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Kishor, Roop, Purchase, Diane ORCID logoORCID: <https://orcid.org/0000-0001-8071-4385>,
Saratale, Ganesh Dattatraya, Saratale, Rijuta Ganesh, Ferreira, Luiz Fernando R., Bilal,
Muhammad ORCID logoORCID: <https://orcid.org/0000-0001-5388-3183>, Chandra, Ram and
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Ecotoxicological and health concerns of persistent coloring pollutants of textile industry wastewater and treatment approaches for environmental safety

Roop Kishor ^a, Diane Purchase ^b, Ganesh Dattatraya Saratale ^c, Rijuta Ganesh Saratale ^d, Luiz Fernando Romanholo Ferreira ^{e,f}, Muhammad Bilal ^g, Ram Chandra ^a, Ram Naresh Bharagava ^{a,*}

^a *Laboratory of Bioremediation and Metagenomics Research (LBMR), Department of Microbiology (DM), Babasaheb Bhimrao Ambedkar University (A Central University), Vidya Vihar, Raebareli Road, Lucknow 226 025 U.P., India*

^b *Department of Natural Sciences, Faculty of Science and Technology, Middlesex University, The Burroughs, Hendon, London NW4 4BT, England, UK* ^c *Department of Food Science and Biotechnology, Dongguk University, Ilsandong-gu, Goyang-si, Seoul, Gyeonggi-do 10326, Republic of Korea*

^d *Research Institute of Biotechnology and Medical Converged Science, Dongguk University, Ilsandong-gu, Goyang-si, Seoul, Gyeonggi-do 10326, Republic of Korea* ^e *Graduate Program in Process Engineering, Tiradentes University (UNIT), Av. Murilo Dantas, 300, Farolandia, 49032-490 Aracaju-Sergipe, Brazil* ^f *Institute of Technology and Research (ITP), Tiradentes University (UNIT), Av. Murilo Dantas, 300, Farolandia, 49032-490 Aracaju-Sergipe, Brazil* ^g *School of Life Science and Food Engineering, Huaiyin Institute of Technology, Huaian 223003, China*

ABSTRACT

Textile industry wastewater (TIWW) is considered as one of the worst polluters of our precious water and soil ecologies. It causes carcinogenic, mutagenic, genotoxic, cytotoxic and allergenic threats to living organisms. TIWW contains a variety of persistent coloring pollutants (dyes), formaldehyde, phthalates, phenols, surfactants, perfluorooctanoic acid (PFOA), pentachlorophenol and different heavy metals like lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn) and nickel (Ni) etc. TIWW is characterized by high dye content, high pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS), total suspended solids (TSS), total organic carbon (TOC), chlorides and sulphates. Thus, requires adequate treatment before its final discharge into the water bodies to protect public health and environment. The treatment of TIWW is a major challenge as there is no particular economically feasible treatment method capable to adequately treat TIWW. Therefore, there is a need to develop a novel, cost-effective and eco-friendly technology for the effective treatment of TIWW. This review paper emphasizes on the different textile industry processes, wastewater generation, its nature and chemical composition, environmental impacts and health hazards and treatment approaches available for TIWW treatment. It also presents various analytical techniques used to detect and characterize TIWW pollutants and their metabolites, challenges, key issues and future prospective.

Keywords:

Textile industry, Wastewater, Persistent coloring pollutants, Environmental and health concern, Treatment approaches

* Corresponding author. (R.N. Bharagava) *E-mail addresses:* bharagavarnbbau11@gmail.com, ramnaresh_dem@bbau.ac.in

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1. Introduction

The textile industries (TIs) are the major sources of the global economy in many countries like China, India, Pakistan, Brazil, Bangladesh and Malaysia, but unfortunately, these are also the major sources of environmental pollution [1,2]. TIs utilize a large volume of potable water and a wide range of synthetic chemicals at different stages during the textile production process [3,4]. TIs generate a large quantity of highly colored wastewater containing a variety of hazardous persistent coloring pollutants (PCPs) that goes into the aquatic resources [5–7]. In major textile countries, the wastewater/effluent is discharged into the rivers, which finally opens into the sea. For example, in India, Kanpur city is a major hub of textile industries that discharges large volumes of wastewater into drains and canals, which opens into the Ganga River and finally, emptying into the Bay of Bengal [5].

Thousands of synthetic dyes are used in TIs during the dyeing process. Globally, $\sim 7 \times 10^7$ tons of different dyes is produced annually, and more than 10,000 tons of synthetic dyes are used in TIs [8]. Besides dye molecules, textile industry wastewater (TIWW) also contains a high load of salts, alkalis, binders, dispersants, volatile organic compounds

(VOCs), surfactants, chlorobenzenes, reducing agents, dioxin, phthalates, phenols, pentachlorophenol, detergents and heavy metals [9–11]. This TIWW, if discharged directly into the water bodies, causes serious environmental threats and toxic effects in living beings.

Different natural fibres such as jute, cotton, silk, wool and a variety of synthetic fibres like polyamide, polyester, viscose, nylon and acrylic are used by TIs [12,13]. A large number of highly toxic chemicals such as sizing, brightening, anti-creasing, sequestering, stabilizers, softening and finishing agents are used in TIs at different stages [2,14]. In addition, many synthetic dyes such as azo, vat, direct, reactive, sulphide, acidic and basic dyes are extensively used in TIs. These dyes are not totally attached to the target fibres during textile dyeing process and get discharged into the aquatic resources like river, pond, streams and lakes along with the wastewater [15,16]. Dyes are hazardous chemicals for environment and human health. An overview of different stages of wastewater generation in TIs, its toxicity in human health and environment and various treatment approaches are summarized in Fig. 1.

TIWW has a very complex matrix and contains a variety of aromatic compounds, color content and toxic metals like arsenic (As), lead (Pb), chromium (Cr), antimony (Sb), cadmium (Cd) and mercury (Hg) [6,8]. Heavy metals are used in the production of color pigment of textile dyes [11,12]. These pollutants are transported to a long distance along with the wastewater, persist in environment (water/soil) for long period of time and pose severe health hazards in living organisms as well as decrease soil fertility and photosynthetic activity of aquatic plants leading to the development of anoxic conditions for aquatic fauna and flora both [3,6,17]. Thus, there is an urgent need to develop cost-effective and eco-friendly treatment approaches for the adequate treatment of TIWW before its final disposal into the environment. Therefore, this review paper provides a detailed knowledge on different textile processing steps, wastewater generation, its nature and chemical composition, environmental impacts and health hazards along with the various existing and advanced treatment technologies for the better management of TIWW for the environmental sustainability. It also presents various analytical techniques used to detect and characterize the TIWW pollutants and their metabolites produced during the wastewater treatment processes, key issues and challenges.

2. Textile industries: an overview

Globally, TIs contribute ~ 120 million employments directly and market share of value around \$2000 billion worldwide. In India, TIs are amongst the oldest industries in the country and the world's second largest groups of producers of textile products/fabrics. India shares $\sim 5\%$ of the global export and nearly 5% of the global textile and apparel trade. In India, ~ 3400 textile units contribute to $\sim 4\%$ of the country's National's Gross Domestic Product (GDP), 27% of the country's export income and $\sim 14\%$ of the overall Index of Industrial Production-IIP [1, 6]. These industries also act as the second largest group of employers after agriculture, providing ~ 45 million direct and 60 million indirect employment to both rural as well as urban peoples [1,18]. Currently, the size of Indian textile market estimates to be $\sim$ US\$ 108 billion and expected to reach $\sim$ US\$ 209 billion by 2021 [1]. Moreover, TIs also share nearly 24% of the world's spindle capacity, 8% of the global rotor capacity and have the highest loom capacity with 61% of the world's market share economy.

Fig. 1. Processing in textile industry, wastewater generation, its toxicity and various treatment approaches.

2.1. Different stages, processes and chemicals used in TIs

Textile manufacturing is a complex process, which involves different stages and chemicals in the production of a variety of products [7,14,19, 20]. These stages require large volumes of water and chemicals. The different stages of textile manufacturing processes are as below.

2.1.1. Sizing

It is the first step in production of textile from man-made or natural fibres like polyester, silk, jute, cotton and wool by adding special carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), polyacetate and polycyclic acids. These substances provide the high potency to fibers.

2.1.2. Desizing

It is the second step, which uses enzymes and many auxiliary chemicals to remove unwanted chemicals and sizing materials and enhance the absorbency of fibres. Currently, bacterial enzymes and mineral acids are more prevalent than traditional methods in desizing applications.

2.1.3. Scouring

It is a cleaning process used to remove impurities from fibres. In this process, alkali agents such as glycerol, ethers, sodium hydroxide, detergent, or soap are used for the removal and washing of impurities like fats, waxes, oils, and surfactants as well as non-cellulosic materials.

2.1.4. Bleaching

It is a chemical process used for the removal of unwanted coloring materials from fibres. Currently, H_2O_2 and peracetic acid are used as bleaching agent to enhance the whiteness of fibers.

2.1.5. Mercerization

In this process, cold or hot caustic soda (NaOH) is extensively used to improve the physical and chemical properties of fibres namely lustre, strength, dyes affinity and fibre's appearance.

2.1.6. Dyeing and printing

At this stage, a variety of auxiliary chemicals are used to improve the attachment of dye molecules with fibres. Dyeing is the major process in textile production industries for the addition of colors to fabrics. Different dyes such as azoic dye, vat dye, reactive acid dye, sulfur dye, basic dye, direct dye, pigments and metal complex dyes are extensively used in TIs worldwide [6,11,15]. Phthalates, dyes, metals, solvents, formaldehyde and urea are commonly used in printing stage [12].

2.1.7. Finishing

It is the final stage of textile production process in which different types of protecting and maintenance chemicals such as biocides, synthetic organic or inorganic chemicals are used to improve and maintain the specific properties of fibers like stain proofing, softening, water proofing, flame retardance and protection from microbial activities as well as UV damage.

2.2. Wastewater generation and its characteristics

TIs discharge large volumes of highly colored and potentially toxic wastewater. In India, ~ 830 million m^3 /year of ground water is used and ~ 640 million m^3 /year of wastewater is discharged [21]. While in China, $\sim 8.65 \times 10^9$ m^3 /year of ground water is used and $\sim 1.84 \times 10^9$ m^3 /year of wastewater is discharged by the TIs [22]. It is estimated that China, United States and United Kingdom annually discharge ~ 26.0 , 12.4 and 1.0 million tons of textile waste, respectively [23]. In TIs, dyeing and washing stages are the major sources of wastewater generation. A normal TI generally consumes ~ 1.6 million liters of ground water to produce 8000 kg of textile fabric per day, out of which ~ 30 – 40% water is used in dyeing process, 60 – 70% of washing stage and ~ 10 – 50% of unused dyes are released into the aquatic resources along with the generated wastewater [6,12,20]. The printing, bleaching, scouring and finishing processes in TIs also discharge a large volume of wastewater upto 1 – 10 million liters per day. According to the World Bank, ~ 17 – 20% of wastewater is released into the environment from the dyeing and finishing processes [6].

More than 2000 – 22000 kg of highly toxic acidic dyes is discharged from the washing process of polyamide textiles and ~ 2000 – 22000 kg of direct dyes is released from the washing stage of cotton manufacturing industries [24]. In addition, more than 500 tons of dyestuffs are also discharged along with the wastewater released from the TIs. TIWW is characterized by the high dye content, high temperature, pH, BOD, COD, TDS, TS, SS, TOC, TSS, chlorides and phosphate etc. [8,25,26]. TIWW also contains sulphates, nitrates, electrical conductivity, turbidity, alkalinity, salts, acid, bases, mordants, surfactants, VOCs, chlorobenzenes, phenols, dioxin, bleaching, fixing, and finishing agents along with various metals like Cr, Cd, Pb, Sb, As, Cu, Ni and Zn etc. [6, 11–13,17,26,27]. However, the nature and chemical composition of TIWW is largely depends on the chemicals used as well as processes adopted by the TIs. The physico-chemical characteristics of TIWW reported by various researchers are given in Table 1.

2.3. Persistent coloring pollutants (PCPs) in TIWW

TIs discharge a variety of PCPs (dyes) along with the wastewater into the aquatic resources, which act as a major sources of environmental pollution and health hazards [18,20]. Globally, $\sim 280,000$ tons of different synthetic dyes are discharged from TIs into the environment [15]. Dyes are synthetic organic compounds that are used to add color to substrate like cloth, paper, leather and other objects. Textile dyes are aromatic, heterocyclic and persistent in nature and possess different chromophore groups such as azo ($-\text{N}=\text{N}-$), nitro ($-\text{N}=\text{O}$), carbonyl ($-\text{C}=\text{O}$), quinoid groups and auxochrome groups like hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$), amine ($-\text{NH}_2$) and sulphonate ($-\text{SO}_3\text{H}$) etc. [6,18]. Dyes such as methyl orange, congo red, methylene blue, azure B, reactive dye, direct red, remazol red, scarlet, malachite green, acid orange and remazol brilliant blue R are extensively used in TIs [2,7]. These dyes are highly resistant to light, water, chemicals, detergents and microbial activities [6,19].

Textile dyes are mainly categorised into two groups: natural and man-made or synthetic dyes. Natural dyes are environment friendly, but are little used in dying process, whereas synthetic dyes are used extensively, but unfortunately are not eco-friendly due to their complex and stable structure, resistant for microbial degradation, hazardous effects on environment and living organisms [4,40]. Synthetic dyes are used in textile, leather, paints, photographs, dyeing, paper, food, cosmetic, plastic, prints, carpet and medicine industries due to their bright colors, chemical stability, excellent color fastness and easy applications [40, 41]. Based on their molecular structures, particle charges and application methods, dyes can be classified into different groups.

Based on the molecular structures, textile dyes are classified into azo dyes (congo red, methyl orange and reactive black 5), indigoid dyes (acid blue 71 and vat red 6), anthraquinone dyes (alizarin, reactive blue 4 and acid blue 25), triarylmethane dyes (basic red 9, malachite green and crystal violet) and nitro and nitroso dyes (naphthol yellow S and mordant green 4). Based on charges, dyes are classified into the anionic dyes (methyl orange, direct and acid dyes), and cationic dyes (methylene blue, crystal violet) and neutral dyes (dispersed dyes) [6,13]. Among these dyes, azo dyes are the largest and most versatile group of synthetic dyes accounting $\sim 80\%$ of total dyes used in TIs. According to Sarayu et al. [42], ~ 3500 different synthetic dyes are used in various industries, out of which, $\sim 84\%$ belong to the sulphonate azo dye group. Besides above-mentioned PCPs, many other

pollutants such as active substances, reducing surfactants, inhibitors, salts, phenols, phthalates, fixing agent, bleaching, finishing agents and detergents are also reported to be present in TIWW.

Table 1

Physico-chemical characteristics of a typical textile industry wastewater.

Parameter	Recorded value	References
pH	8.75 ± 1.29	[8,14,25,28]
EC	7.1 ± 1.72	[14,25,29,30]
COD	1268 ± 121	[31,32,33,34]
BOD	237.2 ± 32.1	[25,35,29,34]
TDS	8850 ± 756	[27,31,32,34]
TSS	253.2 ± 43.5	[25,29,33,36]
TS	5076 ± 344	[25,29]
TOC	222.2 ± 53.3	[4,14,25,29] [36–38]
Cl ⁻	51.6 ± 16	
Alk	396 ± 132	[36,37]
NO ₃ ⁻	116.1 ± 109	[37,30]
SO ₂₋₄ ⁻	240.6 ± 75.4	[14,25,28,37]
PO ₄₃ ⁻	12.4 ± 3.2	[25,29,33,36]
TN	24.4 ± 11.7	[25,29,33,36]
Cr	2.74 ± 0.4	[8,11,32,39]
Cd	0.62 ± 0.3	[8,11,25,29]
Pb	0.35 ± 0.3	[8,31,32,30]
Phenol	0.52 ± 0.22	[14,25,29]
Zn	0.37 ± 0.37	[11,14,30]
Cu	0.54 ± 0.5	[11,30]
As	2.21 ± 0.4	[8,31,32,39]

Note: All the values are means of triplicates (n = 3) ± SD.

*Except pH, all the parameters are expressed in “mgL⁻¹”, but the conductivity is expressed in “µmho/cm”.

*EC: Electrical Conductivity; BOD: Biochemical Oxygen Demand; COD: Chemical Oxygen Demand;

TDS: Total Dissolved Solids; TSS: Total Suspended Solids; TOC: Total Organic Carbon; TS: Total solids; Alk.: alkalinity.

Table 2

Application and toxicity of different chemicals used in textile industries.

Chemicals	Applications	Toxicity
Chlorinated solvents e.g. Trichloroethane (TCE)	Applied in scouring of fabric (removal of impurities from fibres)	Affect central nervous system, liver, kidneys and also may interfere with atmospheric activities (ozone-depletion)
Carbon disulphide (CS ₂)	Applied in manufacturing of viscose rayon fibres	Neurological and psychiatric symptoms, gastrointestinal and sexual disorders, reproductive toxicity, birth defects, leukaemia, chronic skin conditions, kidney diseases
Alkylphenols, nonylphenol ethoxylates (NPEs) and nonylphenols (NPs)	Applied as scouring agents (wool), laundry detergents, emulsifiers and dye-dispersing agents for dyes, and also to protect or stabilise polymers	Highly toxic to aquatic life and disrupt endocrine system in humans/animals, increased incidence of breast cancer, abnormal growth patterns and neuro-developmental delays in children
Chlorobenzenes (e.g. hexachlorobenzene (HCB))	Applied as dyeing carrier, dyestuff, and in preparation of azo pigments	Carcinogenic (Group 2B possibly human carcinogen as per International Agency for Research on Cancer (IARC)) International Agency for Research on Cancer (IARC), affect liver, thyroid and central nervous system and also an endocrine disruptor
Phthalates (DINP: di-isononyl phthalate, and BBP: butyl benzyl phthalate)	Applied in printing and dyeing operations and coating of textiles to makes the cloths soften	Carcinogenic, endocrine disrupters and aquatic toxicant, affect reproductive system and impair fertility
Heavy metals (Sb: antimony, Cd: cadmium, Pb: lead, Hg: mercury, As: arsenic, Ni: nickel and Cr: chromium = priority pollutants)	Applied in preparation of pigments and dyes applied in colouring of textiles	Genotoxic, carcinogenic and mutagenic, reproductive disorders, DNA damage, damage blood cells, kidney, liver and environmental damage
Azo dyes (e.g. methyl nitro, orange, remazol, reactive dyes etc.)	Applied in dyeing of textile fibres, mainly for cotton but also viscose, silk, wool and synthetic fibres	Carcinogenic, mutagenic, and genotoxic, aquatic toxicant, adverse effects include allergic dermatoses, respiratory diseases asthma, and variable immunoglobulin levels
Organotin compounds (DBT: dibutyltin, TBT: tributyltin, and TPhT: triphenyltin)	Applied as biocide to prevent the heavy duty textiles and reduce body odour posed by the microbial breakdown of sweat	Affect immune and reproductive systems, severe skin, eye and mucous membrane irritation, muscular weakness and breathing problems
Perfluorinated chemicals (PFCs): perfluorooctane sulphonate (PFOS), a banned persistent organic pollutant (POP) in Stockholm Convention	Applied to make the textiles both water and stain- proof	Carcinogenic, affect liver and immune, endocrine and reproductive system, reduced birth weight, fertility and sperm quality, attention deficit hyperactivity disorder (ADHD), changes in thyroid hormone levels and increased total and non-HDL (bad) cholesterol levels
Formaldehyde	Applied in textile finishing (to make cloths softer, water-resistant, and more crease-resistant and prevent shrinking)	Human carcinogenic as per IARC, National Cancer Institute (NCI) and U.S. Environmental Protection Agency (EPA), allergies, skin irritant, dermatitis, irritate mucous membranes and the respiratory problems
Volatile organic compounds (VOCs: toluene, methyl isobutyl ketone, xylene, methyl ethyl ketone, dichloromethane, 1,1,1-trichloroethane)	Applied in preparation of solvent-based inks or pastes used during printing and drying of textiles	Off-gassing is a major problem for workers (occupational exposure), skin/eye irritation, depression such as dizziness, nausea, headaches, drowsiness, tremors, slurred speech, staggering, weakness and personality changes and toes to unconsciousness and numbness in the fingers and repeated exposure to moderate to high amount may cause kidney and liver damage
Short-chain chlorinated paraffins (SCCPs): classified as POPs under Stockholm Convention	Applied as a flame retardant, waterproof and rot- proof to heavy textiles, like military tents	Bio-accumulative nature, aquatic toxicant, endocrine disruptor, affect kidney, liver and thyroid gland, and may cause cancer (Group 2B probable human carcinogen as per IARC)
Chlorophenols (e.g. pentachlorophenol (PCP)): cauterized as group B2 probable human carcinogen as per USEPA	Applied as a preservative (fungicide) on heavy- duty textiles and fibres	Carcinogenic, affect the immune, cardiovascular and nervous system, kidney, blood, liver, and eyes and cause dermatitis
Brominated Flame Retardants (BFRs: polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecane (HBCD) e.g. hexabromobiphenyls	Applied to make textiles less flammable to prevent burning	Carcinogens, neurodevelopmental toxicity, thyroid effects, endocrine disruption, classified as POPs under United Nation Environment Programme (UNEP),
Dioxins	Applied as a preservative agent for textile fibres like cotton and other fibres during sea transit, and in cotton bleaching and also used in preparation of dyestuffs	Cancer in Lung and liver, diabetes, cardiovascular disease, early menopause, porphyria, endometriosis, reduced testosterone and thyroid hormones, altered immunologic response, tooth, skin and nails abnormalities, altered growth factor signalling and also altered metabolism
Organophosphorus compounds e.g. tributylphosphate (TBP)	Applied as a strong wetting agent and in preparation of pigment pastes used in printing	Eye, nose and skin irritation, irritation of mucous membranes, and also causes bladder cancer in rats
Silver and nano silver compounds	Application of silver nanoparticles as antimicrobial or antibacterial agents in textiles	Bacterial resistance, ecotoxicity, affect lungs, neuronal cells, lung epithelial cells, guidelines and regulations need to be developed

3. Ecotoxicological and health concern of textile industry wastewater pollutants

TIs consume large volumes of fresh water and generate huge quantity of dark colored wastewater that acts as a major source of environmental pollution [6]. TIWW usually has high BOD and COD, contains suspended and dissolved solids and various toxic metals as well as a complex mixture of PCPs, acid, base, salts and many auxiliary chemicals, making it complex and highly toxic in nature [11,17,26]. The Ministry of Environment and Forest, Government in India has documented that TIWW is the most polluting wastewater compared to the other wastewaters. Approximately 72 different types of highly toxic pollutants are present in TIWW, of which ~30 pollutants are resistant to microbial degradation leading to severe environmental and health hazards [43]. The applications and toxicological effects of different chemicals used in TIs are given in Table 2.

Various toxic metals such as Cr, Sb, Cu, Zn, Pb, Cd, and Ni are reported to be present in TIWW and affect plant growth parameters like seed germination, seedling growth as well as decrease in microbial activity/diversity [8,17]. These metals are also accumulated in living tissues through a food chain, posing severe effects on human and animal's health such as diarrhea, liver, neuromuscular, hemorrhage, dermatitis, central nervous system disorder and kidney malfunction [3,6]. The untreated or partially treated TIWW, if discharged directly into the aquatic resources, causes coloration of water leading to the reduction in the penetration power of sunlight, decrease in photosynthetic activity of aquatic plants as well as dissolved oxygen content resulting in the anoxic conditions and thus, affecting the normal life of aquatic fauna and flora [2,31,34].

The nonylphenol ethoxylates (NPEs) used as surfactants at washing stage for scouring fibres are well reported as endocrine disrupting chemicals and can lead to the hormonal imbalance in living beings [44]. Textile dyes/wastewater causes allergic reactions, carcinogenic, mutagenic and cytotoxic effects in plants, rats, fish's, molluscs, microbes as well as in mammalian cells [43]. These can also affect various organs like liver, kidney, brain, nervous system and reproductive system in human and animals [6,13,26]. Azo dyes and their various degradation products are reported to cause severe health hazards such as haemorrhage, nausea and ulceration of skin and also cause cancers of spleen and urinary bladder in human and mammalian cells [2,6]. The persistent organic pollutants (POPs) such as additives, dioxin, detergents, pesticide, phenol, surfactants, mordants, fasteners, salts, formaldehyde and finishing chemicals discharged in TIWW are also reported to be lethal to human/animal's health [7,18].

Malachite green (MG) is reported as a PCP, which severely affects human beings due to reduction in food intake, growth and fertility rate as well as damages in kidney, spleen, heart and liver [32]. It also causes increase in white blood cells (WBCs) count, anemia, decrease in red blood cells (RBC) count (dyscrasia), inflicts lesions on eyes, skin, lungs and bones [45, 46]. Because of these toxic effects, MG dye has been banned in many countries and not allowed by US Food and Drug Administration, but it is still used in several countries. Tartrazine is a type of azo dye, which is used in food, pharmaceuticals, textile and cosmetic industries and causes various health problems like allergy, asthma, skin eczema, immunosuppression, hypersensitivity, carcinogenic and mutagenic effects in living organisms [6].

Acid black 210 and its metabolite (4-nitroaniline) are characterized as a human carcinogen [47]. Azure-B dye is widely used in TIs, which intercalates within the helical structure of DNA, duplex RNA and partitions to the lipid membrane of cells [47]. Basic red 9 is a triarylmethane dye used in textile, cosmetic, leather, printing, paper and ink industries and reported as potential carcinogen [6], allergen, mutagen and skin irritating agent and also develop tumors in bladder, liver and mammary glands [43]. Bharagava et al. [5], reported that crystal violet (CV) dye is persistent in nature and known for its carcinogenic, clastogenic nature and tumor growth promoting effect in fishes. According to the International Agency for Research for Cancer (IARC), benzidine dye acts as a powerful carcinogen for living beings [49]. It is banned for more than 20 years due to its carcinogenic nature, but it is still regularly used in many countries [50]. Reactive orange (RO) and congo red (CR) dyes are extensively used in dyeing industries and reported to affect the algal and bacterial growth [32,51]. Methylene (MB) blue dye is reported to increase blood pressure, hypertension and myocardial depression [40]. Some dyes like erythrosine and xanthene are reported to cause allergic, neurotoxic, carcinogenic, xenoestrogenic and DNA damage in animals/humans [6]. According to KEMI [24], ~3500 highly toxic chemicals are commonly used in TIs during the production processes. Among these, ~1000 is registered under Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). It is estimated that ~10% of these textile chemicals are potential toxic for human health and ~5% of these substances are highly toxic to environment.

4. Various methods reported for the treatment of TIWW

A number of physico-chemical, biological and advanced oxidation methods have been reported by various researchers for the treatment of TIWWs. These approaches can be used either individually or in combination to improve/accelerate the treatment of TIWWs.

4.1. Physico-chemical treatment methods

The physico-chemical methods like adsorption and coagulation/ flocculation are reported effective for color removal from TIWW [40, 53]. The adsorption method transforms pollutants from one phase to another phase [54, 55] whereas,

coagulation/flocculation methods decolorize the selective dyes like sulfur and dispersive dyes, but are not effective in the decolorization of acid, reactive, direct and vat dye [6]. Thus, these treatment methods are not sufficient in many ways. For example, these methods are highly expensive, time consuming, less applicable and produce huge amount of highly toxic sludge as secondary pollutant, which causes serious contamination in environment and pose severe effects on human/animal's health [2,3,40].

The major advantages of adsorption and coagulation/flocculation methods include easy to use, well proven, utilize readily available chemicals, easy operating conditions and good color removal efficiency; while disadvantages are: high cost, pH sensitive, inability to destroy and generate large amounts of waste materials (sludge) [6,9]. The cost of TIWW treatment using adsorption method is ~5.0–200 US\$ m³ of wastewater [54]. The cost of a particular treatment method plays an important role in the extent of pollutants removal/degradation from TIWW. The cost of different treatment methods includes the cost of chemicals, amount of chemicals used, energy consumption, electrode materials, membrane materials, disposal/management of sludge generated during the treatment process [16,22]. However, the treatment cost of a wastewater also depends on the nature and chemical composition of wastewater, method to be followed and amount of wastewater to be treated.

4.2. Biological treatment approaches

Biological approaches are green, eco-friendly, inexpensive treatment methods that can be used effectively in treatment of industrial wastewaters. Due to their genetic diversity and versatility, these are the most effective and alternatives for the degradation and mineralization of wastewater pollutants [2,56]. The biological treatment process can be carried out under the aerobic, anaerobic or facultative anaerobic conditions by using different category of microorganisms or their enzymatic machinery [18,40]. The microorganisms such as bacteria, fungi, yeast and algae reported in Table 3 have been widely used by various researchers in treatment of TIWWs. These microorganisms can decolorize, degrade, detoxify and mineralize an array of wastewater pollutants by using their different metabolic pathways and biosorption processes [15]. Further, these are also capable to reduce BOD, COD, TDS, TSS, TOC, turbidity and detoxify various metals from the synthetic and real TIWW [3,6].

Among these microorganisms, bacteria have strong potential for the treatment of TIWWs because these are easy to culture with fast life phase and capable to grow on different substances [57]. Further, bacteria can degrade or convert many toxic compounds into non-toxic products [5]. For example, many bacterial species like *Arthrobacter*, *Pseudomonas*, *Bacillus*, *Aeromonas hydrophila* and *Lysinibacillus* are reported capable to remove dyes, dissolved solids and heavy metals as well as reduce their toxicity upto a significant level [5,15,57]. Further, for the effective treatment of TIWW, various workers have reported that microbial consortium is more effective as compared to the axenic cultures (Table 3). In a microbial consortium, individual strain may attack dyes molecules at different positions. Moreover, the degradation products, which appeared due to the metabolic activity of one strain, may be utilized as substrate by another [77]. In a study, a bacterial consortium was found capable to degrade and decolorize the direct blue 2 dye more rapidly than single bacterial culture [15]. Recently, some researchers have developed bacteria-yeast, fungal-yeast, bacteria-fungal and bacteria-algal consortia that were found effective to remove color and COD significantly [77].

Sepehri et al. [78] have developed an algae-bacteria consortium of *Chlorella vulgaris* and nitrifier-enriched-activated sludge (NAS) for the treatment of wastewater having low C/N ratio under autotrophic conditions. They used different ratios of developed consortium referred as B0, B10, B50, B70, B90 and B100. Among these ratios, B10 and B90 were found to be most effective resulting 100% removal of NH₄⁺-N within 7 days by B10 ratio and highest carbon capture (156 mg) by B90 ratio in a photobioreactor, while pure culture of *C. vulgaris* showed only 87.5% removal of PO₄³⁻-P after 14 days. In this system, algae eliminate many competing microbial species like pathogens and enhance the dissolved oxygen (DO) concentration (4 mg/l), which is utilized as an electron acceptor by bacteria, thus stimulating the biodegradation of many chemicals. Result showed that aeration favoured the enhanced nutrient removal, increased carbon capture, reduced metabolite generation and decrease in sludge production and this system using advanced technologies like membrane bioreactors can also be considered for the wastewater treatment at industrial scale. However, the development and utilization of microbial consortium provide better superiority as compared to the pure microbial culture in TIWW treatment.

The treatment of wastewaters is generally carried out in a vessel/ bioreactor. Bioreactor is a vessel/tank in which biological treatment process is carried out under adequate aeration and agitation conditions resulting in degradation/mineralization of pollutants. Batch, fed-batch, continuous, sequencing batch and multistage bioreactors are commonly used in treatment of TIWW. Bioreactors support natural process of cells by mimicking and maintaining their natural environment to provide optimum growth conditions [79]. The main advantages of biological treatment processes are green, eco-friendly, low cost, no sludge generation, complete mineralization and globally acceptable, but also has disadvantages like long treatment time and ineffective against toxic compounds [80]. The cost of biological treatment of TIWW comes very low (~0.1 €/FU).

Table 3 Different microbial agents used by various researchers in treatment of textile industry wastewater/dyes.

Microbial agents	Textile wastewater/ dyes	Mechanism	Optimized conditions (dye conc., pH, temp, agitation, time)	Decolorization and treatment efficiency (%)	References
Pure bacterial culture					
<i>Pseudomonas aeruginosa</i> RS1	Reactive Yellow 145	Decolorization	50 mgL ⁻¹ , pH 7, 37 °C, static and 24 h	85	[7]
<i>Pseudomonas putida</i>	Textile wastewater	Decolorization	pH 7, 35 °C, 80 rpm, aerobic and 90 h	Color (87), and COD (69) 97	[58]
<i>Bacillus</i> sp. KM201428	Reactive Black 5	Biotransformation	3.9 mgL ⁻¹ , pH 9, 25 °C and 120 h	100	[59]
<i>Halomonas</i> sp. GT	Acid Brilliant Blue	Degradation	100 mgL ⁻¹ , pH 7.5, 30 °C and 96 h	98	[56]
<i>Exiguobacterium profundum</i> strain CMR2	GR	Biodecolorization	100 mgL ⁻¹ , pH 7.5, 30 °C and 96 h	90	[60]
<i>Serratia liquefaciens</i>	Reactive Blue EFAF	Decolorization	50 mgL ⁻¹ , pH 5–10, 160 rpm and 24 h	90	[48]
<i>Neisseria</i> sp.	Azure B	Decolorization	100 mgL ⁻¹ , pH 7.6, 30 °C, 120 rpm and 48 h 100 mgL ⁻¹ , pH 7, 37 °C, 160 rpm, static and 6d 50 mgL ⁻¹ , pH 7, 35 °C,	99	[61]
<i>Aeromonas hydrophila</i>	Bezema Red S2-B	Decolorization	110 rpm, static and 8 h		[5]
	Crystal violet				
Fungal and yeast culture					
<i>Phanerochaete</i> sp.	Textile wastewater	Biotransformation	pH 5, 30 °C and 2.5 h 200 mgL ⁻¹ , pH 4, 50 °C,	99	
<i>Trametes versicolor</i>	Reactive Blue 19	Biodegradation	120 rpm, shaking and 210 min	85	[62]
<i>Pleurotus ostreatus</i> HAUCC 162	Malachite Green	Decolorization	100 mgL ⁻¹ , pH 6, 25 °C and 24 h	91.5	[63]
<i>Pichia kudriavzevii</i> CR-Y103	Reactive Orange 16	Degradation	50 mgL ⁻¹ , pH 6, 30 °C,	100	[64] [65]
<i>Mucor hiemalis</i>	Textile effluent	Detoxification	120 rpm, shaking and 24 h 100 mgL ⁻¹ , 35 °C, 150 rpm and 60 h	TS (76) and COD (91.35)	[66]
<i>Pleurotus pulmonarius</i>	Malachite Green	Decolorization	100 mgL ⁻¹ and 36 h	68.6	[67]
<i>Pichia occidentalis</i> G1	Acid red B	Degradation	50 mgL ⁻¹ , pH 5, 30 °C, 160 rpm and 16 h	98	[68]
Algae and microalgae					
<i>Scenedesmus</i> sp.		Biosorption	200 mgL ⁻¹ , pH 9, 30 °C and 120 rpm	87.69	[52]
<i>Spirulina platensis</i>	Methylene Blue	Decolorization	100 mgL ⁻¹ , pH 6, 30 °C and 48 h	46.74	[69]
<i>Scenedesmus obliquus</i>	Remazol brilliant Blue R		200 mgL ⁻¹ , pH 6, 25 °C,	93.5	[70]
	Astrazon Red		200 rpm and 48 h		
<i>Chlorella vulgaris</i>	Dye effluent	Biodegradation	pH 8, 30 °C and 10d	99.99	[71]
<i>Phormidium autumnale</i> UTEX1580 Seaweed	Indigo dye	Decolorization	25 °C and 14d	91.22	[72]
<i>Chlorella pyrenoidosa</i> NCIM 2738	Textile effluent	Decolorization	10 mgL ⁻¹ , pH 5, 37 °C, 2000 rpm and 300 min 50 mgL ⁻¹ , pH 3, 25 °C and 30 min	84.37	[73]
	Reactive Red 120	Adsorption		96	[74]
Mixed culture and microbial consortium					
Bacterial mixed culture (<i>Pseudomonas</i> sp. RS1 and <i>Thiosphaera</i> sp. ATCC 35512)	Reactive Yellow 145		50 mgL ⁻¹ , pH 7, 160 rpm, static and 96 h	99	[7]
Bacterial consortium (<i>Shewanella</i> sp. ST2, <i>Oceanimonas</i> sp. ST3, <i>Enterococcus</i> sp. ST5, and <i>Clostridium bufermentans</i> sp. ST12)	Methyl Orange and reactive Yellow 84	Degradation and decolorization	100–2000 mgL ⁻¹ , pH 4–8, 35–50 °C, static and 48 h	90 and 96	[51]
Aerobic/anaerobic Algae-bacterial photobioreactor	Disperse Orange-3 and disperse blue-1	Decolorization	100 and 60 mgL ⁻¹ , pH 7.2,	90	[75]
Bacterial consortium (<i>Gammaproteobacteria</i> , <i>Betaproteobacteria</i> , and <i>Bacilli</i>)	Direct Blue 2B	Decolorization and detoxification	38 °C, 300 rpm and 8d 100 mgL ⁻¹ , pH 7.57, 38.70 °C, static and 48 h		[15]
Bacterial consortium (<i>Bacillus licheniformis</i> , <i>Bacillus subtilis</i> , <i>Paracoccus tibetensis</i> , and <i>Pseudomonas</i> sp.)	Viscose fibre wastewater	Degradation	30 °C, 180 rpm, shaking and 14d	87	[76]

4.3. Enzymatic treatment

Many enzymes are reported to involve in the degradation and detoxification of industrial wastewater pollutants as well as remediation of contaminated sites [6,51]. A variety of microorganisms are capable to produce different types of extra- and intracellular enzymes during the degradation processes. Enzymes such as azoreductase, laccase, peroxidases and polyphenol oxidases are well reported to degrade the industrial wastewater pollutants [18,51,64]. Azoreductase and laccase are the most effective enzymes in the remediation of persistent azo dyes and wastewater than other enzymes [15,81].

Azoreductase (EC 1.7.1.6) is a major class of azo dye degrading enzyme, which is considered as flavoproteins and classified as flavin- dependant and flavin-independent azoreductase. Flavin-dependant azoreductase are classified based on the electron donors such as NADH, NADPH or both. Azoreductase has great potential to degrade and decolorize a number of azo dyes by catalyzing the cleavage of azo linkage ($-N=N-$) under aerobic or anaerobic conditions. During the decolorization of azo dyes, the reducing agents such as FADPH, NADPH and NADH act as electron donors and also participate in the breaking of azo linkage at both extra and intracellular sites of the bacterial cell membrane. The degraded aromatic products are highly stable under anaerobic conditions and further mineralization of these colorless aromatic products take place under aerobic conditions [56,82]. For instance, *Halomonas*, *Bacillus circulans* and *Bjerkandera adusta* are capable to degrade and decolorize different azo dyes containing wastewaters by producing azoreductase enzyme [56,81].

Laccase (EC1.10.3.2) is a promising multicopper oxidase enzyme, which is most effective in the treatment of different dyes such as crystal violet, methyl violet, and cotton blue etc. as well as TIWW. It is non- specific in nature and neither use oxygen as electron acceptor, nor need co-factor [63,64]. ABTS (2, 2-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid) is a low molecular weight compound and acts as a redox mediator for laccase enzymes. The presence of this redox mediator enhances the treatment efficiency of enzymes by many folds [51]. Navada and Kulal, [62], reported that laccase produced by *Phomopsis* sp. can be used as mediator during the degradation of textile wastewater pollutants.

Further, other enzymes like lignin peroxidase (LiP), veratryl alcohol oxidase, tyrosinase, NADH-DCIP reductase and polyphenol oxidase are also reported to play important roles in the degradation of various pollutants from TIWW [15,51,83]. In addition, the utilization of different enzyme combinations offers a significant advantage over the use of single enzyme [51]. Enzymatic degradation and mineralization of TIWWPs have often seen as inexpensive viable options and expanding technologies due to their cost-effectiveness and environmental compatibility. The main advantages of enzymatic treatment are eco-friendly and possibility to effect complete remediation of pollutants, whereas disadvantages include long treatment time requirement, sensitive to temperature, pH, inactive against toxic compounds and not applicable at large scale [85].

4.4. Microbial mechanism of dye degradation and decolorization

Various researchers have reported that many bacterial species are capable to degrade and detoxify different dyes from real as well as synthetic TIWW with the help of intracellular and extracellular enzymes. For example, an isolated *Enterococcus faecalis* YZ 66 strain showed high potential for degradation and detoxification of direct red 81 (DR81) dye [86]. *E. faecalis* is a gram-positive and facultative anaerobe capable to survive and grow under extremely unfavorable environmental conditions. Bacterial degradation of azo dye DR81 is initiated by the reductive cleavage of azo bond ($-N=N-$) by producing azoreductase enzyme in the presence of redox mediator under anaerobic environment.

It results in the generation of various low molecular weight, colorless, highly stable and aromatic amines such as sodium-4-aminobenzenesulfonate, 1,4-benzenediamine and 7-benzylamino-3- dibenzyl-1-4-hydroxy naphthalene-2-sulfonic acid. Further, the degradation of sodium-4-aminobenzenesulfonate takes place by deamination process resulting sodium benzenesulfonate whereas 7-benzylamino-3- dibenzyl-1-4-hydroxy naphthalene-2-sulfonic acid is degraded by laccase enzyme into 1-phenylmethanamine-ethene and 8-aminonaphthol and finally, these get converted into a low molecular weight volatile product i.e. naphthalene. The proposed degradation pathway of direct red 81 dye by *E. faecalis* is shown in Fig. 2(A).

Cao et al. [15], developed a potential bacterial consortium YHK (*Betaproteobacteria*, *Gammaproteobacteria* and *Bacillus*), which was effective for the degradation of Direct Blue 2B (DB2B). DB2B azo dye was primarily decolorized by the symmetric braking of azo bonds by azoreductase enzyme under microaerophilic condition. The symmetric cleavage of DB2B dye results in the formation of two different colorless aromatic amines i.e., disodium 3,5 diamino-4-hydroxynaphthalene-2, 7-disulfonate (A) and benzidine (B) (Fig. 2B). The product (B) was further transformed into 4-aminobiphenyl by deamination process whereas product (A) was further degraded and detoxified by laccase and veratryl alcohol oxidase enzymes resulting in the formation of 8-aminonaphthalen-1-ol and finally this intermediate was converted into naphthalen-1-ol as end product of DB2B dye.

Furthermore, crystal violet (CV) a triphenylmethane dye, which is extensively used in TIs, was effectively degraded by a bacterium, *Aeromonas hydrophila*, isolated from textile wastewater [5]. The degradation pathway of crystal violet dye by the isolated bacterium *A. hydrophila* is shown in Fig. 2C in which it was first transformed into phenol-2-6-bis (1,1-dimethylethyl) followed by further conversion into 2,6-dihydroxyacetophenone and finally into benzene as final product.

Fig. 2. Proposed biodegradation mechanism of Direct Red 81 dye by *Enterococcus faecalis* YZ66 (A), Direct Blue 2B dye by bacterial consortium YHK (B) and Crystal violet dye by *Aeromonas hydrophila* (KU720586) (C). (A) Adopted from [86], (B) Adopted from [15], (C) Adopted from [5].

4.5. Microbial fuel cells

Microbial fuel cells (MFCs) system employed various microorganisms as catalysts to oxidize various organic and inorganic compounds along with the generation of electrons and protons that are directly transported to an electrode [13,87]. It represents a novel, advance and sustainable approach for the efficient treatment of industrial wastewaters along with the power generation with reduced CO₂ emission [88]. MFCs seemed to be the most promising technology for the degradation and decolorization of TIWW pollutants and for this many electrodes have been investigated in MFCs for the effective treatment of wastewater. Out of the used electrodes, oxygen (O₂) and platinum (Pt) were found to be the most suitable electron acceptor in MFCs system, but these have many limitations like high cost, poor kinetics of oxygen reduction reaction (ORR) and create toxicity to the environment [13, 26]. Thus, various researchers have used different electrodes such as nickel, manganese and copper for the oxygen reduction reactions (ORRs) in MFCs [35,88].

Miran et al. [87] have observed that a sulfate-reducing mixed communities comprising of *Proteobacteria*, *Desulfovibrio* and *Deltaproteo bacteria* have a great potential to decolorize 89.4%, 48.2% and 52.7%, respectively of Acid red 114 dyes with generation of electrical energy upto 258 ± 10 mW/m². The major advantages of MFCs are the complete mineralization of pollutants, electricity generation, reduced sludge generation and CO₂ emission [89], while the major disadvantages are the high cost for operation, energy recovery, system development and it is not applicable at extremely low temperature because the microbial activities are very slow at lower temperature [90,91].

4.6. Genetically modified organisms (GMOs)

TIWW contained a variety of potentially toxic POPs, which are resistant for biodegradation due to their complex chemical structure and high stability [18,19]. There are several technologies applied for the treatment of TIWW. But these approaches are not always effective [8, 26]. Therefore, an effective treatment method utilizing genetically modified organisms (GMOs) may offer a potential solution.

Many researchers have developed different GMOs (transgenic strains) and used in treatment of TIWW. For instance, LacTT gene from *Thermus thermophilus* SG0.5JP17–16 was inserted into *Pichia pastoris* making it more effective to remediate reactive black, congo red, reactive black WNN and remazol brilliant blue R [92]. A thermo-alkali-stable laccase gene purified from *Klebsiella pneumoniae* was cloned into *E. coli* and used for the rapid degradation of bromophenol blue, mordant black 9, reactive brilliant blue X-BR, cotton blue, azo phloxine, reactive brilliant blue K-GR, congo red, reactive brilliant blue KN-R, malachite green and reactive dark blue M-2GE from TIWW [82]. Laccase purified from *Pleurotus sp.* MAK-II showed high stability towards different dyes like diazo dye, congo red, anthraquinone, remazol brilliant blue R and decolorization in presence of violuric acid as redox Mediator [93]. The major advantage of GMOs is the good potential to accelerate decolorization efficiency and disadvantages include uncertain long term health effects, reduced biodiversity, cross pollination and damage environment due to horizontal gene transfer.

4.7. Plant treatment/phytoremediation

Phytoremediation is a green, solar energy driven, eco-friendly and cost-effective method, which uses different classes of plants for treatment of harmful pollutants [43]. Plants are well reported to remediate dyes, dissolve solids and heavy metals from TIWW [8]. Further, many plant species has the potential to convert/degrade toxic persistent and emerging pollutants into non-toxic products by adsorption, accumulation and degradation process [31]. Many plants act as hosts for aerobic and anaerobic microorganisms, supplying chemical nutrients, providing shelter and oxygen. Plants in stress conditions can activate efficient enzymatic machinery, which can take up hazardous chemicals as substrates and completely degraded and detoxify them into non-toxic products [77].

Many plants such as *Glandularia pulchella*, *Vetiveria zizanioides*, *Physalis minima*, *Scirpus grossus*, *Blumea malcolmii*, *Ipomoea aquatic*, *Lemna minor*, and *Azolla pinnata* are used in the remediation of various carcinogenic and mutagenic textile dyes from TIWW [32,43]. Further, a mixed culture of fungi and bacteria with in vitro development of plants system was found to be more effective in the decolorization of TIWW [31]. Recently, the combination of plants *Typha angustifolia*-*Paspalum scrobiculatum*, *Fimbristylis dichotoma*-*Ammannia baccifera* were found to achieve superior decolorization of methyl orange dye along with a significant reduction in ADMI, BOD, TDS, COD and TSS from TIWW than single plants use [8,29]. Phytoremediation has some major advantages like eco-friendly, solar-driven approach, cost-effective, low maintenance, negligible nutrient used, possible recovery and reuse of valuable metals, less waste to dispose off, applicable for laboratories, pilot and field study; while disadvantages include slow process, difficulty to achieve acceptable levels of decontamination, toxic metals leached into groundwater and possibility of food chain contamination [8,43].

4.8. Constructed wetland

Constructed wetland (CW) is a man-made system utilizing the natural ability of plants to remediate/treat wastewater pollutants. CW employed natural substances including wetland vegetation, bedding materials and its associated microbial flora for the remediation of persistent organic and inorganic contaminants [77]. Although, the bedding materials like gravel, zeolite rock and

sand are used to enhance the treatment efficiency [31]. Different macrophytes like *Phragmites australis*, *Typha angustifolia*, *Panicum elephantipes* and *Myriophyllum spicatus* are extensively used in CW treatment process [25]. The wetland plants provide habitat and nutrients to rhizo- and endophytic microorganisms while, microorganisms help host plants to gain more biomass by reducing the contaminant stress, performing plant growth promoting services and accelerate treatment performance [94]. CWs are generally of two types i.e., horizontal sub-surface flow (HSFCW) and vertical sub-surface flow (VSFCW), which functions under both aerobic as well as anaerobic conditions. In aerobic conditions, organic load is removed adequately, but color is not reduced significantly; whereas in anaerobic condition, the situation is reversed where color is removed effectively, but organic compounds are not degraded effectively [25,29].

For instance, vertical-flow pilot-scale constructed wetland augmented with bacterial endophytes was found effective to remove and reduce color, dissolved solids and heavy metals from the real TIWW [94]. For example, the horizontal and vertical-flow pilot-scale constructed wetland planted with *Phragmites australis* was found effective to remove 89% of COD, 91% of BOD and 96% of TDS from textile bleaching effluent containing 13.7 mg/l PO_4^{3-} [25]. Furthermore, the floating wetlands also showed the highest efficiency to remove 92% of COD, 91% of BOD, 87% of trace metals and 86% of color from TIWW containing $16.4 \pm 3.6 \text{ mg l}^{-1}$ of PO_4^{3-} [29]. In present time, the CWs developed with microbial fuel cell (CW-MFC) were able to decolorize 96% of acid red 18, 67% of acid orange 7% and 60% congo red along with the generation of bioelectricity [88].

The major advantages of CWs are eco-friendly, efficient color removal, self-regeneration, no energy requirement, recharging ground water, providing excellent habitat for aquatic and wildlife, no biosolids and sludge generation, but also has disadvantages like involve large land area, costly to design and construction, facilitate mosquito breeding, high monitoring requirement, require skill and management, need long period to establish vegetation and optimum treatment efficiency [25].

5. Advanced oxidation processes

Advanced oxidation processes (AOPs) are considered as emerging, fast and competitive methods for the removal of refractory contaminates. AOPs were first evaluated for the treatment of drinking water in 1980 s and became widely applicable in the treatment of industrial wastewaters [2,12]. In AOPs, different oxidizing agents such as O_3 , H_2O_2 and many catalysts such as Fe_2O_3 , ZnO , CdS , TiO_2 , GaP , and ZnS as well as high energy radiation like UV light are used [54,77,95].

In AOPs, the highly oxidative and non-reactive species such as hydroxyl ($\text{OH}^\bullet$) and sulfate radicals ($\text{SO}_4^\bullet$) are produced, which act as mediator in electron transfer, hydrogen abstraction and radical addition reactions [12,16]. Thus, AOPs are effective to degrade or transform many refractory compounds into carbon dioxide and water [12,95]. Currently, many AOPs including ozonation, photo-fenton, photo-catalytic, sono-catalytic, electro-coagulation and electro-oxidation process, which are widely applied in the degradation and mineralization of various persistent dyes, dissolved solids, and heavy metals from TIWW. But, these are expensive, high chemical demanding, use complicated procedures, applied high electrical energy and generate large amount of sludge as secondary pollutant [77].

5.1. Ozonation

Ozonation is a chemical oxidation process used to remove pollutants from industrial wastewaters. Ozone (O_3) is a strong oxidizing agent and non-selective in nature that can decompose the persistent pollutants from TIWW [28,95]. During wastewater treatment, it produces highly reactive species like hydroxyl and other radicals, which rapidly decolorize and detoxify persistent dyes, dissolve solids and heavy metals [19, 54]. Many studies have reported that ozonation can effectively decolorize and remove a variety of dyes, TOC, BOD, COD, TDS, TS, and Sb, Cr, Cd, and Pb from TIWW [28,95,96].

The major advantages of ozonation process are fast color removal, and no alterations in volume while disadvantages are: it is applicable in gaseous state only, short half-life (20 min), sensitive to pH and sludge disposal problems [6,54] and the total treatment cost estimated is $\sim 3.4 \text{ €/FU}$.

5.2. Photo-Fenton process

Photo-Fenton (PF) process ($\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$) has emerged as a highly effective method for industrial wastewater treatment. It is able to degrade and decolorize many pollutants such as dyes, COD, BOD, TOC and TDS as well as various metals from TIWW [77,97,98]. But, this method also has some drawbacks like: (1) TIWW is alkaline in nature, but PF process is effective in acidic condition; (2) the colored pollutants reduce light penetration power; (3) ferric-organic complexes can be formed and thus, decreases radical generation efficiency; (4) the high load of inorganic ions such as SO_4^{2-} , CO_3^{2-} , and Cl^- may result the formation of inorganic ion-ferric complexes leading to decrease in radical generation [6,42,64]. These drawbacks can be minimized by the addition of oxalic acid to PF treatment process.

Ferrioxalate complexes block the production of stable complexes between ferric ions and organic species [37]. These also increase the quantum yield, enhance regeneration of ferric ions and thus, produce a large amount of hydroxyl radicals [6,33,54].

For instance, the PF/Ferrioxalate process is capable for the treatment of synthetic cotton-textile wastewater [37,99]. The addition of oxalic acid to PF process is limited with the iron precipitation and also promotes the degradation and mineralization of TIWWPs.

PF method has major advantages such as efficient in color and COD removal, mineralization of persistent compounds, more effective than fenton processes at lower dose of ferrous sulfate due to additional benefit of UV radiation and disadvantages like high operation cost, less catalytic power and ineffective in case of copper phthalocyanine dye. The treatment cost of photo-fenton was estimated based on the raw material, energy consumption and disposal of precipitate generated during the treatment process [77]. The total treatment cost was estimated ~ 3.4 €/FU. 5.3. *Photo-catalytic treatment*

It is an emerging approach with a great potential for the treatment of different xenobiotic contaminants. In UV-TiO₂ process, the photoactivation of semiconductors is initiated by irradiation with electron-hole pairs appearing as a result of band gap excitation [16,19,37]. The oxidation and reduction processes are possible at or near the surface of the photo excited particles [77]. The light generated possible hole may react with electron donors to generate hydroxyl radicals [12]. Hydroxyl radicals can oxidize organic compounds leading to their mineralization into non-toxic forms [77,100]. In this process, various semiconductor catalysts such as TiO₂, CdS, ZnO, CuNPs, GaP, SA/TiO₂, Fe₂O₃, TiO₂/UV, α -Bi₂O₃-ZnO, S₂O₈²⁻/Fe²⁺ and ZnS are used and generate highly reactive species such as H₂O₂, O₃, OH[•], and O⁻² [2,6,19]. These species are highly effective in mineralizing and detoxifying various POPs, refractory organic and organic pollutants from TIWW [33,37].

Among various semiconductors, TiO₂ is widely used in wastewater treatment [65]. For example, Fazal et al. [19], reported a biochar-TiO₂ composite for the treatment of wastewater with 99.20% photodegradation efficiency of dye-simulate wastewater. Saratale et al. [100], synthesized CuO/Cu(OH)₂ nanostructures using co-precipitation techniques and utilized in the photocatalytic degradation of reactive green 19 A dye as well as treatment of TIWW.

The major advantages of photo-catalytic treatment are short time consuming, little or no chemicals consumption, efficient for persistent compounds, high stability and considerable COD reduction. For example, a photocatalytic process removes 100% color from the real TIWW within 30 min. It also removes 87% COD within 3 h and consume less chemicals like Fe²⁺ = 0.2 mM and S₂O₈²⁻ = 4 mM [101]. While disadvantages are the high treatment cost, limited applications subjected to light, catalysts fouling, formation of by-products and problem of fine catalyst separation from the treated effluent (slurry reactors) [2, 77].

5.4. *Sono-catalytic process*

Sonolysis is a simple chemical method used in wastewater treatment, but it is limited by poor elimination efficiency, high cost and not environmentally safe [99,102]. Sono-catalytic process is widely used to reduce and detoxify toxic persistent compounds from TIWW. Many semiconductors such as CdSe, CdS/TiO₂, and KNbO₃ have been successfully used as catalyst to reduce organic load, suspended solids, dye content and other hazardous chemicals [6,77]. In recent years, many nano-composites such as Fe₃O₄-graphene/ZnO/SiO₂, CdSe/GQDs and TiO₂-BC have been used to remove a variety of dyes such as methylene blue, methyl orange, rhodamine B and reactive blue 69 dyes, dissolve solids and inorganic refractory chemicals from TIWW [6,16,103]. Asgari et al. [16], developed a sono-photolytic-activated ZnO/persulfate (US/UVZnO/PS) composite to remove and mineralize acid blue 113, COD and TOC from the real textile wastewater at optimum conditions.

The major advantages of this process are the short time requirement, efficient to toxic or non-biodegradable compounds while disadvantages are high treatment cost and require high amount of dissolved oxygen [77]. The total cost estimated to achieve 90% decolorization of AB113 dye by US/UV/ZnO/PS processes is ~154.6 \$/m³. This cost was estimated based on the amount of Kg of ZnO or PS used [16].

5.5. *Electro-coagulation treatment*

Electro-coagulation (EC) is an electrochemical process that broadly used in treatment of persistent textile wastewater due to its high efficiency. It is an efficient method to treat persistent contaminants such as dyes, heavy metals, phenols, surfactants, pesticides and pharmaceuticals from wastewaters [104]. The EC setup consists of cathode and anode electrode that are connected to the external monopolar or bipolar power supply [104]. In EC process, electrical energy is used to dissolve iron (Fe) and aluminum (Al) to remove hazardous pollutants from TIWW [54,105]. At cathode, hydroxide ions are formed, which helps to remove flocculants from wastewater [106] and metal ions generated from the sacrificial anode act as destabilizing agents and neutralize the electric charge of contaminants resulting in the removal of pollutants from wastewaters [104]. Different electrodes such as iron, stainless steel, aluminum, mild steel and graphite can be used in EC treatment process in single as well as in different combinations such as Al/Al, Fe/Al and Fe/Fe for the effective degradation and mineralization of various toxic refractory pollutants from synthetic as well as real textile wastewater [14,54,107]. The main criteria followed to choose the electrode are low cost, good performance, high efficiency, easy handling and availability [108]. Iron and aluminum are most widely used as electrode materials in EC process. Iron electrode is more suitable in neutral and alkaline medium while aluminum electrode used in acidic medium [14]. For instance, the use of aluminum in TIWW treatment significantly removes color and reduces BOD, COD and TSS [54].

Recently, Bener et al. [14] used EC process for the treatment of real textile wastewater for its possible reuse in agriculture irrigation. This process was found effective to remove 94.9% color, 83.5% turbidity, 64.7% TSS, 42.2% TOC and 18.6% COD from treated wastewater. The various operating parameters like electrode materials, time of electrolysis, pH of electrolytes, current density, electrode's connection mode and distance between electrodes affect the treatment efficiency of EC process [14].

The EC treatment method has some major advantages like no chemical requirement, short treatment time, smooth operation, minimal footprint and requirement of a low dose of colloidal particles. Besides these advantages, the EC method also has some disadvantage like high operation cost, cathode passivation and generation of toxic sludge as secondary pollutant [14,104]. The operating cost to achieve ~95% decolorization of real textile wastewater was found to be 1.5 \$/m³ with a treatment time (7200 s) and applied current (0.5 A) [14]. The cost of EC process was calculated by considering the amount of energy consumption, electrode materials and addition of external chemicals for enhancing the treatment efficiency [14,104].

5.6. Electro-chemical oxidation

Electro-chemical oxidation (EO) provides an alternative treatment of toxic or non-biodegradable wastewater like TIWW. During the treatment process, a highly reactive species (OH•) is produced, which broadly decolorizes and mineralizes different coloring substances, dissolved solids and toxic metals from TIWW [34,105]. The anodic oxidation process applies both direct as well as indirect ways to remove color, toxic chemicals along with the reduction in COD, BOD, and TDS from synthetic wastewaters [77,109]. For example, Abdessamad et al. [110] achieved 100% COD removal from TIWW by using anodic oxidation process.

EO uses many types of electrodes like Ti/IrO₂, Ti/SnO₂, Ti/PbO₂, BDD, graphite and PbO₂, Ti/RuO₂ and SnO₂ as anode in treatment of textile wastewater [6,34]. These electrodes have potential for the oxidation of pollutants and high oxygen over potential (1.9 V) [34]. BDD appears to be a more effective electrode in the removal and mineralization of TIWW pollutants because it has high stability, generate high potential O₂ overvoltage (2.7 V) and inactive surfaces with less adsorption capacity [37]. However, BDD is highly expensive while other electrodes are reported as poor performer with low oxygen over potential [34]. Ti/RuO₂ is a potentially stable and has high chemical and mechanical strength, high oxygen over potential (~2.0 V) and produces strong oxidants such as HOCl, Cl₂ and ClO⁻ etc. It is highly efficient in decolorization and degradation of various dyestuffs and reduces dissolved as well as suspended organic and inorganic pollutants from TIWW [34,77,108].

EO method has major advantages such as high decolorization efficiency, efficient for persistent or toxic pollutants, no additional chemical requirement, while disadvantages like high operation cost, toxic metabolites generation and steam stripping. EO treatment may result in the removal of 100% color, 85% COD and 69% TOC from TIWW within 30 min with operating cost of ~4.8 USD/m³ [108].

6. Membrane technologies

Membrane technologies (MTs) use various classes of permeable membranes in purification and reclamation of industrial wastewaters. Many emerging membranes such as reverse osmosis (RO), nanofiltration (NF), microfiltration (MF) and ultrafiltration (UF) are widely utilized in separation and desalination of dyeing and TIWW [11]. All these membranes are found effective in the removal of color, organic salts and suspended impurities from TIWW [111,112].

Sahinkaya et al. [113] have used reverse osmosis (RO) technique in treatment of TIWW and obtained 94% decolourization of textile wastewater. However, NF is more effective method as compared to RO treatment because it requires lower pressure [109]. For instance, UH004, PA6DT-C and polyamide nanofiltration membranes are capable to remove different dyes such as methylene blue, direct, reactive blue 2 dyes, reactive black 5, reactive blue 15, reactive orange 16, reactive yellow 145 and reactive red 194 from synthetic wastewaters [111,114]. Currently, a pilot scale ceramic UF/NF process is applied in the treatment of real TIWW with the reduction efficiency of 90.1%, 82.2%, 82% and 76.8% and 90.1%, 82.2%, 82% and 76.8% for COD, color, total hardness and TOC from the real wastewater of disperse printing and reactive printing washing baths, respectively [4]. Further, Hubadillah et al., [11], developed a potential hydroxyapatite (HAp)-based bio-ceramic hollow fiber membranes (h-bioCHFM) that are found effective to remove 99.9% color, 80.1% COD, 99.4% turbidity, 30.1% conductivity and 100% heavy metals from TIWW.

MTs has some major advantages like no chemical requirement, effective in color and multiple contaminants removal, complete water/ wastewater purification and produce a high-quality treated wastewater, while disadvantages are membrane fouling, clogging, scaling and cleaning, poor production efficiency, pre-treatment requirement, high pressure requirement, concentrated sludge production and high cost of membrane replacement [4]. Approximately 90.1% of COD, 82.2% of color, 82% of total hardness and 76.8% of TOC were removed by NF (ceramic membrane) method and the treatment cost was estimated ~ 1099406 USD \$/year [4]. This treatment cost was estimated based on the cost of membranes, membrane installation, and operation.

7. Membrane bioreactors

Membrane bioreactors (MBRs) are a combination of biological approach and membrane filtration, which is widely used in treatment of wastewaters [112]. In MBR, the microbial communities play a crucial role in degradation and mineralization of various persistent coloring compounds present in TIWW [115]. Membranes separate the microorganisms, macro-molecules as well as allow the water and dissolved species to pass through [84]. MBR is a simple, cost-effective and reliable method, which produce high quality recyclable treated water [115]. It has a strong potential to remove high nutrient load, organic chemicals and coloring pollutants. But, its major disadvantage is the fouling of membrane in bioreactor i.e. deposition of cells on the membrane, exertion of extracellular polymeric substances (EPS) and soluble microbial products (SMP), which largely depends on the density of microbial cells and microbial population structure [116]. Sepehri and Sarrafzadeh [116], applied a nitrifying-enriched activated sludge (NAS) for the mitigation of membrane fouling in MBR and observed that the nitrifiers community significantly reduced the membrane fouling by enhancing the permeation (2.5 times) in comparison to the conventional activated sludge process and thus, enhance the performance of MBR. In case of a wastewater containing low C/N ratio, the dominant nitrifies population and nitrifying bacteria produce a very low concentration of organic metabolites such as extracellular polymeric substance (EPS) and soluble microbial products, significantly enhancing the permeation which was higher (2.5 times) than the conventional activated sludge process.

Enhanced membrane bioreactor (e-MBR) in combination with two anoxic bioreactors (ARs), aerated bioreactor (AMBR), UV-unit and a granular activated carbon (GAC) filter was found effective in removal of ~99% COD, 95% color, 73% phosphorus and 97% nitrogen from TIWW [115]. Yurtsever et al. [112], used a microbial community of anaerobic (AnMBR) and aerobic bioreactors (AeMBR) technology to remove color and degrade hazardous ROPs from TIWW. However, the aerobic process is restricted by the low aerobic biodegradability of textile wastewater due to the presence of azo dyes because the azo dyes are not degraded in aerobic conditions [112]. Microbial anaerobic process is efficient for TIWW decolorization, but it produce highly toxic intermediate products [117]. In this context, a novel anaerobic-aerobic algal-bacterial photobioreactor was developed for the treatment of synthetic wastewater. This technology was capable to decolorize 99.1% of disperse orange 3% and 96.3% disperse blue 1. In photobioreactor, the symbiotic interaction is based on the mutualistic exchange of CO₂ and O₂ between bacteria and microalgae. Furthermore, the pollutants adsorption onto microalgae cell wall can facilitate the dye mineralization whereas; bacteria can improve algal growth by producing growth-promoting factors [117].

MBRs has major advantages including compact nature, reliable, small footprint, biogas production, high quality of treated effluent, lower sludge generation, higher nutrient removal, high degradation rate of organic and inorganic pollutants over conventional activated sludge process, while disadvantages like aeration limitations, stress on sludge in external MBR, membrane fouling and higher operation cost [115]. The unit cost per m³ of wastewater treated could be lowered to 0.46 M USD/y [22].

8. Combined treatment approaches

Combined treatment approaches use physical, chemical and biological methods in combination that results in better degradation and mineralization of textile dyes and TIWW treatment compared to other methods in single use [13,77]. TIs discharge huge amount of highly colored wastewater with various persistent chemicals like dyes, softeners, surfactants, salts, heavy metals and disinfectants [43]. The reported treatment methods are not always effective and also have some serious disadvantages. For example, AOPs are effective and efficient, but may not be feasible due to the high cost, incomplete mineralization and generation of large amount of toxic products (sludge). Besides this, biological treatment is widely used in the degradation and decolorization of TIWW, but this process takes long time for the complete mineralization and transformation of pollutants [117]. Therefore, combined treatment approaches like physical, chemical and/or biological methods can be used for the better degradation and mineralization of TIWW as compared to the other methods in single use [13,77]. For example, the combination of AOP and biological process seems to be an effective alternative approach to treat persistent compounds [117]. In this process, AOP breakdown the complex structure of pollutants by free radical attack, generating products, which are more biodegradable and then biological process further degrade and mineralize such products into the small, simple and non-toxic metabolites by involving oxidoreductive enzymes [2,117].

Ceretta et al. [2] used an integrated biological and photocatalysis system to remove 95.5% of color and 99.8% of TOC from the real TIWW. A combination of ceramic UT-NF system was found effective in removal of 83.5% color, 89% COD, 86.4% TOC and 68% hardness from real printing wastewater [4]. Wang et al. [96], developed a hybrid system of catalytic ozonation with regenerated granular activated carbon (rGAC) and biological activated carbon (BAC) for the treatment of textile wastewater [83]. Sun et al. [13], evaluated a combined system of plasma oxidation and microbial fuel cell (MFC) and found effective to remove and mineralize 97.7% of methylene blue dye with the generation of electrical energy upto 519 mWm⁻². Different physico-chemical, AOPs and biological methods used in combination for the treatment of TIWW are summarized in Table 4. The major advantages of combined treatment processes are fast treatment efficiency, efficient for toxic or non-biodegradable pollutants and maximum removal of contaminants while disadvantages are the high treatment cost and sludge generation. The total cost

estimated to achieve 90% decolorization of AB113 dye by US/UV/ZnO/PS processes is ~ 154.6 $\$/\text{m}^3$ and this cost was estimated based on the amount of Kg of ZnO or PS used [16].

9. Comparative discussion of various treatment methods

Adsorption and coagulation/flocculation are excellent methods for the decolorization of TIWW. These methods convert pollutants from one phase to another or concentrate them within one phase [54]. But, these processes are high cost and generate large amount of toxic sludge as secondary pollutants in comparison to biological methods [80]. Biological processes using naturally occurring bacteria, fungi, yeast and algae were found to be eco-friendly, cost effective and globally acceptable methods. These are capable to decolorize, degrade, mineralize and transform different pollutants into non-toxic, simple form in comparison to physico-chemical methods [5]. But, biological processes require long treatment time as well as being sensitive to toxic compounds as compared to AOPs [77]. Enzymatic treatment is a potential tool to convert or transform many complex pollutants into simple, non-toxic and inorganic compounds [85], but this method are time consuming and sensitive to pH, temperature and toxic pollutants in comparison to AOPs and physico-chemical methods [14]. MFCs are a novel, advance and sustainable approach for the remediation and mineralization TIWW along with the power generation with reduced CO_2 emission [88]. But, this method also has long treatment time, high operation cost for energy recovery, system development and it is not applicable at extremely low temperature because microbial activities are very slow at lower temperature compared to AOPs [90,91].

GMOs are an effective treatment method utilizing genetically modified organisms (GMOs) for the treatment of TIWWPs. This method has strong potential to decolorize and detoxify many textile dyes and wastewater, but it has harmful effects on natural environment due to the horizontal gene transfer in comparison to other treatment methods [6]. Phytoremediation is an eco-friendly, solar energy driven and cost-effective method, which uses plants to remediate TIWW [43]. But, it is land area-demanding, slow as well as sensitive to toxic compounds in comparison to AOPs. CWs are the man-made system utilizing the natural ability of plants to remediate/treat wastewaters. CWs method is an eco-friendly and remediates organic and inorganic pollutants into non-toxic, simple compounds in comparison to physico-chemical methods.

Furthermore, AOPs like ozonation, photo-fenton process, photo-catalytic, sono-catalytic, electro-coagulation and electro-chemical oxidation process are considered as fast, emerging and competitive methods for the treatment of persistent and non-biodegradable compounds [54]. These methods are capable for the rapid and fast decolorization of different toxic and refractory pollutants as compared to the biological and physico-chemical methods [6,77]. Among these different kinds of AOPs, the photocatalytic oxidation/treatment showed the highest degradation efficiency [124]. MTs are found to be effective in removal of color, organic salts and suspended impurities from TIWW [103,112]. But, these only transfer pollutants from one phase to another phase [54]. MBRs are the most effective method to remediate organic and inorganic pollutants in comparison to physico-chemical methods, but these methods are not always effective due to the membrane fouling. Combined treatment approaches use physico-chemical, AOPs and biological methods in combination that results in better treatment of TIWW as compared to the physico-chemical, biological and AOPs methods in single use [116], but these are highly expensive and not environmentally safe due to the generation of toxic waste products (sludge) as secondary pollutant.

10. Possible recycling and reuse of treated TIWW

Water is an essential compound to sustain all living creatures on the planet. Approximately 97% of the water resources are salty and not drinkable. More than 2% of the world's water is tied up in glaciers and ice caps and only less than 1% water is potable. Currently, the level of potable water is decreasing day by day due to the continuous increase in water pollution and overuse of water in industries. Industries use a large volume of potable water in different production process [2]. For example, ~ 1.6 million L of fresh water is used in TIs to produce 8000 kg of textiles and discharge as a wastewater along with persistent dyes, salts, VOCs, phenols, surfactants and toxic metals into natural water bodies [2,54].

Further, 20% of the world's population is suffering from water deficiency and 40% from contaminated water by industrial discharge [125]. To solve such issues, many techniques are developed for adequate treatment of wastewaters that allows reuse of treated water with many economic and environmental benefits. For example, EC process is used in the treatment of real textile wastewater. It effectively decolorizes wastewater and allows the treated wastewater for recycling and reuse in the wool dyeing process and agricultural irrigation [126]. UF/NF ceramic membrane process has potential to recover and reuse hot textile wastewater that significantly reduces water consumption as well as electricity charges [4]. Rosa et al. [12], applied AOP for the recycling of TIWW of $\sim 22.47\%$. These treatment technologies reduce water consumption, chemicals and treatment cost along with the environmental threats, public health concern as well as improved the industry image before the society.

Table 4

Combined treatment approaches for TIWW/dyes.

Combined treatment approaches	Textile wastewater and dyes	Optimum parameters	Treatment efficiency	References
Ultrafiltration + nanofiltration (UF-NF) treatment	Real textile printing wastewater	UF/NF = pH = 0–14/0–14, pore size = 0.05 μm /1 kDa, channel diameter (mm) = 0.3/0.3, channel number 19/ 19, active layer = $\text{AlO}_3/\text{TiO}_2$, and support layer = $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{ZrO}_2$	Color (83.5%), COD (89%), TOC (86.4%), and hardness (68%)	[4]
Biological + photocatalysis treatment	Real textile wastewater	Biological = pH = 7, T = 25 °C, 125 rpm and 24 h, Photocatalysis = ZnO/PPy = 25:1, simulated dyes wastewater = 50 mg/L,	Color (95.7%), and TOC (99.8%)	[2]
Plasma oxidation (PO) + microbial fuel cell (MFC)	Methylene blue	PO = diameter = 25 and 45 mm, height = 120 and 360 mm, dye = 300 mg/L, and voltage 25–40. MFC = chamber long/diameter = 4/3, dye = 300 mg/L, pH = 7, T = 450 °C and 30 min	97.7%	[13]
Ozonation + regenerated granular activated carbon (O ₃ /rGAC) treatment	Textile wastewater	Ozonation = diameter = 4 cm, height = 50 cm, ozone dosage = 18.5 mg/L, and 5 min. BAC = diameter = 11.5 cm, height = 55 cm, aeration = 3:1, and 25–100 min	Compared to ozonation, O ₃ /rGAC was 1.6–2.0 more efficient for removal of organic load, color, recalcitrant chromophores and toxic wastewater pollutants	[96]
Adsorption + photocatalysis	Textile wastewater	Photocatalysis = Dye = 5.0 mg/L, rpm = 140, voltage = 500 W, pH = 6–7, T = 25 °C, and T = 60 min. Adsorption = dye = 5.0 mg/L, pH = 6.1, T = 27 °C, rpm = 140, and 30 min	99.20%	[19]
Electrocoagulation (EC) + ozonation (O ₃) treatment	Textile wastewater reuse	EC = reactor = 2 L, current density = 20 mA/cm ² and 100 mA/cm ² , voltage range = 0–150 V, and T = 23 $\pm$ 5 °C. O ₃ = stirred cell = 1 L, rpm = 200, and feeding parameter = Co_3 42 mg/L, Q_{in} 40 L/h	95%	[54]
Fenton + ultrafiltration (UF) treatment	Textile wastewater	UF = membrane (FP100 and FP200), water flux = 0.053 and 0.0732. Fenton = vessels = 9 L, rpm = 300,	Color (>99%), COD (48 mg/L), and TOC (1.2 mg/L)	[118] [98]
Coagulation-flocculation (C-F) sequential + Fenton or photo-fenton	Textile wastewater	TMP = 0.5 or 1 bar, and 60 min $\text{Al}_2(\text{SO}_4)_3$ =	87%	[119]
(AOP) treatment	Textile wastewater	700 mg/L, pH = 9.96, Fe^{2+} concentration = 1 mM, H_2O_2 dose = 2 mL/L (19.6 mM), and pH = 3 and 90 min 36.0 L $\text{m}^{-2} \text{h}^{-2}$, 2 M NaCl	95%	[120]
Forward osmosis (FO) + coagulation/flocculation (CF)		1.5 A and 0.3 mol dm^{-3} NaCl	Photo-assisted method was more efficient for the removal of COD (86%) and TOC (92%) than the electrochemical method alone (72% and 62%)	
Photo-assisted electrochemical + simultaneous chlorine photolysis treatment				
Biological + chemical treatment	Textile wastewater	pH 3 for 100% sample	Colour (> 92%) and COD (87%)	[121]
SBR (sequencing batch reactor) + Fenton process as post treatment	Azo dye AR18 (AR18) and	H_2O_2 and zero valent iron (ZVI) with ultrasonic irradiation	Colour (100%) and COD (97%)	[122]
Combined anaerobic-ozonation process	(500 mg/L)	100–1000 textile wastewater mgL^{-1} , 3 days HRT during biological treatment followed by 6 min ozonation	Colour (100%) and COD (90%)	[123]
	Textile wastewater			

11. Various analytical techniques used to detect and characterize TIWW pollutants and their metabolites

TIWW is well reported to contain a variety of PCPs, out of which some are degraded and mineralized while some get converted into metabolic products ([8,13]. These metabolites are required to be characterized and identified with help of various analytical techniques to understand their nature for the safety of environment and public health. UV–vis spectroscopy is the primary technique used to measure the decolorization of textile dyes. The major visible light absorbance peaks were completely disappeared and new peaks appeared as the evidence of dyes removal [34]. American Dye Manufacturers Institute (ADMI) tristimulus filter method is used to calculate the decolorization of real and synthetic TIWW [8]. Fourier transform infrared (FT-IR) analysis is used for the identification of functional groups present in parent compounds and their metabolites produced during the treatment process [7]. High-performance liquid chromatography (HPLC) is employed for the detection, identification and quantification of organic compounds present in TIWW [105]. The GC-MS and LC-MS/MS techniques are used to characterize as well as identify the low molecular weight organic compounds and their metabolites [8,34]. In addition, the nuclear magnetic resonance (NMR) a powerful analytical technique is used to confirm the presence and position of protons in organic compounds

and their metabolites. Details of different techniques used by various researchers for the characterization and identification of TIWW pollutants as well as their metabolites are listed in [Table 5](#).

12. Challenges and key issues

TIs are facing serious challenges from the public and governmental sectors like increased cost of raw textile products, stringent environmental regulations, increasing demand of various types of textile fabrics, lack of advanced processing techniques and waste treatment technologies in developing countries, lack of specific dedicated industrial areas for the positioning of textile industries, poor capacity utilization leading to the higher financial cost and over heads charges, and the lack of financial support from the Government. The mitigation of these challenges requires large scale financial supports from the Government for proper functioning of TIs, especially for small scale industries. TIs should also use ecofriendly/natural coloring/auxiliaries agents of biological origin instead of synthetic agents as it may be helpful in the reduction of treatment cost. TIs should adopt recycling/reuse of treated wastewater to minimize the use of fresh ground water for economic and environmental benefits. There is a need to revisit the textile processing industries to ensure the sustainability in the core of industries as these are the key driver of many nations' economy.

Table 5

Various analytical techniques used to detect and characterize the textile industry wastewater pollutants.

Analytical techniques	Metabolic products identified	Dye degraded
UV-vis, FT-IR and GC-MS, HPLC and GC-MS	Phenol, 2, 6-bis (1,1-dimethylethyl) and 2, 6-dihydroxyacetophenone and benzene	Crystal Violet (CV)
UV-vis, FT-IR, HPLC and LC-MS	1 and 2-[(3-diazenylphenyl) sulfonyl] ethanesulfonate 8-[(4-chloro-1,3,5-triazin-2-yl)amino] naphthalene-1-ol and benzene-oxosulfane oxide	Remazol Red (RR)
UV-vis, FT-IR, HPLC and LC-MS	1,1-biphenyl-4,4-diylidiazene, sodium 4-amino-3-hydroxynaphthalene-1-sulfonate and 1-aminonaphthalene-2-naphthalene-2-ol	Congo Red (CR)
UV-vis, FT-IR, HPLC and LC-MS	Sodium 4-(phenyldiazenyl)benzenesulfonate, 4-(phenyldiazenyl) benzenesulfonate and 4-sulfanyphenol	Methyl Orange (MO)
HPLC and GC-MS	L-proline, N-valeryldecyl ester, 3,5 di-tert-butyl-4-trimethylsiloxytoluene and 1,2-benzenedicarboxylic acid and diisooctyl ester	Dt. T Blue GLL (BGLL)
LC-ESI-MS/MS	Phthalic acid (product) and 4-hydroxy-2-oxovaleric acid	Direct Black G (DBG)
UV-vis, FT-IR and LC-MS	N, N-dimethyl p-phenylenediamine, 4-(dimethylamino) phenol, 4-diazenylbenzene sulfonic acid, and 4-amino sulfonic acid	Methyl Orange (MO)
UV-vis, FT-IR, HPLC and LC-MS	Biphenyl diamine and 1,20-diaminonaphthalene-4-sulfonic acid	Congo Red (CR)
UV-vis, FT-IR, TLC and GC-MS	1,2,7 triamino-8-hydroxy-3,6- naphthalenedisulfonate, 1-sulphonic,2-(4-aminobenzenesulphonyl and oxalic acid	Reactive Black 5 (RB5)
UV-vis, FT-IR, HPLC and GC-MS	1,3,5-triazine 2,4-diol, naphthalene 2-diazonium 1,5-disulfonic acid sodium 1-naphthol-3-sulfonate, naphthalene diazonium and naphthalene	Reactive Orange 4 (RO4)
UV-vis, FT-IR, HPTLC and GC-HRMS	Naphthalene-1- yldiazene, naphthalene, 1-(2-methylphenyl)- 2phenyldiazene, and diphenyldiazene	Solvent Red 24 (SR124)
UV-vis, FT-IR, HPLC and GC-MS	sodium-4-aminobenzenesulfonate, 1,4-benzenediamine and 7-benzylamino-3-dibenzyl-1-4-hydroxy naphthalene-2- sulfonic acid, 1-phenylmethanamine-ethene and 8-aminonaphthol, naphthalene	Direct Red 81 (DR81)
FT-IR, HPLC, HPTLC and GC-MS	4(5-hydroxy, 4-amino cyclopentane) sulfo benzene and 4(5-hydroxy cyclopentane) sulfo benzene	Reactive Yellow-84A (RY-84A)
UV-vis, FT-IR, HPLC and GC-MS	Methanesulfinic acid, 4-[(6-amino-4-chloro-1,2,3,4-tetrahydro-1,3,5-triazin-2-yl) amino] decahydronaphthalene-2,7- disulfonate, 4-[(4-chloro-1,3,5-tiazin-2-yl) amino] naphthalene-2,7-disulfonate], and 4-chloro-1,3,5-tiazin-2-amine, 1,3,5- triazine	Remazol Red (RR)
UV-vis, FT-IR, GC-MS and ¹ H NMR	[2-amino-8- (2- (4- (6- (7-amino-3,6,8-trihydroxynaphthalene-1-ylamino) pyridine-2-ylamino) phenylamino) pyrimidin-4ylamino) naphthalene-1,3,6,-triol], and 8-(4,6-dichloro-1,3,5-triazin-2-ylamino)- 2diazenylnaphthalene-1,3,6-triol	Reactive Red (RR)
UV-vis, FT-IR, HP-LC and GC-MS	N-ethyl-4-[(2- methyl-4-nitrophenyl) diazenyl] aniline, 4-[(2-methyl-4-nitrophenyl) diazenyl] phenol, 1-(2-methyl-4- nitrophenyl)- 2- phenyl diazene, 2-methyl 4-nitroaniline	Textile wastewater
UV-vis, FT-IR, HP-LC and GC-MS	[GG-A], {ethyl [(4-oxo-3-4-dihydroquinolin-2-yl) methyl] amino} acetaldehyde [Rt-19.383-MW, 244, m/z - 244]	Scarlet RR (SRR)
HPTLC, HPLC, FT-IR and GC-MS	5-Sulfone diazonium, 4-methyl-2-m-tolyamino-cyclopentanol	Golden Yellow HER (GYHER)
UV-vis, FT-IR, HPLC and ¹ H NMR	Methyl metanilic acid, 4-aminobenzoic acid and Benzoic acid	Remazol Orange (RO)
UV-vis, HPLC and GC-MS	6-(acetylamino) naphthalene-2-sufonic acid, 2-(4-aminophenyl) ethanesulfonic acid, aniline	Reactive Orange 16 (RO16)

Adopted from: [\[5,8,13,31,34,83,106\]](#).

13. Concluding remarks and future perspectives

TIs are major sources of environmental pollution. Millions of gallons of highly polluted/colored wastewater are discharged from TIs regularly all over the world. TIWW contains high concentration of different toxic persistent or xenobiotics pollutants, which persists in the environment for a long duration, posing severe environmental and public health hazards. Treatment of TIWW is a big challenge as there is no particular and economically feasible technique for the adequate treatment of TIWW. Although, many traditional and emerging treatment methods have been reported for the treatment of TIWW, but physico-chemical methods seem to be effective in color removal from TIWW, but these incur high operating cost and generate undesirable secondary pollutants (sludge).

On the other hand, microbial remediation is a cost effective, ecofriendly and globally acceptable approach, but less effective and has long treatment time. Therefore, more research is required from laboratory scale to pilot scale to minimize the environmental as well as public health hazards. Phytoremediation and constructed wetlands are green, emerging and environment friendly tools for the remediation of a variety of recalcitrant organic and inorganic wastes effectively. In addition, different AOPs have been reported as the most promising methods for the treatment of persistent/xenobiotics textile pollutants, but these are also restricted by the high operating cost and generation of secondary pollutants.

MTs and MBRs are extensively utilized to achieve the desired quality of treated water for recycling. Transgenic microbial strains having special genes for the effective removal of dyes from wastewater can also effective in treatment of TIWW. Furthermore, the combined approaches of physical, chemical and biological methods have also emerged as the potential tools for the degradation and detoxification of TIWW. Besides these, the use of hazardous, poor degradable/non-degradable dyes and auxiliaries should also be avoided in TIs as it may be helpful in the reduction of treatment cost for environmental cleanup.

Declaration of Competing Interest

Authors have no conflict of interest.

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