CHAPTER

2

Distillery Industry

2.1 INTRODUCTION

The distillery industry uses sugarcane molasses, cereals, and other agro products for producing alcoholic beverages. The production of fermented and distilled drinks throughout the world is based on materials that can be grown locally and is best suited to prevailing climatic conditions. In the distillery, ethyl alcohol is manufactured by fermenting molasses. Molasses come from sugar manufacturing units, which are either based on sugarcane or beet sugar. The molasses is fermented by yeast after suitable dilution. The unwanted bottom product of distillation is called stillage or spent wash or alcohol distillery waste. Distillery waste in the form of 'spent wash' or 'stillage' is one of the most complex, troublesome and strongest industrial organic effluents. The polluting strength is very high due to the high content of biodegradable organic materials, such as sugar, lignins, hemicelluloses, dextrins, resins and organic acids.

The distillery effluent contains melanoidin—a dark brown pigment. The empirical formula of melanoidin is $C_{17-18}H_{26-27}O_{10}N$. It is a product of non-enzymatic reaction between sugars and amino compounds. The molecular weight distribution is between 5000 and 40000. It is acidic, polymeric and composed of highly dispersed colloids, which are negatively charged due to the dissociation of carboxylic acids and phenolic groups. The dark brown colour and COD are the major pollutants in the distillery effluent, and are not reduced by conventional treatment processes.

Physicochemical treatment methods have not been found satisfactory. The biological aerobic and anaerobic treatment methods have been found to be effective up to a certain extent, and huge anaerobic lagoons, aeration tanks and solar drying pits are installed to solve the problem of pollution in cane molasses distilleries. Since biological methods are unable to degrade the colouring compounds, in many traditional processes and alternative methods are being used and new treatment processes are being developed for effluent treatment. Complete

In 1932, a large number of sugar factories were established in the country, particularly in Maharashtra and Uttar Pradesh where good irrigation facilities existed for the cultivation of sugarcane. India has emerged during recent years as the largest sugarcane producer in the world. This has resulted in the accumulation of molasses, which is evident from the twofold increase in the number of alcohol industries in India during the last decade. Distilleries in India are concentrated in the states of Maharashtra, U.P., Andhra Pradesh, Madhya Pradesh, Tamil Nadu and Karnataka. There are 285 distilleries in India, producing 2.7 billion litres of alcohol and generating 40 billion litres of wastewater annually. The proportion of wastewater, generally known as spent wash, is nearly 15 times the total alcohol production. This massive quantity, approximately 40 billion litres, of effluent is disposed untreated, causing considerable stress on water-bodies and leads to widespread damage to aquatic life. According to a recent estimate, the alcohol production in India has reached the 2.7 million litre mark

The distillery industry today broadly consists of two parts, potable liquor and industrial alcohol. The potable distillery, producing country liquor has a steady but limited demand with a growth rate of about 8 percent per annum. The industrial alcohol industry, on the other hand, is showing a declining trend because of the high price of molasses which is invariably used as a substrate for producing alcohol. The alcohol produced is now being utilised in the ratio of approximately 52 percent for potable liquor and the balance 48 percent for industrial use. Over the years, the potable liquor industry has shown remarkable results in the production of quality spirits. The most important of these is alcohol, which bears immense significance as a basic chemical for the rapidly advancing chemical industry and as a readily available source of energy. Therefore, in the present scenario as well as in the future, the demand for alcohol will increase in the country and so also will the number of distilleries producing alcohol.

2.3 PROCESSES AND PRODUCTION IN DISTILLERY INDUSTRY

Distilleries use different kinds of raw material such as sugarcane juice, sugarcane molasses, sugar beet molasses and wine or corn for the production of alcohol. The cycle of raw materials starts from farms, through product formation and fermentation to the distillery for the production of alcoholic beverages and finally spent wash. The sugar manufacturing process broadly involves the extraction, clarification and concentration of sugarcane juice. The concentrated juice is finally, crystallized and dried. The manufacturing process produces molasses, bagasse and press mud as waste. The manufacturing process in a distillery involves the dilution of molasses with water, followed by fermentation. The product is then distilled to obtain rectified spirit or neutral alcohol. The distilling process begins with noble raw materials, grains, which are initially ground in order to make a mash, and it is at this point that the starch is converted into sugar. The fermentation process then follows.

2.3.1 The Grinding

The process in the mill is completed based on height that helps in delivering the raw materials from one stage to another stage. The mill is located on two floors, one above the other. The grains, delivered in bags, are lifted through a trapdoor to the upper floor and emptied into a rotating brushing machine in order to separate the grains from the chaff. The grains are then pulverised by the hammer mill and the resulting flour is blown into 3 hoppers with a capacity of 1.200 kg each. Ingredients for the malt wine are rye, malt (barley) and maize, for the grain alcohol, wheat and malt.

2.3.2 The Saccharification of the Starch

The flour is mixed with water in the mash tun. The mash is brought to a boiling point by direct addition of steam, after which the mash is cooled down to approximately 69°C. Through the addition of malt-germinated barley, the saccharification process is induced and it continues for about 1 hour at a temperature of 61°C. The mash is then cooled down to 30°C and pumped into fermentation tanks.

2.3.3 The Fermentation Process

The fermentation room has four tanks. The cooled mash, after being pumped into the tanks, is mixed with water to reduce the sugar concentration. Without the dilution of the mash with water, the yeast would perish due to high alcohol concentration, hence resulting in an incomplete conversion of the sugar into alcohol. Baker's yeast added to this mixture, results not only in the transformation of sugar into alcohol and carbon dioxide, but also in the production of other aromatic components. Fermentation lasts for about 72 hours.

2.3.4 The Distillation Process

The fermented mash is pumped into a condenser, where it is pre-heated before reaching the top of the distillation columns. Each of the two copper distillation columns is about 6 metres high and contains as much as 15 plateaus, which provide for an equal distribution of the mash and the steam injected below. The heating of the fermented mash causes the alcohol to evaporate (boiling point 79°C). The rising steam, used to pre-heat the mash, takes with it the volatile components, which are cooled down in the first condenser. The second cooled water condenser cools them to room temperature. The residue or draft flows from the bottom of the columns into tanks. These residues are natural and nutritious waste products that are used as fodder for cattle. The phlegm (first distillation) contains about 57% volume of alcohol and flows into a measurement tank located in a sealed area. Only excise clerks are allowed to unseal this area, which they do in order to determine the exact quantity of alcohol produced. The phlegm is then pumped into storage tanks, for further processing. A second distillation process results in the conversion of the phlegm into malt wine or grain alcohol. The process is completed through a discontinuous process in a still pot or through a continuous process in a rectification column. The production process for these two products is the same upto the measurement tank located in the sealed area. Only the grain recipes are different. The fermented solution contains about 6–12% ethyl alcohol, which is recovered by distillation.

In case of molasses, the consumption of molasses depends upon per KL (kilolitre) of alcohol produced which varies from 4.53MT to 6.28 MT (million tons). The water consumption shows a very wide variation from 14.69 KL to 512.88 KL per KL of alcohol. Since the quality of molasses used varies, the production of alcohol is also checked on the basis of the quantity of Total Reducing Sugar (TRS) whose Fermentable Part (FS) ultimately gets converted into alcohol and, therefore, is a better criterion for judging the efficiency. The distilleries generate highly polluted effluent in the form of spent wash during the process of alcohol production, and this is the main concern from the environmental angle in this industry. The spent wash generated per KL of alcohol varies from 10.87 KL to 38.34 KL, against the prescribed norm of 12 KL/KL of alcohol. In India, 285 distilleries generate 40 billion litres effluent in a year. The distillery wastewater has the potential to produce 1100 million cubic metres of biogas. The wastewater can be used for the irrigation of agricultural crops and can produce more than 80,000 tonnes of biomass, annually. The requirement of alcohol in the country for all purposes however, stands at about 1200 to 1300 million litres in a year, which works out to about 40 percent the licensed capacity. The bulk of the capacity thus remains dormant and can be utilised for the production of anhydrous alcohol for being used as oxygenate/fuel. The utilisation of ethanol as oxygenate is the prime need of the country because, the enormous increase in the number of motor vehicles has been a major cause of air pollution, particularly in metropolises and big cities. As air pollution is posing a serious threat to the health of community, it is absolutely necessary to devise ways and means of curbing pollution. The cheapest and best way to solve this objective is to utilise ethanol as oxygenates in admixture with petrol/diesel.

The source of other wastes is from floor washings, recovery units of yeast and other by-products. The distillation process results in the generation of a strong organic effluent. Alcohol is a member of a class of organic compounds containing carbon, hydrogen and oxygen, considered hydroxyl derivatives of hydrocarbons, produced by the replacement of one or more hydrogen atoms by one or more hydroxyl (-OH) groups. There is a potential to utilize the hydrocarbon for food, feed and fuel and other commercial and daily-use products. The use of different materials and processes results in a wide variety of effluents.

2.4 CHARACTERISTICS OF WASTE AND EFFLUENT

The distillery wastewater known as spent wash is characterised by its colour, high temperature, low pH, high ash content and high percentage of dissolved organic and inorganic matter, of which 50% may be present as reducing sugars. The spent wash is produced as a result of the fermentation and distillation of molasses. It is acidic in nature, having very high BOD (40,000-50,000 mg/l) and COD (10,000-125,000 mg/l). The dry spent wash contains water (90-93%), solids (7-10%), sugar (2-20%) and proteins (10-11%). The metals present in spent wash are Fe (348 mg/ltr), Mn (12.7 mg/ltr), Zn (4.61 mg/ltr), Cu (3.65 mg/ltr), Cr (0.64 mg/ltr), Cd (0.48 mg/ltr) and Co (0.08 mg/ltr), with electrical conductivity in the range of 15-23 dS m^{-1}. The colour of spent wash may be due to molasses used for fermentation, anthocyanins and tannins and most importantly, caramels, melanoidins and decomposition products such as hydroxyl methyl furfural. Organic compounds extracted from spent wash using alkaline reagents are humic in nature and similar to those found in the soil, except that fulvic acid predominates over humic acid.

The formation of coloured compounds in sugarcane processing is mainly due to sugar degradation reactions. Monosaccharides, mainly glucose and fructose are important compounds in colour formation reactions. Heating monosaccharides under acidic or basic conditions leads to degradation reactions, forming highly reactive intermediates, which can undergo further condensation and polymerisation reactions to form coloured polymers. The colourants formed from sucrose can be divided into enzymatic colourants, such as melanins, and non-enzymatic colourants, such as melanoidins, alkaline degradation products of hexoses (HADPs) and caramels.

2.4.1 Melanoidins

The amino compounds present in juices do not lead to any colour formation reaction, but in the presence of monosaccharides and other carbonyl compounds formed from them, the Maillard reaction takes place and browning products appear. The formation of melanoidins is the result of polymerisation reactions of highly reactive intermediates formed during the Maillard reaction. A wide range of reactions takes place, including cyclisations, dehydrations, retroaldolisations, rearrangements, isomerisations and further condensation, which lead to the formation of brown nitrogenous polymers and co-polymers, known as melanoidins. The molecular weight of the coloured compounds increases as browning proceeds.

2.4.2 Alkaline Degradation Products of Hexoses

The hexose alkaline degradation products, together with the melonidins are responsible for upto 80% of colour in sugar beet juices. Monosaccharides in aqueous alkaline solutions undergo both reversible and irreversible transformations. The reversible reactions, ionisation, mutarotation, enolisation and isomerisation, result in the formation of the enediol anions which are generally considered common intermediates in isomerisation reactions of monosaccharides. Enediol species are considered to be intermediates in the isomerisation of monosaccharides, as well as starting intermediates in the alkaline degradation reactions.

2.4.3 Caramels

Caramels are thermal degradation products of sugars. They are colloidal compounds with a tendency to remain preferentially on the crystal surface, thus affecting the quality of white sugar. Heating concentrated sucrose syrups at temperatures above 210°C forms caramels. The generation of colour in caramelisation requires that sugars, normally monosaccharide structures, should first undergo intramolecular rearrangements. Depending on the time and temperature, yellow or brown solutions are obtained. In the sugar degradation reactions, osuloses are formed, which are considered to be intermediates of caramelisation. Osuloses lead to the formation of typical components of caramel colour and caramel flavour. The osuloses are involved in the formation of three typical *O*-heterocyclic compounds: hydroxymethylfurfural (HMF), hydroxydimethylfuranone (HDF) and hydroxyacetylfuran (HAF) from D-glucose. During thermally induced caramelisation, transglycosidation and the formation of oligomers by polymerisation are important.

2.4.4 Distiller Grains and Slop

After settling and decanting of the liquid, the unfermented grain particles left behind are known as wet distiller's grains. The decanted liquid is known as "thin slop" or wet distiller's solubles. Distilleries produce huge amounts of slop as part of the alcohol production process. The raw slops are high in BOD and usually very dark in colour. This makes treatment necessary, before the wastes can be disposed of in the environment. Unfortunately, this is often not done effectively and there has been widespread public outcry at the pollution that has resulted. Researchers have investigated a range of treatment options for the sugarcane slops to find out which would best balance the needs of the distilleries, farmers and the environment. Their goal was to find a treatment option that would have minimal costs for the distillery, produce maximum increase in crop yields for farmers and have as little pollution impact on the environment as possible. The technologies for the treatment of distillery effluent have been adopted, depending upon the availability of land, filler material for compost and mode of disposal.

Despite stringent standards imposed on effluent quality, the untreated or partially treated effluents very often find access to water-bodies. The spreading of maize. The study revealed that the application of distillery effluents resulted in increased leaf area, chlorophyll content, nitrate reductase activity, total dry weight and grain yield.

Distilleries producing huge quantities of foul smelling wastes (effluents) are recognised as one of the most potential agro-based industries in India. However, these distillery effluents contain organic and inorganic nutrients and have been reported to have a beneficial effect on crop yields. A field experiment with groundnut as test crop was conducted to evaluate the manurial potential of three distillery effluents: raw spent wash (RSW), biomethanated spent wash (BSW) and lagoon sludge (LS) vis-à-vis recommended fertilizers (NPK + Farm Yard Manure (FYM)) and a control (no fertilizer or distillery effluent). It was found that all the three distillery effluents increased total chlorophyll content, Crop Growth Rate (CGR), total dry matter, nutrient uptake (N, P and K) and finally seed yield, as compared to the controlled but inhibited nodulation and decreased nitrogen fixation. However, the distillery effluents did not influence protein and oil contents. It was concluded that these distillery effluents, because of their high manurial potential, could supply nutrients, particularly potassium, nitrogen and sulphur, to the crops and thus reduce the fertilizer requirement of crops. Nevertheless, the crop performance and yield with three distillery effluents was overall less than that produced by recommended fertilisers, NPK + FYM, probably on account of the failure of the effluents to supply balanced nutrition to the plants for achieving their potential growth capacity.

The physico-chemical characteristics of spent wash and the possibilities of treating distillery effluent by anaerobic method have been studied. The chemical composition of distillery spent wash is a very important deciding factor for the growth of specific microorganisms which can be applied for the treatment of effluent. Biokinetic coefficient for a two-stage anaerobic digester has been carried out on a bench-scale model, for the treatment of distillery effluent. The post-methanation effluent, has considerable organic load, making its disposal a great problem. Crops show good response to distillery effluent if it is used after proper dilution.

2.6 TREATMENT OF DISTILLERY INDUSTRY EFFLUENT

Most of the distilleries are facing the environmental issue of treatment and disposal of distillery-spent wash. Many technologies have been tried for the treatment of spent wash, however, none of these methods have been found effective and economically viable to achieve the standard norms set by the Central Pollution Control Board, Government of India.

2.6.1 Primary Treatment

Primary treatment methods selectively remove materials which could interfere with the physical operation and subsequent treatment processes. The processes are based on the exploitation of the physical properties of the contaminants and are generally used at the initial stage of effluent treatment. It helps in improving the treatment efficiencies by reduction of surface area. Screening, flow equalization, comminution, mixing, flotation, flocculation and sedimentation are methods used during the initial stages of effluent treatment.

Chemicals are also used in conjugation with physical treatment in which sedimentation is performed by the addition of coagulant and other additives, such as alum, lime, ferric chloride, activated charcoal etc. Different chemical treatment methods were investigated, based on the chemical properties of the pollutants, and as a result, chemical treatment with Fe(III) and anionic polymer and then with H_2O_2 +Fenton reagent which were selected as the best options because of their performance and economics.

Strong oxidants like ozone and hydrogen peroxide were used. Though they result in decolourisation, they are not accepted at present because of economic reasons. Inorganic flocculants, such as iron sulphate, iron chloride and aluminium sulphate aid the separation of colouring matter. Oxidation by ozone, combined with hydrogen peroxide, is found to be very effective in the degradation of some aromatics present in wastewater, and in the removal of colour. However, due to the generation of sludge, accumulation of metals, cost and related contaminants, chemical methods are not successful.

2.6.2 Secondary Treatment

In secondary treatment which is also known as biological treatment, soluble and colloidal forms of organic matter are removed. Both aerobic and anaerobic microorganisms are used in secondary treatment. Anaerobic digestion is the most suitable option for the treatment of high strength organic effluents. The presence of biodegradable components in the effluents, coupled with the advantages of anaerobic process over other treatment methods makes it an attractive option. In addition, a modification in the existing reactor designs has been suggested for improving the efficiency of digestion.

Anaerobic and aerobic treatment systems can remove most of the biologically removable organics, CODs and colour. Biologically treated distillery wastewater is non-biodegradable. Anaerobic treatment of effluents from different alcohol-producing industries over a long period, is performed. Since most of COD and colour in biologically treated distillery wastewater is non-biodegradable, identification and optimisation of biotechnological treatment methods is a necessity of the present times.

Aerobic treatment: The wastewaters of molasses-based alcohol distilleries contain brown coloured melanoidin pigments that are one of the major pollutants. Melanoidins have antioxidant properties and are toxic to many microorganisms in wastewater treatment. Many researchers have tried to isolate microorganisms, which have the ability to remove pollutants and decolourise melanoidins from distillery effluent. A wide variety of microorganisms have been implicated in decolourisation. It has been reported that fungi *Coriolus* sp. No. 20, *Aspergillus fumigatus* G-2-6, *Aspergillus oryzae* Y-2-32 and *Rhizoctonia* sp. D-90, and bacteria, including *Lactobacillus hilgardi* showed melanoidin-decolourising activity. The potential of these microorganisms to remove melanoidin from molasses wastewater (MWW) is clear, but their actual use in genetic stability and maintenance of colour removal activity is not clear. *Rhizoctonia* sp. D-90 was applied for treating the MWW in a fed-batch system, but the maintenance of the mycelium for a long period was difficult due to bacteria contamination. *Phanerochaete chrysosporium* ATCC 24728 used for decolourisation indicated reduction in colour after 8-10 days. Rotating biological contractor for decolourisation using *Trametes versicolour* removed colour (82%) and COD (77%) has been demonstrated. *Coriolus hirsultus* pellets grown in a melanoidins containing medium produced extracellular H_2O_2 upto 43mM, indicated the possible role of enzymes in decolourisation. The culture fluid contained two extracellular peroxidases which helped in decolourisation. *Geotrihcum candidum* decolourised molasses after 12 days. Decolourisation of intensely brown coloured molasses spent wash (MSW) by *Flavodon flavus*, a white rot basidiomycete fungus isolated from a marine habitat, has been reported. *Bacillus smithi* decolourises 33.5% molasses pigments. *Bacillus cereus*, *Bacillus subtilis* and *Aeromonas* sp. have been reported for decolourisation of industrial effluent of distillery. Most of the studies reported so far indicate an efficient removal of colour from post-methanation tanks of the distillery effluent.

Decolourisation by microorganisms is strongly influenced by culture conditions. The major culture parameters affecting decolourisation are growth substrate, nitrogen availability, oxygen concentration and mode of cultivation of biomass. The efficiency of colour removal has not been proved successful without proper optimization of culture parameters. The process of decolourisation of MSW is improved by this fungus by immobilisation. Polyurethane foam-immobilised-fungus decolourised 10% diluted MSW by 60% and 73% by days 5 and 7, respectively. Besides decolourisation, the fungus also removed the toxicity of MSW. Toxicity bioassay of the fungus-treated molasses spent wash, using an estuarine fish *Oreochromis mossambicus* showed no liver damage, in contrast to untreated effluent, which showed moderate liver damage. There is report of benzo(a)pyrene, a polycyclic aromatic hydrocarbon (PAH) in the MSW and this appears to be one of the causes of toxicity of the MSW. The concentration of PAH in the MSW decreased by 68% by day 5, on treatment with the fungus. A possible mechanism of decolourisation of MSW is via the action of glucose oxidase accompanied by the production of hydrogen peroxide that may ultimately act as a bleaching agent.

Decolourising activity was seen in low-nitrogen medium, nutrient-rich medium and sugarcane bagasse medium. The percentage decolourisation of MSW particulate carrier materials, e.g. fluidised bed reactors and anaerobic expanded bed reactors; and entrapment of sludge aggregates between packing material supplied to the reactor, e.g. down flow anaerobic filter and upflow anaerobic filter.

Fixed film reactors: In stationary fixed film reactors, the reactor has a biofilm support structure (media) such as activated carbon, PVC (Polyvinyl Chloride) supports, hard rock particles or ceramic rings for biomass immobilisation. The wastewater is distributed from above/below the media. Fixed film reactors offer the advantages of simplicity of construction, elimination of mechanical mixing, better stability at higher loading rates, and capability to withstand large toxic and organic shock loads. The reactors can recover very quickly after a period of starvation. The main limitation of this design is that the reactor volume is relatively high as compared to other high rate processes, due to the volume occupied by the media. Another constraint is clogging of the reactor, due to a increase in biofilm thickness and/or concentration high suspended solids in the wastewater.

Upflow Anaerobic Sludge Blanket Reactor (UASB): UASB technology is being used extensively for effluents from different sources, such as distilleries, food processing units, tanneries and municipal wastewater. The active biomass in the form of sludge granules is retained in the reactor by direct settling for achieving high MCRT, thereby achieving highly cost-effective designs. A major advantage is that this technology requires less investment, as compared to an anaerobic filter or a fluidised bed system. Among notable disadvantages, it has a long start-up period, along with the requirement for a sufficient amount of granular seed sludge for faster start-up. Moreover, significant wash-out of sludge is likely during the initial phase of the process, and the reactor needs skilled operation.

A UASB reactor essentially consists of gas–solids separator (to retain the anaerobic sludge within the reactor), an influent distribution system and effluent draw-off facilities. Effluent recycling (to fluidise the sludge bed) is not necessary as sufficient contact between the wastewater and sludge is guaranteed, even at low organic loads with the influent distribution system. Also, significantly higher loading rates can be accommodated in granular sludge UASB reactors, as compared to flocculent sludge bed reactors. In the latter, the presence of poorly degraded or non-biodegradable suspended matter in the wastewater results in an irreversible sharp drop in the specific methanogenic activity because the dispersed solids are trapped in the sludge. Despite expected toxicity problems arising from the high concentrations of COD, sulphide and salts, anaerobic treatment with the UASB (upflow anaerobic sludge blanket) process has proved to be successful in treating distillery effluent up to a limited extent.

Anaerobic fluidized bed reactor: In the anaerobic fluidised bed, the media for bacterial attachment and growth is kept in the fluidised state by drag forces exerted by the upflowing wastewater. The media used are small particle sized sand, activated carbon, etc. Under fluidised state, each media provides a large surface area for biofilm formation and growth. It enables the attainment of high reactor biomass hold-up and promotes system efficiency and stability. This provides an opportunity for higher organic loading rates and greater resistance to inhibitors. Fluidised bed technology is more effective than anaerobic filter technology as it favours the transport of microbial cells from the bulk to the surface and thus, enhances the contact between the microorganisms and the substrate. These reactors have several advantages over anaerobic filters, such as elimination of bed clogging, a low hydraulic head loss combined with better hydraulic circulation and a greater surface area per unit of reactor volume. Finally, the capital cost is lower due to reduced reactor volumes. However, the recycling of effluents may be necessary to achieve bed expansion, as in the case of expanded bed reactors. In the expanded bed design, microorganisms are attached to an inert support medium such as sand, gravel or plastics, as in fluidised bed reactors. However, the diameter of the particles is slightly bigger as compared to that used in fluidised beds. The principle used for the expansion is similar to that for the fluidised bed, i.e. by a high upflow velocity and recycling.

The anaerobic digestion process is affected significantly by the operating conditions. As the process involves the formation of volatile acids, it is important that the rate of reaction be such that there is no accumulation of acids, which would result in the failure of the digester. This, in turn, is governed by the loading rate and the influent strength. Temperature and pH are other important variables as the methane producing bacteria are sensitive to these as well. An increased growth rate of the methanogens at higher temperatures makes the thermophilic anaerobic digestion process a suitable alternative to mesophilic digestion.

It is now widely recognised that microbiological processes involved in anaerobic digestion centre around methanogenic bacteria and differ significantly from acid forming bacteria, in terms of physiology, nutritional requirements and sensitivity. A diphasic fixed film reactor with support media has been used for the treatment of distillery spent wash. With such diphasic processes, it is possible to provide optimum environmental conditions for these bacterial groups, thereby enhancing overall efficiency. To operate such a system, conditions in the first reactor must be made sufficiently unfavourable to methane formers so as to force them to grow only in the second reactor, which is achieved by the application of chemical or kinetic controls. Dialysis techniques can also achieve physical separation of microbial groups. The methane forming bacteria could effectively be sheltered by close monitoring of acid fermentation reactor effluent and by eliminating the potential problems before the methane forming bacteria are subjected to stress. Various applications of diphasic process of different types of industrial wastes, including high strength soluble wastes have been applied. Since the development of UASB process in the 1970s, this process has been widely applied for the treatment of industrial effluents. Effluents from alcohol producing industries are usually highly polluted and therefore, in principle very suitable for anaerobic treatment. Removal of colour and COD from effluent is a great problem in the treatment of distillery effluent. The application of anaerobic digestion, together with genetically potential aerobic fungi and bacteria might be a significant remedial measure for the removal of colour and COD from distillery effluent. So far, limited reports of aerobic fungi and bacteria actively involved in the removal of major contaminants of distillery effluent are available. Therefore, it would be appropriate to isolate and identify genetically potential aerobic fungi and bacteria from the effluent of distillery, and apply them in conjugation with anaerobic treatment of distillery effluent for the removal of colour and COD in a sequential way.

2.6.3 Tertiary or Alternative Treatment

A variety of treatment methods and strategies like thermal pretreatment, wet air oxidation, concentration–incineration, anaerobic treatment, etc., have been suggested or tested for the treatment of the distillery wastewater. All these schemes on their own are either incomplete, or are impractical or unviable. Thus, there is an urgent need for assessing of the possibility of combining of the available partial treatment schemes for the complete treatment.

Chemical oxidation: Colour removal from biologically pretreated molasses wastewater, by means of chemical oxidation with ozone has been investigated. Batch experiments have been performed in order to analyse the influence of ozone dosage and reaction time on colour removal, molecular weight distribution and decolourisation kinetics. Depending on the applied ozone dosage, colour removal from 71% to 93% and COD reduction from 15% to 25%, was reached after 30 minutes reaction time. TOC values remained constant throughout ozonation. Ozonation of synthetic melanoidin under the same experimental conditions provided similar colour removal efficiencies.

Cavitation: One method that remains unexplored for the distillery wastewater treatment is the use of cavitations chemistry by ultrasound. Sonochemical oxidation employs the use of ultrasound resulting in the cavitation phenomena, which is defined as the phenomena of the formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small intervals of time (microseconds), releasing large magnitudes of energy at millions of such locations in the reactor. Ultrasound irradiation effectively destroys the contaminants in water because of localised high concentrations of oxidising species, such as hydroxyl radicals and hydrogen peroxide in the solution and high-localised temperature and pressure. The combination of the physical and chemical effects of cavitation allows the application of ultrasound in water and effluent treatment. However, the time-scale and the dissipated power necessary to obtain complete mineralisation of the pollutants in the case of ultrasound treatment are not economically acceptable. Hence, ultrasound is found to be more effective when lagooned effluents, respectively, at a flocculant dosage of 4% v/v. The reduction in Total Organic Carbon (TOC) was 21% for fresh slops and averaged to more than 73% for the biodigester and lagooned effluents. The presence of relatively high amounts of fluoride ions affected the decolourisation of fresh slops; supplementing CaO at a rate of 30 g/*l* improved the decolourisation of the distillery slops, resulting in 93% colour removal.

Emulsion Liquid Membrane (ELM): Emulsion Liquid Membrane (ELM) is a highly sophisticated, but energy-saving separation technique. Many studies have been carried out for the separation of heavy metal ions, chemicals, organic acids, etc. by using this technique. In this technology, solutes are not only removed, but also concentrated. The external phase to be treated is contacted with an emulsion dispersed in globules. Each emulsion globule consists of droplets of an aqueous internal stripping phase encapsulated in an organic membrane phase containing a surfactant as micelle interfacial layer. During this contact, solute transport occurs through the membrane phase into the internal stripping phase where it is concentrated. Since extraction and stripping are done in a single step, ELM technology is preferred in treating effluents. Effluents from distilleries, tanneries and milk processing plants have been posing serious problems, and extensive efforts to overcome them are in progress. Use of emulsion liquid membrane in effluent treatment has received wide attention due to its ease of operation.

Photodegradation: This phenomenon is ascribed to active oxygen species generated by a photo-initiated electron-transfer reaction. Photodegradation is generally accelerated in the presence of transition metal ions. In addition, ascorbic acid reacts with O_2 in the presence of transition metal ions, giving O_2^-, H_2O_2, and OH. Since ascorbic acid and metal ions are common components in many foods, it seems that the Cu^{2+}/O_2 and ascorbic acid/Cu^{2+}/O_2 systems would be good systems to use for both biological and food models.

It is well known that riboflavin, some kinds of essential amino acid, and protein in milk are photodegraded under UV and visible light. Another example is the off-flavour formation in beer, exposed to sunlight. However, there have been few reports on the photodegradation of melanoidin. Colour intensity of model melanoidin was influenced by manganese and iron and decolourised by oxygen and light. Some kinds of amino acid were photodegraded in the presence of melanoidin, playing the role of a photosensitiser.

Solar energy method: Scientists at Nimbkar Agriculture Research Institute in Phaltan, India, have developed a method of treating distillery effluent using suitable chemicals and solar energy. A laboratory-scale reactor set up at the Institute campus can treat 50 l of diluted anaerobically digested distillery effluent and can make it completely colourless and odourless in 2-3 days. Moreover, the Chemical Oxygen Demand (COD) of the effluent is also reduced to less than 150 ppm. The propriety chemical (2% w/w) is mixed with diluted distillery effluent and the mixture is fed to the reactor. The break-up of the toxins is the result of photochemical reactions by solar energy. NARI scientists took their cue from work on solar detoxification of groundwater and industrial wastes using titanium dioxide catalyst. This method, however, did not give satisfactory results with distillery wastes and hence the NARI team instead used another chemical, which gave good results.

2.6.4 Wetland Method

A field-scale, 4-celled, horizontal subsurface Constructed Wetland (CW) was installed to evaluate removal efficiencies of wastewater constituents in an industrial distillery effluent. Total and dissolved solids, NH_4-N, TKN, P and COD were measured. This CW design provides four serial cells with synthetic liners and a river gravel base. The first two unplanted cells provide preliminary treatment. Specific gravel depth and ensuing biofilm growth provides anaerobic treatment in Cell 1, and anaerobic treatment in Cell 2. Cell 3 was planted with *Typha latifolia* with an inserted layer of brick rubble (for phosphorus removal). Locally grown reed, *Phragmites karka* was planted in Cell 4. COD was reduced from Cell 1 to the outlet of Cell 4. Likewise, other parameters like total and dissolved solids, ammonium and total nitrogen, and total P indicated declining trends at the 4-celled CW effluent. This study reveals how high strength distillery wastewater strongly impacts morphology, aeration anatomy in the chiseled plant tissues, reed growth, and the composition of the biofilm in the specialised substratum. The reliability of a CW for organic and nutrients reduction, in association with a poorly performing conventional system, has been discussed. There is an immense potential for appropriately designed constructed wetlands for improving high strength wastewaters in India.

2.7 PROSPECTS OF BIOUTILISATION OF DISTILLERY EFFLUENT FOR PRODUCTS

Industrialisation can be considered a desirable option, owing to its contribution to the national economic growth. However, it exerts considerable pressure upon the natural resources and waste generated is a major environmental concern. The disposal of effluents without appropriate treatment could have long term adverse effects, especially upon the local vegetation and aquatic life. Thus, it is imperative for highly polluting industries to adopt a suitable waste treatment process for the clean disposal of high-strength wastewater. Research conducted over the past several years by biotechnologists addresses its mission to investigate opportunities to obtain value added products from distillery effluent.

2.7.1 Production of Food and Feed

Concentrated spent wash is used as an animal feed additive in Europe and North America, producing alcohol from beet molasses. This practice has not been within a short period of time. When the wet solubles are dried back onto the grains, a product known as Distillers Dried Grains (DDGs) is produced. This is the most common distillery by-product available. Biomethanation Spent Wash (WSW) is concentrated in an open field, by evaporation to obtain lagoon sludge which is used as fertiliser and manure. Distillery effluents contain organic and inorganic nutrients and have been reported to be beneficial in increasing crop yields. However, not much is known about the relative effects of RSW, BSW and LS on crop growth and yield.

Composting technology may be one of the best options. It could result in zero pollution and can produce valuable organic and inorganic ingredients to enhance soil fertility. The concentrated spent wash (60% W/W) has sufficient calorific value and can burn by itself without any external input of energy. This process results in potash rich ash which can be used as a fertiliser. While farmers in Maharashtra and Andhra Pradesh utilise the distillery effluent primarily through direct spent wash applications and making spent wash cakes or spent wash press mud compost, in Uttar Pradesh the post-methanation effluent is applied to the crops. In certain areas, the scarcity of the water has forced the farmers to use the effluent as a substitute for irrigation water, but over the years the use of this has led to the realisation of its potential as a fertiliser also. It would be more pragmatic to consider the land application of post-methanation effluent as an effective waste treatment strategy which bears the potential to replace the expensive energy intensive secondary treatment.

2.7.7 Biocatalysis

With extensive expenditure of energy, nature has biosynthesised many complex molecules by the use of enzymes, the biocatalysts of great specificity and stereoselectivity. Enzymes are considered to be "green" catalysts as their reactions are not environmentally hazardous and are thus, favoured over chemical catalysts, whenever possible. Biocatalysis offers viable, environmentally friendly pathways to new and useful products from renewable resources. Phenolic acids, such as ferulic acid and *p*-coumaric acid, are among the most abundant aromatic chemical substances found in distillery and other industrial effluents. Phenolic cinnamic acid derivatives represent a major renewable chemical resource from which biocatalysis approaches can prepare value-added chemical products that are available today only from petrochemical sources. Three new feruloylated disaccharides were characterised following mild acid treatment. A buffer-organic solvent two-phase system was used with *Bacillus pumilus* to flavoured decarboxylate ferulic acid to vinylguaiacol. Vinylguaiacol is an extremely valuable flavour chemical, useful for the synthesis of other value-added aromatic products.

p-coumaric acid (CA) is another abundant phenolic natural product that exhibits both chemoprotectant and antioxidant properties. Microbial distilleries have been established in India to utilize the molasses, which are recognized as one of the most polluting agro-based industries, emitting huge quantities (40 billion litres) of highly foul smelling Raw Spent Wash (RSW).

Ethanol-blended petrol is being supplied through retail outlets in nine States and four Union Territories of India. These states are Andhra Pradesh, Goa, Gujarat, Haryana, Karnataka, Maharashtra, Punjab, Tamil Nadu and Uttar Pradesh. The four Union Territories include Chandigarh, Dadra & Nagar Haveli, Daman & Diu and Pondicherry. Petrol blended with 5 percent ethanol would be supplied by petrol pumps all over the country under the second phase, towards the end of the year. The content of ethanol blending would be increased to 10 percent in the third phase of the programme. For every litre of alcohol, around 13–15 l of effluent is produced. During the recent years, India has emerged as the largest sugar producer in the world. Molasses, being a by-product of the sugar industry, it bears an immense significance for the production of alcohol that is a raw material for the rapidly advancing chemical industry. The production of ethanol for fuel has increased and continues to expand in the United States, as compared to recent years. The primary source of the fuel ethanol is the dry milling distillation of corn grain. Ethanol is used as an automotive fuel by itself and can be mixed with gasoline to form what has been called "gasohol". Fuel ethanol, the most common blend contains 10% ethanol and 85% ethanol mixed with gasoline. Over 1 billion gallons of ethanol are blended with gasoline every year in the United States. Because the ethanol molecule contains oxygen, it allows the engine to more completely combust the fuel, resulting in fewer emissions. Since ethanol is produced from plants that harness the power of the sun, ethanol is also considered to be a renewable fuel. Therefore, ethanol has many advantages as an automotive fuel.

2.7.10 Production of Biogas

Biogas is recovered as a pre-treatment option from high strength raw spent wash through the full-scale application of a biomethanation system comprising anaerobic fixed film reactors. This, combined with subsequent concentrations through Multiple Effect Evaporators (MEE), and utilisation of concentrated effluent for biocomposting of press mud (another by-product of the industry) for the production of biomanure, contributes to the elimination of effluent discharges. In the present scenario anaerobic digestion is gaining wider acceptance over aerobic treatment, due to the production of biogas.

2.7.11 Production of other Commercial and Household Materials

Most industrial ethanol is denatured to prevent its use as a beverage. Denatured ethanol contains small amounts, 1 or 2 per cent each, of several different unpleasant or poisonous substances. The removal of all these substances would involve a series of treatments more expensive than the federal excise tax on alcoholic beverages (currently about $20 per gallon). These denaturants render ethanol unfit for some industrial uses. In such industries, undenatured ethanol is used under close federal supervision for the production of several commercial products. Several options to improve the methods of dunder disposal, are being considered, including incremental improvements to the existing spray irrigation system; installation of an incinerator to evaporate and burn the dunder, to generate steam and produce a granular fertilizer; installation of an ocean outfall pipeline; installation of an anaerobic digester to generate methane and reduce the biological oxygen demand of the dunder; construction of a new distillery using new technology; or cessation of distillery operations altogether. In addition, the conversion of dunder to a by-product called *Biodunder*, which was sufficiently concentrated to be used as a canefield potassium fertilizer; elimination of odour and contamination of local waterways; increased plant productivity; improved quality of ethanol produced by the plants; reduction in steam usage within the plant by 30%; and reduction in water consumption by 70%, have all been performed by US based distillery plants.

2.8 CONCLUSION

Molasses is one of the most important raw materials used in fermentation industries due to its low cost and ready availability. Molasses Waste Water (MWW) from the above industries, however, contains high pollution load and a large amount of dark brown pigment, melanoidins, which is poorly decolourised by physiochemical methods and the usual biological treatments, such as activated sludge systems, aerated lagoons, and anaerobic methods viz. anaerobic lagoon, anaerobic digester, anaerobic contact reactor, anaerobic filter, Upflow Anaerobic Sludge Blanket reactor (UASB) and anaerobic fluidised and expanded bed reactors. Benzo(a)pyrene, a Polycyclic Aromatic Hydrocarbon (PAH) and phenolic compounds are also seen in the molasses wastewater, and this appears to be one of the causes of toxicity to flora and fauna. The high organic load of the effluent causes eutrophication. When disposed in soil, MSW acidifies soil and affects agricultural crops. About 2.7 billion litres of alcohol is produced by about 285 distilleries in India, serving as a basic chemical for a large number of chemical industries, therefore, increasing the demand for alcohol in the future. Molasses spent wash in such effluents is nearly 15 times in volume of the total alcohol production, about 40 billion litres of MSW effluent, if disposed of untreated in water courses can cause great stress on aquatic life. Anaerobic digestion of MSW-containing effluents results in dark brown sludge which is used as a fertilizer, and other value added products biogas, food and feed and commercial products. In addition, several other bioproducts can be obtained from the effluents of distillery industries by biotechnological innovations.

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