Recent Advances in Physicochemical and Biological Treatment Approaches for Distillery Wastewater

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Abstract

Molasses-based distilleries are amongst the most polluting industries worldwide generating huge volume of high strength wastewater. Discharge of this wastewater, enriched with toxic androgenic and carcinogenic pollutants including melanoidins, phenolics, endocrine disrupting chemicals, organic acids, heavy metals and other recalcitrant hazardous compounds, into the environment without adequate treatment posing a risk to human, animals, microorganisms, and plants.

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Thus, proper wastewater treatments are mandatory to remove contaminants before its discharge into the environment. Numerous physicochemical methods have been implemented for remediation or detoxification of distillery wastewater, which is viewed as a challenging job with respect to cost, technical complexity, and sludge generation in huge quantity with subsequent disposal problems. Therefore, there is an urgent need for safe management of hazardous distillery wastewater; the technologies must be economically viable, ecologically sound, and socially acceptable. This book chapter presents an overview of the generation of effluent, its chemical characteristics and environmental hazards. In addition, we have also discussed the existing treatment approaches and challenges for safe disposal of distillery wastewaer into the environment.

Keywords
Endocrine-disrupting chemicals · Melanoidins · Ligninolytic enzymes · Methanogenesis

6.1 Introduction

The worldwide demand for energy and the uncertainty of natural resources has led to the eco-friendly development of alternative liquid biofuels. Ethanol is one of the excellent candidates since it reduces dependence on fossil-fuel reserves. In developing countries like India, distilleries are one of the major agro-based polluting industries; in addition, they are a high consumer of fresh water and utilize the sugarcane molasses as the feedstock for ethanol making (Arimi et al. 2014; Kumar and Chandra 2018; Chandra and Kumar 2017a,b). However, there is serious environmental trouble with ethanol production from sugarcane molasses fermentation which is generally connected to the generation of dark brown-colored wastewater, known as a spent wash (SW) or raw wastewater/effluent (Kumar and Chandra 2018; Chandra and Kumar 2017a, b, c). It has been reported that SW produced from distilleries has a high organic load as compared to other raw material used for ethanol production (Kumar and Sharma 2019. There are three different organic wastes generated from the molasses based-distilleries which include yeast sludge, spent malt grain wash, and SW. A typical sugarcane molasses-based distillery generates 12–15 liters of SW for every liter of the ethanol produced. It stated that about 40.4 billion liters of SW are produced with a generation of 3.25 billion liters ethanol from 319 distilleries located in the tropical and subtropical region of India. SW is a dark brown-colored wastewater characterized by a specific obnoxious odor with high organic and inorganic load at acidic pH (Table 6.1). Wilkie et al. (2000) stated that COD is 4–5 times higher in sugarcane molasses-based SW as compared to sugarcane juice stillage. SW composition generally depends on the raw material used for sugar extraction as well as the distillation and fermentation processes adopted in distilleries for ethanol production. The dark brown-colored SW is one of the most obvious indicator of water and soil pollution. Apart from color, SW possesses a high

Table 6.1 Physicochemical characteristics of various types of waste generated by alcohol-producing molasses-based distilleries (Acharya et al. 2011; Mohana et al. (2007); Singh and Dikshit (2011) Chandra and Kumar (2017a, b)

Parameter	Spent wash	Anaerobically digested spent wash	Anaerobically digested spent wash sludge
Color appearance	Dark brown	Dark brown	Dark brown
Color intensity(co-Pt unit)	150,000	80,000	–
Odor	Like molasses	Unpleasant	–
pH	3.0–4.07	7.9–8.2	8.00–8.1
EC (μS cm^{-1})	–	33	2.29–4.12
Temperature (°C)	90	30	89
BOD (mg L^{-1}/mg kg^{-1})	40,000–60,000	8000–12,000	–
COD (mg L^{-1}/mg kg^{-1})	90,000–190,000	45,000–52,000	–
TS (mg L^{-1}/mg kg^{-1})	83,084–190,000	47,422–72,500	–
Sodium (mg L^{-1}/mg kg^{-1})	–		42.13–56.16
Chloride (mg L^{-1}/mg kg^{-1})	2200–8500	7842–7997	1272.74–1824.4
Phenol (mg L^{-1}/mg kg^{-1})	4.20–10,000	6893–7202	501.34
Sulfate (mg L^{-1}/mg kg^{-1})	5760–9000	180–3875	145.07
Phosphate (mg L^{-1}/mg kg^{-1})	5.36–2700	46–1625	2268.83
TN (mg L^{-1}/mg kg^{-1})	2800–7000	4096	2.468
TOC (mg L^{-1}/mg kg^{-1})	25,368	31,090	17.318
Reducing sugar (g%)	–	0.40–0.17	–
TVS	80,000–120,000		–
TSS (mg L^{-1}/mg kg^{-1})	13,000–15,000	29,810	–
TDS (mg L^{-1}/mg kg^{-1})	90,000–150,000	17,612	–
Ammoniacal nitrogen	–	2800	190
Trace elements			
Mn (mg L^{-1}/mg kg^{-1})	4.556	43.63	126.30–238.47
Cr (mg L^{-1}/mg kg^{-1})	1.05 ± 0.031	–	BDL-21.825
Zn (mg L^{-1}/mg kg^{-1})	BDL-2.487	1.24	43.47–210.15
Cu (mg L^{-1}/mg kg^{-1})	BDL-0.337	BDL-0.75	73.62–847.46
Fe (mg L^{-1}/mg kg^{-1})	163.947	57.50	2403–5264.49
Pb (mg L^{-1}/mg kg^{-1})	BDL	0.23	16.33
Cd (mg L^{-1}/mg kg^{-1})	BDL	1.30	BDL-1.440
Ni (mg L^{-1}/mg kg^{-1})	BDL-1.175	0.31	13.425–15.60

BOD biological oxygen demand, *COD* chemical oxygen demand, TS Total solids, TN Total nitrogen, *TSS* total suspended solids, *TS* total solids, *TDS* total dissolved solids, *TOC* total organic carbon, *TVS* total volatile solids, *EC* electrical conductivity, *Mn* Manganese, *Cr* Chromium, *Zn* Zinc, *Cu* Copper, *Fe* Iron, *Pb* Lead, *Cd* Cadmium, *Ni* Nickel, *BDL* Below detection limit

concentration of reducing sugars, hemicelluloses, lignin, resins, dextrin, polysaccharides, organic acids, phenolic compounds, anthocyanins, tannins, fatty acids, sterols, and resins (Chandra and Kumar 2017a). High chemical oxygen demand (COD), biological oxygen demand (BOD), and persistent dark brown color of SW poses environmental, water, and soil pollution problems including a threat to plant and animal lives, and thus safe disposal of such kind of wastewater is challenging. In accordance with the environmental protection act and rules of the Ministry of Environment, Forests and Climate Change and Central Pollution Control Board (CPCB), Govt. of India, it is mandatory to treat hazardous SW before it is disposed into the environment. Indian government policies on pollution prevention have forced distilleries to look for an effective and sustainable technology for decreasing the SW characteristics. It is usually subjected to conventional aerobic and anaerobic secondary treatment approaches such as activated sludge, anaerobic digestion, and anaerobic lagoons processes, which easily remove organic matter (OM) and also reduce the BOD and COD of SW. However, these treatment methods do not decompose or decolorize melanoidins present in SW due to their recalcitrant nature and presence of other complex co-pollutants. Thus, adequate treatment is warranted before the wastewater is discharged into the environment. Hence, this book chapter is focused on the generation and characteristics of distillery wastewater (DW) pollutants, their environmental hazards as well as various existing physicochemical and biological treatment approaches used for DW. Further, the emerging treatment approaches used for DW have also been discussed.

6.2 Ethanol Manufacturing Process and Effluent Generation

Ethanol can be produced from various feedstock, including sugar-based materials (i.e., sugarcane juice and beet molasses), starch-based material (i.e., corn, barley, wheat, rice, and cassava), and cellulosic materials (i.e., crop residues and sugarcane bagasse). In India, distilleries used diluted sugarcane molasses (15–16%) as a chief feedstock material for ethanol production (7–8% v/v). In general, ethanol production consists of three steps: (i) feed preparation (fermentable sugar containing diluted molasses solution), (ii) fermentation (conversion of sugars to ethanol), and (iii) distillation (separation and purification of ethanol). For ethanol production, sugarcane molasses, and nitrogen and phosphate-containing food supplements are taken in a fermentation broth. Further, the fermentation process is carried out by yeast (*Saccharomyces cerevisiae*) culture, which converts the sugar into ethanol, and the yeast sludge settles down at the end of the process. The fermented mass contains 7–8% ethanol, which is separated in a distillation column as the top product, and brownish liquid as the bottom product known as SW (Fig. 6.1). In molasses-based distilleries, the fermentation process can be carried out by three modes; (i) batch, (ii) fed-batch, (iii) continuous mode. In a batch process, sugarcane molasses is diluted with water to reduce the sugar content from the existing 40–45% to 10–15%, and then yeast inoculum at about 10% concentration (v/v) is added with this diluted sugarcane molasses. Further, this diluted molasses is allowed to ferment for 30–40 hrs. After completion of fermentation, the yeast sludge is separate from the bottom of the

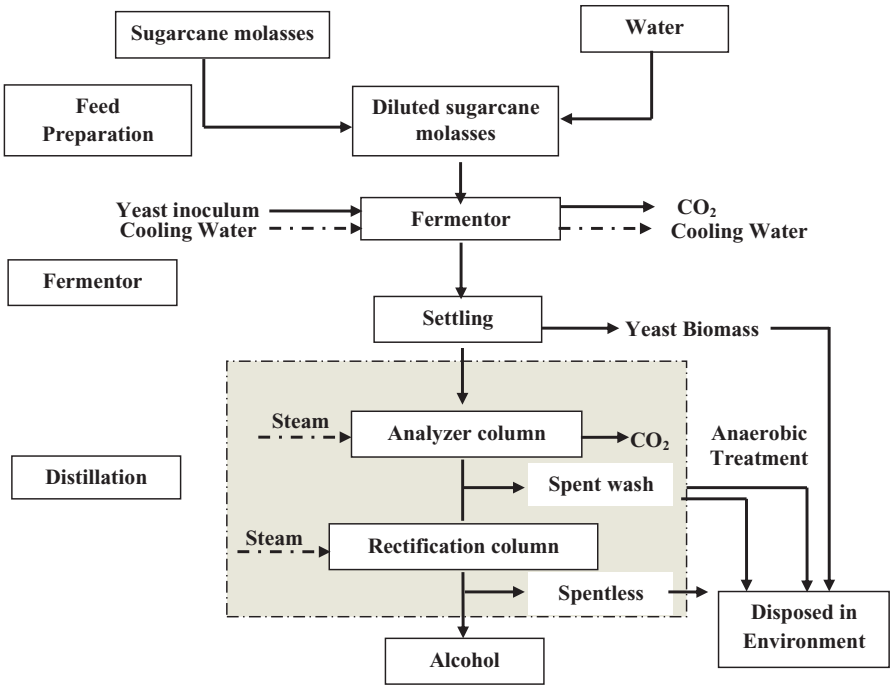

Fig. 6.1 Manufacture of ethanol from sugarcane molasses and generation of wastewater

fermenter (bioreactor) while the bioreactor wash is sent to the analyzer column for distillation with steam where a mixture of steam and ethanol vapors is collected at the top of the column and spent wash drained out from the bottom. The mixture of steam and ethanol is fed to the rectification column where rectified spirit (RS) is formed due to condensation of water and ethanol vapors. The condensed steam is discharged as spent lees (Fig. 6.1). In a fed-batch process, a combination of batch and a continuous mode, substrates (nutrients) are supplied (fed) to the bioreactor during cultivation and the product(s) remain in the bioreactor until the end of the run. Continuous mode is carried out by continually adding culture medium, substrates, and nutrients into a bioreactor containing microorganisms. During this process, the culture volume must be constant and the products formed after fermentation are continuously taken from the media. Absolute ethanol or fuel ethanol is generated by the dehydration of RS through molecular sieve technology where RS is passed through preheater to raise the temperature to 65 °C, then fed into the recovery column and heated through boiler by steam to produce alcohol vapors. Further, the alcohol vapors are superheated with steam and then passed through one of the pairs of molecular sieve beds in auto-mode. The water (H_2O) molecules are absorbed by the molecular sieves beds and become saturated within 5–6 min. When the first molecular sieve bed is saturated with H_2O, automatically ethanol vapors will pass through the second bed. The ethanol vapors having alcohol concentration of about 99.70% are condensed and stored in the collection tanks. The desorbed liquid contains 70–75% ethanol, which is partially used for

creating a vacuum and remains recycled to the recovery column. During ethanol production, a huge amount of solid waste matter as a yeast sludge is formed in the distilleries, which cause pollution when it is disposed into the environment. Yeast sludge is rich in protein and contains a considerable amount of essential amino acids and drying sludge grains are marketed as livestock feed and make it the best source for the production of single cell protein. Generally, during ethanol production, distillery operations use water for various process and non-process applications. The process applications include preparation of sugarcane molasses for fermentation, yeast propagation, and steam requirements for distillation, while the non-process applications involve boiler water, wash water, cooling water used in making potable ethanol. The wastewaters discharged from the analyzer column, yeast sludge, spent less, water treatment plant, waste wash water, cooling water, boiler as blowdown, bottling plant, and other wastes as termed as SW. In distilleries, the major source of wastewater generation is the distillation step wherein a huge volume of dark brown-colored wastewater is generated. Average SW generation is highest in the batch process (11.1–15.0 liters per liter ethanol production), higher in the continuous process (8.5–11.0 liters per liter ethanol production), and lowest in the bio-still process (6–8 liters per liter ethanol production). Figure 6.1 illustrated the manufacturing process of ethanol from sugarcane molasses, along with the wastewater generation.

6.3 Distillery Wastewater: Nature and Chemical Characteristics

Over the last few decades, the occurrences of pollutants due to discharge of DW in the aquatic ecosystem and their toxic effects to human health as well as wildlife organisms have become major issues of increasing concern in India and other developing countries (Kumar and Sharma 2019). The majority of distilleries coexist with sugar mills and utilize sugarcane molasses as a starting material for ethanol production. In distilleries, a major fraction (~90%) of the fermented wash going to distillation column is discharged as SW (Chandra and Kumar 2017b). The characteristics of SW vary significantly according to the fermentation feedstock, and the fermentation/distillation processes adopted. SW is characterized with unpleasant odor; deep brown color; high level of BOD, COD, TDS, total solids (TS), total nitrogen (TN) sulfate and phosphate; and the presence of various heavy metals (HMs) ions such as iron (Fe^{3+}), zinc (Zn^{2+}), copper (Cu^{2+}), nickel (Ni), manganese (Mn^{2+}), and lead (Pb^{2+}) and numerous endocrine-disrutping chemical (EDCs) (Tables 6.1 and 6.2).

The high organic load of SW is primarily composed of melanoidins (Maillard reaction products; MRPs), thermal degradation products (hexose alkaline degradation products; HADP), and sugar condensation reaction products (overheated sugars; caramels) (Hatano et al. 2013; Hatano and Yamatsu 2018; Kumar and Chandra 2018). The MRPs formed through the nonenzymatic browning reaction also known as Maillard reaction occurs between amino acids and reducing sugars and caramels at elevated temperatures that are responsible for deep brown color and odor in the SW (Kumar and Chandra 2018, 2020). Besides, the color of SW is also generally attributed to the existence of a wide variety of naturally polymeric colorants such as

Table 6.2 Organic pollutants identified by gas chromatography-mass spectrometry (GC-MS) technique in (a) acetone (b) ethyl acetate (c) isopropanol (d) methanol (e) ethanol and (f) n-hexane extracted sample of distillery spent wash (Chandra and Kumar 2017a, b, c)

SI. No.	Retention time	Identified compounds
(a)		
1.	8.66	1,3-Propanediol, TMS ether
2.	9.88	Propanoic acid, 3-[(TMS)oxy)-TMS ether
3.	10.27	Butanoic acid, 3-methyl-2-[(TMS)oxy]-TMS ether
4.	11.54	D-Erythrotetrofuranose, tris –O-(TMS)
5.	11.87	Pentanoic acid
6.	13.78	Butanedioic acid, bis(TMS) ester
7.	15.52	Resorcinol, O-bis(TMS)
8.	16.01	2,3-Butandiol, bis-O-(TMS)
9.	17.34	Malic acid (O-(trimethylsilyl)-bis(trimethylsilyl ester)
10.	17.54	2-Methyl-1,3-Butanediol 2TMS
11.	19.60	2-Furancarboxylic acid, 5-[[(TMS) oxy] methyl], TMS ester
12.	20.19	2,3,5-tri-O- TMS-arabino-1,5-lactone
13.	22.18	Cyclooctene, 1,2-bis(trimthylsiloxy)
14.	22.15	Tricarballylic acid TMS
15.	22.81	D-ribo-Hexanoic acid, 3-deoxy-2,56, tris-O-(TMS), lactone
16.	23.54	Benzoic acid, 3,4-bis [(TMS)oxy], TMS ester
17.	24.19	Tert-butylhydroquinone, bis (TMS) ether
18.	24.87	Trimethylsilyl 3,5-dimethoxy-4-9 TMS oxy)benzoate
19.	26.48	Vanillypropionic acid, bis (TMS)
20.	30.61	Benzeneacetic acid, α,4-bis[(TMS) oxy]-methyl ester
(b)		
1.	8.23	L-lactic acid, TMS ether, TMS ester
2.	8.48	Acetic acid, [(TMS)oxy], TMS ester
3.	10.33	Butanoic acid, 3-methyl-2-[(TMS), TMS ester
4.	10.70	Valeric acid, 5-methoxy, TMS ester
5.	11.86	2-Hydroxysocaproic acid, TMS ether,
6.	12.24	Ethyl(TMS) succinate
7.	12.90	1,3-Propanediol, TMS ether
8.	13.78	Butanedioic acid, bis(TMS)ester
9.	13.94	Diethyl methylsuccinate
10.	15.22	Lactic acid dimer, bis(TMS)
11.	16.00	Silane, [1,4-phenylenebis(oxy)]bis(trimethyl)
12.	16.56	2-Methyl-1,3Propanediol 2TMS
13.	18.59	2-Furancarboxylic acid, 5 -[[(trimethylsilyl)oxy] methyl], TMS ester
14.	19.18	Benzenepropanoic acid, α-[(TMS)oxy], TMS ester
15.	20.09	Benzoic acid, 4-[(TMS)oxy], TMS ester
16.	20.25	Ethyl-TMS dipropylmalonate
17.	20.62	Bicyclo[4.3.0]nonane −2-one,[Z]-cis-8-(phenyl-1-trimethylsilylmethylene)

(continued)

Table 6.2 (continued)

SI. No.	Retention time	Identified compounds
18.	20.98	2-Hydroxyheptanoic acid 2TMS
19.	21.32	D-erythro-Hex-2-enoic acid, 2,3,-di-O-methyl-5,6-bisO-(TMS)-ϒ-lactone
20.	22.23	Tricarballylic acid 3TMS
21.	22.65	Benzoic acid, 3-methoxy-4-[(TMS)oxy], TMS ester
22.	24.89	Trimethylsilyl 3,5 dimethoxy-4-(TMS oxy)benzoate
23.	25.96	3-Vanil-1,2-Propanediol 3TMS
24.	27.01	B-D-Galactopyranoside, methyl 2,6-bis-O-(TMS)-cyclic butyboronate
25.	27.83	Silane, (preg-5-ene-3β,11β,17,20β-tetraylteraoxy) tetrakis (trimethyl)
(c)		
1.	8.49	Propanoic acid, 2–9 (TMS)oxy],- TMS ester
2.	13.75	Butanedioic acid, bis(TMS)ester
3.	15.32	Butane, 1,2,4-tris (trimethylsilyloxy)
4.	16.01	2-Methyl-1,3-Propanediol- 2- TMS
(d)		
1.	10.14	Propanoic acid, 3-[(TMS)oxy], TMS ester
2.	10.44	Butanoic acid, 3-methyl-2-[(TMS)oxy], TMS ester
3.	10.93	2-Methylbutanoic acid, 3-(t-butlydimethylsilyloxy),-methyl ester
4.	11.71	Erythro-pentitol, 2-dedoxy-1,3,4,5-tetrakis-O-(TMS)
5.	16.04	3,6-Didoxa-2,7-Disilaoctane, 2,2,4,5,7,7-Hexamethyl
6.	19.95	Cyclooctene, 1,2-bis-(trimethylsilyloxy)
7.	20.22	2,3,5,-tri-O-trimethylsily-arabino-1,5-lactone
8.	22.85	D-ribo-hexanoic acid, 3-deoxy-2,5,6 tris-O-(TMS)-lactone
(e)		
1.	8.48	D-lactic acid-Di TMS
2.	12.39	Ethyl (trimethyl)succinate
3.	13.76	Butanedioic acid, bis (TMS)ester
4.	16.03	3,6-Dioxa-2,7-disilaoctane,2,2,4,7,7-pentamethyl
5.	17.77	Erytritol per-TMS
6.	20.21	2,3,4,5-tetrahydroxypentanoic acid-1,4-lactone, tris (TMS)
7.	21.07	Cyclooctene, 1,2-bis(trimethylsiloxy)
8.	22.76	D-Ribo-Hexanoic acid, 3-deoxy-2,5,6-tris-O-(TMS) lactone
9.	23.12	α-D-Galactopyranose, 1,2,3-tris-O-(TMS), cyclic methylboronate
(f)		
1.	12.31	Benzene, 1-ethyl-3,5-disopropyl
2.	12.87	Eicosane
3.	35.69	3,4-Dihyroxymandelic acid, ethyl ester, tri-TMS
4.	36.56	Octadecane,3-ethyl-5(2-ethylbutyl)
5.	37.57	Celidonil, Deoxy

carotenoids, chlorophyll, resins, fatty acids, heme pigment, anthocyanins, tannins, riboflavin, betalains, quinone pigments, polyphenols, melanin, and metal sulfides (Borja et al. 1993; Arimi et al. 2014; Pant and Adholeya 2007). Among these colorants, melanoidins are major nitrogenous, high molecular weight (5–40 kDa), polymeric, acidic, negatively charged imparting organic compounds present at high concentration in SW. Melanoidins are toxic to microorganisms and recalcitrance to biological wastewater treatments; therefore, DW must be treated before disposal into the environment. It has been demonstrated that various HMs such as Mn^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, and Fe^{3+} bind with melanoidins to make an organometallic complex and, consequently, enhance the toxicity of SW into the environment (Hatano et al. 2016; Migo et al. 1997; Chandra et al. 2018a, b, c, d). Polyphenols and melanoidins may also be the source of the formation of aromatic halogenated disinfection by-products (DBPs) during chlorine disinfection of DW. Liu and Zhang 2014 reported that aromatic halogenated DBPs showed higher developmental toxicity and growth inhibition than aliphatic halogenated DBPs. However, the colloidal nature of caramels makes the SW resistant to biological degradation and toxic to aquatic and terrestrial organisms. The obnoxious odor of DW mainly occurs due to the presence of indole, skatole, and other sulfur compounds. In addition, some toxic chemicals such as tricarballylic acid 3TMS; benzoic acid 3-methoxy-4-[(TMS)oxy], TMS ester; benzenepropanoic acid; α-[(TMS)oxy], TMS ester; 2-furancarboxylic acid, 5-[[(TMS)oxy] methyl], TMS ester; vanillylpropionic acid, bis(TMS); 2-hydroxysocaproic acid; and butanedioic acid bis(TMS) ester are also present in SW (Yadav and Chandra 2012). These organic compounds are well reported as potential EDCs by the US Environmental Protection Agency (USEPA) (2012). Hence, due to its toxic nature, SW must be treated properly before it is disposed into the environment (Tewari et al. 2007). In order to lower the high BOD and COD level, presently many distilleries are recycling this wastewater for getting fuel in the form of methane (Joshi et al. 1994). SW received after anaerobic digestion is called post-methanated distillery effluent (PMDE) or biomethanated distillery effluent (BMDE), which contains a higher level of BOD, COD, TDS, and phenols, with dark brown color, strong odor, and alkaline pH. Besides organic content, BMDE also contains a high level of nitrogen, potassium, sulfur, and phosphorus, which can lead to eutrophication of aquatic ecosystem. In addition, BMDE retains a high amount of various HMs (Table 6.1). This means that SW after anaerobic digestion retains high organic and inorganic load and it is not safe for discharge into the environment (Chandra et al. 2018a; Kaushik and Thankur 2009). Besides the effluent, sugarcane molasses-based distilleries produce huge amount of anaerobically digested SW sludge which has been reported for high concentration of phenolics, melanoidins, and complex OM along with metallic ions (i.e., Cd^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+} and Zn^{2+}) and nonmetallic ionic compounds (i.e., Na^{+}, Cl^{-}, SO_2^{-4}, PO_3^{-4}) (Table 6.1). Recently, distillery sludge is reported to contain high amount of plant-derived hexadecanoic acid; octadecanoic acid; n-pentadecanoic acid; stigmasterol; β-sitosterol trimethyl ether; heptacosane, lanosta-8, 24-dien-3-one, 1-phenyl-1-propanol, and 1-methylene-3-methyl butanol; dotriacontane; dodecanoic acid; 2-ethylthio-10-hydroxy-9-methoxy-1,4 anthraquinone; 5α-cholestane, 4-methylene; and campesterol TMS as potential

EDCs reported by the USEPA (Chandra and Kumar 2017a, c; Chandra et al. 2018b). All these features combined with the huge volume of DW and sludge disposed of distilleries causes important environmental issues. Therefore, the elimination and biodegradation of organic and inorganic toxic compounds are necessary for the safe disposal of DW into the environment.

6.4 Environmental Pollution and Toxicity Profile of Distillery Wastewater

Distilleries generate a huge volume of wastewater during ethanol production, and most of the distilleries dispose their partially treated or untreated wastewater into water bodies causing environmental threats to organisms. Due to high pollution nature of DW, MoEF listed alcohol industries at the top among the "Red category" industries (Tewari et al. 2007). Regarding environmental pollution, the government of India made rules and regulations in 1976 and again revised them in 1983. The Bureau of Indian Standards (BIS) provides guidelines to state and central government authorities which would help to decide boundaries on effluent disposal and to the industry for selecting effective technology and the degree of treatment required for DW before their disposal. In an aquatic ecosystem, the DW reduced penetration of sunlight in lagoons, lakes, and rivers, which in turn decreases both dissolved oxygen and photosynthetic activity, thereby aquatic life suffers, resulting in deterioration of water quality and loss of productivity to such an extent that the water becomes unusable (Kumar and Gopal 2001; Chandralata et al. 2004; Ramakritinan et al. 2005; Kumar and Chandra 2006; Kumar and Sharma 2019). Disposal of DW on land is equally hazardous; it inhibits germination of seeds and depletes vegetation by decreasing the soil alkalinity, salinity, and manganese availability (Jadhav and Savant 1975; Chandraju and Basavaraju 2007; Bharagava and Chandra 2010; Narain et al. 2012; Srivastava and Jai 2010; Arora et al. 1992; Kannan and Upreti 2008). Chandra and Kumar (2017b) reported the toxic effects of SW at different concentrations on seedling growth of *P. mungo* L. and *T. aestivum*. In a another study, Chandra and Kumar (2017a) also reported the presence of androgenic-mutagenic compounds and potential autochthonous bacterial communities during in situ bioremediation of anaerobically digested distillery sludge and also tested the toxicity of in situ degraded sludge leachate by using *Allium cepa* L. root meristematic cell. They showed a reduction of toxicity in degraded samples of sludge and leachate, confirming the role of autochthonous bacterial communities in the bioremediation of distillery waste in situ. Nonjudicious use of PMDE adversely affected crop growth and decreased physicochemical properties (Jagdale and Sawant 1975; Joshi et al. 2000; Tripathi et al. 2011). However, the judicious application of PMDE improved crop productivity and alleviated environmental pollution problems (Devarajan et al. 1994; Davamani et al. 2006). The impact of distillery waste on the environment and their eco-friendly and advanced cleaner technologies used to combat the threat are illustares in Fig. 6.2.

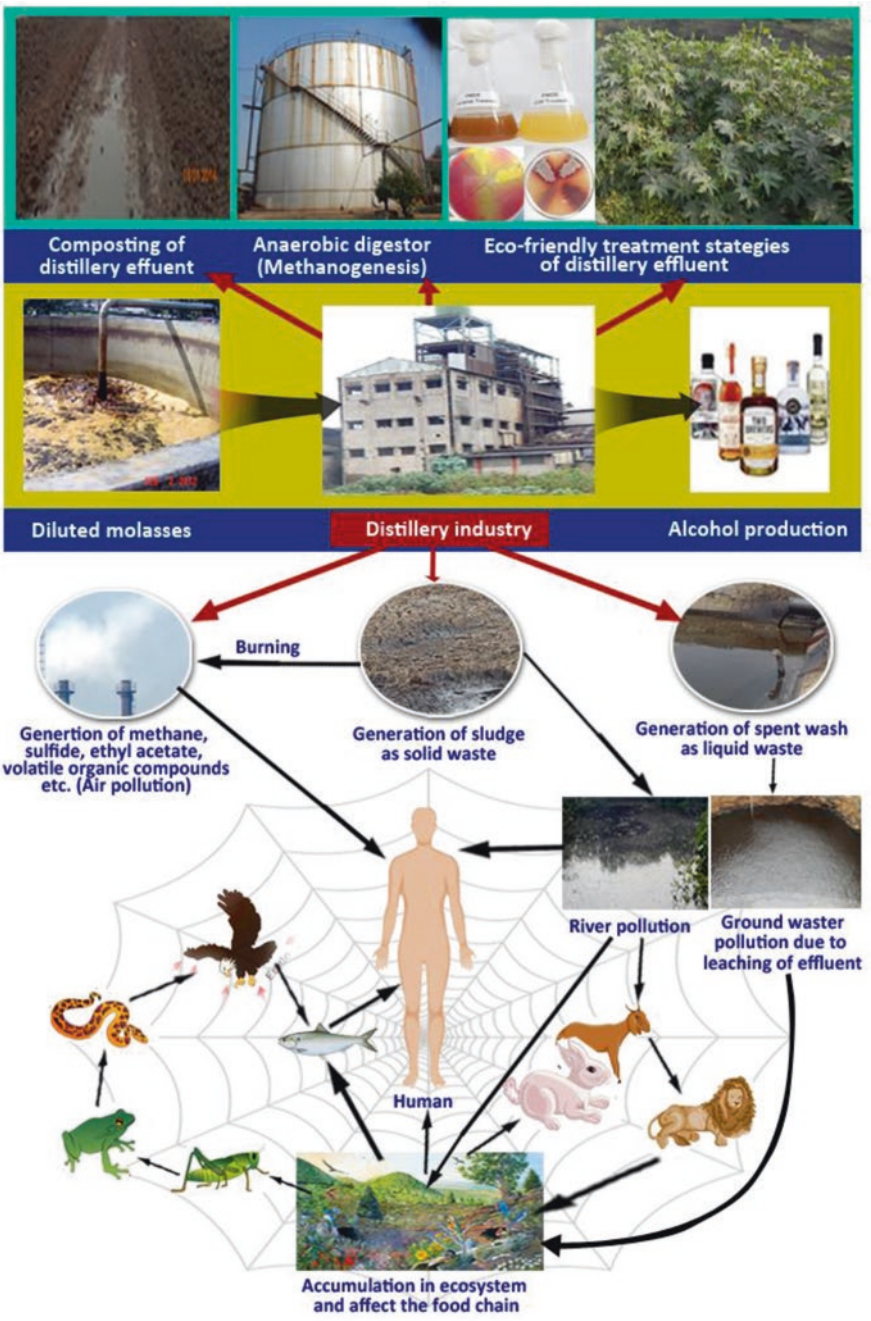

Fig. 6.2 Discharged distillery waste and its environmental impact and treatment technologies to combat the threat

6.5 Treatment Approaches for Distillery Wastewater

DW is a major threat to the environment, and it is therefore essential to adequately treat the DW prior to its safe disposal into the environment. This can be achieved by using biological, physical, and chemical approaches, either alone or in combination (Fig. 6.3).

6.5.1 Biological Treatment Approaches

Biological approaches have been recognized as eco-friendly and most effective methods for the treatment of highly polluted DW whereby organic substances are used as food by growing microorganisms such as bacteria, fungi, yeast, and cyanobacteria. The end result is a decrease in the number of organic pollutants and an increase in the number of microorganisms, carbon dioxide (CO_2), water (H_2O), and other by-products of microbial metabolism (Kumar et al. 2018; Kumar and Chandra

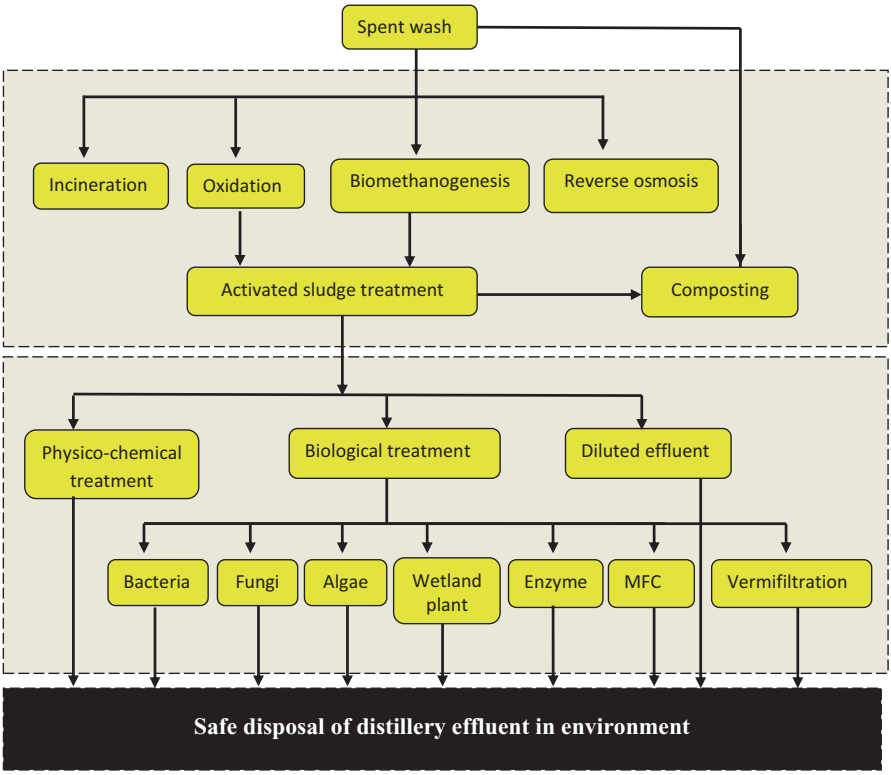

Fig. 6.3 Different physicochemical and biological approaches used for treatment of distillery wastewater

2020. The role of anaerobic and aerobic biological treatment approches in DW treatment are discussed in the following sections.

6.5.1.1 Anaerobic Treatment

Distillery SW retains high BOD/COD ratio (1.11–1.25), TDS, and high concentration of inorganic solids with low pH and high temperature. In order to decrease its high COD and BOD level, presently many distilleries are recycling this effluent for getting fuel in the form of methane (CH_4) through anaerobic digestion (AD). AD is a multifaceted treatment process requiring the potential activity of different group of microorganisms interacting in a bioreactor. The breakdown of OM in an anaerobic reactor typically involves four major degradation phases: (i) hydrolysis, (ii) acetogenesis, (iii) acidogenesis, and (iv) methanogenesis. In the first three phases, organic pollutants are hydrolyzed and/or fermented into intermediate short-chain fatty acids which are further degraded to acetate and hydrogen and carbon dioxide. Further, in the fourth phase, acetate and H_2/CO_2 are converted into methane. Anaerobic treatment is a broadly accepted an effective exercise, and different high-rate anaerobic reactor designs have been tried for DW treatment. One of the methods that are used to treat DW is the application of upflow anaerobic sludge blanket (UASB) reactor. The UASB process is an attractive treatment because of low cost, high treatment efficiency, biogas generation, and ability to handle high organic loading rates (OLRs) and requires shorter hydraulic retention time (HRT) than other reactors (Keyser et al. 2003; Acharya et al. 2008). The UASB reactor has four major components, i.e., sludge bed, sludge blanket, gas-solid separator, and settlement compartment. A two-stage process with an anaerobic filter followed by a UASB reactor was investigated by Blonskaja et al. (2003). The acidogenic and methanogenic phases were clearly separated ensuring better conditions for the methanogens. COD reduction was 54% and 93% in the first and second stage, respectively. Table 6.3 provides a summary of different reactor configurations used for the anaerobic digestion of SW. The limitations of anaerobic treatment processes are the requirement of high dilution due to the presence of many antimicrobial compounds (Bharagava and Chandra 2010). AD can remove a substantial amount of organic load when applied in treating DW, but it is ineffective in color reduction and several recalcitrant pollutants. Therefore, further treatment is required to remove the remaining dark color and COD, BOD, etc. However, researchers have reported various alternatives for further treatment of BMDE through aerobic route and resource the recovery.

6.5.1.2 Aerobic Treatment

Aerobic processes are usually applied as post-aerobic treatment of BMDE, based on pollutant degradation by the utilization of specific microorganisms, either as pure strains or as a consortium. These processes generally depend on the oxidative activities of microorganisms, viz., fungi, yeast, bacteria, and cyanobacteria, used by the various researchers for the treatment of raw SW as well as BMDE in the presence of oxygen (Chandra and Kumar 2015a).

Table 6.3 Performance efficiency of various anaerobic reactors used for the treatment of spent wash

	Reduction %			
Reactor	BOD	COD	HRT	References
Upflow anaerobic fixed film bioreactor	–	64	–	Acharya et al. (2008)
Bench-scale UASB reactor	95	69	–	López et al. (2018)
Expanded granular sludge bed reactors	–	80–90	–	López et al. (2018)
Thermophilic UASB reactor	>80	39–67	–	Harada et al. (1996)
UASB reactor	–	83.87	24 hrs	Thiyagu and Sivarajan (2018)
Anoxic-aerobic ultrafiltration membrane bioreactors	–	93	20–39 hrs	Wolmarans and de Villiers (2002)
UASB reactor	84–89	72–91	20 hrs	Saini and Lohchab (2017)
UASB reactor	–	90–95	–	Moletta (2005)
Anaerobic filter and UASB reactor	–	90	1.3 days	Blonskaja et al. (2003)
Anaerobic granular sludge reactor	–	80–90	1 day	Collins et al. (2005)
Anaerobic filter followed by a UASB reactor	–	54 and 93		Blonskaja et al. (2003)
Downflow fixed-film reactor	60–73	85–97	3.3–2.5 days	Bories et al. (1988)
UASB reactor	89.11	68.35	2 days	Saner et al. (2014)

BOD biological oxygen demand, *COD* chemical oxygen demand, *HRT* hydraulic retention time, *UASB* upflow anaerobic sludge blanket, *hrs*, hours

6.5.1.2.1 Fungal Treatment

In the last two decades, the fungi species belonging to basidiomycetes and ascomycetes class have been used in the decolorization of natural and synthetic melanoidins in connection with the color reduction of DW. The aim of fungal treatment is to reduce the COD and BOD of DW and at the same time to obtain some valuable products, such as fungal biomass for protein-rich animal feed, extracellular organic acids, or some specific fungal metabolites. Several fungi species such as *Geotrichum candidum* (Kim and Shoda 1999), *Trametes* sp. (Gonzalez et al. 2000), *Coriolus hirsutus* (Miyata et al. 2000), *Flavadon flavus* (Raghukumar and Rivonkar 2001), *A. niveus* (Angayarkani et al. 2003), *Phanerochaete chrysosporium* (Dhaiya et al. 2001; Thakkar et al. 2006), *Pleurotus florida, Aspergillus flavus* (Pant and Adholeya 2009a), *Neurospora intermedia* (Kaushik and Thakur 2013), *Fusarium verticillioides* (Pant and Adholeya 2009b) and yeast *Citeromyces* sp., *Candida tropicalis* (Tiwari et al. 2012), and *Candida glabrate* (Mahgoub et al. 2016) have been reported for the degradation and decolourisation of melanoidins containing DW. A list of yeast and fungi species used by various researchers for decolorization and degradation of DW is given in Table 6.4. The degradation and decolorization of melanoidins by fungus have occurred due to the prevalence of ligninolytic enzymes, i.e.,

Table 6.4 Various yeast and fungi species capable for COD, BOD reduction and decolorization of distillery wastewater

Microorganisms	Incubation time	Reduction %			References
		Decolorization	BOD	COD	
Yeast	2–5 days	60.00	–	–	Mahgoub et al. (2016)
Candida tropicalis RG-9	24 hrs	75.00	–	–	Tiwari et al. (2012)
Issatchenkia orientalis	7 days	60.00	–	–	Tondee and Sirianutapiboon (2008)
Fungi					
Trametes sp. I-62	7 days	73.30	–	61.70	Gonzalez et al. (2000)
Emericella nidulans var. lata (DF3)	–	38.00	–	–	Kaushik and Thakur (2009)
Neurospora intermedia (DF4)	–	31.00	–	–	Kaushik and Thakur (2009)
Phanerochaete chrysosporium	10 days	85.00	–	–	Fahy et al. (1997)
Aspergillus oryzae MTCC 7691	–	75.71	51.00	86.19	Chavan et al. (2013)
Geotrichum candidum Dec 1	–	80.00	–	–	Kim and Shoda (1999)
Cladosporium cladosporioides	–	62.50	–	73.60	Ravikumar et al. (2013, 2011)
Flavodon flavus (Klotzsch) Ryvarden	8 days	80.00	–	–	Raghukumar and Rivonkar (2001)
Penicillium pinophilum TERI DB1	–	50.00	–	–	Pant and Adholeya (2007)
Alternaria gaisen TERI DB6	–	47.00	–	–	Pant and Adholeya (2007)
Penicillium florida EM 1303	–	86.00	–	–	Pant and Adholeya (2007)
Phanerochaete chrysosporium JAG-40	6 days	80.00	–	–	Dahiya et al. (2001)
Coriolus versicolor	–	71.5	–	90.00	Kumar et al. (1998)
Aspergillus species	–	–	–	–	Wagh and Nemade (2018)
Aspergillus nidulans Var. nidulans	7 days	79.6	–	62.00	Adikane and Patale (2014)
Stenotrophomonas maltophilia	–	–	–	–	Thiyagu and Sivarajan (2018)
Aspergillus niveus	–	56.00	94.00	97.14	Angayarkanni et al. (2003)
Coriolus versicolor Ps4a	4	75.00	–	–	Aoshima et al. (1985)
Neurospora intermedia,	–	–	–	–	Kaushik and Thakur (2009)
Emericella nidulans var. lata	–	–	–	–	Kaushik and Thakur (2009)
Aspergillus fumigatus	–	–	–	–	Mohammad et al. (2006)

BOD biological oxygen demand, *COD* chemical oxygen demand, *hrs Hours*

manganese peroxidase (MnP), laccase (Lac), and lignin peroxidase (LiP), which metabolize melanoidins and other refractory organic compounds present in the DW as sole carbon and nitrogen sources (Miyata et al. 2000; Bonugli-Santos et al. 2012; Pant and Adholeya 2007, 2009a, b). The Lac and MnP have a broad range of substrate oxidizing enzymes able to cleave large varieties of several chemical bonds present in phenolic and nonphenolic recalcitrant compounds (Wong 2009). Miyata et al. (1998) demonstrated that synthetic melanoidin is decolorized by the sharing of manganese-dependent and -independent peroxidases of *Trametes* (*Coriolus*) *hirsutus* pellets, and the extracellular H_2O_2 along with the participation of Lac enzyme. MnP and Lac protein both act on pollutants in synergy resulting in the degradation and depolymerization of melanoidins (Miyata et al. 2000; González et al. 2008). González et al. 2008 and Miyata et al. (2000) have demonstrated that the presence of melanoidins and other similar compounds can induce the expression of MnP and Lac genes. González et al. (2008) report the induction of Lac by molasses wastewaters and molasses melanoidins in the *Trametes* sp. I-62. Tapia-Tussell et al. (2015) also reported the expression of Lac genes in the *T. hirsutus* strain Bm-2, in the presence of phenolic compounds, as well as its effectiveness in removing colorants from vinasse. In the presence of all phenolic compounds (i.e., guaiacol), increased levels of laccase-encoding mRNA were 40 times higher than those in the control. So far ligninolytic enzymes have been known to be produced by various fungi, but most of them have failed to bring about complete mineralization of melanoidins and other organic pollutants present in DW. However, the long growth cycle; long hydraulic retention time, requiring nitrogen limiting conditions; and low pH range (3.0–5.0) for complete decolorization of DW still limit the performance of the fungal decolorization system.

6.5.1.2.2 Bacterial Treatment

Bacterial cultures have a very high potential for biodegradation and decolorization of DW due to their higher environmental adaptability, faster growth rate, and high metabolizing capability of melanoidins. Thus, the degradation and decolourisation of synthetic and natural melanoidins was reported by various researchers using the axenic and mixed bacterial consortium. Pioneering work on SW decolorization by bacteria was done by Kumar et al. (1997). They observed that two aerobic bacterial isolates LA-1 and D-2 brought about maximum decolorization (36.5% and 32.5%) and COD reduction (41% and 39%) under optimized conditions in eight days. Various bacterial groups, such as *Bacillus* sp. (Kambe et al. (1999*), Pseudomonas putida, Aeromonas* sp. (Ghosh et al. 2002), *Lactobacillus plantarum* (Tondee and Sirianutapiboon 2008), *Alcaligenes faecalis* (Santal et al. 2011), *Pseudomonas* sp. (Sankaran et al. 2015), *Bacillus* sp. (Krzywonos 2012), and *B. badius* (Mehta et al. 2014), have been reported for the degradation and decolorization of melanoidin-containing DW. Some of the bacterial species investigated for their ability for decolorization and degradation of DW are summarized in Table 6.5. Bacterial decolorization is promising and faster compared to fungal decolorization, but an individual bacterial strain usually cannot degrade melanoidins completely, and the metabolites are often more toxic compared to parental compounds, which need to

Table 6.5 Bacterial species capable of COD, BOD reduction and decolorization of distillery wastewater

Microorganisms	Incubation times	Decolorization	Reduction %		References
			BOD	COD	
Pure bacterial isolates					
Paracoccus pantotrophus	5–6 days	–	–	81.2	Santal et al. (2016)
Pseudomonas sp.		26.08	–	–	Sankaran et al. (2015)
Alcaligenes faecalis SAG_5	5 days	72.6	–	–	
Pseudomonas aeruginosa		92.77	–	–	Charles et al. (2015)
Bacillus subtillis	24 hrs	85.00	–	–	Tiwari et al. (2012b)
Lactobacillus plantarum no. PV71–1861	7 days	68.12	–	–	Tondee and Sirianutapiboon (2008)
Lactobacillus plantarum		44.00	–	–	Krzywonos and Seruga (2012)
Acetogenic bacteria BP103	5 days	72.00	58.50	82.20	Sirianuntapiboon et al. (2004)
Bacterial consortium					
Proteus mirabilis, *Bacillus* sp., *Raoultella planticola* and *Enterobacter sakazakii*	10 days	75.00	–	71.00	Yadav and Chandra (2012)
B. licheniformis Bacillus sp. and *Alcaligenes* sp.		70.00	–	–	Bharagava and Chandra (2010)
Klebsiella pneumoniae, Salmonella enteric, Enterobacter aerogenes, and *Enterobacter cloacae*	168 hrs		25.51	53.43	Kumar and Chandra (2018); Chandra et al. (2018a)
Acinetobacter sp., Pseudomonas sp., *Comamonas* sp., *Klebsiella oxytoca, Serratia marcescens*, and *unidentified bacteria*	48 hrs	26.50	–	–	Jiranuntipona et al. (2009)
Pediococcus acidilactici and *Candida tropicalis*	24 hrs	82.15	–	–	Tiwari et al. (2014)

(continued)

Table 6.5 (continued)

Microorganisms	Incubation times	Decolorization	Reduction % BOD	Reduction % COD	References
Pseudomonas aeruginosa PAO1, *Stenotrophomonas maltophila*, and *Proteus mirabilis*	24 hrs	67.00	–	51	Mohana et al. (2007)
Bacillus (C1 and C2)					Krzywonos (2012)
Bacterial communities					
Microbacterium hydrocarbonoxydans, Achromobacter xylosoxidans, Bacillus subtilis, B. megaterium, B. anthracis, B. licheniformis, A. xylosoxidans, Achromobacter sp., *B. thuringiensis, B. licheniformis, B. subtilis, Staphylococcus epidermidis, Pseudomonas migulae, Alcaligens faecalis, B. cereus*	30 days	75.50	–	85–86	Chaturvedi et al. (2006)
Pseudomonas, Enterobacter, Aeromonas, Stenotrophomonas, Acinetobacter, and *Klebsiella* sp.		44.00	–		Ghosh et al. (2004)

BOD biological oxygen demand, *COD* chemical oxygen demand, *hrs* hours

be further decomposed. Therefore, the utilization of bacterial consortia offers significant advantages over the use of pure bacterial cultures in degradation and decolorization of melanoidins, as different bacterial strains may attack the melanoidin molecules at different positions or may use decomposition products produced by another strain for further decomposition. Various biological studies have been earlier carried out by a number of researchers using bacterial consortium that included *Pseudomonas aeruginosa*, *Stenotrophomonas maltophilia*, *Proteus mirabilis* (Mohana et al. 2007), *Klebsiella oxytoca*, *Serratia marcescens*, *Citrobacter* sp., (Jiranuntipon et al. 2008), *B. licheniformis*, *Bacillus* sp., *Alcaligenes* sp. (Bharagava et al. 2009), and *Proteus mirabilis*, *Bacillus* sp., *Raoultella planticola*, and *Enterobacter sakazakii* (Yadav and Chandra 2012) to treat DW. In recent years, the ligninolytic system of bacteria with respect to their enzymatic potential for the bioremediation degradation of synthetic melanoidins and BMDE pollutants has been

extensively studied (Pant and Adholeya 2009b). LiP, MnP, and Lac are the three major lignin-degrading enzymes with great potential in industrial applications (D'Souza et al. 2006). Out of the three, mainly Lac and MnP play a major role in the degradation of melanoidins (Kumar and Chandra 2018). Chandra and Kumar (2018) reported that MnP is profusely present at the initial phase of bacterial growth, while laccase was produced in a later phase of growth during melanoidin degradation and decolorization.

6.5.1.2.3 Cyanobacteria/Algal Treatment

Cyanobacteria are prokaryotic, gram-negative, photoautotrophic eubacteria having the ability to take up their nutrients from DW as sole carbon and nitrogen source, and thereby decolorizing the wastewater resulting in the reduction of color, BOD, and COD. Another advantage of using cyanobacteria is that, apart from the degradation of the melanoidin, it also oxygenates water bodies thereby reducing the energy need of the aerobic treatment. Kalavathi et al. (2001) reported degradation and decolorization of melanoidin in DW by the *Oscillatoria boryana* BDU 92181. This marine cyanobacterium degrades melanoidins due to the production of hydrogen peroxide, perhydroxyl, hydroxyl, and active oxygen radicals, resulting in the 60% decolorization of the DW. They further identified enzymes from microalgae, namely, glucose oxidase, MnP, and two MIP, involved in maximum production of hydrogen peroxide. In addition, riboflavin, manganese sulfate, methyl viologen, reduced glutathionine, and ascorbic acid could be used by *O. boryana* BDU 92181 for improving the degradation rate of melanoidins. A study conducted by Patel et al. (2001) examined the 26%, 81%, and 96% decolorization of DW through bioflocculation by *Synechocystis* sp., *Lyngbya* sp., and *Oscillatoria* sp., respectively. Valderrama et al. (2002) used a combined treatment of *Lemna minuscule* and *Chlorella vulgaris* for color removal from DW. They reported 52% color removal from DW by this combined treatment. Solovchenko et al. (2014) have investigated the possibilities of DW bioremediation along with a new *C. sorokiniana* sp. cultivated in a semi-batch mode in a high-density photobioreactor. A decrease in COD of the DW from 20,000 to ca. 1500 mg L^{-1} was achieved over 4 days with a decline in nitrate (>95%), phosphate (77%), and sulfate (35%). Recently, Krishnamoorthy et al. (2017) have shown the treatment of anaerobically digested DW with *Oscillatoria* sp. This organism reduced COD up to 55% of anaerobically digested DW. Although biological methods provide an eco-friendly approach for DW treatment, these methods also have some technical difficulties as far as in situ administration of pollutant is concerned.

6.5.1.2.4 Phytoremediation Approaches

Phytoremediation is an in situ, cost-effective, and eco-friendly technique to eliminate hazardous HMs and organic pollutants from the contaminated environment (Chandra et al. 2015, Chandra and Kumar 2018; Chandra et al. 2018b, c, d). It is an emergent green technology that employs plants and their associated microbiota to remove, reduce, immobilize, and/or degrade harmful environmental pollutants (Ma et al. 2011; Glick 2010). This can reduce the health risk from contaminated

water, sediments, sludge, and soil through contaminant degradation or removal (Chandra and Kumar 2015b; Alkorta et al. 2004; Rajkumar and Freitas 2008). For the removal of DW contaminants, there is some significant work done by Billore et al. (2001) for a horizontal flow gravel bed constructed wetland (CW) to treat DW. After secondary conventional treatment, the concentrations of COD and BOD_5 in DW amounted to 2540 and 13,866 mg L^{-1}, respectively, and, therefore additional treatment was essential. The CW treatment system achieved BOD_5, COD, total P, and, total Kjeldahl nitrogen (TKN) reductions up to 84%, 64%, 79%, and 59%. This study recommended that CW may be a sustainable tertiary treatment technique for the remediation of contaminants present in DW. Similarly, Trivedy and Nakate (2000) used wetland plant *T. latipholia* for treatment of DW in a CW treatment system. This treatment system resulted in 47% and 78% decrease in BOD and COD, respectively at incubation of 10 days. Increasing concentration of DW significantly reduced the biomass of growing plants, with the highest accumulation of Fe being recorded in plants growing in 100% concentration of DW. *Potamogeton pectinatus*, an aquatic macrophyte, was used to accumulate Mn, Zn, Cu, and Fe and efficiently clear out the DW (Singh et al. 2005). Chaturvedi et al. (2006) reported the phytoremediation potential of *P. australis* grown on DW-contaminated site. She also characterized the diverse bacterial species from the rhizospheric zone of *P. australis.* The culturable bacterial species were helpful for the degradation and decolorization of noxious pollutants that exist in the distillery effluent. They observed a 75.5% reduction of color by the same bacterial species along with a concomitant reduction in BOD, COD, sulfate, phenol, and HMs values. Bharagava et al. (2008) studied the HMs accumulation efficiency and its physiological effects in *Brassica nigra* L. (Indian mustard) plants grown in soil irrigated with different concentrations (25%, 50%, 75%, 100%, v/v) of PMDE after 30, 60, and 90 days treatment. This study concluded that *B. nigra* L. accumulated elevated concentrations of Zn, Ni, Mn, Fe, Cu, and Cd due to the increased amount of cysteine and ascorbic acid (work as antioxidants) in root, shoot, and leaves of *B. nigra* L. at all the concentrations and exposure periods of PMDE except at a 90-day period. Chandra and Yadav (2010) conducted a pot culture experiment to evaluate the accumulation pattern of Cu, Pb, Ni, Fe, Mn, and Zn in *T. angustifolia* grown in Zn, Mn, Fe, Ni, Pb, and Cu-rich aqueous solutions of phenols and melanoidins. They concluded that *T. angustifolia* could be an efficient phytoremediator for HMs from melanoidin, phenol, and metal-containing industrial effluent at optimized conditions. Recently, Hatano et al. (2016) observed the chelating property of melanoidin-like product (MLP) and to assess the facilitatory influence on the phytoextraction potential of *Raphanus sativus* var. *longipinnatus* (Japanese radish). They found that MLP binds with all the tested HMs ions, and the metal ion-binding capability of MLP toward Cu^{2+} was found to be the maximum among them. In a separate study Hatano and Yamatsu (2018) evaluated the facilitatory effect of MLP on phytoextraction potential of three *Brassica* species grown in a medium containing Pb or Cd. They reported that biomass and Pb^{2+} uptake in the nutrient medium containing 1 mM Pb nitrate were significantly increased by the addition of MLP, and all the Pb^{2+} from the medium was accumulated in the root tissues. They concluded that MLP was able to detoxify Pb^{2+} and to improve their bioavailability in *Brassica* species.

6.5.1.2.5 Vermifiltration

Vermifiltration technology is an alternative DW treatment method widely used in developing countries due to its low cost and eco-friendly nature. Manyuchi et al. (2018) reported that the TDS, TSS, TKN, BOD, and COD were significantly reduced by more than 90% during the 40 h vermifiltration process. The treated DW can be used for irrigation purposes. In addition, vermicompost, a bio-fertilizer which is rich in N (1.87%), P (0.66%), and K (0.87), was produced as part of the vermifiltration process.

6.5.1.2.6 Microbial Fuel Cells

Microbial fuel cells (MFCs), which exploit living microorganism as electrode catalysts, have the potential to recover energy from biomass wastes and distillery wastewater. It has recently attracted considerable attention as green energy devices for generating electricity from various organic and inorganic materials. Simultaneous electricity generation and DW treatment were accomplished using a thermophilic MFCs. Recently, molasses DW was examined as an organic fuel for electricity production in a mesophilic MFCs (Zhang et al. 2009; Mohanakrishna et al. 2009). Ha et al. (2012) studied the treatment of DW using a bacteroidetes-dominant thermophilic MFCs. The results suggest that thermophilic MFCs, which require less energy for cooling the DW, can achieve high efficiency for electricity generation and also reduce sulfate along with oxidizing complex organic substrates. Bacterial diversity analysis by pyrosequencing of the 16S rRNA gene showed that known *Deferribacteres* and *Firmicutes* members were not dominant in the thermophilic MFCs fed with DW; instead, uncharacterized *Bacteroidetes* thermophiles were up to 52% of the total reads in the anode biofilm. Recently, Mohamed et al. (2018) have investigated the effect of buffers and feed pH of the DW on the overall performance of the MFCs. The results demonstrated that anolyte of MFCs at pH 8 showed to achieved a maximum power density of 168 mW/m^2, which was due to the presence of microbial communities and its exoelectrogenic activity. In addition, the COD, TDS, and color elimination have achieved a maximum of 68.4%, 15.4%, and 26.4, respectively, at pH 8.

6.5.1.3 Emerging Treatment Approaches

6.5.1.3.1 Membrane Filtration

Membrane filtration (MF) is a term used to describe the removal of particulates from a feed stream (Chang et al. 1994). Tertiary treatment of aerobically treated DW by nanofiltration (NF) was carried out in a spiral wound NF membrane module, which was done by Rai et al. (2008) under different operating conditions. They obtained COD, TDS, and color removal in the range of 96–99.5%, 85–95%, 98–99.5%. respectively. The membrane-based NF and RO processes can be used to reduce the K^+ COD, TDS, and the content of DW by 99.99%, 99.90, and 99.80, respectively (Nataraj et al. 2006). Nakhla et al. (2006) studied the applicability of a submerged vacuum ultrafiltration membrane technology in combination with the biological treatment system. This system achieved 99% COD and 95–96.5% BOD

removal. Submerged NF for removal of melanoidins from the BMDE was evaluated by Liu et al. (2013). The melanoidins could be effectively removed from the BMDE by SNF. However, MF technology cannot be directly applied to treat DW due to its high TDS.

6.5.1.3.2 Oxidation Processes

Oxidation processes are a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) pollutants in DW by the formation of highly reactive oxidant species, mainly hydroxyl radicals (•OH), a powerful, ubiquitous in nature, nonselective, electrophilic behavior, redox potential of 2.8 V, and highly effective oxidants which accelerating the oxidation and destruction of a wide range of contaminants from wastewater by abstracting hydrogen atom from aliphatic carbon, or adding hydrogen atom to the double bonds and aromatic rings.

6.5.1.3.2.1 Ozone Oxidation

Ozone oxidation, also known as ozonation, is a promising technology for the treatment of DW. Ozone is a potent oxidant for wastewater treatment; when ozone comes in contact with wastewater, it reacts with organic compounds in two different ways: (i) direct oxidation as molecular ozone and (ii) indirect reaction through the formation of secondary oxidants like free radical species, viz., the •OH radicals. Both ozone and •OH radicals are strong oxidants and are capable of oxidizing a number of compounds, and, finally, COD value is reduced (Pena et al. 2003). The color elimination from DW was most likely due to the fact that ozone is able to break down the conjugated –C=C- bonds, thus breaking the chromophore of the melanoidins (Kim et al. 1985). Oxidation by ozone could achieve 80% decolorization of PMDE with simultaneous 15–25% COD reduction (Pena et al. 2003). Benitez et al. (2003) reported the reduction of COD and total aromatic compound up to 5–25.2% and 16.8–51.4% under optimum conditions by an ozonation process. A catalyst has also enhanced the efficiency of the ozonation process. Sangave et al. (2007) have used an ultrasound (US) plus ozone treatment process to treat DW pretreated with thermal pretreatment and AD process. The result demonstrated that 13% COD reduction was attained at the end of 48 h of aerobic oxidation, while 45.6% COD reduction was obtained in ozone-treated DW. Asaithambi et al. (2012) used a hybrid technique of ozone-assisted electrocoagulation for the elimination of COD and color in the industrial effluent. They reported a maximum elimination of COD (83%) at a current density of 3 Adm^{-2}, initial pH (6.0), and initial COD concentration 2500 ppm, and the ozone mixture flow rate was 15 L min^{-1}, while the complete elimination of color was found within 2 h of process time. Kumar et al. (2006) have reported that COD was removed up to 95% from treated PMDE through ozone treatment. Sreethawong and Chavadej (2008) have used iron oxide to enhance the ozone oxidation process. They reported a maximum 80% COD and 50% color reduction during the process.

6.5.1.3.2.2 Hydrogen Peroxide Treatment

The chemical decolorization of model melanoidins by H_2O_2 treatment was studied by Hayase et al. (1984). They reported about 64% and 97% decolorization of melanoidin using H_2O_2 at pH 7.0 and pH 10.0, respectively. They suggested the degradation of melanoidins by active oxygen species, i.e., H_2O_2, which is generated by the oxidation of glucose ($C_6H_{12}O_6$) into gluconic acid by the glucose-oxidase enzyme. They demonstrated that H_2O_2 reacts with hydroxyl anion (OH^-) to give per hydroxyl anion (HOO-), which nucleophilically attacks carbonyl groups (COOH) of melanoidins.

6.5.1.3.3 Photocatalytic Treatment

Photocatalytic degradation is an attractive treatment process for wastewater. Charles et al. (2015) studied the degradation of OM in the form of the color of SW using nano-photocatalyst nano-Al_2O_3/kaolin prepared from aluminum oxide (Al_2O_3) nanoparticle and kaolin clay. Optimization of the process parameters using Taguchi Orthogonal Array (TOA) design resulted in a maximum of 80% SW decolorization. A vanadium-doped TiO_2 (V-TiO_2) photocatalyst has been used for the degradation of SW and industrial dyes (Takle et al. 2018). The degradation of colored compounds in the SW was monitored by gel permeation chromatography, which showed the degradation of high molecular weight compounds into low molecular weight fractions.

6.5.2 Physicochemical Treatment Approaches

Physicochemical treatment methods are a combination of physical and chemical technologies used for wastewater treatment by adding chemicals. Elimination of suspended solids from the DW is a physical operation, while reduction of the dissolved solid is a chemical process. Several physicochemical methods, viz., coagulation/flocculation, electrocoagulation, thermolysis, membrane filtration, oxidation by ozone, chlorine dioxide, hydrogen peroxide, and radiation, and adsorption to material such as chitosan and activated carbon, have been shown to reduce the pollutant load of DW.

6.5.2.1 Adsorption

Activated carbon (AC) is the most extensively studied adsorbent prepared from agro-waste materials such as rice husk ash, fly ash, sugarcane bagasse, wood ash, and wood sawdust. This adsorbent has been reported to adsorb a wide array of organic compounds, i.e., phenolics, heavy metals, and other various organic pollutants and bio-organisms. Therefore, the adsorbent is used for the elimination of organic and inorganic pollutants in form color, COD, BOD, and HMs from DW (Chandra and Pandey 2000; Satyawali and Balakrishnan 2007, 2009; Mane et al. 2009). Comparative studies of color removal from DW using bagasse fly ash and commercial AC showed 58% color removal with 30 g/dm^3 of bagasse fly ash and 80.70% color removal with 20 g/dm^3 of commercial ACs. Lalov et al. (2000)

reported 98% color and 99% COD removal from DW by using natural carbohydrate polymer chitosan as an anion exchanger at 30 min contact time. ACs are not low-cost materials; hence, in spite of their good efficiency and applicability for adsorbing a wide variety of materials, their use can sometimes be restricted due to economic considerations.

6.5.2.2 Coagulation/Flocculation

Coagulation is the use of chemicals to cause pollutants to agglomerate and subsequently settle out during sedimentation. The removal of COD and color-containing compounds from DW was reported using inorganic coagulants, viz., aluminum chloride ($AlCl_3$), $FeCl_3$ (ferric chloride), calcium oxide (CaO), ferrous sulfate ($FeSO_4$), and polyaluminium chloride (PAC) (Chaudhari et al. 2007). Treatment of DW using iron sulfate [$Fe_2(SO_4)_3$] as a coagulant results in 40% removal of pollutants (Pikaev et al. 2001). Migo et al. (1993) studied the use of commercial inorganic flocculent [Fe(OH)n$(SO_4)3_{-n/2}$]m, a polymer of ferric hydroxide, for melanoidin removal from DW. Decolorization yields of 94%, 87%, and 32% were obtained for the lagoon, biodigester, and fresh slops effluents, respectively, at a flocculant dosage of 4% v/v. In addition, the reduction of TOC was 21% for fresh slops effluent and averaged to more than 73% for the biodigester and lagoon effluents. A 55% reduction in COD by using integrated Fenton-coagulant/flocculation process in distillery wastewater treatment has been reported by Beltrain de Heredia et al. (2005). *Moringa oleifera* seeds were also used as a coagulant for removal of color from SW (Krishna Prasad 2009). Armini et al. (2015) used manganese oxides, a strong oxidizer that oxidize aromatic amine to quinones and dimer products, for the color removal from melanoidin-rich DW. It can also oxidize the long-chain amines to nitrone, which may further dimerize to bigger compounds and precipitate out of the solution by MnOx. Different coagulants used by various researchers for the COD and decolorization of DW are shown in Table 6.6.

6.5.2.3 Electrochemical/Electrocoagulation

The electrochemical treatment methods (i.e., electrocoagulation) use electron as the main reagent as well as the presence of supporting electrolytes, to eliminate the OM from DW (Prasad and Srivastava 2009). This process involves the consumption of metals from the anode, with simultaneous formation of OH^- and H_2 occurring at the cathode. In the electrochemical treatment process, the pollutants are eliminated by either direct or indirect oxidation process (Kobya and Gengec 2012). In a direct oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction, while, in an indirect oxidation process, strong oxidants, viz., hypochlorite (ClO^-)/chlorine (Cl), O_3, and H_2O_2 are electrochemically generated, and these oxidants destroyed the pollutants. Among the oxidants, ClO^- is cheaper, and DW has a certain amount of chloride (Cl^-). The electrochemical method converts Cl^- to ClO^-/Cl, through the supply of electrical current. The Cl and ClO^- oxidize the pollutants and are then reduced to chloride ions. Thakur et al. (2009) studied the effect of pH 3.5–9.0 on the electrochemical

Table 6.6 Reduction of COD and color from distillery wastewater investigated by different researchers by using a different coagulant

				Coagulant Performance		
S.No.	Feedstock	Type of distillery wastewater	Coagulant	COD reduction (%)	Color reduction (%)	References
1.	Molasses	–	$FeCl_3.6H_2O$	89.00	98.00	Liang et al. (2009a)
2.	Molasses	ATW	Aluminum sulfate	66.00	86.00	Liang et al. (2009b)
3.	Molasses	–	ACH/ polyDAMAC	56 0.00	70.00	Fan et al. (2011)
4.	Molasses	AADW	$FeCl_3.6H_2O$	90.00	90.00	Liakos and Lazaridis (2014)
5.	Molasses	ATW	$FeCl_3.6H_2O$	86.00	96.00	Liang et al. (2009)
6.	Sugar beet molasses	ATW	CaO	89.50	84.30	Inanc et al. (1999)
7.	Rice grain	–	$FeCl_3.6H_2O$	78.00	80.00	Prajapati et al. (2015)
8.	Cassava	ATW	$FeCl_3.6H_2O$	78.80	94.00	Zhang et al. (2017)

ATW anaerobically treated wastewater, *AADW* anaerobically digested wastewater, *DOM* dissolved organic matter, *COD* chemical oxygen demand

treatment of PMDE. The 31.5%, 43.71%, and 48.9% COD decline was obtained at pH 9.0, 6.5, and 3.5, respectively, with a current density of 117 A/m^2 in 60 min. Similarly, the effect of pH on the treatment of BMDE was studied by Kumar et al. (2009). The 32.66%, 39.95%, and 44% COD reduction was obtained at pH 2.0, 5.0, and 8.0, respectively, with a current density of 133.94 A/m^2 in 90 min. Prajapati and Chaudhari (2014) reported 87% color reduction and 93% COD reduction in DW using iron electrode at optimum condition.

6.5.2.4 Thermolysis

The treatment of DW by thermolysis is done due to the existence of a diverse range of compounds such as minerals, lignin, hemicellulose, proteins, lipids, and reduced carbohydrates in DW (Chaudhari et al. 2008). Lele et al. (1989) have studied the thermolysis process for treatment of SW at temperatures in the range of 160–250 °C and autogenous pressures. They observed that there was no further COD reduction after a treatment time of 2 h. The authors reported zero-order COD reduction kinetics as 6.67, 10.40, 10.8, and 14.40 kg/m^3 h at 160, 200, 230, and 250 °C, respectively. The thermolysis treatment of PMDE in the absence of air at 150 °F resulting in 35% COD reduction in t = 0.6 h has also been reported by Dhale and Mahajani (2000). Chaudhari et al. (2005) reported COD reduction of PMDE at 100 °C and atmospheric pressure by using different catalysts such as Mn/Cu oxide, Mn/Ce

oxide, $CuSO_4$, and CuO. About 70%, 65%, 35%, 38%, 40%, and 36% COD reduction was obtained at pH 2.0, 2.0, 4.0, 6.0, 8.0, and 10, respectively, using CuO catalyst. Similarly, the treatment of SW with COD reduction of 58%, 60%, 51%, 36%, 30%, and 32% at pH 1, 2, 4, 6, 8, and 10, respectively at 140 °C and autogenous pressure was reported by Chaudhari et al. (2008).

6.6 Combined Biological Treatment Approaches

Since the SW contains recalcitrant highly colored pigments which cannot be separated or degraded with conventional treatment methods, there is always a lookout for advanced treatment methods. Besides, the drawbacks associated with these methods are instable decolorization efficiency, excess use of chemicals, operational difficulty, sensitivity to variable water input, and a huge amount of sludge generation with subsequent disposal problems, and occasional formation of hazardous by-products/secondary pollutants. Therefore, there are still demands to develop substitute means of decolorization and bioremediation of DW such as pioneering eco-friendly methods capable of providing a more complete cleanup of the pollutant in a more economic fashion. Investigation in implementing a hybrid method of treating the DW has gained its soundness rather than an individual treatment. In order to increase the biodegradation ability of the process, a two-stage sequential/phase separation/sequential method has demonstrated to be an efficient approach for bioremediation of DW. Numerous scientific reports indicated that the use of a hybrid technique by using bacteria, fungi, yeast, and plant or their combinatorial systems is more successful than the individual one. For instance, Ghosh et al. (2002) investigate the treatment of DW in a two-stage bioreactor by using *Pseudomonas putida* followed by *Aeromonas* sp. strain EMa. In the first stage, *P. putida* decreased the color and COD of DW up to 60% and 44.4, respectively, whereas in the second stage, *Aeromonas* sp. strain Ema reduced the effluent COD up to about 44.4%. Kaushik et al. (2010) investigated the treatment of DW in three-stage bioreactors by using fungus followed by bacteria. The potential use of fungi (*Cladosporium cladosporioides*) and cyanobacteria (*Phormidium valdernium*) for treatment of DW in a two-stage sequential step was also reported by Ravikumar and Kartik (2015). A maximum 68.5% decolorization and 81.37% COD reduction were achieved in the first-stage bioreactor during the batch experiment. Further, the SW from bioreactor was treated with cyanobacteria in the second stage and resulted in COD reduction (3652 mg L^{-1}) of 89.5% and 92.7% decolorization, respectively. Authors recommended that sequential treatment using the combination of fungi and cyanobacteria resulted in better decolorization and degradation of SW. Combination of wetland treatment technology after bacterial degradation offers an excellent system for the elimination of color from DW and reduction of BOD, COD, TDS, and HMs for safe disposal. A two-stage sequential treatment for sugarcane molasses-based PMDE was reported by Pant and Adholeya (2009a). In the first step, DW was treated in a hydroponic-based system using two plant species (*Vetiveria zizanioides* and *Phragmites karka*) to decrease the high nitrogen content up to 84% of the

wastewater. The roots of these growing plants showed profuse growth on effluent. After that, this first stage treated DW was subjected for treatment by fungal isolates; 86.33% decolorization was obtained with *Pleurotus florida* Eger EM1303 followed by *Aspergillus flavus* TERIDB9 (74.67%), with a significant reduction in COD as well. Table 6.7 summarizes the two-stage sequential results of DW decolorization by using different organisms.

6.7 Reuse and Recycling of Distillery Effluent

In India, three popular methods are employed by distilleries to handle their wastewaters:

(i) Collection of DW in storage tanks, followed by irrigation.
(ii) DW treatment in settling lagoons, which are placed after AD, is found to be useful to settle the solids by gravity, evaporation processes, and application of resultant sludge on land. The outcome of evaporation is the formation of concentrated sludge that can be used as biofertilizer. Besides, distillery sludge is further incinerated to generate power, and the potassium-rich ash is recovered from the combustion of sludge.
(iii) The concentrated DW is used to make powders to use as raw material for power generation and mixed compound fertilizer. The overflow from settling lagoons is sent to RO plant where the permeate (water) of RO is recycled to the ethanol production unit, reducing the water requirement in distilleries. The reject of the RO plant is mixed with the press mud and marketed as a biocompost or discharge of the effluent to a local municipal treatment facility.

However, these three methods have their associated drawback and environmental risks. Tretament of lagoons through solar evaporation requires a huge ground region and also needs to take into consideration the weather conditions prevailing in the region, because settling lagoons are also non-functional during the monsoon. Moreover, treatment of DW in lagoons generates greenhouse gas emissions, and for irrigation practices may in some cases negatively affect the structure of aquifers, soils as well as groundwater quality.

6.7.1 Composting

Composting is a sustainable approach for bioconversion of organic residue of DW into compost (manure) through microorganisms (i.e., bacteria, actinomycetes, and fungi), and this manure may be utilized as nutrients for plant growth and development in the agricultural field. This approach not only solves the pollution and disposal problems arising from the DW and adopted by several Indian distilleries associated with sugar mills but also helps in saving the cost on chemical fertilizers (Bhalerao et al. 2006; Jadhav et al. 1992). Composting of DW is carried out using

Table 6.7 Treatment of distillery wastewater in two-stage sequential treatment by using different organisms

Effluent	First stage	Second stage	BOD	COD	Color	Dec	Incb	Reference
PMDE	Bacterial consortium	*Phragmites communis*	94.5%	96.0%	–	86.33%	–	Chandra et al. (2012)
BMSW	*Vetiveria zizanioides* and *Phragmites karka*)	*Pleurotus florida* and *Aspergillus flavus*	–	–	–	–	–	Pant and Adholeya (2009a)
PMDE	*Bacillus thuringiensis*	*Spirodela polyrrhiza* Schliden	–	–	–	–	–	Kumar and Chandra (2004)
PMDE	*Bacillus thuringiensis*	*Typha angustata* L.	98.00%	99.00%	–	–	7 days	Chandra et al. (2008)
SW	*Emiricella nidulans* var. lata. And *Neurospora intermedia*	*Bacillus* sp.	–	93.00%	82.00%	–	30 hrs	Kaushik et al. (2010)

PMDE post-methanated distillery effluent, *SW* spent wash, *BOD* biological oxygen demand, *COD* chemical oxygen demand, *BMSW* biomethanated spent wash, *hrs* hours, *Dec* decolourisation, *Incb* incubation period

pressmud, obtained from sugarcane juice before the crystallization of sugar in sugar mills. It is the best source material for microbial growth and contains dark brown-colored, amorphous, lightweight, spongy material with 74%–75% OM, 20% volatile solids, 71% moisture, and 9% ash. In composting, DW either directly or after AD is sprayed on pressmud and mixed thoroughly using an aerotiller, which makes the pressmud aerable and enhances the decomposition process. The composting process of pressmud using PMDE wash has two unique features distinguishing it from other composting processes. One is the specially developed mixed microbial culture of fungi, bacteria, and actinomycetes, selected for their ability to rapidly degrade DW. The second is the conventional blending and mixing of the refuse comprising pressmud and liquid SW using the aerotiller machine. The integrated effect of farm yard manure (FYM), bio-compost, and BMDE as a source of plant nutrients and their effect on sugarcane yield, juice quality, nutrient uptake, and soil properties were investigated by Sinha et al. (2014). The quality of juice, viz., sucrose and purity, remains unaffected. The application of BMDE and bio-compost brings remarkable changes in the properties of soil and thus enhances the fertility of soil and productivity of sugarcane significantly.

6.7.2 Ferti-Irrigation

In India, most of the distillery units have opted DW for ferti-irrigation to improve soil health and crop productivity and alleviate environmental pollution problems. Some farmers in northern and western India living in the areas adjoining distilleries often use SW and SW-containing products as a source of manure without considering its impact on the soil and groundwater quality. However, DW also contains significant amounts of phosphorus (P), nitrogen (N), sulfur (S), and potassium (K^+), as well as easily biodegradable OM and micro- and macronutrients, viz., Zn, Cu, K, N, and Fe, which are essential for plant growth (Devarajan et al. 1994; Zalawadia and Raman 1994; Pathak et al. 1999; Yadav et al. 2010). Its application to soil at low concentration has been reported to be beneficial to increase mustard yield (Malaviya and Sharma 2011), wheat and rice (Pathak et al. 1998), rice (Deverajan and Oblisami 1995), sugar cane yield (Mohamed Haron and Subash Chandra Bose 2004), and physiological response of soybean and groundnut quality (Ramana et al. 2001). The use of DW in agriculture as a supplement for irrigation or soil amendment water in a judicious way to enhanced crop production as well as biological, chemical and physical properties of soil (Joshi et al. 1996; Jadhav and Savant 1975; Narain et al. 2012; Raverkar et al. 2000; Chidankumar et al. 2009; Ramana et al. 2001; Jain and Srivastava (2012). Singh et al. (1980) found that addition of SW without dilution was very effective in increasing water intake rate of the sodic calcareous soil. Zalawadia and Raman (1994) found that the application of DW in soil improved its water-retention characteristics. Ayyasamy et al. (2008) conducted a pot experiment to study the effects of different concentrations of sugar factory effluent on seed germination, seedling growth, and biochemical characteristics of green

gram and maize. The higher effluent concentrations (above 60%) were found to affect plant growth, but diluted effluent (up to 60%) favored seedling growth. Previous studies revealed that the application of untreated DW to mung beans (*Vigna radiata*) and rice (*Oryza sativa* L.) suppressed seed germination and seedling growth, suggesting that pretreatment of the effluent to degrade OM before application to crops might yield better results (Arora et al. 1992; Kannan and Upreti 2008). Distillery application increased the dry matter yield and N recovery of Italian ryegrass compared to the inorganic NH_4-NO_3 fertilizer treatment (Douglas et al. 2003). Asano et al. (2014) reported that a large quantity of ammonium nitrogen (NH_4^+-N) was increased in rice-derived DW after inoculation with *A. caelatus*, *A. oryzae*, *A. tamarii*, and *B. subtilis* strain. Chauhan and Rai (2010) also indicated that irrigation with DW impaired the groundwater quality of Gajraula region, especially of agricultural zone, making it unsuitable for drinking purpose. Kumari et al. (2016) conducted field studies on *Brassica compestris* to assess the potential of the diluted PMDE. The results indicated that there was not much variation in pH, electrical conductivity, and nitrate of soil, whereas TDS, COD, and nitrate conductivity of the well water increased slightly but well within the permissible limit. However, there was a significant enhancement in the root hairs, the area of the leaf, diameter of the root and shoot, plant biomass, as well as number and length of pods. The application of BMDE @150 m^3 ha^{-1} can reduce fertilizer requirement, especially N by 75%, K_2O by 100%, and P_2O_5 by 20% (More et al. 2008). In ferti-irrigation, the yield of *Tritium aestivum* increased by 33% (Kumari et al. 2009) as compared to the control using diammonium phosphate and urea suggesting that the diluted DW is capable of replacing the application of chemical fertilizer when used under controlled conditions without any adverse effect on the soil and groundwater quality (Kumari et al. 2012). The use of DW as a soil amendment has generated interest in recent times. Most crops give higher yields with wastewater irrigation and decrease the need for chemical fertilizers, resulting in net cost savings to farmers. So it is an important aspect to understand the specificity of crop-effluent relationship for their appropriate application in irrigation practices. Kumar and Chopra (2012) have studied the ferti-irrigation effect of different concentrations of DW (5%, 10%, 25%, 50%, 75%, and 100%) on agronomical practices of *Trigonella foenum-graecum* L. (Fenugreek) along with control (bore well water). It was observed that there was a significant outcome on moisture content, PO_3^{-4}, SO_2^{-4}, NO_2^{-3}, TKN, Fe^{2+}, Mg^{2+}, Ca^{2+}, K^+, Na^+, CO^{-2}, HCO^{-3}, TOC, Cl^-, pH, and EC, and insignificant effect on WHC and bulk density after irrigation of soil with different DW concentrations up to 90 days. The agronomical parameters such as crop yield, LAI, chlorophyll content, dry weight, pods, flowers, number of leaves, root length, and shoot length of *T. foenum-graecum* were recorded to be in increasing order at low concentration of the DW, i.e., from 5% to 50%, and in decreasing order at higher DW concentration, i.e., from 75% to 100% as compared to control. The authors concluded that the long-term use of PMDE in agricultural fields may pose a serious threat to the groundwater quality.

6.8 Conclusion

The disposal of untreated or partially treated DW into the environment results in soil and water pollution leading to adverse effects on aquatic life and local vegetation. Thus, there is an urgent need to look into economically viable and easy-to-use technology for DW treatment. Several inexpensive secondary and tertiary treatment technologies including physicochemical and biological methods have been investigated for potential treatment of DW. However, these technologies are not techno-economic feasible options for mitigating the problems associated with the treatment and disposal of DW due to its complex nature of pollutants, which cannot be easily degraded by single-step treatment processes. Therefore, adequate treatment of DW by a novel two-step treatment/phase separation/sequential method by using organisms and their combinatorial systems has proven to be an effective approach for bioremediation of DW. The efficacy of the two-step treatment approach has been demonstrated under the pilot scale. This approach was found to be effective also in the field scale, and it is likely that during the next 5–10 years, its use will become widespread.

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