Environmental pollution and health hazards from distillery wastewater and treatment approaches to combat the environmental threats: A review

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Highlights

- Endocrine disrupting chemicals of distillery wastewater.
- Environmental and health hazards of distillery wastewater pollutants.
- Analytical techniques used for distillery wastewater pollutants analysis.
- Physico-chemical, biological and emerging treatment methods of distillery wastewater.
- Merits and demerits of various distillery wastewater treatment approaches.

Environmental pollution and health hazards from distillery wastewater and treatment approaches to combat the environmental threats: A review

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Abstract

Distillery industries are the key contributor to the world's economy, but these are also one of the major sources of environmental pollution due to the discharge of a huge volume of dark colored wastewater. This dark colored wastewater contains very high biological oxygen demand, chemical oxygen demand, total solids, sulfate, phosphate, phenolics and various toxic metals. Distillery wastewater also contains a mixture of organic and inorganic pollutants such as melanoidins, di-n-octyl phthalate, di-butyl phthalate, benzenepropanoic acid and 2-hydroxysocaproic acid and toxic metals, which are well reported as genotoxic, carcinogenic, mutagenic and endocrine disrupting in nature. In aquatic resources, it causes serious environmental problems by reducing the penetration power of sunlight, photosynthetic activities and dissolved oxygen content. On other hand, in agricultural land, it causes inhibition of seed germination and depletion of vegetation by reducing the soil alkalinity and manganese availability, if discharged without adequate treatment. Thus, this review article provides a comprehensive knowledge on the distillery wastewater pollutants, various techniques used for their analysis as well as its toxicological effects on environments, human and animal health. In addition, various physico-chemicals, biological as well as emerging treatment methods have been also discussed for the protection of environment, human and animal health.

Keywords: Melanoidins, Chemical pollutants, EDCs, Environmental problems, Health hazards, Treatment approaches

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1. Introduction

Distillery industries (DIs) are the key contributors to the world's economy, but these industries also considered as one of the major source of environmental pollution worldwide. In India, there are ~ 319 distilleries with annual production of 3.25×10^9 L of alcohol and 40.4×10^{10} L of wastewater (Chandra et al., 2012; Uppal, 2004). The global production of bioethanol in 2007 was 50 billion liters whereas, in 2008, it reached 60 billion liters representing almost 4% of the world's gasoline consumption (Mussatto et al., 2010; Balat and Balat, 2009). DIs generate a huge volume of dark colored wastewater characterized by its dark brown color, acidic pH (5.4-4.5), high BOD (40,000- 50,000 mg/L), COD (80,000-100,000 mg/L), total dissolved solids (TDS), total solids (TS), total suspended solid (TSS), with high nitrogen, potassium, phosphates, calcium, and sulfate content (Table 1). The high BOD and COD values of DWW are mainly due to the presence of high organic content such as proteins, reduced sugars, polysaccharides, lignin, melanoidins, and waxes along with a complex mixture of recalcitrant organic pollutants (Chowdhary et al., 2017).

In distillery wastewater (DWW), melanoidins are the major coloring pollutants causing serious environmental problems and health threats in human and animals (Tamanna and Mahmood, 2015; Saranraj and Dtella, 2014). Melanoidins are recalcitrant compounds of sugar and amino acids, formed during the processing of sugar cane juice in sugar factories and molasses in distillery industries (Arimi et al., 2015; Saranraj and Dtella, 2014; Onyango et al., 2012; Wang et al., 2011; Agarwal et al., 2010; Mohana et al., 2009; Plavsic et al., 2006). Besides melanoidins, some other toxic chemicals such as di-n-octyl phthalate, di-butyl phthalate, benzenepropanoic acid and 2-hydroxysocaproic acid are also reported in DWW (Chandra and Kumar, 2017b; Yadav and Chandra, 2012). These toxic chemicals particularly phthalates are well reported as endocrine disrupting compounds (ECDs), which causes hormonal imbalance resulting several physiological as well as metabolic disorders affecting the reproductive fitness of human and animals (Dixit et al., 2015; Yadav and Chandra, 2012; Alam et al., 2010).

However, the characteristics of DWW are largely depended on the raw materials, chemicals used and processes adopted by DIs (Arimi et al., 2015; Satyawali and Balkrishnan, 2008). Arimi et al. (2014) described in detail the various steps of wastewater generation in DIs utilizing sugarcane molasses as raw material for alcohol production (Fig. 1) (Arimi et al., 2014). Besides sugarcane molasses, DIs also use grains, grapes, sugarcane juice, and barley malt etc. for alcohol production, which mainly accomplished into four steps such as feed preparation, fermentation, distillation, and packaging (Satyawali and Balkrishnan, 2008; Skerratt, 2004; Berg, 2004; Tano and Buzato, 2003).

When untreated/partially treated DWW discharged into the environment, it causes serious ecotoxicological and health threats. In water bodies, it reduces the penetration power of sun light causing a reduction in photosynthetic activity and depletion in dissolved oxygen (DO) content (Saranraj and Dtella, 2014; Chandra et al., 2008a) whereas in soil system, it reduces the fertility of agricultural land. Due to these environmental and health threats, DWW should be adequately treated for the degradation and detoxification of organic and inorganic pollutants prior to its final discharge into the environment. Various physico-chemical methods reported for the treatment of DWW are not feasible to meet the discharge standards set by various environmental protection agencies. On other hands, the biological methods like aerobic/anaerobic treatment processes were found somewhat capable to reduce BOD/COD load of DWW, but the substantial concentration of organic and inorganic pollutants and dark color left behind require further treatment (Safari et al., 2013).

Hence, this review article was mainly focused on the generation and characteristics of DWW pollutants, various analytical techniques used for their identification, their ecotoxicological and health threats as well as various treatment approaches, and challenges for the management of DWW.

2. Chemical pollutants in DWW

The major color contributing pollutants present in DWW are melanoidins, an amino-carbonyl polymer, produced during the processing of sugarcane juice in sugar industries and molasses in DIs (Fig. 2). Melanoidins are produced by a series of non-enzymatic chemical reactions known as Maillard reactions and products produced as Maillard Reaction Products (MRPs). Melanoidins are the mixture of low and high molecular weight compounds ranging from 40 kDa - 40000 kDa (Chandra et al., 2008a). The elemental composition, structure as well as the molecular weight of MRPs is largely depends on the nature and molar concentration of reacting molecules and reaction conditions i.e. pH, temperature, and reaction time etc. (Silvan et al., 2006; Chandra et al., 2008a). The size of MRPs may vary from small molecules to very large polymers (Wang et al., 2011; Wagner et al., 2002). Various authors have reported that low and high molecular weight MRPs isolated from dry heated glucose-glycine systems (125 °C, 2 h) and aqueous sugar-lysine model systems (121°C, 1h, pH 9.0) have genotoxic and cytotoxic effects on cells at higher concentration (Glosl et al., 2004; Jing and Kitts, 2000). Besides MRPs, a variety of mutagenic, carcinogenic, cytotoxic and endocrine disrupting chemicals are also reported in DWW (Table 2) (Dixit et al., 2015; Yadav and Chandra, 2012; Alam et al., 2010).

Endocrine disrupting chemicals (EDCs) are the chemical agents, which interferes the synthesis, secretion, transport, binding, or elimination of natural hormones in human and animal body that play a key role in various physiological and cellular functions such as homeostasis, reproduction, development and behavioral activities (Kavlock et al., 1996). There are a number of organic compounds in DWW, which have been identified as EDCs such as di-butyl phthalate, di-n-octyl phthalate, butanedioic acid and 2-hydroxysocaproic acid etc. (Table 3) (Chandra and Kumar, 2017b; Yadav and Chandra, 2012). These EDCs can alter the regulation of various hormonal activities, which play a significant role in metabolism, sexual development, hormones production and their utilization in growth, stress response, gender behavior, and reproduction processes (Kabir et al., 2016; Somm et al., 2009). Phthalates have been well documented to induce the lipid peroxidation, oxidative stress, and interference with insulin receptor, altered glucose tolerance induction and reduced glucose oxidation. These also undergo a rapid transformation process in normal environment rather than in abiotic environment (Kabir et al., 2016). Therefore, there is an urgent need for awareness and critical research on EDCs present in industrial wastewaters.

3. Analytical techniques available for the detection and characterization of DWW pollutants

DWW contains a number of organic and inorganic pollutants produced during the alcohol production processes in DIs, which can be detected, characterized and identified by using various analytical techniques such as high performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS/MS), infrared spectroscopy (IR), protonic nuclear magnetic resonance (^{1}H NMR), fast atom bombardment-mass spectrometry (FAB-MS), matrix assisted lesser desorption ionization-time of flight (MALDI-TOF), and atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) etc. (Table 4). The HPLC can be used for the separation, identification as well as quantification of organic pollutants present in a complex industrial wastewater (Bharagava et al., 2009). The GC-MS is being used for the characterization and identification of low molecular weight compounds (volatile compounds) from industrial wastewaters, which are soluble in organic solvents such as dichloromethane, ethyl acetate, diethyl ether, methanol, acetone, n-hexane etc. (Chandra and Kumar, 2017b). LC-MS/MS technique is used for the characterization and identification of high molecular weight compounds, which are not soluble in organic solvents, but soluble in water (Chandra et al., 2012; Bharagava and Chandra, 2010a). Infrared (IR) spectroscopy can be used for the identification of functional groups such as alcoholic (-OH), -C-H, ketonic (=C=O), aldehydic (-CHO), carboxylic (-COOH), carbon carbon double bond (-C=C-) and an asymmetric -NO_2 group etc., respectively in the form of stretching frequencies. On the other hand, the ^1H NMR showed the presence and position of protons in organic pollutants (Chandra et al., 2012). FAB-MS can also be used for the detection and characterization of organic pollutants from wastewaters and this method is very simple as the samples are directly introduced into the ion source. But, the drawback of this technique is that it can't be used for the detection and characterization of many organic pollutants at a time and thus, this technique has been replaced by electro-spray ionization (ESI) technique that offers the advantage of a very soft ionization. MALDI-TOF technique is used for the detection and characterization of proteinaceous compounds. On the other hand, the AAS and ICP-MS are used for the detection and quantification of metallic (Cu, Cr, Zn, Fe, Ni, Mn, Pb, Hg, As etc.) and non-metallic pollutants from industrial wastewaters (Chandra et al., 2008a; Chandra et al., 2008b).

4. Ecotoxicological and health hazards of DWW pollutants

DWW contains a high concentration of recalcitrant organic pollutants generated during the processing of sugarcane juice in sugar industries and alcohol production in DIs. DWW also contains natural color contributing compounds such as polyphenols, caramels, melanoidins and alkaline degradation products of hexoses (ADPH) etc. (Arimi et al., 2014; Dai and Mumper, 2010). These polyphenolic compounds have antioxidant, anti-microbial, anti-carcinogenic, free radical scavenging and metal chelating properties (Silvan et al., 2006; Borrelli et al., 2003). Phenolic compounds are also reported to react with proteins during beer storage and form high molecular weight compounds and hazes (Siqueira et al., 2011; Dai and Mumper, 2010; Jimoh et al., 2008).

The presence of polyphenols in DWW is largely depends on the source of molasses and sugar content in feed flow (Bustamante et al., 2005; Jimenez et al., 2004; Martin et al., 2003). Polyphenols are categorized into three broad classes: phenolic acids, flavonoids, and tannins. The phenolic compounds detected in molasses based DWW includes benzoic acid and its derivatives (e.g., gallic acid), cinnamic acid and its derivatives (e.g., coumaric acid, caffeic acid, chlorogenic acid and ferulic acid) (Incedayi et al., 2010; Payet et al., 2006). Besides these polyphenols, DWW also contains melanoidins as major recalcitrant coloring compounds (Arimi et al., 2015; 2014).

4.1. Ecotoxicity

The discharge of DWW in water bodies without adequate treatment causes severe water pollution. Due to its high BOD, COD values, high sulphate, phosphate, and nitrogen content, it causes eutrophication of contaminated water resources (Ramakritinan et al., 2005; Mahimaraja and Bolan, 2004). For DWW, Mahimaraja and Bolan (2004) have estimated the LC_{50} value of 0.5% by using a bio-toxicity test on fresh water fish *Cyprinus carpio var. communis*. Subsequently, it was reported by some other researchers that respiratory process in *Cyprinus* *carpio* under DWW stress get affected resulting in a shift towards the anaerobic conditions at organ level during the sublethal intoxication (Ramakritinan et al., 2005)

DWW also causes soil pollution and acidification in the case of inappropriate land discharge. Further, it is also reported by various researcher that it inhibits seed germination, reduce soil alkalinity, cause soil manganese deficiency and reduces the growth and yield of crop plants (Chowdhary et al., 2017; Onyango et al., 2012; Bharagava and Chandra, 2010b; Agrawal et al., 2010; Mohana et al., 2009). In addition, Bharagava and Chandra (2010b) have also reported that post methanated distillery effluent (PMDE) have deleterious effects on seed germination and seedling growth parameters in *Phaseolus mungo* (L). The inhibition in seed germination at higher PMDE content might be attributed to high salt concentration and TDS, which increases high osmotic pressure (OP) and anaerobic conditions, respectively. These conditions affect various biochemical and physiological activities such as movement of solute, respiration and enzymatic process of seed germination. It has been also reported that high PMDE concentration also acts as an inhibitor for plant growth hormone(s) (auxin and gibberline), which play an important role in plant growth and development (Subramani et al., 1997). Moreover, Bharagava et al. (2010b) have reported that at higher PMDE concentration, the entrance of potentially toxic trace elements into the protoplasm may result in the reduction of intermediate metabolites, which are responsible for the reduction in plant growth parameters.

4.2. Health hazards

Besides soil and water pollution, the residents of DWW contaminated area also face severe health problems such as irritation of eyes, skin allergies, headache, fever, vomiting sensation, and stomach pain etc. All these problems might be due to the presence of high concentration of dissolved impurities like carbonates, bicarbonates, sulphates, calcium chloride, magnesium, iron, sodium, and potassium along with the colloidal impurities like coloring compounds, organic waste, finely divided silica and clay (Chaudhary and Arora, 2011).

DWW due to the presence of a number of anti-nutritional and toxic MRPs such as melanoidins has been also reported to cause severe health problems in human and animals directly/indirectly (Taylor et al., 2004). Melanoidins present in DWW in high concentration have mutagenic, carcinogenic and cytotoxic effects on cells (Silvan et al., 2006; Somoza, 2005). Some researchers have reported that excessive glycation process also destroys the essential amino acids, inactivation of enzymes, cross-linking of glycated extra-cellular matrix, inhibition of regulatory molecule binding sites, altered macromolecular recognition, abnormalities in nucleic acid function, endocytosis and increased immunogenicity etc. (Silvan et al., 2006; Taylor et al., 2004). In addition, melanoidins were also found to be involved in the progression of various diseases such as cardiovascular complications, diabetes mellitus and Alzheimer's disease (Somoza, 2005).

However, the genotoxic compounds can act at various levels in cells (causing gene, chromosome, or genome mutations), necessitating the use of a range of genotoxicity assays designed to detect these different types of mutations (Bartling et al., 2005; Taylor et al., 2004). Brands et al. (2000) have demonstrated that heated sugar-casein model melanoidins consisting variable sugars exhibit different mutagenic activity. For example, ketose sugars (fructose and tagatose) showed a remarkably high mutagenic activity as compared to their aldose isomers (glucose and galactose) and generated reactive oxygen species results in the breaking of DNA strands and mutagenesis. In addition, some other MRPs were also reported to induce chromosomal aberrations in *Chinese hamster* ovary cells and gene conversion in yeast cells. The mutagenicity and DNA strand breaking activity of glucose-glycine model melanoidins was also demonstrated by Hiramoto et al. (1997), who reported that LMW fractions act as lipid sink and induced DNA damage, where the effect increases with increase in concentration.

5. Treatment approaches for DWW

DWW is a major source of soil and water pollution and thus, it becomes imperative to treat it adequately before its final discharge into the environment. This can be achieved by using various physical, chemical and/ or biological treatment processes either alone or in combination for the effective treatment.

5.1. Physico-chemical treatment methods

5.1.1. Coagulation/flocculation

Coagulation is the destabilization of colloidal particles by neutralizing the forces that keep them apart by using coagulating agents and sometimes by the coagulant aids (e.g. activated silica, bentonite, polyelectrolytes, starch etc.). As a result, the particles collide to form larger particles (flocs) whereas flocculation is the action of polymers to form bridges between the flocs, and bind particles to form large agglomerates or clumps. A number of coagulants such as aluminium sulfate ($AlSO_4$), ferric chloride ($FeCl_3$), ferrous sulfate ($FeSO_4$), alum, iron aluminum, calcium salts, polyaluminium chloride (PACl) etc. are reported to be used in the treatment of DWW. These coagulants are reported to reduce the organic load (COD) and suspended solids (SS) from DWW (Wagh and Nemade, 2015; Prajapati and Chaudhari, 2015; Arimi et al., 2014; Agarwal et al., 2010; Satyawali and Balakrishnan, 2008; Pandey et al., 2003).

However, coagulants are pH specific and their effectiveness depends on their type, concentration, and characteristics of wastewater to be treated. Chaudhari et al. (2005) have reported 72.5%, 60% and 55% COD reduction and 92%, 86% and 83% color reduction from DWW using polyaluminium chloride (PACl), $AlCl_3$ and $FeCl_3$. Sowmeyan and Swaminathan

(2008) have tested $FeCl_3$ and $AlCl_3$ for the effective treatment of DWW and reported 93% & 76% reduction in color and total organic carbon, respectively. Moreover, the highest color removal (upto 98%) from biologically treated DWW was reported by using the conventional coagulants such as ferrous sulfate, ferric sulfate, and alum under alkaline conditions (Pandey et al. 2003). Further, Prajapati et al. (2015) have reported 80%, 90%, 70%, and 92% COD reduction and 81.8%, 80.64%, 74.19% and 81.8% color reduction from DWW by $FeCl_3$, alum, $AlCl_3$, and $FeSO_4$ at concentration of $60mM/dm^3$ at pH 5, 5, 6, and 5, respectively. David et al. (2015) have also applied a green methodology for DWW treatment using *Moringa oleifera* seed extract as the coagulant in conjunction with chemical coagulants i.e. aluminium sulphate and calcium sulphate and found 97% color reduction.

5.1.2. Adsorption

Adsorption is a surface based physical phenomenon used for the removal of organic pollutants from industrial wastewaters. Extensive literature is available on the studies using adsorbents such as chemically modified sugarcane bagasse, powdered activated carbon (PAC), activated charcoal, pyochar, chitosan etc. for DWW treatment (Prajapati and Chaudhari, 2015; Agarwal et al., 2010; Satyawali and Balakrishnan, 2008; Mandal et al., 2003; Lalov et al., 2000; Chandra and Pandey, 2000). Activated carbon (AC) has been reported as an efficient adsorbent due to its extended surface area, microporous structure, high adsorption capacity as well as high degree of surface reactivity (Arimi et al., 2014; Agarwal et al., 2010; Satyawali and Balakrishnan, 2008). AC is widely used for the removal of color, polyphenols and specific organic pollutants from various industrial wastewaters (Prajapati and Chaudhary, 2015; Satyawali and Balakrishnan, 2008). Chandra and Pandey (2000) has reported >99%, 70% and 90% reduction in color, BOD, and COD, respectively by using commercial activated charcoal having a surface area of 1400

m^2/g from anaerobically treated distillery spentwash. Lalov et al. (2000) used chitosan as an adsorbent at the concentration of 10 g/l for 30 min contact time for the effective treatment of DWW and found 98% and 99% reduction in color and COD, respectively. Further, Mane et al. (2006) have reported 50% color reduction from DWW using chemically modified bagasse (0.5 g/100 ml wastewater) using 2-diethylaminoethyl (DEAE) chloride hydrochloride and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) for the effective treatment of DWW. Shivayogimath and Inani (2014) have also reported 95.4%, 62.83% and 89.8% COD, color, and TDS reduction, respectively from DWW by using bagasse activated carbon.

5.2. Biological treatment approaches

Biological treatment approaches are eco-friendly methods for the mitigation of industrial pollutants and involve the stabilization of wastes by degrading them into harmless substances either by anaerobic or aerobic processes.

5.2.1. Anaerobic process

The anaerobic digestion is the most appropriate approach for the mitigation of high organic carbon content such as distillery and pulp and paper industry wastewater. The anaerobic digestion process is mainly used to produce biogas from spentwash. The high organic content of molasses spentwash makes the anaerobic treatment more attractive in comparison to direct aerobic treatment process (Satyawali and Balakrishnan, 2008; Mohana et al., 2007). The anaerobic digestion is a process in which the organic compounds present in DWW are digested by microorganisms to produce biogas (CH_4 60% and CO_2 40% approximately). On an average, $1m^3$ of spentwash produces ~38-40 m^3 of biogas. The other products of anaerobic digester include treated spentwash and digested sludge, which is highly rich in nutrients. This digested sludge can be used as green manure since, it contains the high nutrient content (Nandy et al., 2002). The most widely used anaerobic process for DWW treatment is up-flow anaerobic sludge blanket (UASB) (Satyawali and Balakrishnan, 2008; Mohana et al., 2007; Wilkie et al., 2000).

The limitations of anaerobic treatment processes are the requirement of high dilution due to the presence of many antimicrobial compounds such as 2,3-dimethylpyrazone, 2,2-bifuran-5-carboxylic acid, 2-nitroacetophenone, 2,2-bifulan, 2-methylhexane, methylbenzene, 2,3-dihydro-5-methylfuran, p-chloroanisole, 3-pyrroline and acetic acid etc. These compounds can be transformed by bacteria into other products including: 2-nitroacetophenone, p-chloroanisole, indole, 2- methylhexane and 2,3-dihydro-5-methylfuran etc. (Jimenez et al., 2004; Bharagava and Chandra, 2010a). Despite of high COD removal from diluted DWW, the chemical inhibitors remain in DWW even after the anaerobic digestion process. Therefore, a further treatment is required to remove the remaining dark color and COD, BOD etc. Another strategy is the pretreatment of DWW with ozone, UV light plus titanium dioxide before the aerobic digestion in order to improve the efficiency of anaerobic treatment processes (Arimi et al., 2014; Jimenez et al., 2004; Martin et al., 2002). It is thus, preferable to treat the DWW anaerobically first and then with other treatment methods. Arimi et al. (2015) have used natural manganese oxides (MnOx) in anaerobic digestion process to remove DWW pollutants. Further, more information on anaerobic digestion processes can be found in Table 6 and other reviews (Satyawali and Balakrishnan, 2008; Melamane et al., 2007; Wilkie et al., 2000).

5.2.1.1. Conventionally used system

Some conventionally used digesters like continuous stirred tank reactors (CSTR) are the simplest closed anaerobic reactors with the provision of a gas collection. CSTR also known as sealed-tank digester equipped with treatment facility. DWW treatment has been reported in single and as well as biphasic system, resulting in a significant reduction in pollution parameters such as COD and BOD with the provision of a gas collection (Jo et al., 2015; Mendez-Acosta et al., 2010; Mohana et al., 2009; Pathade, 2003). However, the hydraulic retention time in a CSTR- type reactor is determined by the growth rate of microorganism growing in the system. It means to achieve the high degradation rate of DWW, a very high HTR value will be required because the high HTR values make the CSTR concept less feasible and less effective for the treatment of DWW. As CSTR requires long retention time and less gas yield during the treatment process (Siddique, 2012; Kleerebezem and Macarie, 2003).

5.2.1.2. Single and biphasic system

The treatment of DWW in an anaerobic system can be controlled by the single or biphasic system. In single phasic systems, only one reactor involve in the microbial degradation of organic pollutants, whereas biphasic system has two reactors i.e. one for acidogenic and other for methanogenic microorganisms. In biphasic reactors, the most promising thing is that fermentation steps can be optimized at each stage in separate fermenters. Due to this, the effectiveness and kinetics of biphasic reactors become much higher in comparison to single phasic reactors because in this system all process occurs in same environmental conditions. In both phases (primary and secondary), the end products produced are acetate, lactate, ethanol, CO_2, H, C3, higher volatile fatty acid and methane, CO_2, respectively (Mohana et al., 2009; Gosh 1990). Thus, the biomethanation using biphasic system seems to be most appropriate treatment method for DWW because of its multiple advantages such as easy maintenance of optimal conditions for buffering between the production of organic acid and their utilization, steady performance, and high methane gas production.

5.2.2. High rate anaerobic reactors

5.2.2.1. Upflow anaerobic sludge blanket (UASB) reactors

The UASB reactors have become more popularized in the recent years for the treatment of various types of wastewaters including DWW (Petta et al., 2017) The USAB reactors are high rate anaerobic wastewater treatment reactors, which are extensively used for the treatment of DWW worldwide. The UASB reactors have four main components such as sludge bed, sludge blanket, gas solid separator, and settlement compartment. The biomass layers settled at the bottom of the reactors are called as sludge bed whereas the suspension of sludge particles mixed with produced gas is called as sludge blanket. However, the operation of UASB is mainly dependent on the formation of active and settleable granules (Fang et al., 1994). The function and efficiency of USAB reactors are dependent on several factors like temperature, pH, wastewater composition, and organic loading rate. Recently, Petta et al. (2017) have observed that the UASB reactors combined with the anoxic-aerobic ultra filtration membrane bioreactors (UF-MBR) achieve the treatment efficiency up to 97% with the production of methane 340 L of CH_4/kg COD. The efficiency UASB depends on the active and settleable granules that contain the aggregation of anaerobic bacteria, self-immobilized into a compact form. These granules enhance the settleability of biomass leading to an effective retention of bacteria in UASB reactors (Akunna and Clark, 2000). However, the most attractive features of UASB reactor design include, its independence from the mechanical mixing of digester contents, recycling of sludge biomass as well as the ability to deal with the perturbances caused due to the high loading rates and temperature fluctuations (Sharma, and Singh, 2000). For the successful performance of UASB reactors, it should be operated at a low loading rate of 4-8 kg COD $m^{-3}d^{-1}$ and COD removal rate should be monitored carefully. Wolmarans and de Villiers (2002) have reported that USAB reactors can achieve 90% COD removal from DWW under high loading rate.

5.2.2.2. Anaerobic batch reactors

The anaerobic batch reactors have not been generally used for the treatment of DWW and thus, the potential, operational feasibility and scale-up of such reactors need to be studied. However, Moletta, (2005) has achieved 90-95% COD reduction during the anaerobic digestion with the organic loading between 5-15 kg COD/m^3 of digester/day with biogas production from 400-600 per kg COD removal with 60- 70% methane content. Recently, Tansengco et al. (2016) have reported 60% and 86% COD and BOD reduction along with the generation of 72% methane gas during the treatment of DWW in Anaerobic Sequencing Batch Reactor (ASBR), at 8 h of reaction time. In addition, a semi continuous batch digester was also designed to study the biomethanation of DWW within the range of mesophilic and thermophilic temperatures Banerjee and Biswas (2004). In this study, authors have reported 86.01% BOD reduction with 73.23% methane gas production at the BOD loading rate of 2.71 kg m^{-3} and 50 °C.

5.2.2.3. Anaerobic filters

The anaerobic filters are more popular in comparison to aerobic wastewater treatment methods because these generate less amount of solid residue. The anaerobic filters are packed column having static medium to support the colonization of anaerobic microbial consortium for wastewater treatment. These filters are based on an attached growth process, which immobilizes microorganisms on the surface of packing materials to produce a biofilm (de Lemos Chernicharo, 2007). Thus, in anaerobic filters, the selection of packing materials is important because it plays an important role in the effective performance of anaerobic filters as various characteristics of filter media such as porosity, and surface area has significant effects on the attachment of biomass (Loupasaki and Diamadopoulos, 2013).

The anaerobic filters work in up and downflow mode were the latter achieves better sustained and reliable operation because the downflow has the capacity to reduce the clogging of packed material during the treatment of wastewater carrying the very high content of suspended solid (Nicolella et al., 2000). Yu et al. (2006) achieved 82% COD removal from DWW under laboratory condition by upflow anaerobic filter at a temperature ranging from 19-27 °C, BV = 37.68 kg COD/ (m^3.d and HRT of 8h. Further, a lab scale anaerobic reactor packed with small sized and low-density polyethylene (0.93 g/cm^3, Bioflow 30) as supporting materials resulted in 80% COD removal at BV of 30 kg COD m^3.d. However, the biomass retention capacity obtained was 4-6 g dry solids per g support representing a fixed biomass of 57 g solids/L of reactor volume (Thanikal et al., 2007).

5.2.2.4. Bihydrogen production

Industrial wastewaters are well reported to have a high organic load, BOD, and COD, which causes various harmful effects on the environment, but these parameters, can also act as a source of beneficial by-products generation. Approximately, 5.2 million tons of solid waste is generated per day worldwide, which can be used for the generation of useful by-products (Modak, 2011). Many investigators have proposed and selected hydrogen gas as an alternative renewal source of energy and also looking toward the new alternatives to generate hydrogen gas from organic pollutants by using microorganisms (Choudri and Baawain, 2016; Fountoulakis and Manios, 2009; Wang and Zhao, 2009). Recently, many authors have reported the hydrogen gas production utilizing DWW as C, N, and energy source by anaerobic treatment process (Wicher et al., 2013; Mishra and Das, 2014; Mishra et al., 2015). However, the main advantages of microbiological methods of hydrogen generation rely on the possibility of utilization of industrial and municipal wastewaters, significant decrease of costs of production and simplicity of the processes.

5.2.3. Aerobic process

5.2.3.1. Bacterial treatment

Bacterial treatments employing pure bacterial culture have been reported frequently in the past and recent years. Bacterial degradation and decolorization of industrial wastewaters is an environment-friendly and low-cost alternative to the physico-chemical treatment processes of wastewaters. In recent years, many researchers used bacterial consortium and pure culture for the effective degradation/decolorization of DWW. The bacterial consortium comprising of *Pseudomonas aeruginosa* PAO1, *Stenotrophomonas matophila* and *Proteus mirabilis* is reported for 67% and 51% reduction in color and COD within 24 h and 72 h, respectively at 37 °C from DWW (Mohana et al., 2007). Jiranuntipon et al. (2008) have reported 9.5, 1.13, 8.02, and 17.5%, color removal from Viandox sauce (13.5% v/v), caramel (30% w/v), beet molasses wastewater (41% v/v), and sugarcane molasses wastewater (20% v/v) within 2 days by using a consortium of *Klebsiella oxytoca*, *Serratia mercescens*, and *Citrobacter* sp. In addition, they also achieved 26.5% color removal from DWW by using the consortium of *Acinetobacter* sp., *Pseudomonas* sp., *Comamonas* sp., *Klebsiella oxytoca*, *Serratia marcescens*, and unidentified bacterium in 48 h under aerobic condition (Jiranuntipon et al., 2009). However, a detailed list of bacteria used by various researchers in the treatment of DWW is given in Table 5.

5.2.3.2. Fungal treatment (Mycoremediation)

There are a number of fungal species such as *Aspergillus fumigatus G-2-6, Emericella nidulans var. lata, Geotrichum candidum, Trametes sp., Aspergillus niger, Citeromyces sp., Flavodon* *flavus* etc., which have been used by various worker for the treatment of DWW (Bezuneh 2016; Pal and Vimla, 2012; Raghukumar et al. 2004; Patil et al. 2003; González et al. 2000).

Fungal treatment is used to reduce COD, BOD, and degradation of organic compounds as well as to obtain some valuable byproducts such as protein-rich, fungal biomass, which can be used as animal feed or some other specific fungal metabolites. Filamentous fungi have lower sensitivity to variations in temperature, pH, nutrients, and aeration and have lower nucleic acid content in biomass (Satyawali and Balakrishnan, 2008).

Ravikumar et al. (2011) have reported that *Cladosporium cladosporioides* was capable to reduce 52.6% color and 62.5% chemical oxygen demand from DWW at optimum conditions i.e. 5 g/L of fructose, 3 g/L of peptone, 5 pH and 35 °C. Further, these authors again used *Cladosporium cladosporioides* at different conditions i.e. fructose concentration 7 g L^{-1}, peptone 2 g L^{-1}, 6 pH and 10% (w/v) inoculum concentration and found 62.5% and 73.6% reduction in color and COD, respectively (Ravikumara et al., 2013). In addition, Shukla et al. (2014) also reported 97.2% color reduction from DWW by using *Aspergillus niger* (ATCC No. 26550 and NCIM No. 684) with the help of combined coagulants.

However, some white rot fungi also reported to secret ligninolytic enzymes (LiP, MnP & Laccases), which are capable of degrading xenobiotics and organometalic-pollutants (Chandra and Chowdhary, 2015). Moreover, various fungal species investigated for their ability to degrade/decolorize DWW are given in Table 5.

5.2.3.3. Algal treatment (Phycoremediation)

The treatment of DWW with microalgae attracts the researchers not only by treating the waste, but also by its products/byproducts, which are in high demands for social welfare (Sankaran et al. 2014). Solovchenko et al. (2014) have investigated the possibilities of DWW bioremediation along with a new *Chlorella sorokiniana* sp. cultivated in a semi-batch mode in a high-density photobioreactor. Microalgal treatment becomes effective only after the anaerobic treatment of spentwash, since the process is energy efficient and has ability to fulfill its nutrients requirement from biomethanated spentwash and energy requirement from sun light. The treatment of anaerobically treated 10% DWW using the microalgae *Chlorella vulgaris* followed by *Lemna minuscula* resulted in 52% color reduction (Valderrama et al. 2002). Further, Kalavathi et al. (2001) examined the degradation of 5% melanoidin by a marine cyanobacterium *Oscillatoria boryana* BDU 92181.

Saha et al. (2005) observed that *Oscillatoria willei,* when grown under lower nitrogen content, but with optimum phenolic compounds, showed an increased oxidative stress with an increase in ligninolytic and anti-oxidative enzymes such as lignin peroxidase, laccase, polyphenol oxidase, superoxide dismutase, catalase, peroxidase and ascorbate peroxidase. This study concluded that these enzymes were responsible for the decolorization of substrate phenol upto 52% in 7 days by the Cyanobacterium *O. wille*i.

Sankaran et al. (2014) have given the phycoremediation mechanism of DWW (Fig. 3). Thus, coupling microalgae biomass production with nutrient removal/pollutant degradation may represent an important milestone in the bioenergy goals since the wastewater market is immense (Sankaran et al. 2014).

5.2.4. Constructed wetlands (CWs)

Plants have high metal accumulation potential from the contaminated sites, which was observed by TEM analysis of various naturally growing plants (Fig. 5) (Chandra and Kumar, 2017a). Constructed wetland as a natural process, environment friendly with a simple construction and low maintenance is one of the interesting technique. The treatment of DWW through constructed wetlands is the most biological active ecosystem worldwide (Sayadi et al., 2012; Choudhary et al., 2011). Mulidzi et al. (2010) showed the impact of shorter retention time on the performance of constructed wetlands in terms of BOD, COD and other elements removal. The results had shown an overall 60% COD removal throughout the year. Results also showed the significant removal of other elements namely; potassium, nitrogen, electrical conductivity, calcium, sodium, magnesium, and boron from DWW wastewater by constructed wetlands.

Billore et al. (2001) have demonstrated a four-celled horizontal subsurface flow (HSF) CW for the treatment of DWW after anaerobic treatment. The post-anaerobic treated effluent had BOD of 2500 mg/l and COD 14,000 mg/l. A pre-treatment chamber filled with gravel was used to capture the suspended solids. All the cells were filled with gravel up to varying heights and cells, third and fourth were planted with *Typha latipholia* and *Phragmites karka,* respectively. The overall retention time was 14.4 d and the treatment resulted in 64%, 85%, 42%, and 79% reduction in COD, BOD, total solids, and phosphorus, respectively.

5.2.5. Biocomposting

In this process, press mud generated from sugar mills is utilized to produce compost by mixing with DWW (Torres-Climent et al., 2015). Both anaerobic and aerobic composting systems are being used for the treatment of DWW. In some treatment plants, composting with effluent treated through the bio-methanation plant is also practiced. Biocomposting is one of the most valuable thermophilic processes, resulting in a product rich in humus, which is used as fertilizer in agriculture fields. The spentwash, either directly, or after biomethanation is sprayed in a controlled manner on sugarcane pressmud. The latter is the filter cake obtained during the juice clarification in sugar industries. Jimnez and Borja, (1997) reported that the aerobic pretreatment of beet and molasses spentwash with *Penicillium decumbens* resulted ~74% and 40% reduction in phenolics content and color, respectively. This is a popular option adopted by several Indian distilleries attached to sugar mills with adequate land availability.

5.2.6. Enzymatic mechanism of DWW decolorization

There are several enzymes (e.g., Peroxidases, Oxidoreductases, Cellulolytic enzymes, Cyanidase, Proteases, Amylases, etc.) reported from different sources to play an important role in waste treatment processes (Chandra and Chowdhary, 2015; Dec and Bollag, 1994). The ligninolytic system consists of two main groups of enzymes: peroxidases (lignin peroxidases and manganese peroxidases) and laccases (Chandra and Chowdhary, 2015; Baldrian, 2006). The bacterial laccases play an important role in bioremediation of industrial waste because these oxidize both toxic and non-toxic substrates. Laccases are also included in the cleaning of industrial effluents, mostly from paper and pulp, textile and DIs. Among the biological agents, laccases represent an interesting group of ubiquitous oxidoreductase enzymes showing great potential for biotechnological applications (Chandra and Chowdhary, 2015; Sangave and Pandit, 2006; Gianfreda et al., 1999). On DWW decolorization, many studies have suggested the involvement of various enzymes with different mechanisms as Watanabe et al. (1982) have reported the involvement of an intracellular enzyme produced by *Coriolus* sp No. 20 that requires active oxygen molecule and sugars for its activity. This intracellular enzyme was identified as sorbose oxides with molecular weight 2,00,000 kDa. The purified enzyme was found capable to decolorize DWW in presence of glucose, galactose, sarbose, xylose, and maltose. DWW is reported to be decolorized by the active oxygen species (O_2^-, H_2O_2) produced by the reactions catalyze by oxidases because the reaction with pure enzymes was accompanied by the oxidation of glucose into gluconic acid. It could be due to the production of sugar oxidases rather than the sorbose oxidase because the crude preparation utilizes arabinose, fructose, and mannitol while sarbose oxidase does not utilize these sugars. Further, Aoshima et al. (1985) have reported the decolorization of DWW by *Coriolus* versicolor Ps4a, which might be due to an intracellular enzyme induced by DWW pollutants. This intracellular enzyme is reported to consist of two major components i.e. 1st a sugar independent enzyme that forms two-third part while other is sugar independent part that contributes one-third part of the enzyme. Ohmomo et al. (1985) purified a DWW decolorizing enzyme from *Coriolus versicolor* Ps4a and reported that this was an intracellular enzyme consisting of a major P-fraction and a minor E-fraction. The P-fraction consist at least five enzymes, which were of two types that may/may not require sugar for their decolorizing activity. In addition, Miyata et al. (1998) have also studied the DWW decolorizing by *Coriolus hirsutus* pellet, which was mainly due to the production of extracellular hydrogen peroxide (H_2O_2) and peroxidases. The culture filtrate was found to have two major extracellular peroxidases, one manganese independent peroxidase (MIP) and other is manganese dependent peroxidase (MnP). Since both MIP and MnP exhibited DWW decolorizing activity in presence of H_2O_2 and thus, it can be concluded that the decolorization of DWW by C. *hirsutus* involved the production of extracellular H_2O_2 and peroxidases. Therefore, the knowledge of enzymes in bioremediation of various industrial wastes will open many opportunities for large-scale application.

5.2.7. Miscellaneous approaches for color removal from DWW

Sirianuntapiboon et al. (2004) have isolated a strain No. WR-43-6 (*Citeromyces* sp.), which showed the highest decolorization yield i.e. 68.91% from a solution containing molasses pigment in presence of glucose 2.0%, sodium nitrate 0.1% and KH_2PO_4 0.1% respectively at 30 °C for 8 days. Further, this bacterium also found capable for removal of color (75%), BOD (76%), and COD (100%) from the stillage of an alcohol factory.

Satyawali and Balakrishnan (2007) have prepared 19 carbon samples by the acid and thermal activation of various agro based by-products such as bagasse, bagasse fly ash, saw dust, wood ash, and rice husk ash for the color removal from the biomethanated distillery effluent. They found that phosphoric acid carbonized bagasse B (PH) has resulted maximum color removal (50%). In addition, various commercial activated carbons AC (ME) and AC (LB) have resulted 80% color removal from biomethanated DWW. Besides color removal, these activated carbons were also found effective for the reduction in COD, TOC, phenol, and total nitrogen content.

Kaushik and Thakur (2009) have isolated 5 different bacterial strains from a distillery mill site and tested for their COD and color removal efficiency. Out of these 5 bacterial strains, one bacterium (*Bacillus* sp.) was found capable for 21 and 30% color and COD reduction from distillery spent wash. Further, under the optimized parameters such as pH, temperature aeration, carbon, nitrogen, inoculum size, and incubation time by the Taguchi approach, the same bacterium was found effective for 85%, and 90% color, and COD reduction respectively within 12 h of incubation period.

Apollo et al. (2013) achieved maximum colour reduction (88%) from DWW by the combined treatment with anaerobic up-flow fixed bed reactor and annular photocatalytic reactor (as post-treatment technique). They also found that during single (UV photodegradation) treatment process, the colour reduction was 54% and 69% from DWW and MWW, respectively. But, when UV photodegradation apply as pre-treatment to the anaerobic digestion process, it reduced the biogas generation and also COD reduction. Farshi et al. (2013) have reported 97-98% colour reduction from DWW by using electrochemical treatment at different optimized conditions i.e. electrode distance 1 cm, pH 4, current density 2 A/dm^2 for 3 hrs. The removal of melanoidins form stimulated and real wastewaters (biologically treated and untreated) was studied by coagulation/flocculation method by Liakos and Lazaridis (2014). In this study, the authors achieved 90% colour removal at pH 5 by coagulation method with different concentration of ferric ions. However, the real wastewater could be decolorized by 100 mM [$Fe^{3+]}$ while stimulated wastewater by 300 mM [Fe^{3+}]. After the completion of flocculation experiment, the generated ferric hydroxide residue was washed, solubilized and re-used in new cycle. The maximum colour reduction from the real treated, real untreated, and stimulated effluent was 95%, 90%, and 45%, respectively by applying 0.5 A current intensity (Liakos and Lazaridis 2014).

David et al. (2015) have reported that *Pseudomonas aeruginosa*, which produces Polyhydroxybutyrate (PHB) in presence of excess carbohydrate source. PHB is an intercellular polymer, which is utilized by microorganisms as an energy storage molecule when common energy sources are available in limited amount and this bacteria in presence of PHB resulted in resulted 92.77% color removal from DWW. DWW mainly consist of recalcitrant coloring compound (melanoidins), and other organic colorant, which are not easily degraded in biological treatment process. Arimi et al. (2015) achieved significant reduction in colour, dissolve organic carbon, and melanoidins 92.7%, 63.3%, and 48%, respectively at pH 5 and a concentration of 1.6 g/l. In this experiment, the above mentioned physico-chemical parameters were reduced by using six coagulants, out of which, ferric chloride was found to be more effective resulting 92.7% colour reduction. In another study, Arimi et al. (2015) have developed an effective polishing step for the removal of colorants from melanoidin-rich DWW by using natural manganese oxides. In this process, low molecular weight coloring compounds removed first followed by high molecular weight colorant removal with a significant dependence on pH.

Georgiou et al. (2016) have reported the decolorization of DWW by the immobilized laccase enzyme. In this study, authors have immobilized the laccase enzyme covalently on alumina or controlled pore glass-uncoated particles and achieved 71% and 74% decolorization, respectively in 48 h of incubation period. In addition, immobilized laccase on glass achieved 68% degradation of baker's wastewater in 24 h. Chen et al. (2016) achieved 97.1% color reduction from 50% (v/v) DWW by combined micro-electrolysis process with the help of biological treatment method. In this study, fungal biomass and ligninolytic enzyme (LiP, MnP, and laccase) are also played an important role in enhancing the DWW de-colorizing efficiency. El-Dib et al. (2016) achieved 78% and 83% reduction in colour and chemical oxygen demand by using organic-inorganic nanocomposite (chitosan immobilized bentonite with chitosan content). In this study, the used modified chitosan immobilized bentonite (mCIB) and Bentonite (mbent) were prepared by intercalating cetyl trimethylammonium bromide (CTAB) as a cationic surfactant. Further, FTIR, XRD and SEM were used to study the interlayer structure and morphology of prepared samples. Out of all the used sorbents, the modified CIB_3 was found to be more effective in decolorization of distillery wastewater. Santal et al. (2016) isolated *Paracoccus pantotrophus* and found that these bacterial strains were highly effective to decolorize melanoidins up to 81.2 ± 2.43% in presence of carbon (glucose), and nitrogen (NH_4NO_3) source.

Recently Zhang et al. (2017) achieved ~94.0% colour reduction and ~78% reduction of dissolve organic matter from DWW with the treatment by ferric chloride ($FeCl_3$) as coagulant. During treatment process, this coagulant was found to react preferably with melanoidins (major colorant) via either surface complexation or neutralization of electric charge or by both mechanisms. Krzywonos et al. (2017) achieved 38% colour reduction from vinasse by using *Bacillus megaterium* ATCC 14581 and medium component $(NH_4)_2SO_4$, KH_2PO_4, yeast extract, peptone glucose, and vinasse. Out of these factors, four promising factors were chosen as follows: $(NH_4)_2SO_4$, KH_2PO_4, glucose, and vinasse for further optimizing process for color removal. Nure et al. (2017) have reported the significant reduction in colour (64%) and chemical oxygen demand (61%) from melanoidin solution by using activated carbon, which was produced from bagasse fly ash (BFA). In this study, the surface area of used BFA was determined as 160.9 ± 2.8m^2/g with about 90% of particle < 156.8 μm in size. However, BFA was characterized by using Fourier transform infrared spectroscopy (FTIR) and showed the carbonyl (R-C=O) and hydroxyl (OH^-) groups, while X-ray diffraction and scanning electron microscopy analysis showed amorphous nature and heterogeneous and irregular shape of pores, respectively. In addition, microbial fuel cells (MFCs) are also becoming as promising technology, which produce electricity with simultaneous removal of pollutants in terms of COD, color and total dissolved solids etc. from the wastewaters (Feng et al., 2008; Wen et al., 2010; Samsudeen et al., 2015).

5.3. Emerging treatment approaches

5.3.1. Oxidation process

There is a number of oxidation processes, which are being used for the treatment of DWW such as ozone, hydrogen peroxide, Fenton's reagent and ozone combined with hydrogen peroxide (Asaithambi et al., 2015; Arimi et al., 2014; Afify et al., 2009; Dwyer et al., 2008). Ozone treatment alone reduces 76% color, where ozone in presence of low concentration of hydrogen peroxide removes 89% color (Santal et al., 2013; Dwyer et al. 2008). But, bicarbonate ions are reported to have the inhibitory effects on these decolorizing reactions (Coca et al., 2005). The sonication of DWW as a pre-treatment step, converts complex molecules into a more utilizable form by cavitation process and thus, significantly enhances the decolorization of DWW (Sangave and Pandit, 2006).

Vineetha et al. (2013) found that photodegradation of DWW by solar radiation resulted in 79% color reduction under the optimum conditions of H_2O_2, pH, and catalyst. In a recent study, Asaithambi et al. (2015) found that ozone-photo Fenton system was effective to reduce 100% color and chemical oxygen demand (COD) within 4 h.

5.3.2. Membrane treatment

In recent years, membrane processes have been widely used in various applications, especially for the treatment of wastewaters. The use of membrane technologies is accompanied with a high removal efficiency, optimal costs and simple devices handling (Prodanovic and Vasic, 2013).

A two-stage biological treatment followed by membrane modules has been recently developed for the effective treatment of DWW, which have following functions:

a. Biological removal of organic pollutants is carried out in bioreactor by the adapted microbial communities;

b. The membrane module performs the separation of microorganisms from treated wastewater. The membranes constitute a physical barrier for all the suspended solids and therefore, enable not only the recycling of activated sludge to the bioreactor, but also the production of permeate that is free from suspended solids, bacteria, and viruses.

Rai et al. (2008) reported that tertiary treatment of aerobically treated DWW by nano-filtration (NF) technique was carried out in a spiral wound NF membrane module under different conditions and resulted in COD, TDS, and color removal within the range of 96-99.5%, 85-95%, and 98-99.5%, respectively.

The total membrane area was $0.2m^2$ and the system was operated at a fluid velocity of 6.08 m/s, and 0.5 bar transmembrane pressure. Besides the COD reduction, the pre-treatment also improved the efficiency of anaerobic process possibly due to the removal of inhibitory substances. Kumaresan et al. (2003) employed the emulsion liquid membrane (ELM) technique in a batch process for spentwash treatment. In another study, the treatment of vinasse from beet molasses by electrodialysis using a stainless steel cathode, titanium alloy anode and 4% (w/v) NaCl as electrolytic agent resulted in 88% COD reduction at pH 9.5, but it decreased drastically at higher feeding rates (Vlyssides et al., 1997). In addition, reverse osmosis (RO) has been also employed for DWW treatment. In a recent study, Nataraj et al. (2006) reported a pilot trial on distillery spentwash using a hybrid nanofiltration (NF) and RO process. Both, the NF and RO stages employed a thin film composite (TFC) membrane in spiral wound configuration with module dimensions of 2.5 inches diameter and 21 inches length. NF was primarily effective in removing color and colloidal particles accompanied by 80%, 95% and 45% reduction in total dissolved solids (TDS), conductivity and chloride concentration, respectively at an optimum feed pressure of 30-50 bars. The subsequent RO operation at a feed pressure of 50 bar resulted in 99% reduction each in COD, potassium and residual TDS (Prodanovic and Vasic, 2013; Satyawali and Balakrishnan, 2008).

Despite the knowledge of treatment technologies for DWW there is also need to know about the merits and demerits (Table 7).

6. Challenges for the biodegradation and bioremediation of DWW pollutants

The DIs is reported to produce only ~7-9% of alcohol from sugarcane molasses and major portion ~91-93% contribute as wastewater. This huge volume of wastewater requires a long time for treatment due to the non-availability of fast and feasible treatment techniques. Due to very high BOD, COD and TDS values, the Effluent Treatment Plant (ETP) remains to fail to reduce these pollution parameters within the permissible limits set by various environmental protection agencies. DWW contains high melanoidins content, the major coloring compounds, which are highly recalcitrant in nature i.e. resistant to biological/microbial degradation. The management of large amount of sludge generated during the physical, chemical and biological treatment of DWW is also a big challenge for DIs. Further, the lack of advanced and feasible treatment techniques for the effective treatment of DWW within a limited time is a major challenge for sustainable development. In addition, the poor capacity utilization also leads to the higher financial cost and overheads charges. Moreover, the very high expenditure on operation and maintenance of wastewater treatment plants is also not affordable and hence, the Governments should also provide the financial support to industries for sustainable development.

7. Conclusion

This review manuscript concludes that DWW contains a complex mixture of organic and inorganic pollutants and acts as a major source of environmental pollution. DWW causes coloration of water resources, reduces photosynthetic activities, and dissolved oxygen content, whereas, in the soil, it reduces soil fertility and seed germination. The organic and inorganic pollutants such as melanoidins and endocrine disrupting compounds (phthalates) present in DWW are well reported to have cytotoxic, genotoxic, carcinogenic and mutagenic effects on human and animal health. Thus, it requires adequate treatment before its final discharge into the environment. Physico-chemical methods available are capable of both color and organic load reduction, but these methods are highly costly and generate a large amount of sludge as secondary pollutants. Hence, biological methods are gaining its momentum in the arena of wastewater treatment methods due to cost effective and eco-friendly nature, but these methods are time-consuming. Therefore, there is an urgent need to address the limitations in existing treatment methods and to develop the integrated treatment processes that can provide a solution to DIs for the management and treatment of generated wastewater.

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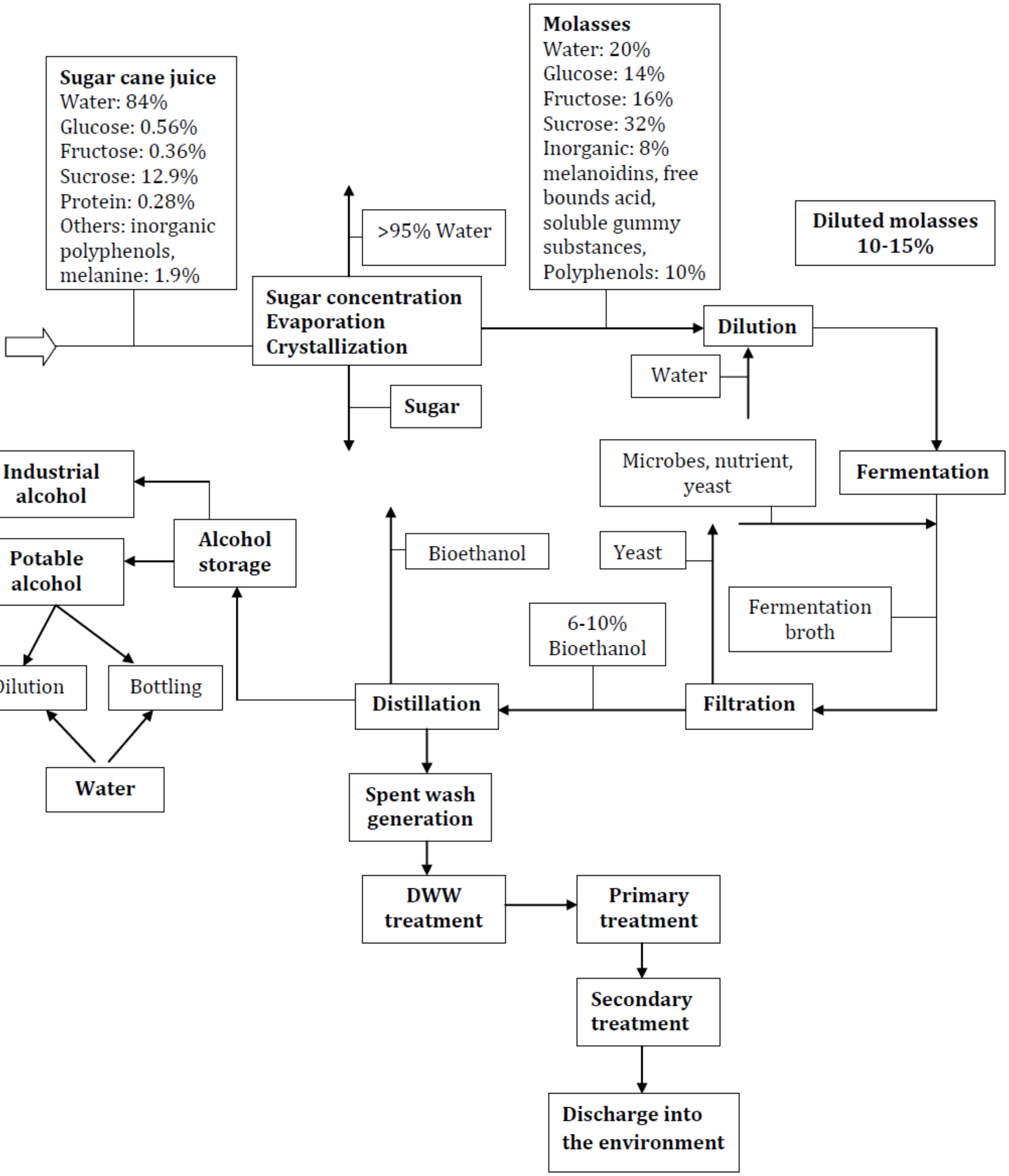

Figure 1: Steps during alcohol production and wastewater generation in distillery industry (Modified from Arimi et al., 2014).

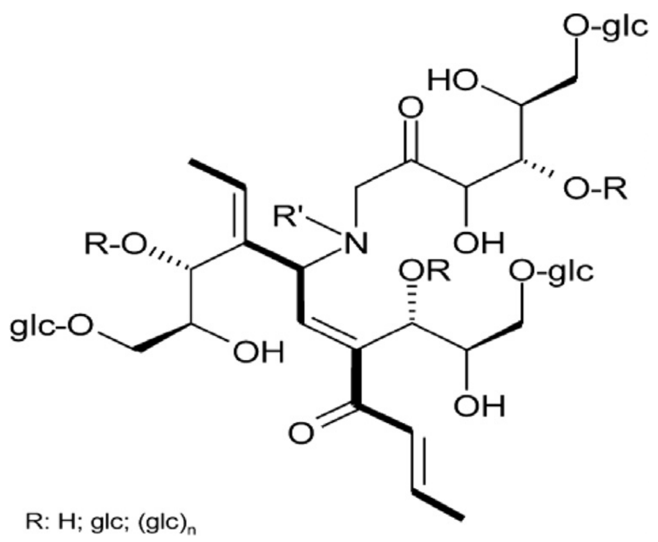

Figure 2: Basic structure of melanoidin (Adapted from Cammerer et al., 2002)

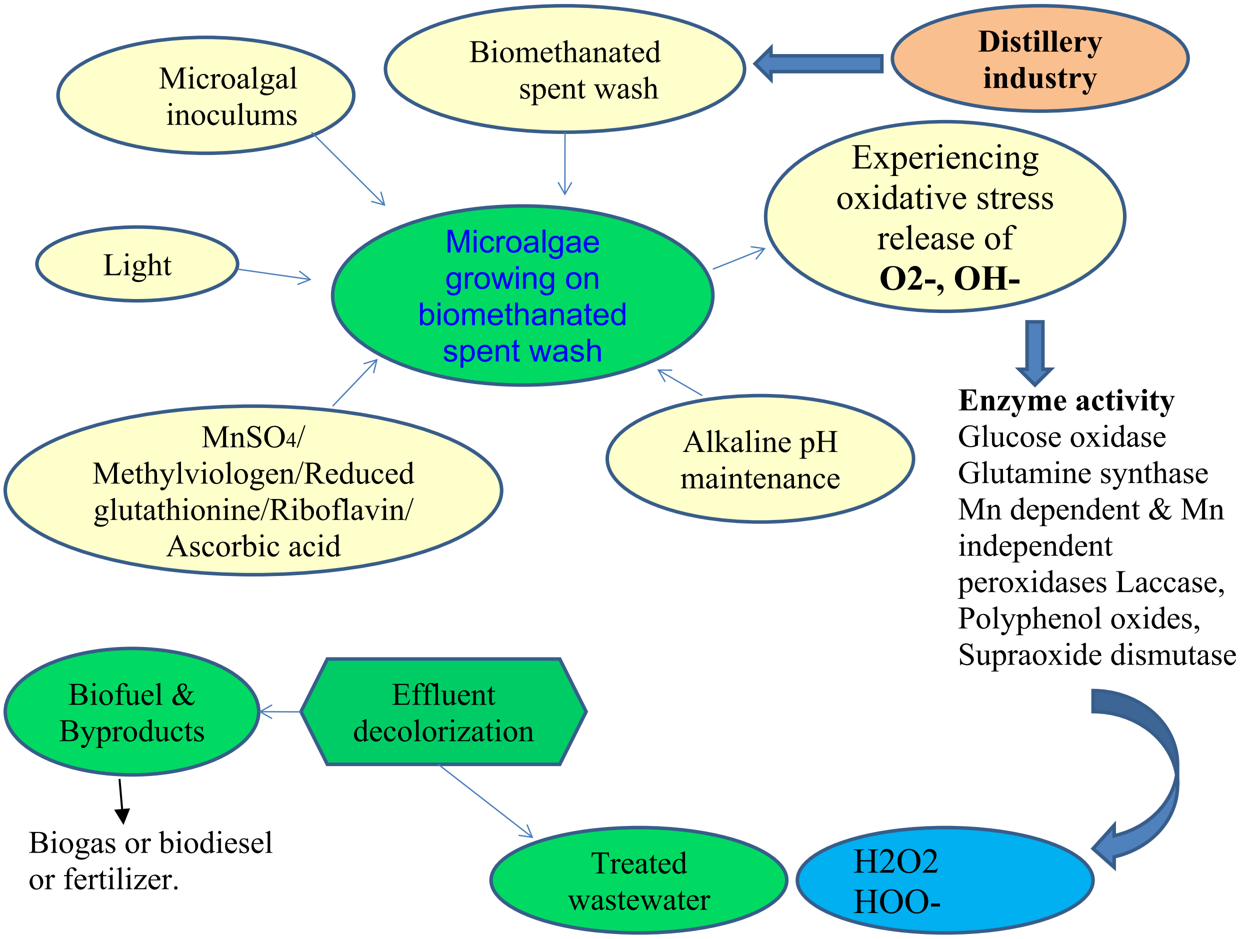

Figure 3: The mechanism of melanoidin containing biomethanated spent wash treatment using microalgae (Modified from Sankaran et al. 2014).

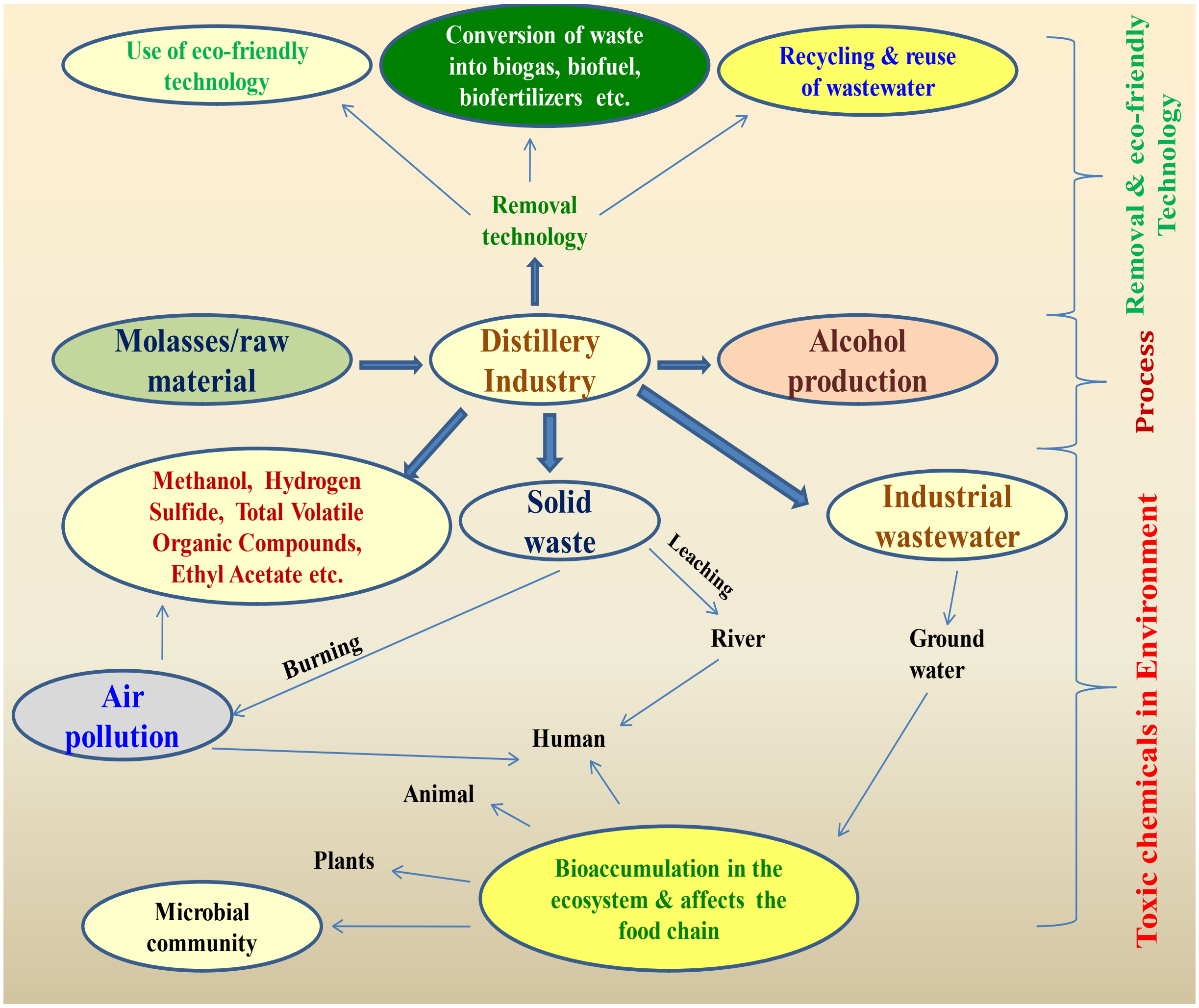

Figure 4: Environmental impact of distillery wastewater and technologies to fight the threat.

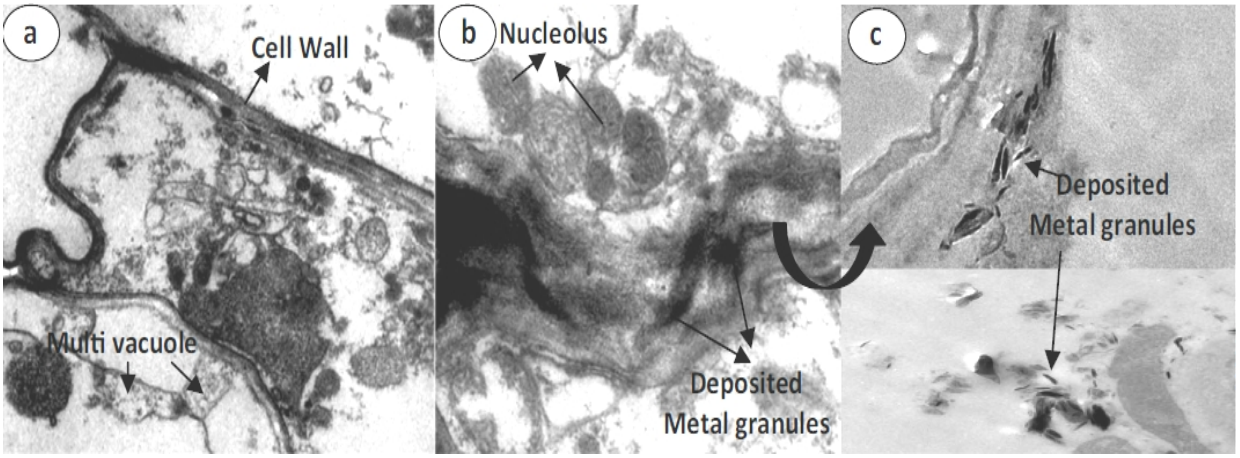

Figure 5: TEM images of native plants root after phytoextraction of heavy metals. a-c Congress grass (*Parthenium hysterophorous*) (Adapted from Chandra and Kumar 2017a).

Legends:

Table 1: Physico-chemical characteristics of various types of distillery wastewater

Table 2: Organic pollutants identified by various researcher in distillery wastewater

Table 3: Organic compounds detected and characterized by using different solvents and GC-MS-MS analysis of distillery wastewater by various authors

Table 4: Various analytical techniques used for the detection and characterization of distillery wastewater pollutants

Table 5: Microorganisms capable for decolorization of distillery wastewater

Table 6: Performance efficiency of various anaerobic reactors for the treatment of distillery wastewater

Table 7: Various treatment approaches/technologies with their merits and demerits used for the treatment of distillery wastewaters

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Tables

Table 1: Physico-chemical characteristics of various types of distillery wastewater

	Wastewater Types					
Parameter	**Distillery wastewater**	**Wine distillery wastewater**	**Vinasse**	**Raw spent wash**	**Lees stillage**	**Molasses wastewater**
BOD$_5$ (g/l)	30	0.21-8.0	42.23	-	20	-
COD$_T$ (mg/l)	100-120	3.1-40		37.5	-	80.5
COD$_S$ (mg/l)	-	7.6-16	97.5	-	-	-
TOC (mg/l)	-	2.5-6.0	36.28	-	-	-
pH	3.0-4.1	3.53-5.4	4.4	4-5	3.8	5.2
EC	346	-	-	2530	-	-
Alkalinity (meq/l)	-	30.8-62.4	-	2	9.86	6000
Phenol (mg/l)	-	29-474	477	-	-	450
VFA (g/l)	1.6	1.01-6	-	-	0.248	8.5
VS (g/l)	50	7.340-25.4	-	-	-	79
VSS (g/l)	2.8	1.2-2.8	-	-	0.086	2.5
TDS mg/l	-	-	51,500	-	-	51,500
TS (g/l)	51.5 – 100	11.4-32	1.5-3.7	2.82	68	109
TSS (g/l)	-	2.4-5.0	-	-	-	-
MS (g/l)	-	6.6	-	-	-	30
MSS (g/l)	-	900	100	-	-	1100
TN (g/l)	-	0.1-64	-	2.02	1.53	1.8
NH4$^+$ (mg/l)	-	140	-	125-400	45.1	-
NO3$^-$ (mg/l)	4900	-	-	-	-	-
TP (g/l)	-	0.24-65.7	-	0.24	4.28	-
PO43$^-$ (mg/l)	-	130-350	-	139	-	-
Iron	0.06	0.05-0.075	-	-	-	0.028

Adapted from (Prajapati and Chaudhari 2015; Arimi et al., 2014; Yadav and Chandra 2012; Melamane et al., 2007; Nataraj et al., 2006; Bustamante et al., 2005; Martin et al., 2002)

Table 2: Organic pollutants identified by various researcher in distillery wastewater

S. No.	Compound Name
1.	3-Amino-2-oxazolidinone
2.	Cyclopropylmethanol acetate
3.	4-Pyridinecarboxlic acid
4.	2-Ethylpyridine
5.	3-(2-Pyridyl)-1-propanol
6.	n-Methyl-2-nitro-3-pyridinamine
7.	3-Ethylpyridine
8.	Nicotinic acid, propyl ester
9.	Isonicotinyl formaldoxime
10.	3-Octadecene
11.	Phthalic acid
12.	DI-N-octyl phthalate
13.	Phthalic acid, butyl-4-octyl ester
14.	Dibutyl phthalate
15.	n-Hexadecanoic acid
16.	1-Eicosanol
17.	13-Tetradecen-1-O-acetate
18.	5,5-Dimethyl hexane
19.	Hexadecamethyl octasiloxane
20.	Benzyl butyl phthalate
21.	1-Hexacosanol
22.	Phthalic acid, dodecyl octyl ester
23.	1,2-Benzenedicarboxylic acid
24.	Phenol
25.	Methylbenzene (toluene)
26.	Butenoic acid
27.	Furfuryl alcohol
28.	2-Hydroxymethylfuran
29..	2-Methoxyphenol (guaiacol)
30.	Methylphenol
31.	Methylbenzaldehyde
32.	Indole
33.	2,6-Dimethoxyphenol (syringol)
34.	1-Hexadecanol
35.	Palmitic acid
36.	Methylindole
37.	2-Ethyl-5-methylfuran
38.	Hydroxypropanone
39.	1,2,3- triethoxy-5-methyl benzene
40.	3,4,5-trimethoxy phenol
41.	2-phenyl ethanol
42.	4,4-dimethyl- 3-(3-oxobutyl)cyclohex-2-enone
43.	2, 2’-bifuran

Adopted from (Fagier et al. 2015; Chandra et al. 2012; Yadav and Chandra, 2012; Bharagava and Chandra, 2010; Wu and Zhou, 2010; Gonzalez et al. 2002)

Table 3: Organic compounds detected and characterized by using different solvents and GC-MS-MS analysis of distillery wastewater by various authors

Solvent system used	Identified Compounds
Acetone	1,3-propanediol 3-oxy- propanoic acid 3-methyl-2-oxy- butanoic acid D-Erythrotetrofuranose Pentanoic acid Butanedioic acid Resorcinol 2,3-Butandiol Malic acid 2-Methyl-1,3-butanediol 2-Furancarboxylic acid 2,3,5-Tri-O- arabino-1,5-lactone Cyclooctene Tricarballylic acid 3-deoxy--2,5,6, tris- O- D-Ribo-hexanoic acid Benzoic acid Tert-butylhydroquinone 3,5-dimethoxy-4-9 benzoate Vanillypropionic acid Benzeneacetic acid
Ethyl Acetate	Ethyl succinate 1,3-Propanediol Diethyl methylsuccinate Lactic acid 2-Furancarboxylic acid Benzenepropanoic acid 4-oxy-Benzoic acid D-Erythro-Hex-2-enoic acid Trimethylsilyl 3,5 dimethoxy-4-benzoate
Isopropanol	Butanedioic acid Butane 2-Methyl-1,3-propanediol
	3-oxy-Propanoic acid 2-methyl-2-oxy-butanoic acid 2-Methylbutanoic acid 2-dedoxy-1,3,4,5-tetrakis- O-erythro-pentitol 2,2,4,5,7,7-hexamethyl-3,6-didoxa 1,2-bis-cyclooctene

Methanol	2,3,5-Tri-O-lactone
	3-deoxy-2,5,6 tris- O-D-Ribo-hexanoic acid
Ethanol	Ethyl-succinate
	Butanedioic acid
	-2,2,4,7,7- pentamethyl-3,6-Dioxa
	Erytritol
	2,3,4,5-Tetrahydroxypentanoic acid-1,4- lactone
	1,2, bis-cyclooctene
	3-deoxy-2,5,6-tris- O-D-ribohexanoic acid
	α-D-Galactopyranose
n-Hexane	Benzene, 1-ethyl-3,5-disopropyl
	Eicosane
	3,4-Dihyroxymandelic acid
	Octadecane,3-ethyl-5(2-ethylbutyl)

Adopted from (Chandra and Kumar, 2017b; Fagier et al. 2015; Yadav and Chandra, 2012)

Table 4: Various analytical techniques used for the detection and characterization of distillery wastewater pollutants

S. No.	Distillery wastewater pollutants	Analytical techniques	References
1.	Organic pollutants	HPLC, GC-MS, Ion-pair RP-HPLC, CEC UV-detection, HPLC differential refractometry detection, HPLC involving derivatization HPAEC coupled electrochemical, and/or DAD, FAB-MS, ESI coupled HPLC and EC, MALDI-TOF, LC-MS, LC-MS with ESI, NBT, ELISA, Ion-pair RP-HPLC, CEC UV-detection, Ion-exchange chromatography, FAB-MS, Colorimetric and fluorimetric methods, FAST, HPLC-DAD, RP-HPLC o-phthalaldehyde precolumn derivatization, RP-HPLC,HPLC-coupled GC-MS, RP-HPLC/LC-ESI-TOF-MS/NMR, HPLC with UV and fluorescence detection, HPLC-DAD, UV, IR spectrometry, MALDI-TOF mass spectrometry.	Chandra and Kumar, 2017b; Wu and Zhou, 2010; Chandra et al., 2008a; Silvan et al., 2006
2.	Inorganic pollutants	AAS, ICP, Ion chromatography, Flame atomic absorption spectroscopy (FAAS)	Hamza et al., 2017; Chandra and Kumar, 2017b; Chandra et al., 2008b

Table 5: Microorganisms capable for decolorization of distillery wastewater

Reported Microorganisms	Comments	Color Removal (%)	Reference
Bacterial species			
Pediococcus acidilactici B-25	Glucose are used as a primary supplementary carbon source	79	Tiwari et al., 2013
Pseudomonas putida	Glucose concentration was critical for decolorization and improved color removal efficiency was obtained by periodic replenishment of glucose	24	Ghosh et al., 2009
Pseudomonas putida	Glucose used as a carbon source, for the production of H_2O_2, which reduced the colour	60	Ghosh et al., 2002
Pseudomonas Fluorescens	The organism performed decolorization with cellulose carrier coated with collagen. Reuse of decolorized cells reduced the decolorization efficiency	94	Dahiya et al., 2001a
Pseudomonas Aeruginosa	The three strains were part of a consortium which decolorized the anaerobically digested spent wash in presence of basal salts and glucose	67	Mohana et al., 2007
Pseudomonas sturzeri	The organism required sugar especially, glucose for decolorization of distillery wastewater	≤ 60.00	Ramachandra, 1993
Pseudomonas sp.	The organism used glucose and fructose as carbon source for decolorization	56.00	Chavan et al., 2006
Bacillus thuringiensis	1% glucose are used as a supplementary carbon source	22	Kumar and Chandra, 2006
Xanthomonas fragariae	The organism used glucose as carbon source and NH_4Cl as nitrogen source.	76	Jain et al., 2002
Acinetobacter sp.	All these organisms were isolated from an air bubble column reactor treating winery wastewater after 6 months of operation. Most isolates from the colonized carriers belonged to species of the genus Bacillus	-	Petruccioli et al., 2000
Acetobacter acetii	The organism required sugar especially, glucose and fructose for decolorization of MWWs	76.4	Sirianuntapiboon et al.,2004
P. aeruginosa	Glucose used as carbon source	67.00	Sarayu et al., 2005
P. aeruginosa	Glucose are used as a supplementary carbon source	69	Pal and Vimala,

			2012
Fungal species			
Penicillium sp.	All fungi produced decolorization from first day of incubation, with maximum being shown by P. decumbent at fourth day with a reduction of 70% of the phenolic content of the wastewater	30	Jimnez et al., 2003
Aspergillus niger UM2	Decolorization was more by immobilized fungus and it was able to decolorize up to 50% of initial effluent concentrations	80	Patil et al., 2003
Flavodon flavus	MSW was decolorized using a marine basidiomycete fungus. It also removed 68% benzo(a) pyrene, a PAH found in MSW	80	Raghukumar and Rivonkar, 2001; Raghukumar et al., 2004
P. chrysosporium	Phenolic concentration and color were decreases under two different growth conditions	56.8 1	Potentini and Rodriguez 2006
Phanerochaete chrysosporium JAG-40	This organism decolorized synthetic and natural melanoidins when the medium was supplemented with glucose and peptone	80	Dahiya et al., 2001
Aspergillus niveus	The fungus could use sugarcane bagasse as carbon source and required other nutrients for decolorization	56	Angayarkanni et al., 2003
Williopsis saturnus strain CBS 5761	Yeast isolates from a rotating biological contactor (RBC) treating winery wastewater. Only 43% COD removal could be achieved		Malandra et al., 2003
Coriolus versicolor sp no. 20	10% diluted spent wash was used with glucose @ 2% added as carbon source	34.5	Chopra et al., 2004
Phanerochaete Chrysosporium	Sugar refinery effluent was treated in a RBC using polyurethane foam and scouring web as support	55	Guimaraes et al. 2005

Marine Basidiomycete NIOCC # 2a	Experiment was carried out at 10% diluted spent wash	100	D'souza et al., 2006
Citeromyces sp. WR-43-6	Organism required glucose, Sodium nitrate and KH_2PO_4 for maximal decolorization	68.91	Sirianuntapiboon et al., 2003
Pleurotus florida	Various fungi grown under solid-state fermentation using agro-residue	86.3	Pant and Adholeya, 2009
Yeast			
Candida tropicalis RG-9		75	Tiwari et al., 2012
Citeromyces sp.	The organism required sugar especially, glucose and fructose for decolorization	75.00	Sirianuntapiboon et al., 2004
Cyanobacteria			
Oscillotoria boryana	The organism required sugar especially, glucose and fructose for decolorization	60.00	Kalavathi et al., 2001

Table 6: Performance efficiency of various anaerobic reactors for the treatment of distillery wastewater

Reactors	COD Reduction (%)	BOD removal (%)	Retention time (days)	Reference
Upflow anaerobic fixed film bioreactor	64%		8	Acharya et al., 2008
Upflow Anaerobic Sludge Blanket (UASB)	90-95%	-	-	Moletta, 2005
Anaerobic granular sludge reactor	80-90	-	1	Collins et al., 2005
Thermophilic UASB reactor	87	-	0.3	Syutsubo et al., 1997
Downflow fluidized bed reactor with ground perlite	85	-	3.3-1.3	Garcia-Calderon et al., 1998
Upflow anaerobic sludge blanket (UASB) reactor	39-67	80	-	Harada et al., 1996
UASB	75	-	-	Sanchez Riera et al., 1985
UASB	90	-	-	Wolmarans and de Villiers, 2002
UASB	93	-	20-39h	Wolmarans and de Villiers, 2002
Granular bed anaerobic baffled reactor (GRABBR)	82-90	90	-	Akunna and Clark, 2000
Anaerobic filter and UASB	90	-	1.3d	Blonskaja et al. 2003
Anaerobic contact filter	73-98	-	4	Vijayaraghavan and Ramanujam, 2000
Diphasic (Upflow) fixed film reactor (granular activated carbon support)	67.1		4	Goyal et al., 1996

Table 7: Various treatment approaches/technologies with their merits and demerits used for the treatment of distillery wastewaters

Treatment Technology	Advantages	Disadvantages
Physico-chemical Treatment		
Adsorption	Simultaneous adsorption and degradation of many pollutants	Temperature and pH sensitive High cost of commercial adsorbents is their main drawback for application
Coagulation/ Flocculation	Simple, and cost-effective Widely accepted Separates many kinds of particles from wastewater Enhances filtration process Uses abundant and low cost chemicals	pH sensitive As^{+3} and As^{+5} must be fully oxidized High energy lost Excess use of chemicals Large amount of sludge generated
Oxidation process	Broad range of organic compounds are oxidized The method has advantages over AOP since it can be used in either the pretreatment step or in the final treatment step	Ozone can selectively attack the double bonds (e.g. C=C, N=C) and functional groups (e.g. $-OCH_3$, -OH, and $-CH_3$) in acid or neutral conditions with limited concentrations, High cost
Membrane treatment	Significant color removal Removal of multiple contaminants	Membrane fouling, clogging, scaling and cleaning Poor production efficiency, Requires pretreatment
Evaporation and Combustion	Due to potassium rich ash it can be used for land application	Poor efficiency
Biological Treatment		
Aerobic treatment/ Anaerobic treatment Reactors	Eco-friendly and cost effective	Requires high dilution Slow process
Bacterial treatment		Time consuming
Fungal treatment		It acquires large space for treatment
Treatment by other microorganisms		

Microalgae	No need to add nutrients	Light dependent process
	Yield biogas or biodiesel or fertilizer are by-product	
Cyanobacteria	Energy obtain from photosynthesis	Slow growth rate
Yeast	Produced ethanol for biofuel industry	Slow growth rate
Enzymatic treatment		
Laccases	Enzyme are naturally produced by microorganism which is ecofriendly	Slow process and thus, cannot be applicable at large scale application
Peroxidases		
Oxidoreductases	Reusable in nature	
Cellulolytic enzymes	Enzymatic biotransformation of industrial pollutants	
Cyanidase		
Proteases		
Amylases		