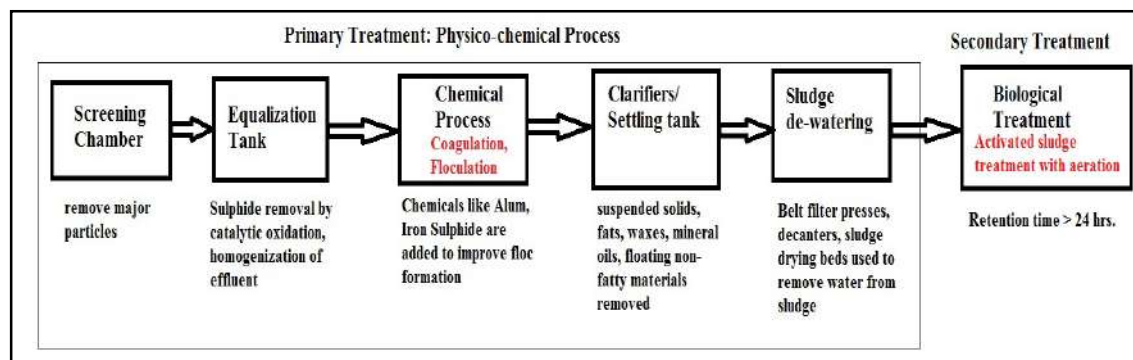
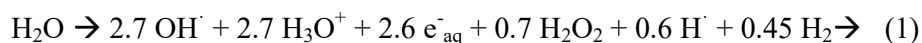


Figure 1: Conventional Waste Water Treatment Process in Tannery Industry

Advanced oxidative processes used for wastewater treatment are UV based AOP [4, 5], Ozone based AOP, Fenton process [6], Radiation treatment (Electron beam treatment and Gamma radiation) which produce oxidative radical OH. The generation of OH radical depends on G value of the process. OH is very non selective and rapidly reacts with numerous species with the rate constant of 10^8 - $10^{10} \text{ M}^{-1} \text{ S}^{-1}$.

Electron beam irradiation generates various free radicals in water along with OH radicals.



The coefficients in the equation (1) are the G values that are defined as number of excited states, radicals, or other products formed or lost in the system, when 100eV of energy is absorbed. Electron beam irradiation produces strong reducing agent e^-_{aq} and $H^\bullet$ radical along with OH radicals which also contribute towards degradation of pollutants in waste water [7]. Figure 2 shows the scheme of radiolysis of water using ionising radiation.

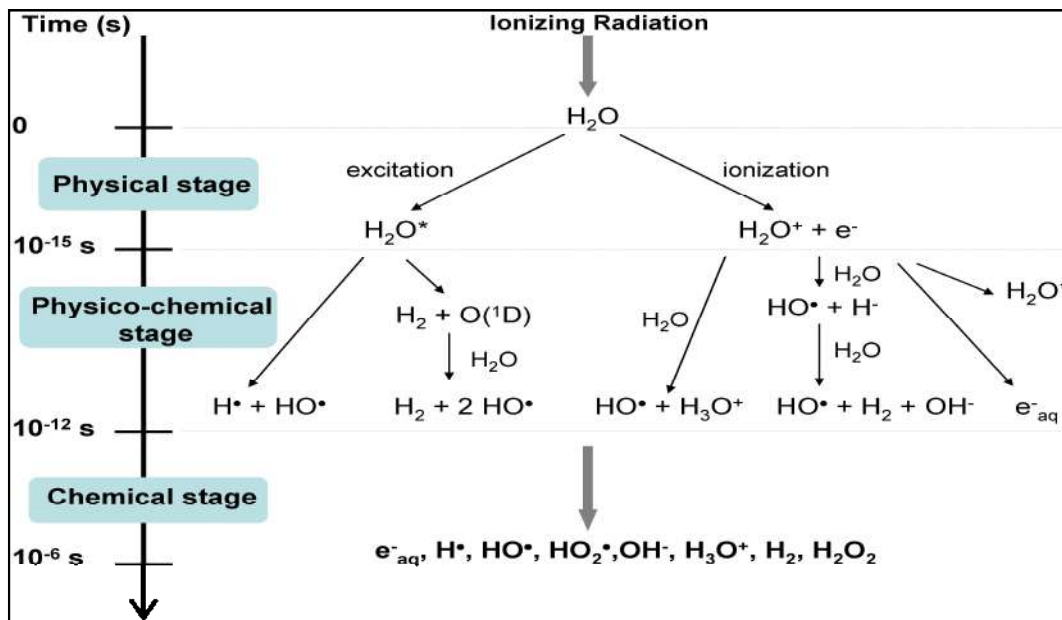


Figure 2: Scheme of Radiolysis of water

The hydrated electron with standard potential $E^0(H_2O/e^-_{aq}) = -2.9V_{NHE}$ and $E^0(H^+/H^\bullet) = -2.9V_{NHE}$ can readily reduce dissolved metal ions to its lower oxidation states [8].

2. Experimental Procedure

The electron beam technology was used to treat industrial waste water and sludge in various plants and they are still in operation. These pilot plants have provided concrete evidence for the effectiveness of EB treatment [9].

Electron Beam Centre, Kharghar, Navi Mumbai houses indigenously developed RF and DC accelerators for various applications. 10 MeV, 3kW RF linear accelerator was developed for various applications such as food irradiation, medical sterilization, polymer cross linking, diamond irradiation, chitosan irradiation and other R&D applications. A 1 MeV DC accelerator is especially designed for wastewater treatment, which has a capacity to treat 2MLD waste water [10]. Figure 3 shows the general scheme of waste water treatment using electron accelerator. Electron accelerator consists of electron gun, accelerating column and scan horn having 'Ti window'. The electron beam is ejected in air through the window. A waste water to be treated is passed under the accelerator using a water jet.

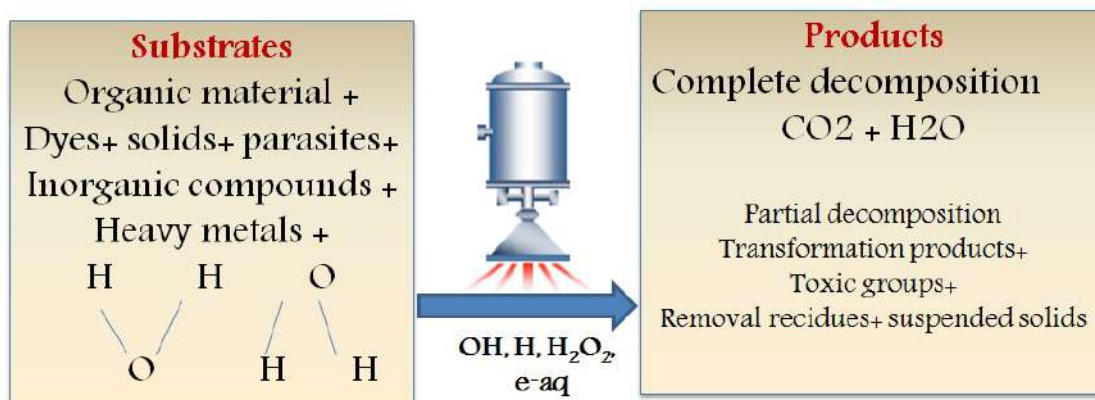


Figure 3: Scheme of waste water treatment using electron accelerator

3. Waste Water Treatment

3.1 Waste water treatment using Electron Accelerator

3.1.1 Experiment with Simulated dye water

A simulated Dye solution is prepared and treated with the 1 MeV DC accelerator. Approximately dose of 1 kGy is received by the samples in each cycle. After about 16 cycles i.e. 16 kGy dose, samples become colourless as shown in the figure 4. The reduction in the colour is due to “Azo bond breaking”. Optical density, OD is measured using UV-VIS spectrophotometer. It shows reduction with increase in the dose (see figure 5).



Figure 4: De-colouration after irradiation

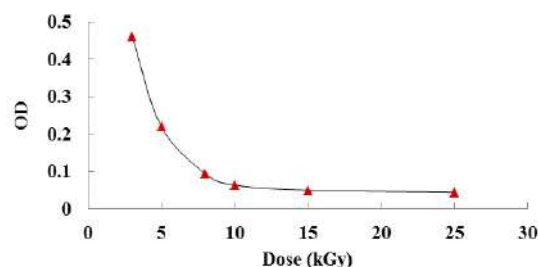


Figure 5: Reduction in optical density

3.1.2 Treatment of Tannery waste water using e-beam

a) Effect of e-beam treatment on Chromium Concentration

Tannery waste water received from Kanpur Tannery contained lot of impurity. The pH, COD, TSS and TDS of the sample were 4.02, 1792 (mg/L), 2040 mg/L and 21862 mg/L respectively. Total chromium content was 384 mg/L. As received sample is analysed using UV-VIS Spectro-photometer. Two prominent absorption peaks are observed at a wavelength of 405 nm and 575 nm corresponding to Chromium [11]. To study effect of pH, NaOH is added to the tannery water sample; pH is increased up to 12. Figure 6 shows the effect of increased pH; quantity of precipitation is increased with pH.



Figure 6: Precipitation of impurities at different pH

Change in the absorption spectrum is studied at different pH values. It is observed that peak at 575 nm is completely disappeared in pH=12 sample. This may be due to the conversion of soluble Cr^{6+} to insoluble Cr^{3+} which is settled down as precipitate. Figure 7 shows the change in Absorbance with pH. A supernatant in neutralized samples (pH=7) is collected and then irradiated at different doses of electron beam.

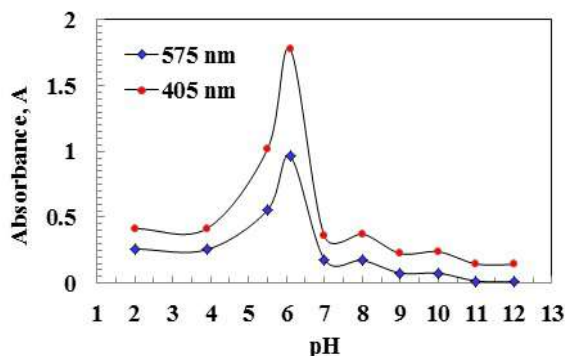


Figure 7: Change in Absorbance with pH

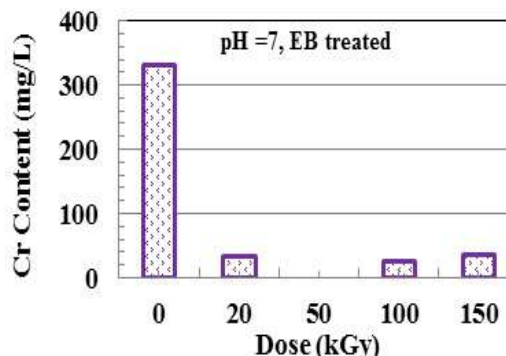


Figure 8: Reduction in total Cr content

Figure 8 shows reduction in Total Cr after e-beam irradiation of pH=7 sample. Total Cr content in neutralized sample was 332 mg/L, it reduced to 34 mg/L at dose of 20 kGy. By increasing dose further up to 150 kGy no change in Cr content was observed. Thus, approx. 90% Chromium reduction is observed at 20 kGy dose [12].

b) Effect of e-beam treatment on the biodegradability of tannery waste water

The samples are treated at different doses of e-beam in as received condition and after neutralizing to pH=7. Samples are irradiated using e-beam accelerator up to 150 kGy. The change in COD value is shown in the figure 9. Maximum COD reduction of ~21% and ~19 % is observed in the samples of pH=4 and 7 respectively. BOD of these samples is measured, it increased with dose. This indicates that biodegradability of the water is increased. Figure 10 shows the ratio of BOD/COD for treated samples; increase of ratio with dose indicates increase in the biodegradability of samples.

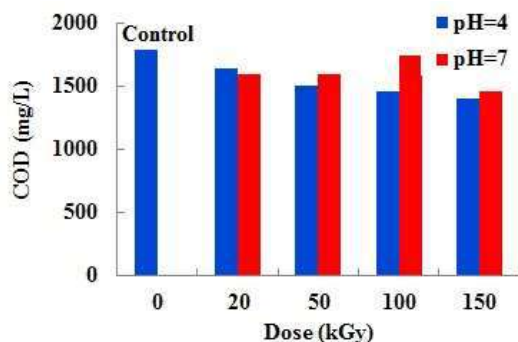


Figure 9: COD reduction with dose

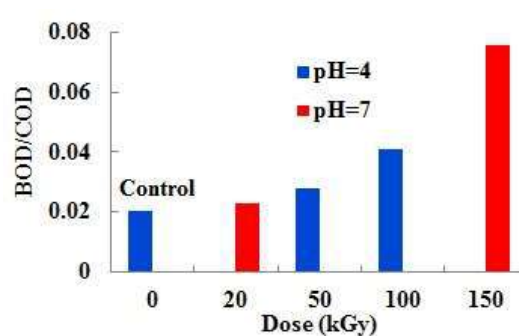


Figure 10: Increase in Bio-degradability

c) Effect of Combined processes on Tannery water

Effect of e-beam treatment in combination with Ozonation is studied. Samples are collected from different tanks of Unnao Tannery plant viz., Equalization Tank, Flocculator, Biological Treatment and Final tank. Samples are treated by e-beam and Ozonation followed by e-beam treatment. Dose is varied from zero to 5 kGy; maximum reduction in COD is observed at 5 kGy. Figure 11 shows the COD reduction with Dose for samples from different tanks. Figure 12 shows % COD reduction in the samples collected from different tanks and treated by different combination process. In all the samples, % COD reduction is more in only e-beam treated samples as compared to (Ozonation+e-beam) samples. In Equalization tank sample, COD reduced from 470 to 220 (53.2 %) while in Final sample COD reduced from 194 to 43 (77.8 %).

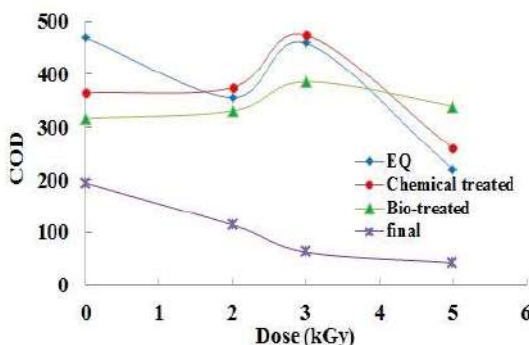


Figure 11: COD reduction with dose

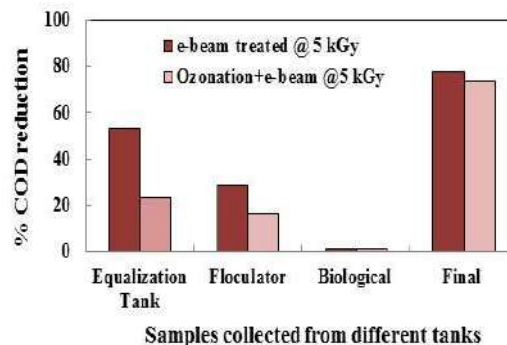


Figure 12: Effect of combined processes on COD

3.1.3 Treatment of Textile waste water using e-beam

Effect of electron beam on the real effluent received from textile industry was studied. Samples are treated by electron beam at a dose of 3 kGy and 5 kGy, with and without addition of $K_2S_2O_8$. COD of samples before and after EB treatment is measured. The earlier studies by J. Paul et. Al. [13, 14] have shown the effectiveness of Gamma radiolysis in the presence of $K_2S_2O_8$ for complete mineralization of organic compounds. Thus same procedure is adapted to study the e-beam radiolysis. The results are given below [15].

- Textile effluent collected from Jodhpur industrial area, India is treated using 10 MeV RF electron beam accelerator at EBC, Kharghar. Samples were irradiated at 3 and 5 kGy dose in as received condition and also by adding 40mM of $K_2S_2O_8$. About 80% reduction in COD was achieved for textile effluent when irradiated at 5 kGy dose with addition of

$K_2S_2O_8$. Figure 13 shows the colour degradation in the samples after e-beam treatment under different conditions. Table 1 shows the measured water parameters.



Figure 13: e-beam treated samples; a) Control, b) 3kGy, c) 5kGy, d) 3kGy + $K_2S_2O_8$, e) 5kGy + $K_2S_2O_8$

Table 1: Measured parameter of Jodhpur Industrial area water samples

No.	Sample Description	pH	TDS	COD
1	Control	7.4	4150	568
2	e-beam treated at 3 kGy	8.6	3810	192
3	e-beam treated at 5 kGy	8.5	3530	220
4	e-beam treated at 3 kGy with 40 mM $K_2S_2O_8$	8.0	7260	124
5	e-beam treated at 5 kGy with 40 mM $K_2S_2O_8$	7.6	7710	120

b) Wash cycle effluent was collected from Technocraft textile industry from Murbad, Maharashtra, India. It was treated with e-beam with addition of $K_2S_2O_8$ and in combination with Ozonation. A table-top Ozone generator was used for the experiment. About ~46% reduction in COD observed with combination of Ozonation, $K_2S_2O_8$ and irradiation by e-beam at 10 kGy dose. Figure 14 shows the colour degradation of water after different processes. Table 2 shows the measured water parameters.

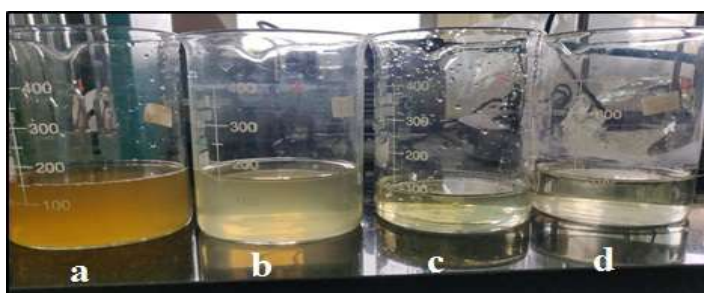


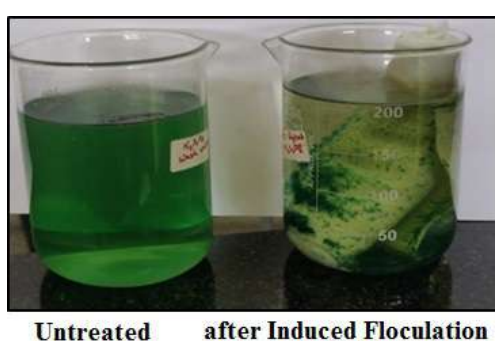
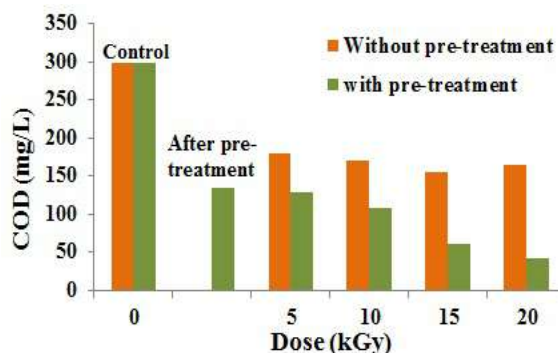
Figure 14: e-beam treated samples; a) Control, b) Ozonation, c) $K_2S_2O_8$, d) $K_2S_2O_8$ + ozone

Table 2: Measured parameter of M/s Technocraft wash cycle water samples

No.	Sample Description	pH	TDS	COD
1	Control	6.7	1640	896
2	Wash cycle water with $K_2S_2O_8$	4.5	4380	736
3	Wash cycle water + Ozonation with $K_2S_2O_8$	3.6	3820	584
4	Wash cycle water e-beam treated at 10 kGy	6.4	1570	760
5	Wash cycle water + Ozonation with $K_2S_2O_8$ +e-beam treated at 10 kGy	4.3	4200	484

3.1.4 Effect of Induced Flocculation as pre-treatment on Textile and Tannery water

New method of induced flocculation as a pre-treatment is studied for textile, tannery effluents using radiation grafted cotton cloth. The radiation grafted cloth was rotated mechanically in effluent water so that micro flocks are precipitated; this can be used as effective pre-treatment method in water treatment plant. This method results in reduction of colour and COD which is a major hurdle in common effluent treatment plants for discharge or reuse of water. The method was tested on real effluents from textile and tannery industry. Experiments are done with real Textile effluent from Jodhpur Industrial Area. Flocculation was initiated by lint on grafted cotton. Adsorption of dyes on lint adds weight and coagulation will start with rotation. Rotation speed of 150 RPM was maintained during treatment. Figure 15 shows the precipitation of Dye after pre-treatment. Figure 16 shows the COD reduction after e-beam treatment with and without pre-treatment. Without pretreatment % COD reduction at 20 kGy dose is ~45 %; with pre-treatment the % COD reduction increases to 86%. Induced Flocculation alone reduces COD value by 55 % after resident time of 10 min. Similar experiment was done on the water received from the Equalization tank of Banther Tannery. Pre-treatment is able to reduce COD value from 1170 to 772 (34%) [16].

**Figure 15: Effect of pre-treatment****Figure 16: COD reduction with e-beam dose**

3.2 Waste Water Treatment using Other AOPs

3.2.1 Waste water treatment using Plasma

BTDG has developed 'Cold Atmospheric Pressure Plasma System: 10 MHz (ICAPPS-10)'. A Plasma Generator is installed in the Chemistry laboratory at EBC, Kharghar for waste water treatment. An experiment is carried out with simulated dye water; a dye water solution of concentration 100 ppm is prepared using magenta colorazo dye. Absorption peaks of dye solution measured by UV-VIS spectro-photometer; two peaks are observed at wavelengths of 334 nm and 548 nm. The corresponding Absorbance values are ~ 0.7 and ~ 0.6 respectively. About 100 ml Dye water is treated using cold plasma generator. Figure 17 shows the plasma torch and the dye solution under treatment. After 45 min. treatment water turned completely colorless. Figure 18 shows reduction in the optical density of dye solution due to breaking of azo bonds. Figure 19 shows reduction in pH; figure 20 shows increase in TDS with time.

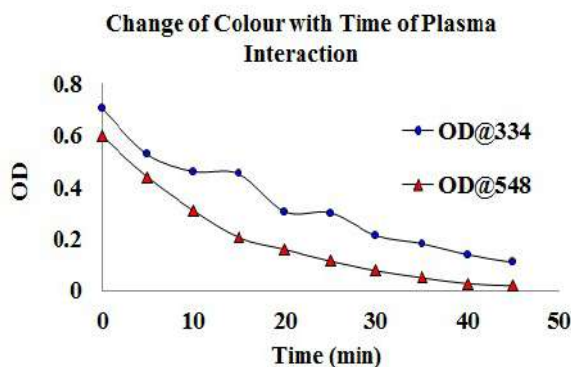


Figure 17: Plasma treatment Figure 18: Reduction in the Optical density

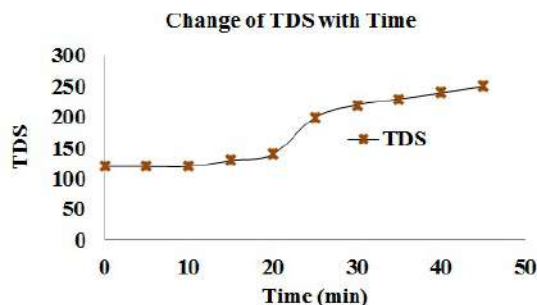
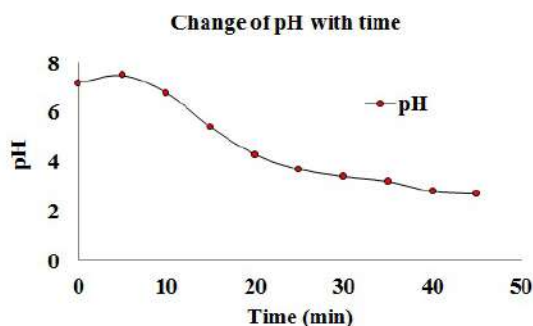


Figure 19: pH reduction with time Figure 20: Change in TDS after with time

Absorbance (OD), pH and TDS of dye solution is observed with time. The Absorbance and pH reduced considerably while TDS value increased with time. After 45 min. plasma treatment % decolouration of dye solution is $\sim 97\%$ at 548 nm. Reduction in pH associated with increase in TDS is indicative of fragmentation of complex dye molecule to smaller components.

3.2.2 Waste Water Treatment using Pulsed Discharge

Pulsed electrical discharges, produced using high voltage pulse power supply, are also used for wastewater treatment. The power supply consists of a resonant converter and high frequency MOSFET switching module. It can generate high voltage pulses up to 22 kV at 30 kHz. The rise time and fall time of the high voltage pulse is $< 2 \mu\text{s}$ and the pulse width is $2 \mu\text{s}$. The power supply is short circuit proof and can withstand variable load conditions from

overloads to arcs. Pulse electrical discharges experiments are carried out with the power supply at 22 kV, 30 kHz for the breakdown of complex phenol with different concentration in wastewater, and also the decolouring of sodium aluminium sulpho silicate dye in water using direct pulsed electrical discharges. Pulsed electrical discharges treatment significantly reduces the organic compound, and also decolours the wastewater. Significant improvements in the degradation of phenols and decolouring rate are seen with the bubbling of oxygen gas into the wastewater while treatment with pulsed electric discharges.

4. Conclusion

Electron accelerator is used to study the colour degradation of dye water and reduction in COD, BOD of various samples. We found that electron beam can efficiently remove colour while COD reduction is more effective when used in conjunction with other methods like pre-treatment or by adding $K_2S_2O_8$. Addition of $K_2S_2O_8$ in textile samples has resulted in higher TDS thus it is necessary to study the effect of other oxidising agents. E-beam treatment could not reduce COD of Tannery water considerably but is able to reduce the chromium content when used with chemical method. Also bio-degradability of tannery water is increased with e-beam treatment. Pre-treatment of waste water using induced flocculation has shown considerable reduction in the COD. Other novel techniques like Plasma treatment and pulse discharge treatment have potential to treat the waste water.

In conclusion, in order to treat waste water effectively using e-beam and to make it viable, it is necessary to know the composition of water so that a suitable pre-treatment and/or combination of processes can be synthesized to minimize the e-beam dose required for complete degradation of waste water.

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Harnessing micro-nano bubbles of ozone for produce-water treatment: A lab-to-land case study

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1.0 Introduction: As India leapfrogs in to the league of developed nation its energy requirement is slated to double by 2045. Though there is increased focus on renewables, oil and especially gas will continue to be an important player in the energy mix (especially for base load applications) in the near future. Till then it is essential to make the process of oil/gas recovery as environmentally friendly as possible. One major challenge is how to manage the water that comes out along with the oil/gas from wells. This water is called produce-water and is contaminated with dissolved and emulsified oil. Management of this water is specially challenging as the nature of contaminant vary from time to time and from well to well. Produce-water constitute around 70-90 % of the total well output and this water must be treated first so as to make it amenable for surface discharge and/or other gain full use. In Indian scenario presently this produce-water is being re injected inside the ground (at great expense of energy) as the water is not suitable for surface discharge/industrial/agricultural use. To reduce this waste full consumption of energy a process is developed to remove dissolved oil and salt from produce-water and make it suitable for gain full use like in agriculture and/or industry.

Literature survey indicates that various techniques have been reported for treatment of produce-water. The list includes Fentons (Neyens and Baeyens, 2003), photo (UV)-Fenton (Pignatello et al., 2006) process. The active species here being hydroxyl radical. Similarly photocatalytic processes using UV light and TiO₂ photocatalyst have been tried (Nath et al., 2012). Ozone gas has also been used to degrade dissolved organics/pollutants in produce-water (Jiménez et al., 2019). However ozone is often used in combination with other oxidants (chemicals) to enhance the overall effectiveness of the process. Use of UF membranes to treat produce-water has also been reported (Wandera et al., 2011). Very good results are obtained using membrane contactors but this route alone may not be sufficient for industrial scale deployment due to challenges of severe membrane fouling in presence of dissolved oil and grease in the feed.

To determine the optimal degradation technique for actual produce-water, we compare three methods: treatment using UF (organic) membranes, adsorption on natural/synthetic resins and natural materials (like clay), and advanced oxidation processes (AOP). Comprehensive laboratory-scale experiments are conducted to evaluate the strengths and weaknesses of each technique. Eventually, the chosen treatment sequence comprises AOP (utilizing micro-nano bubbles of ozone gas) as the primary step, followed by resin bed adsorption in a polishing column (secondary step), and finally reverse osmosis (RO) based desalination (tertiary step) to address total dissolved salt (TDS) issues. AOP targets the bulk removal of dissolved

oil/organic matter, while the adsorption column prevents inadvertent carry-over of oil/grease to the RO unit. The RO step aims to reduce TDS levels to acceptable levels for irrigation use (< 2100 ppm, preferably below 1000 ppm), considering that TDS levels in produce-water are typically high (~10-12 g/L). Upon completion of laboratory-scale experiments and process selection, bench-scale experiments are conducted to assess scalability. This involves testing various ozone dispersing equipments in the ozonation reactor namely sparger with high-speed top mounted agitator, venturi injector, and regenerative turbine pump. Batch experiments (bench scale) are conducted. The secondary polishing step is also tested in a 6-inch column (1.0 m high) filled with suitable adsorbents. The final RO unit is evaluated for its ability to reduce TDS to below 1000 ppm in the permeate. Following successful bench-scale experiments, a pilot-scale unit, referred to as Advanced Effluent Water Treatment Plant (AEWTP), is designed, fabricated, installed, and commissioned. Approximately 10 kL of produce-water is processed over a period of around 3 days (8 hours of operation per day) on a continuous basis, demonstrating a processing rate of 500 LPH. In both bench and pilot-scale operations, total organic carbon (TOC) and TDS levels in the final processed water are below 10 ppm and 1000 ppm, respectively, rendering the water suitable for agricultural use. Germination studies of "mung" seeds and growth studies of germinated plants using the product water are also conducted to verify the suitability of the water. Detailed results from laboratory-scale, bench-scale, and pilot-scale experiments are provided below. All produce-water samples are sourced from an on-shore oil production facility in Mehsana, Gujarat.

2.0 Laboratory scale studies

2.1 Selection of a suitable process for degradation of dissolved oil in produce-water

The first step is the selection of the technique/process for removal of dissolved oil in produce-water. [Table 1](#) provides a gist of the typical results obtained at laboratory scale (2-5 L of processing). The feed is produce-water containing 100-125 ppm of total organic carbon (TOC), 10-12 g/L of total dissolved solids (TDS), and oil and grease (O&G) ~10 ppm.

Table 1: Comparison of three different techniques to degrade dissolved oil in produce-water.

Technique	TOC reduction	Consumables /chemicals	Secondary waste generated
Advanced Oxidation Process (AOP) using ozone micro bubbles	>90 %	None	None. By-product of ozone is oxygen
UF membranes (organic)	70-75 %	None	Reject streams containing high O&G content. Problem of disposal. Also severe problems of membrane fouling while processing the feed containing O&G.
Adsorption on clay	~40-50 %	Clay	Clay is consumable. Problem of disposal if deployed at large scale.

Thus it can be seen that the AOP using ozone micro bubbles is the most promising amongst all in terms of TOC removal and adaptability at large/industrial scale. Also it is a green process while does not lead to generation of any secondary waste stream.

Though ozone injected in the form of micro bubbles is seen yield very good results there are many reports in literature that suggest that use of additional additives/oxidants along with ozone further improves its efficiency (Jiménez et al., 2019). This led us to compare results obtained using micro bubbles of ozone against three other competing AOP techniques -Fenton, photo Fenton, O_3 , and H_2O_2/O_3 . In all experiments pertaining to ozone the injected ozone gas is infused in the form of micro bubbles. Of all four AOP techniques H_2O_2 aided ozonation (ozone micro bubbles) is found to be best and the TOC of the treated water can be reduced to below 10 ppm using this approach. Performance of H_2O_2/O_3 is seen to be better compared to that of Fenton and photo-Fenton process in terms of reduction of TOC. % TOC removal for Fenton, photo-Fenton are roughly 50 % and ~65 % respectively for Fe loading of ~120 ppm. However performance of H_2O_2/O_3 is seen to be only marginally better (section 2.2) than that of O_3 . It may be noted that in both cases O_3 is injected in form of micro bubbles.

The mechanism of ozone based AOP is well studied (Hoigne, 1988). Ozone can react with a pollutant either directly as molecular ozone (oxidation potential being 2.08 eV) or can lead to formation of hydroxyl (OH) radical after a series of reactions (indirect attack). The first route is a selective in nature where the oxidation mechanism depends on the molecular structure of the pollutant whereas the second route involving OH radical is nonselective and can oxidise a variety of unsaturated pollutants. It is this second route that is typically relied upon in ozone AOP. Though ozone alone cannot lead to complete mineralisation of the pollutant (i.e. conversion into CO_2 and H_2O) it can remove unsaturation in the target pollutant molecules (e.g. dissolved organics in produce-water) thereby reducing oxygen demands.

2.2 Parametric study of AOP using micro bubbles of ozone (aided/un-aided)

Ozonation experiments are conducted at a laboratory (1.5 L, batch) scale. Ozone is introduced into a 3-liter stirred tank via a sparger positioned at the tank's bottom, with vigorous stirring employed to ensure dispersion of the injected gas into very fine (micro) bubbles. Fig. 1a illustrates the impact of pH on the Total Organic Carbon (TOC) levels in the resulting treated water. Two pH levels are investigated: 7.8 and 10. The pH of the initial feed stream, set at 7.8, is elevated to 10 through the addition of concentrated NaOH. After a 2-hour reaction time, it is observed that raising the pH to 10 leads to somewhat higher TOC levels in the treated water. This finding suggests that working with the original feed stream is preferable, obviating the need for additional chemicals to adjust pH. Notably, even without modifying the initial feed stream's pH, the TOC can be reduced from 125 ppm to approximately 40 ppm after just 2 hours of ozone treatment, employing a concentration of 120 grams/ Nm^3 . Fig. 1b depicts the influence of hydrogen peroxide (H_2O_2) dosage on the TOC levels of the treated water, utilizing a higher ozone concentration of 180 grams/ Nm^3 in these trials. One experiment involves no addition of hydrogen peroxide, while the other utilizes 0.5% (v/v) H_2O_2 . The results indicate that adding H_2O_2 indeed lowers the TOC levels in the treated water. However, even without H_2O_2 addition, i.e., solely through ozone micro bubble treatment for 2 hours, the TOC could be reduced to 30 ppm. This suggests that the addition of an extra oxidizing agent (hydrogen peroxide) does not yield a significant difference in results. Fig. 1c demonstrates the impact of ozone dosage on the TOC levels of the treated water. Increasing ozone concentration is observed to decrease the TOC levels in the treated water after 2 hours of operation.

Thus, a systematic parametric analysis reveals that there is no need to alter the pH of the feed solution; the feed can be used directly. It is also found that there is no need to add hydrogen peroxide; ozone micro bubbles are sufficient.

An additional experiment is being conducted in which ozone is injected continuously for 3 hours (at a concentration of 120 grams/Nm³). Samples are being taken at regular intervals, and the time profile of TOC in the water being treated is shown in Fig. 2. In fact, Fig. 2 shows the kinetics of the process. It can be seen that there is a continuous decrease in the TOC of the water with time. Finally, after 180 minutes, the TOC of the treated water is 3.42 ppm.

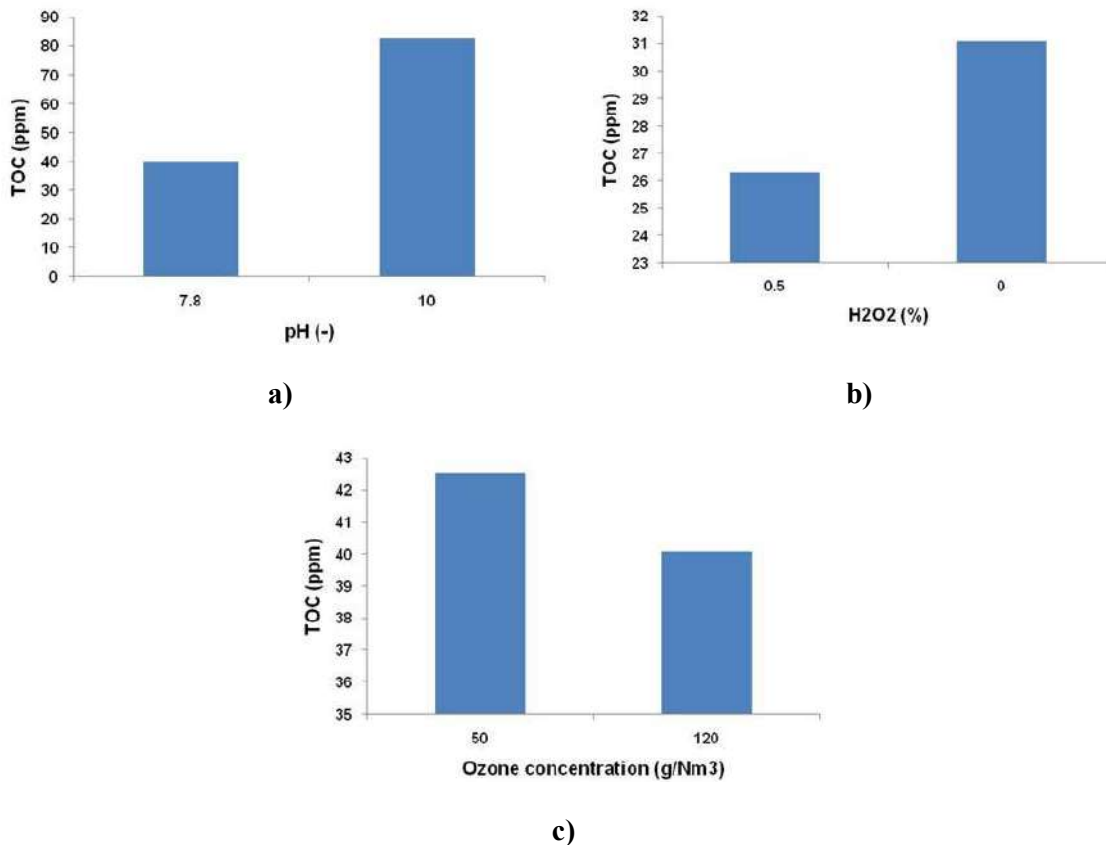


Figure 1: Effect of a) pH, b) presence of H₂O₂ and c) ozone concentration on TOC of treated water (TOC of feed = 125 ppm, treatment time = 2 hours, scale = 1.5 L)

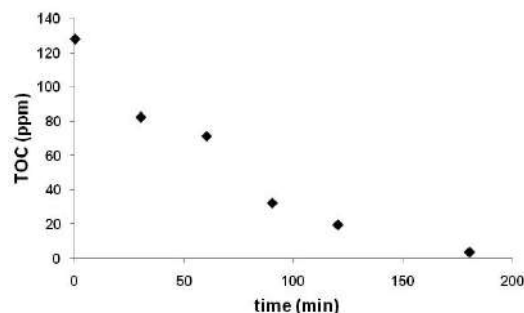


Figure 2: Kinetics of ozone based treatment of produce-water

In all ozonation experiments, not only is TOC significantly reduced, but the color and odor of the feedstock are also completely eliminated. Fig. 3 below compares images of the feed water and the treated water. The treated water is also being tested for COD and O&G. The COD can be reduced from 424 ppm to 112 ppm, corresponding to a removal of 73.5%. The O&G content is also being reduced from approximately 10 ppm to 0.4 ppm.

At this stage it is worth mentioning that the results are valid only if ozone is injected in form of micro bubbles (<100 microns). The oxidation process essentially occurs in the liquid (aqueous) phase. Thus mass transfer of ozone molecules from gas to liquid phase represents a possible resistance and more often than not this mass transfer of ozone from gas to liquid phase is the rate limiting step (Sarayu et al. 2007, Kabdash et al., 2002). Such a resistance leads to very poor utilisation of the generated ozone and thus represents waste of energy. One way to increase the utilisation of gaseous ozone is by creating micron sized bubbles of ozone. Compared to macro bubbles (size greater than ~1 mm or more) micro bubbles (0.05-0.10 mm) drastically increases the interfacial area available for mass transfer of ozone as well as increases the rise/retention time of the gas in the liquid phase. Both these factors help to increase ozone utilisation. Thus injecting micro (or micro-nano bubbles) of ozone into a liquid truly represents a state-of art AOP that can efficiently degrade organic pollutants. The two above mentioned factor essentially ensure that ozone micro bubbles are critical in achieving a green “ozone-only” process to treat produce-water.



Figure 3: Comparison of original (left) and treated (right) water

2.3 Secondary and tertiary steps

These sets of experiments are conducted to test the effectiveness of two different resins (polystyrene-divinylbenzene, PS-DVB and granular activated carbon, GAC) to further polish the effluent from the ozonation reactor. Typical values for specific adsorption capacity attained is 3 and 2.2 mg/g for PS-DVB and GAC, respectively. Column studies are carried

out to determine break through volumes for both resins (omitted here for brevity). It can be seen that though PS-DVB resin leads to a slightly higher adsorption capacity but it is expensive vis-à-vis GAC. Also its long term disposal needs to be studied. In view of these facts and also in light of the fact that difference in specific adsorption capacity is only 0.8 mg/g, activated carbon is selected as the resin material for polishing step.

In the tertiary step involving reverse osmosis, it's crucial to ensure that the O&G content in the feed is close to 0 ppm, and preferably, the TOC value remains below 10 ppm. After the primary and secondary steps, the O&G content is reduced to 0 ppm. Since RO is a standard procedure, laboratory-scale trials using an RO module are not conducted.

3.0 Selection of ozone dispersing equipment at bench/engineering scale

At laboratory scale a high speed stirrer/impeller is sufficient to break down the infused gas into small micron sized bubbles. Infact the efficacy of the “ozone only” process is due to the presence of micro bubbles and may not be valid if ozone micro bubbles cannot be generated at engineering/pilot scales. Three different equipments are compared to test their ability to create micro bubbles of ozone. They are a classical stirred tank with sparger and top mounted agitator, stirred tank with regenerative turbine pump and stirred tank with venturi injector. Experiments are carried out with a feed stock of around 125-140 ppm TOC, O&G ~10-12 ppm and TDS of 10-12 g/L. For all experiments time of treatment is fixed at 3 hours and ozone dosage is fixed at ~100 grams/hr (for venturi injector and top mounted agitator) and ~25 grams/hr for regenerative turbine pump. Scale of operation is ~100-150 L. Experiments are carried both with and without hydrogen peroxide to determine whether use of hydrogen peroxide can be done away with at engineering scale. A set of three specific parameters are used to compare the three equipments.

$$1) \text{ Specific Organic Removal Rate (mg/KW-hr)} = \text{SORR} = \frac{\dot{m}(TOC_{initial} - TOC_{final})}{P}$$

$$2) \% \text{ organic removal (-)} = \text{POR} = \frac{100(TOC_{initial} - TOC_{final})}{TOC_{initial}}$$

$$3) \text{ Specific energy consumption (KW-hr/kg)} = \text{SEC} = \frac{P}{\dot{m}}$$

The results are summarised below in [Table 2](#).

Table 2: Comparison of different ozone dispersing equipment (feed TOC is ~135 ppm)

	Sparger with top mounted agitator	Regenerative turbine pump	Venturi
TOC _{final} (3 hours)	57 ppm	10 ppm	20 ppm

Effect of H_2O_2 addition	Significant (23%)	Very small ($<10\%$)	Small (13%)
POR (%Org Removal)	60.14 %	90.67 %	85.10 %
SORR (Sp Org removal rate)	1081.98 mg/KW-Hr	883.26 mg/KW-Hr	2578.33 mg/KW-Hr
SER (Sp Energy Req)	0.079 KW-Hr/kg	0.121 KW-Hr/kg	0.046 KW-Hr/kg
Scale up	Poor	Good	Good
Bubble size formed	> 1000 microns	0.8 to 50 microns	>250 microns

On comparing the three equipments it is seen that performance of the sparger with top mounted agitator is the worst while that of the regenerative turbine pump is the best. Performance of venturi injector is in between. After a treatment time of 3 hours, in presence of H_2O_2 , TOC of treated water are 57 ppm, 10 ppm and 21 ppm for sparger-agitator system, regenerative turbine pump and venturi injector. Hence from a technical standpoint the most appropriate ozone dispersal equipment is regenerative turbine pump. However in absence of H_2O_2 the corresponding TOC values are 23 %, 4 % and 13 % higher for sparger-agitator system, regenerative turbine pump and venturi injector respectively. This shows that if we use regenerative turbine pump there is genuinely no requirement of H_2O_2 . Moreover it needs to be kept in mind that the stellar performance of the regenerative turbine pump is achieved at a much lower ozone dosage (almost $1/4^{th}$). Though the energy requirement is slightly higher for this equipment considering the advantages (superior organic degradation, no requirement of hydrogen peroxide, low requirement of ozone) we recommend use of regenerative turbine pump as the ozone dispersing equipment at engineering scale. Typically the bubbles formed are in the range of 0.8 to 50 microns. Thus apart from micro bubbles some fraction of the bubble density are in nano metric scale. The basic principle behind creation of micro-nano bubbles is hydrodynamic cavitation. At the location of hydrodynamic cavitation local shear stress is extremely high. It is these local stresses that break down the injected gas into ultrafine bubbles. Apart from this, cavitation is known to lead to generation of hydroxyl radical on its own. These radicals formed due to cavitation will augment those generated by the reaction between dissolved ozone and water. This synergistic effect is the driving force behind the superior performance of regenerative turbine pump.

One problem with this equipment is that gas to liquid flow rate cannot be more than 8%. In case the process requires a higher ozone dosage (from kinetically controlled considerations i.e. intrinsically slow kinetics) we can either increase the number of pumps (increases capital investment) or introduce a venturi injector (classical) which can create micro bubbles > 250 microns). The ozone injector system employed in the pilot scale plant (section 4) is thus a combination of regenerative turbine pump and a classical venturi ozone injector.

4.0 Pilot scale operation (500 LPH)

After finalizing the process and necessary equipments necessary at engineering scale, a pilot-scale Advanced Effluent Water Treatment Plant (AEWTP) is constructed and operated at a feedrate of 500 LPH. Approximately 10 kL of oil-contaminated produce-water from Mehsana site, with initial TOC and TDS levels of around 120 ppm and ~21,000 ppm respectively, is used.

The treatment process consists of three steps:

1) Ozonation (AOP): Micro bubbles of ozone are used to degrade a majority of the organic contaminants (~60-70%). This step includes a feed tank, pump, ozonation reactor, regenerative turbine pump, venturi injector, clarifier, and ozone and oxygen generation units.

2) Adsorption: The discharge from ozonation passes through sand filters and activated carbon resin columns, removing additional organic content (~10-15%). This step involves an intermediate tank, metering pump, and pressurized filters.

3) Reverse Osmosis (RO): TDS levels are reduced, producing permeate comparable to portable water. This step utilizes an RO feed tank, booster pump, and spiral RO module.

The first two steps predominantly remove organic contaminants, with the final step focusing on reducing TDS levels. Fig. 4 below shows the process flow diagram (process schematics) of AEWTP. Fig. 5 shows the photograph of the plant as installed.

4.1 Results of batch studies in ozonation reactor:

Before continuous flow operation in AEWTP experiments are carried out in the primary ozonation reactor to determine the kinetics of the organic degradation process. Ozone injection system is composed of regenerative turbine pump and venturi injector. The batch size is kept at 1000 L. Fig. 6 a shows the time profile of reduction of TOC in one typical experiment (ozone dosage 65 gms/hr, flow rate of 5 LPM, 6 hour of operation). It can be noticed that within 3 hours TOC could be reduced from 123 ppm to around 40 ppm. It is also noticed that further increase in residence time beyond 3 hours is not needed. Systematic experiments at 1000 L scale proved that a faster kinetics is obtained at higher ozone dosage (Fig. 6 b) while presence of H₂O₂ (0.1 vol %) does not make any significant difference in kinetics of TOC reduction (Fig. 6 c). These experiments suggest recommending a higher ozone dosage. However, an excessively high ozone dosage would result in increased investment costs. Therefore, a dosage

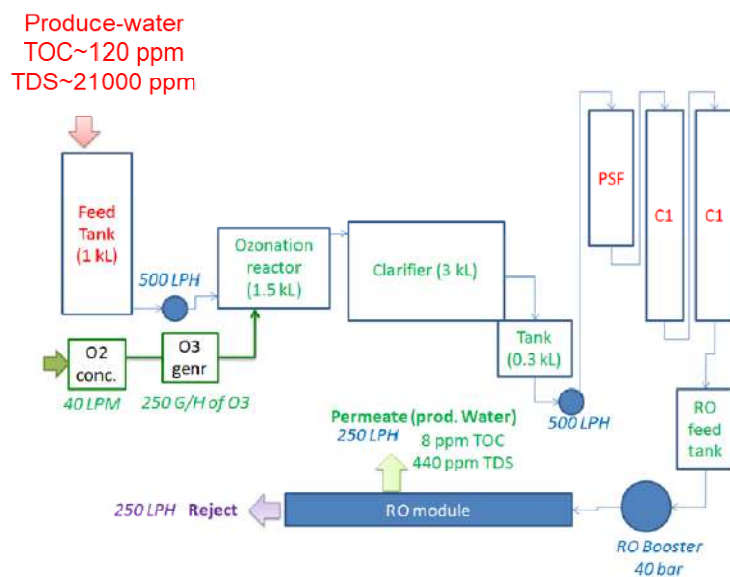


Figure 4: process flow diagram of AEWTP



Figure 5: Photograph of AEWTP ranging from 130 to 150 g/hr is deemed sufficient to reduce TOC to approximately 35-40 ppm for a 1000 L scale of operation. Consequently, for continuous operation utilizing the entire reactor volume (1500 L), an ozone dosage of approximately 250-300 g/hr is recommended.

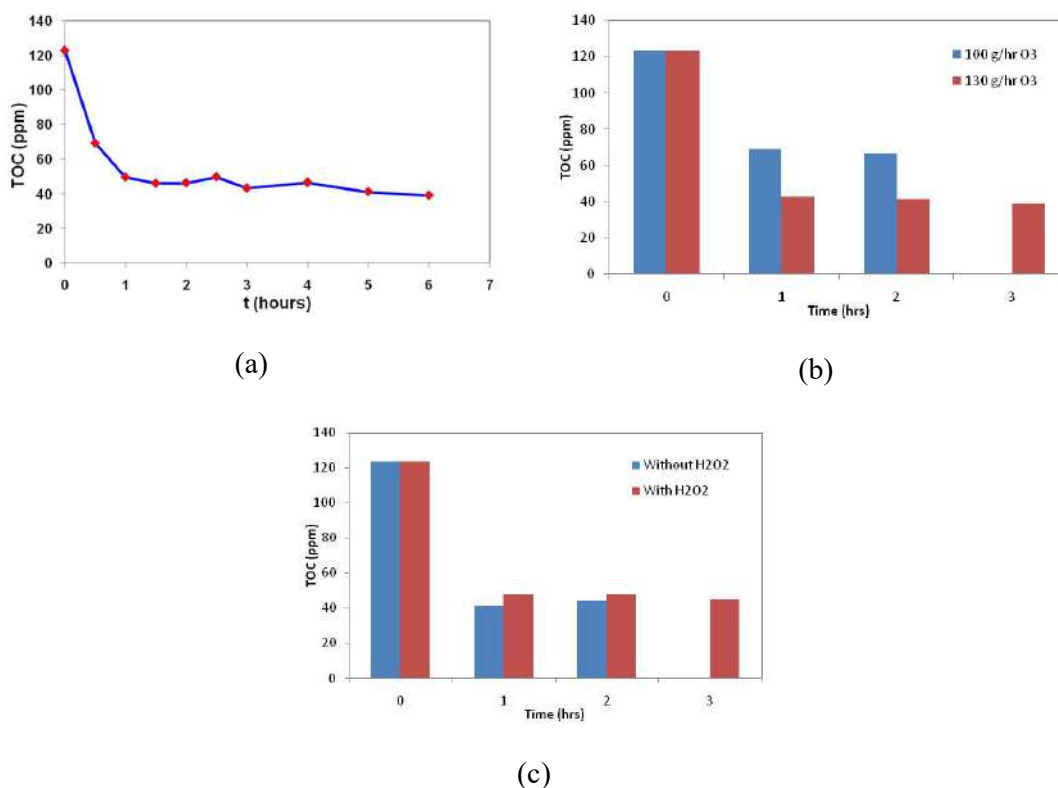


Figure 6: a) Variation of TOC of produce-water with time at 1 kL scale, b) effect of ozone dose rate on TOC reduction and c) effect of presence of H₂O₂ on TOC reduction

Table 3 below presents the averaged results of the treated water immediately at the exit of the ozonation reactor and RO permeate. Key parameters such as TOC, COD, and BOD₅, which are relevant in terms of discharge limits, are recorded. Visually, the product obtained at the exit of the ozonation reactor appears colorless, whereas the feed (produce-water) exhibits coloration (Fig. 7). Rated specific power consumption of the plant is 15.5 kW-hr/m³ of feed processed.

Table 6: Characterisation of feed, intermediate and final product

	Feed	Exit of ozonation reactor (first step)	Exit of RO unit (final step)
TOC (ppm)	120	50	8
TDS (ppm)	20700	20529	404
COD (ppm)	215	140	10.28
BOD ₅ (ppm)	42	34.8	14
pH (-)	8.5	8.7	7.4
EC (micro S/cm)	~35000	~35000	811

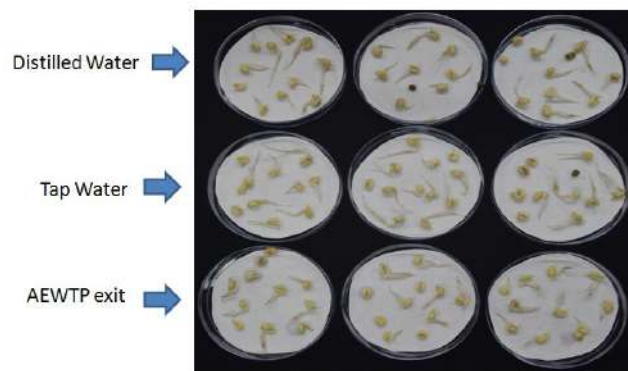
Results show approximately 60% TOC removal and 35-40% COD removal after the ozonation step. Following the RO stage, COD and BOD5 in the permeate measure around 10 ppm, indicating water suitability for irrigation. Although the ozonation step does not affect TDS, the RO unit achieves nearly 98% solute rejection. In fact, the quality of the product water is comparable to that of potable water.



Figure 7: Photograph of AEWTP in operation.

5.0 Suitability of AEWTP product water for agricultural use

The product water (obtained as RO permeate) is evaluated for its suitability in agricultural applications. Germination studies involving "mung" seeds are conducted using tap water, distilled water, and AEWTP product water. Results, along with snapshots of germinating seeds on a petri dish, are depicted in Fig. 8 (a-c). The findings distinctly demonstrate that AEWTP product water performs equivalently to distilled water in terms of shoot vigor index and germination rates. In fact, the shoot vigor index appears to be higher for AEWTP water. The results mentioned in this section are prepared in collaboration with NABTD, BARC



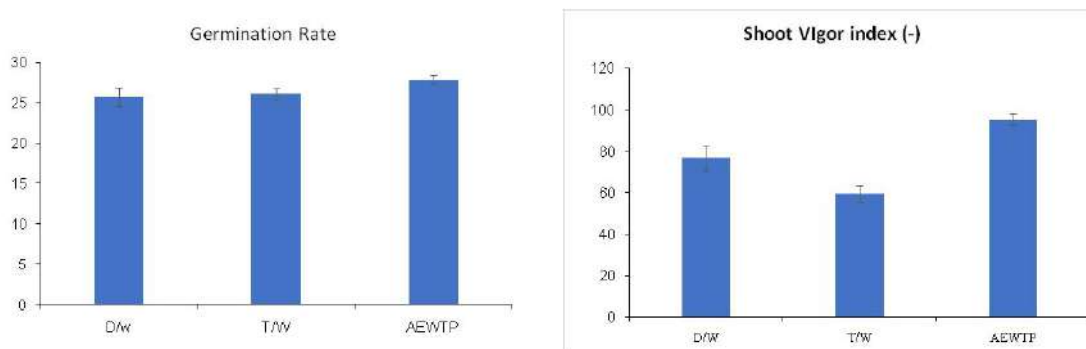


Figure 8: a) Photograph of germinating seeds b) germination rate and c) shoot vigor index in three types of water namely distilled water, tap water and AEWTP product. *(In collaboration with NABTD, BARC)*

Thus it can be concluded that the product from AEWTP (10 m³/day capacity) is able to produce water (5 m³/day capacity) that is suitable for irrigation purpose.

6.0 Conclusion

A multipronged approach is employed to treat dissolved oil contaminated produce-water from on-shore oil producing site (Mehsana), rendering it suitable for irrigation/agriculture. Various methods are compared, and the selected process flow sheet comprises primary, secondary, and tertiary treatment steps. O₃-based AOP is chosen as the primary step, activated carbon-based adsorption columns serve as secondary polishing steps, while reverse osmosis is utilized as the final tertiary step to remove salinity/TDS. Each step is individually optimized at bench-scale, with three different ozone dispersion equipment tested, and the most optimal one (regenerative turbine pump) selected based on achieving a chemical free “ozone only” process. Drawing from laboratory and bench-scale experience, a pilot-scale plant (Advanced Effluent Water Treatment Plant, AEWTP) is designed, fabricated, and commissioned. The unit, comprising all three stages, processes 10 kL of produce-water (TOC120 ppm, TDS21,000 ppm) in a continuous manner. The final product of AEWTP has a TOC and TDS content of <10 ppm and ~400 ppm, respectively, making it suitable for irrigation and/or potable use. The nameplate capacity of AEWTP is 10 m³/day (20-hour operation per day) with a rated power consumption of 15.5 kW. The plant footprint area is approximately 50 m². Product water from AEWTP is tested for germination of “mung” seeds and found to perform as well as, if not better than, distilled and tap water.

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Oxidative Treatment of Industrial Waste Streams Contaminated by Toxic and Recalcitrant Organics

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Abstract

In this short review article, the working principle and advantages of three advanced oxidation processes (AOPs), namely, Fenton's oxidation, electro-persulphate oxidation and wet oxidation are highlighted. These processes are capable of degrading toxic and hazardous organic pollutants. However, there are some limitations associated with each of these processes. One of the major limitations is recovery and recycling of soluble metal catalyst which is generally used to increase reaction rate. Hence, more research is required to address the issues.

1. Introduction

Treatment of industrial waste streams containing hazardous pollutants is challenging worldwide. These pollutants may include organic, inorganic or a combination of both. Several methods have been suggested for the removal of such pollutants. Some of which destroy or degrade the pollutant whereas the others just concentrate the pollutants in other phase (solid or liquid) leading to change in phase of the concerned pollutant(s). Both types of processes are capable to make the wastewater suitable for downstream biological methods, if required. The oxidation and reduction processes are used to degrade the organic pollutants while adsorption transfers the pollutant from liquid to solid phase. This short paper is focussed on oxidative treatment of persistent and toxic organics present in industrial wastewater.

Advanced oxidation processes (AOPs) generally oxidize the organic pollutants into simpler low molecular weight organics and gaseous products (e.g., CO₂). The processes can be designed to only partially degrade the organics if either resource recovery is targeted or the residual stream is to be subjected to eco-friendly biological process for further removal of pollutants. The AOPs have capability of destroying the pollutants completely for which severe reaction conditions are generally required. Alternatively, hybrid systems may also be explored. However, the selection of appropriate process primarily depends upon the wastewater characteristics. The AOPs are gaining attention due to capability of destroying various recalcitrant organic pollutants (Liu et al., 2014). For an efficient AOPs, free radicals should be produced which are responsible for the degradation of pollutants.

The current trend is to partially treat the wastewater so that the concept of circular economy and resource recovery could be strengthened. Using this approach, not only the cost of AOP is reduced but also recovery or utilisation of intermediate (primarily low molecular weight carboxylic acids and macromolecules) is also possible.

The mechanism and applicability of the following AOPs are discussed in subsequent sections: Fenton's oxidation, electro-persulfate oxidation and wet air oxidation.

2. Fenton's Process

Fenton's oxidation is a process which utilizes ferrous ions (Fe^{2+}) and H_2O_2 as catalyst and oxidant, respectively. A combination of the catalyst and oxidant is called as Fenton's reagent. Fenton's oxidation process involves the activation of H_2O_2 to form hydroxyl radicals by iron salts for the destruction of organic pollutants in water. This was first described by H.J.H. Fenton, for the oxidation of tartaric acid by Fenton's reagent (Fenton, 1894).

Following reactions may happen during Fenton's oxidation (Babuponnusami and Muthukumar, 2014).



Initially, the reaction between ferrous iron with hydrogen peroxide induces hydroxyl radicals ($\text{HO}\cdot$). The hydroxyl radicals ($\text{HO}\cdot$) thus generated (oxidation potential = 2.8 V) are stronger oxidant than H_2O_2 . They may react with Fe^{2+} , H_2O_2 or organics. However, the generation of hydroxyl radicals also depends on conversion of Fe^{3+} to Fe^{2+} ions. The rate of equation (2) is very low and often it is considered rate limiting step. The weaker hydroperoxyl radicals ($\text{HO}_2\cdot$) generated according to equation (2) can also oxidize organics. In addition, reactions presented in equations 3-5 may also happen. The $\text{HO}\cdot$ radicals may also be scavenged by ferrous ions, hydrogen peroxide, hydroperoxyl radicals and hydroxyl radical (equations 6-9).

The efficiency of Fenton's process mainly depends on pH, initial concentration of pollutant, temperature, H_2O_2 concentration, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio and reaction time (Barbusinski, 2009).

The process shows optimum performance at wastewater pH of 2-4. If the wastewater pH is more than 5.0 then formation of ferric hydroxo complexes decrease concentration of free soluble iron (Fe^{2+}) thus reducing efficiency (Kang and Hwang, 2000). In case of highly acidic pH conditions (i.e., $\text{pH} < 2$), the reaction is adversely affected due to formation of stable oxonium ions $[\text{H}_3\text{O}_2]^+$ (Kwon et al., 1999; Babuponnusami and Muthukumar, 2014).

The process is considered suitable for hazardous organic pollutants present in low to medium strength wastewaters having chemical oxygen demand (COD) up to 8000 mg/L (Fryda et al., 2003). The energy cost for the process is lower than ozone and UV based AOPs (applicable for similar strength wastewaters). In addition, equipment used for Fenton's oxidation is simple and the reaction is allowed to occur at low temperatures (generally ambient) and atmospheric pressures (Kavitha and Palannivelu, 2004).

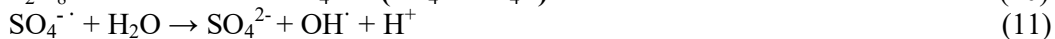
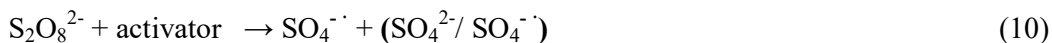
The major limitations of the process are requirement for narrow operating pH range, difficult iron recovery and recycling and production of large amount of sludge.

3. Electro-persulphate (EPS) oxidation

The AOPs based on sulphate radicals ($\text{SO}_4^{\cdot -}$) are also gaining attention in recent times due to the superior performance over $\text{HO}\cdot$ radicals (Hussain et al., 2012). The longer half-life of $\text{SO}_4^{\cdot -}$ radicals (30-40 μs) compared to $\text{HO}\cdot$ radicals (20 ns), higher redox potential (2.6-3.1 V), high solubility and stability render it beneficial for the degradation of organic pollutants (Lee et al., 2020; Karim et al., 2021). The $\text{SO}_4^{\cdot -}$ radicals can be produced in-situ by the activation

of persulphate (PS) which includes both peroxymonosulphate (PMS) and peroxydisulphate (PDS). Highly reactive $\text{SO}_4^{\cdot -}$ radicals are produced by cleavage of peroxy bonds (O-O).

The persulphate ions can be activated by the cleavage of O-O bond electrochemically to produce highly active $\text{SO}_4^{\cdot -}$ radicals (equation 10). It has been reported that the $\text{SO}_4^{\cdot -}$ radicals may react with water over a wide range of pH to produce other radicals (Zhi et al., 2020) as shown in equation 11.



In order to improve performance of EPS treatment, iron can be used as catalyst which may trigger electrochemical activation of persulphate. The transition metal is considered a good choice due to its low cost, easy availability and low toxicity. Iron may be used as a sacrificial anode to activate persulphate. The Fe^{2+} ions released from the anode can be regenerated due to the reduction occurring at the cathode. The in-situ generation of Fe^{2+} requires low energy input along with increase in the utilisation efficiency of Fe^{2+} and persulphate (Cai et al., 2018). Since Fe^{2+} ions are found at anode, cathode and bulk solution, the $\text{SO}_4^{\cdot -}$ radicals can be produced in large concentration. Yuan et al. (2014) reported two-step activation process for persulphate using ferrous ions – (i) from the corrosion of Fe^0 and (ii) from the cathodic reduction of Fe^{3+} . Although the persulphate ion can directly degrade a few organics like phenol, the extent of degradation is expected to be low due to its lesser oxidation potential ($E^\circ = 2.01 \text{ V}$) in comparison to that of the $\text{SO}_4^{\cdot -}$ radicals (Matzek and Carter, 2016).

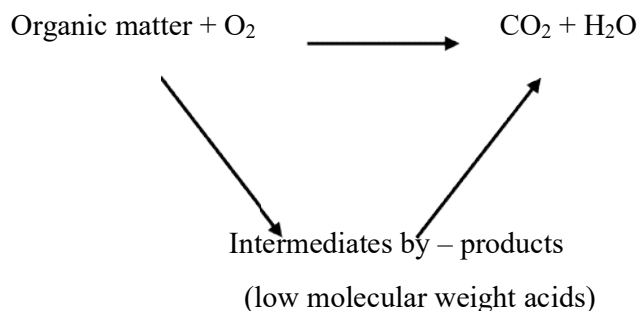
The electrochemical techniques are considered clean and can be applied to the waste streams containing COD up to 100 g/l (Fryda et al., 2003). The technique results minimize secondary pollution in terms of excessive dissolved metal concentration and less or no sludge generation.

4. Wet Oxidation (WO) Process

The WO is another oxidation process which is performed at elevated temperatures (125 - 320°C) and pressure (0.5 - 20 MPa) conditions for the destruction of organics and inorganics (Mishra et al., 1995). The primary objective of the process is to transform highly concentrated waste streams into biodegradable wastewaters. High pressures and temperatures are applied in order to keep the wastewater in liquid phase and to enhance oxygen solubility. The oxidation reactions are exothermic in nature therefore the process becomes self-sustainable in case of high strength waste streams (COD > 10000 mg/L) (Tungler et al., 2015). The economic feasibility of this process is considered to be challenging due to the requirement of high temperature and pressures. However, use of a suitable catalyst brings down the severity of temperature and pressure conditions.

The WO process carried out in presence of catalyst is known as catalytic wet oxidation (CWO). Two types of catalysts are suggested for the process, namely homogeneous and heterogeneous. Homogeneous catalysts are dissolved in the wastewater and the active metal specie interact with pollutants and oxidant to produce active $\text{HO}^{\cdot}$ radicals. In the presence of heterogeneous catalyst, the reaction occurs at the surface of catalyst. The pollutant and oxidant first adsorb on the catalyst and interact with the active metal specie. Subsequently, the intermediates and/ or end products desorb from the surface and provides active sites for the other molecules. The advantage of heterogeneous CWO process is possibility of recycling of the catalyst which is very difficult in case of homogeneous CWO. In the latter case, an additional process is required to remove dissolved metals.

The simplified oxidative degradation pathways for organic pollutants is shown in Figure 1.



WO reaction occurs via $\text{HO}^\cdot$ radical mechanism, which occurs through three-step chain reaction (Bhargava et al., 2006). The steps are: (i) Initiation (ii) Propagation, and (iii) Termination. Some representative reactions are presented below as equations 13-17.

Initiation



Propagation



Termination



where R is alkyl group.

The current trend is to apply WO process as a pretreatment step for treatment non-biodegradable waste in order to convert it into easily biodegradable wastewater so that economics of the process is improved (Garg and Mishra, 2010; Yadav and Garg, 2012; Chandra et al., 2014; Lal and Garg, 2014; Bohite and Vaidya, 2018; Chowdhary et al., 2018; Khatri and Garg, 2021).

5. Summary

The AOPs are potential options for the transformation or destruction of organic and inorganic pollutants which are recalcitrant in nature. Generally, these processes rely on generation of free radicals particularly $\text{HO}^\cdot$ radical which has high oxidation potential. The major issue with $\text{HO}^\cdot$ radicals is of their very less half life. To compensate this problem, the radicals should keep forming in the process which can be promoted by using a suitable catalyst and/or another radical such as $\text{SO}_4^{\cdot-}$ radicals should be produced. The catalyst should be recovered and recycled to make the process economically feasible. Though many research studies have been published on AOPs, still the identification of suitable catalyst(s) at industry level particularly for EPS and wet oxidation has to be accomplished. Given to the current

regulatory policies, AOPs are seen as the most promising options for hazardous waste streams. Hence, the gaps in these processes need to be addressed.

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