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Treatment Processes and Technologies for Decolourization and COD Removal of Distillery Spent Wash: A Review

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Abstract— ***Most of distilleries in India use biomethanation process to treat the spent wash generated during the alcohol process, to ensure the effective treatment all distillery industries follow 1- 3 fold dilutions due to which tremendous amount of spent wash is generated. 8 -15 l of spent wash was generated during 1 l of alcohol, thus distillery industries consume more water and produce waste water on a large scale. Ethanol produced in a distillery industries are around 8 to 15 % by volume, it means about 85 to 92 % waste water contain by volume. Spent wash is the dark brown viscous liquid highly putrid, having very high chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Spent wash contain 2% melanoidin which is form by maillard reaction between amino acid and sugar, melanoidin having high molecular weight and cannot be degradable easily. This paper present an overview of pollution problem caused by distillery spent wash, this paper also summaries number of technologies such as physico-chemical treatment, biological treatment , their status , application and limitations, also includes further investigation for future study have been discussed.***

Key Words: - Biomethanation, melanoidin, caramel, recalcitrant, molasses, spent wash, decolourization.

I. INTRODUCTION

Sugarcane molasses is the byproduct of sugar industry which generated during sugar production, sugarcane molasses contain 50 % fermentable sugar and about 4 to 10 kg of molasses which is required for 1 l of alcohol production [1]. Molasses is the dark brown, putrid, viscous liquid. Sugar molasses is the most common feed stock for industrial fermentation processes, molasses are diluted 1- 3 fold for effective fermentation process and purification of spirit [2]. Spent wash is highly acidic, having strong odour, variety of recalcitrant colouring pigment as melanoidins, metal sulfides and phenolics are responsible for dark brown colour of spent wash. Along all these characteristics spent wash is daily generated with huge quantity, so during the ethanol production around 8 – 15 l of spent wash generated. Melanoidin having high molecular weight nitrogenous brown polymer form by Maillard reaction between the amino acid and sugar [3, 4, 5].Maillard reaction responsible for formation of volatile aromatic compound, brown pigment, and intermediate non volatile compounds called melanoidin [6] Dark brown colour present in melanoidin is hampers the photosynthesis process by blocking sunlight, aquatic plant and animals are highly affected. Spent wash generated from the distillery industry is depending up on the quality of molasses and fermentation process indirectly culture used for fermentation process. General characteristics of spent wash generated during alcohol production are summarized in table.I.

Table I. The typical Characteristics of distillery spent wash [7, 8, 9, 10]

Sr. No	Parameter in (mg/l Except pH)	Range
1	pH	3 – 4.5
2	BOD	50,000 – 60,000
3	COD	1,10,000 – 1,90,000
4	TS	1,10,000 – 1,90,000
5	TSS	13,000 – 15,000
6	TDS	90,000 – 1,50,000
7	Chlorides	8,000 – 8,500
8	Phenols	8,000 – 10,000
9	Sulphate	7,500 – 9,000
10	Phosphate	2,500 – 2,700

Distilleries Effluent Discharge Standards

Ministry of Environment and Forests (Government of India) has specified Standards for different industries taking into account the characteristics of the effluents the drainage water from the land after such treatment has to satisfy a limit of 30 mg/l of BOD. The net addition to the ground water quality should not have a BOD more than 30 mg/l [4, 11].

Table II Effluent Standards for Fermentation and Distillery Industries

Sr. No	Parameter	Standards
1	pH	5.5 – 9
2	Colour and Odour	Absent
3	BOD_3 at 27 ^{0}C mg / l Max	
	1. Disposal into land surface water/ rivers/ streams	30
	2. Disposal on land or for irrigation	100
	3. Suspended Solids mg/l Max	100

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(Ref: The Environment (Protection) Act 1986 and Environmental Protection Rule, 1986; Management of distillery wastewater (CPCB and MoEF) Resource recycles series, September 2001).

Causes of Problem

Generally four types of colour are present in sugar plant pigments, melanoidins, caramels and alkaline degradation products of fructose (ADF) [12] .The last three is factory produced colour pigments.

Table III Coloured & their Characteristics of Post methanated spent wash Effluent Ref:-[21, 13, 14, 12].

Sr.No	Colourant	Characteristics
1	Phenolics	Plant pigments, low molecular weight, may be attached to polysaccharides, pH sensitive, darker at high pH, pale yellow to orange colour, react with iron to produce very dark color, may oxidize to form darker colour.
2	Caramel	Process colourant, thermal degradation of sugar, high molecular weight Low net charge.
3	ADF	Process colourants, reddish to dark brown in colour, low molecular Weight up to polymeric depending on degree of degradation.
4	Melanoidin	Browning reaction products of sugars and amino acid, high molecular Weight.
5	Sulfide	Process colourant, toxic to microorganisms and creating foul smell, Strong binding tendency with metals.
6	Heavy metals	Process colourants, toxic to microorganisms, animals and humans.

II. Process Description

Alcohol Manufacturing Process

Alcohol manufacturing process consists of different steps such as feed preparation, fermentation process, distillation process and packing shown in figure 1.

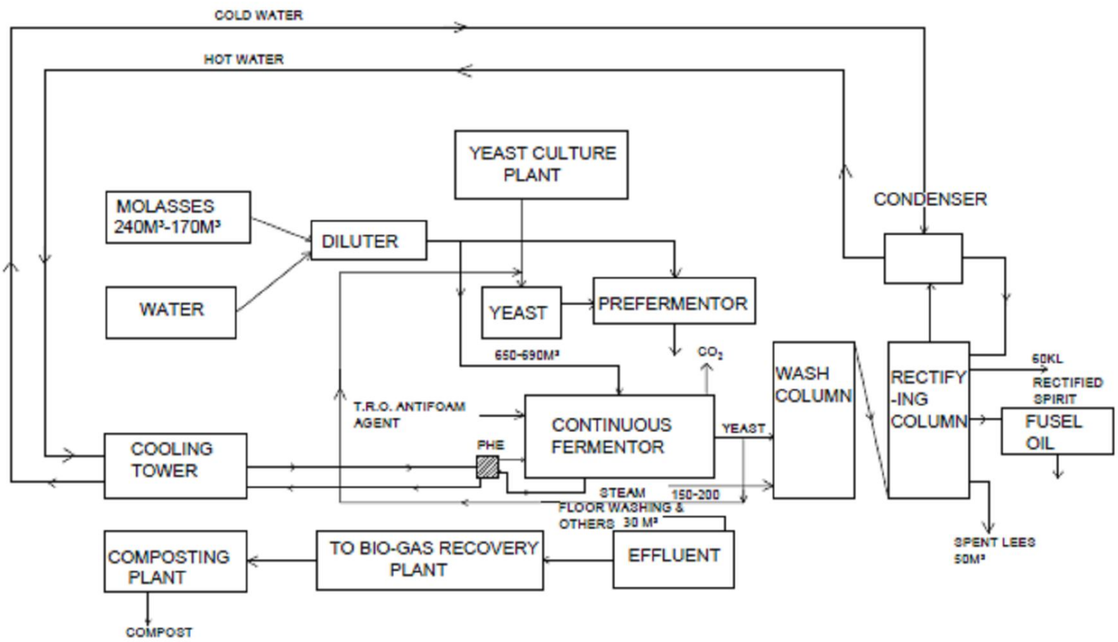

Figure 1. A process flow diagram

Feed Preparation

Raw materials used for ethanol production are sugar, starch and cellulose material Sugars base includes sugar cane, sugar beets, molasses, and fruits can be converted to ethanol directly [17]. Starch base corn, cassava, rice, wheat and barley. Cellulose base such as crop residues, municipal solid wastes, woods and sugar cane bagasse material. Satyawali et al [2] reviewed process, treatment of sugar starch and cellulose biomass based feedstock. Brazil distillery use cane juice as a feedstock for ethanol manufacturing [18]. While Indian distillery use sugar molasses for ethanol production. All over world nearly about 61% ethanol production is from sugar crops [19].

Fermentation

The most widely used sugar for ethanol fermentation is blackstrap molasses which contains about 35 – 40 wt% sucrose, 15 – 20 wt% invert sugar such as glucose and fructose, and 28 – 35 wt% of non-sugar solids. Blackstrap (syrup) is collected as a by-product of cane sugar manufacture. The molasses is diluted sugar cane molasses, beet molasses and sugar cane juice [20]. Chandra raj et. al. (2004), [16], demonstrated zymomonas mobilis culture for ethanol production. In general for alcohol production fermentation process is carried out by using Saccromyes cerevisiae and Saccharomyces pombe bacteria. These bacteria (yeast culture) is developed by using 500 ml molasses for 24 hr. and kept in incubator. Next day bacteria are developed in 5000 ml molasses for 24 hr. like this process continues. For development of yeast slant between pH 3 to 3.2 is more favourable as growth of yeast is faster.

Nutrients are Feed such as 2 kg urea, 2 kg DAP (diammonium phosphate) for bacterial growth. This anaerobic process is carried out under control condition of temperature and pH where reducing sugar broken down to ethyl alcohol and carbon dioxide [2]. Temperature of the process can be maintain 25 to 35°C by using plate heat exchanger or by using spray cooling water on fermenter walls. Time required for batch fermentation typically 24 to 36 hr and having 95 % efficiency. Fermentation process can be carried out in batch mode or continuous mode (CPCB 2003). The waste water comes out as a liquid waste from the residual fermented mesh is known as distillery spent wash or distillery slop [35].

Treatment Technology for distillery Spent Wash

There is a need of modernization and scientific revolution as the tremendous changes occur in the surrounding area of distillery industry and environmental crises problem also terrestrial and aquatic land badly affected due to these industries. To minimize and economical disposal of waste water problem in 21st century number of techniques are developing to treat the distillery spent wash indirectly reduce the overburden pollution of the environment. Today modern and huge numbers of technologies are explored to reduce pollution load of distillery spent wash.

Adsorption

Activated carbon is a well known adsorbent due to its extended surface area, microporous structures, high adsorption capacity and a high degree of surface reactivity [2, 21]. Adsorption techniques are considered to be most effective and proven technology having potential application in both water and waste water treatment [22]. Adsorption is a rapid process of passive sequestration and separation of adsorbate from aqueous or gaseous phase onto the solid phase; Sugarcane bagasse and charcoal use an adsorbent for decolourization of distillery spent wash [23]. Activated carbon is a widely used adsorbent for the removal of organic pollutants from wastewater, but the relatively high cost restricts its usage.

Oxidation process

Different oxidation process is used for treatment of waste water, such as ozone, single hydrogen peroxide, Fenton's reagent and ozone combined with hydrogen peroxide. Ozone treatment was able to reduce 76 % of colour, a combination of ozone with a low concentration of hydrogen peroxide was able to increase the colour removal efficiency up to 89% [6]. Bicarbonate ions were found to be strong inhibitors of decolourizing reactions [24]. Sonication of distillery wastewater as a pre-treatment step to convert complex molecules into a more utilizable form by cavitation [25]. Wet air oxidation as part of a combined process scheme for treating anaerobically digested spent wash [26]. Drawbacks of ozone treatment is high capital cost of installation and generation of large quantity of ozone, Fenton's reagent, single stage treatment with ozone, electrochemical oxidation treatment will not be adequate on a large scale due to high reagent cost for the treatment of industrial effluent [1]. Hydrogen peroxide and Fenton's reagent were not able to reduce colour [6].

Membrane Treatment

Emulsion liquid membrane (ELM) technique in a batch process for spent wash treatment is effective to remove the colour of spent wash, drawbacks of emulsion liquid membrane (ELM) technique are membrane which does not remain intact during operation and uncontrolled ionic strength, membrane fouling, clogging, scaling and cleaning. Electro dialysis has been explored for desalting spent wash using cation anion exchange membrane gives 50 -60 % reduction in potassium content [27]. Nanotechnology is effective for COD and Colour removal, by using nanotechnology 100 % colour is removed and about 97.1 % COD is removed. Nanotechnology is more effective but high capital cost and effect on human health and the environment [28]. Electro dialysis and reverse osmosis process are less economical and pretreatment is required for reverse osmosis.

Electrocoagulation

Kobya et al., (2012) [29], revealed that Colour removal efficiency of electro-coagulation is decreases with increase in concentration of melanoidin; he also mentioned that electrodes consumption increases with increase in concentration of melanoidin. Decolourization efficiency of melanoidin is increases with increase in conductivity, NaCl significantly increases the conductivity. pH and time are the important parameter for decolourization of melanoidin, at low pH decolourization is fast and vice-versa .melanoidin is soluble in dilute alkaline solution but precipitate from an acidic solution. Efficiency of the chemical oxygen demand (COD) removal retarded with increases in pH, spacing between electrodes plays important role in decolourization of melanoidin, COD removal efficiency accelerate with increase in the distance between electrodes [30]. Acidic condition is more favourable for treatment of distillery spent wash due to decreased production of chlorine or hypochlorite at higher pH [31]. Al-Al electrodes are more effective to remove colour of distillery spent wash as compared to Al-Fe, and Fe-Fe electrodes due to Fe ion generated during the EC process from iron electrodes has high solubility at acidic condition and are easily oxidized into Fe, since Fe is difficult to settle [29, 32]. Efficiency of chemical oxygen demand removal and power consumption increases with increase in current density up to certain limit then after operating cost is increases in the power consumption with decrease in current efficiency [33].

Electro coagulation (EC) is a simple and efficient method and has been used for the treatment of many types of wastewater, using Graphite - Graphite electrodes 85.2 % COD removed at pH 6.9 – 7.2 and duration is 180 minutes, by using Al - Al electrode 72.3 % COD removed in 2 hours when pH is 3.[30,31,34,34,35].Al - Al electrode removed 81.3 % COD successfully, Al - Fe electrode remove 71.8 % COD in 2 hour duration when the pH is 3 of the solution [36,37] . 98 % COD removal efficiency was obtained by using Al – Al electrode when the pH of the waste water is 7.2. Electro -coagulation technique can be successfully employed for the treatment of distillery effluent [38]. The electro coagulation process generates a considerable amount of sludge as a secondary pollutant during treatment; hence the alternative process is needed for effective sludge reduction by combining electro coagulation with ozone, ozone is powerful oxidizing reagent and very effective to remove the colour of spent wash. [39]. 94% colour can be removed from bio- digester effluent by using aluminum electrodes without fenton reagent at pH 7 for 140 min and current density 0.03 A/cm^2, he also study advanced oxidation process to treat distillery effluent by using combination of electrochemical and fenton reagent which gives very effective result for removing colour about 97.76% colour removed at pH 7 for 140 min and 0.03A/cm^2 current density [40].

Table IV Modified table Electro coagulation used for treatment of distillery spent wash (Khandegar et al., 2014)[34]

Current density in A/cm^2	Time (Min)	pH	% Colour Removal	% COD Removal	Anode -Cathode	Reference
0.817	120	3	-	81.3,71.8,52.4	Al-Al, Al-Fe,Fe-Fe	30
0.01	140	3	-	56	Al-Al	31
0.143	180	5	-	37	RuO2-Ti – SS	9
1.467	150	6.75	-	61.6	SS-SS	10
0.06	180	6.9-7.2	-	85.2	Graphite-Graphite	34
0.03	180		-	84	Mixed metal oxide (MMO) electrode	39
0.71 0.718	60 60	7.5 7.2	-	60,50 99.88	Al-Al, Fe-Fe Al-Al, Fe-Fe	38
0.03	140	7	94	-	Al-Al	40
0.03	140	7	97.76	-	Al-Al with fenton reagent	40
0.03	240	6	100 89 7	83 60 7	Ozone assisted EC Al-Al electrodes ozonation	33

Table V Summary of various physiochemical treatments used for the treatments of distillery spent wash and their efficiency (Mohona et al (2009) [4] Modified table)

Treatment	% COD removal	colour removal	Reference
Adsorption, Chitosan, a biopolymer was used as anion exchanger	99	98	41
Chemically modified bagasse DEAE bagasse CHPTAC bagasse	 40 25	 51 50	42
Activated carbon prepared from agro industrial waste Phosphoric acid carbonized bagasse was used	23	50	43
Commercially available activated carbon AC(ME) AC(LB)	 76 88	 93 95	
Coagulation-flocculation Flocculation of synthetic melanoidins was carried out by various inorganic ions Polyferic hydroxysulphate (PFS) Ferric chloride(Fecl$_3$) Ferric sulphate (Fe(SO$_4$)$_3$) Aluminium sulphate (Al$_2$(SO$_4$)$_3$) Calcium oxide (CaO) Calcium chloride (CaCl$_2$)	 NR NR NR NR NR NR	 95 96 95 83 77 46	44
Different inorganic ions and wastewater from iron pickling and Titanium process industry were used as coagulents. Addition of polyelectrolyte Ferrous sulphate (FeSO$_4$) Ferric Sulphate (Fe$_2$(SO$_4$)$_3$) Alum Iron pickling waste water Titanium processing waste water	 78 77 64 86 67	 98 96 95 99 99	45
Iron chloride coagulation Iron chloride Aluminium chloride Calcium oxide	38 65 61.3 39.8	47 69 74.4 80.2	46 47
Ferric chloride (FeCl$_3$) Aluminium chloride(Alcl$_3$) Polyaluminium chloride (PAC)	55 60 72	83 86 92	48

Oxidation processes	88	99	49
Fenton's oxidation	15-25	80	50
Ozonation		87	
Coagulation with PAC followed by fungal sequencing batch aerobic reactor (FSBAR)	81	96	82
PAC followed by fungal sequencing batch aerobic reactor (FSBAR) and ozonation			
Ozone and Electro coagulation	83	100	33
Ozone treatment	47	62	83
Ozone + H_2o_2	61	85	
Ozone + H_2O_2 + UV	68	88	
Electrochemical oxidation	80.6	95.6	
Graphite electrodes	90.8	98.5	51
Lead dioxide coated on titanium	92.1	99.5	
Ruthedium dioxide coated on titanium	92.6	-	52
Electro coagulation and electro Fenton			
Membrane technologies			
Reverse osmosis	99.9	-	28
Nanofiltration	97.1	100	

Evaporation and Combustion

According to Bories et al., (2005) [54] , natural evaporation ponds are used for winery and distillery waste water, the organic compounds are oxidized to Co_2 and nitrate is reduced to N_2, in order to prevent the odour in winery and distillery pond, he added nitrate to test on an industrial scale. Santal et al., (2013) [6], says that natural evaporation process forms malodorous compounds induces harmful effects. Cortez. (1997) [55] discovered that on-site combustion of vinasse disposal is an effective method as it contains potassium rich ash that can be used for land application. As vinasse is recalcitrant and has a bad effect on the environment and surrounding area of distillery industry.

Anaerobic Treatment

Physico –Chemical and Biological treatment are used on large scale to treat the distillery spent wash. As COD/BOD ratio is more than 1.5 it indicates biological method is more suitable to treat the distillery spent wash. Biological method can be implemented in two manner one is anaerobic and another is aerobic treatment. In absences of oxygen biological process occurs and energy is extracted from the waste components. Now days anaerobic treatment is effectively used to decomposed waste water and generate biogas [11]. Anaerobic treatment is primary common practice treatment more effectively used as compared to aerobic treatment to treat distillery effluent [56].

Anaerobic lagoon (digester) is the simplest and traditional method used initially on large scale. Rao (1972) [36], carried out the pioneering research work in the distillery effluent management reducing BOD 82 - 92%, but this method having various limitation and drawback such as large area is required, odour nuisance changes of ground water pollution [6]. Hydrolytic fermentative, syntrophic and methanogenic bacteria are the three types of organism present in microbial food chain [57].Mailleret et al., (2003)[58] and [59]. proved that anaerobic treatment having high capacity of degradation, and produce less sludge require less energy and beneficial by generating methane gas which can be utilized for steam generation in the boiler, but this process is having long hydraulic retention time (HRT) and sensitive to organic shock loading due to low pH of spent wash and slow growth rate of anaerobic microbes. Thus anaerobic treatment poor performance process.

Aerobic Treatment

Anaerobic treatment is the primary treatment to treat distillery spent wash but still contain high concentration of COD, suspended solids, chloride, and biochemical oxygen demand. Effluent also contain high ration of C: N which affect the fertility of the land as C: N ratio reduces mineral nutrients so cannot be disposal and discharge directly [59]. Aerobic treatment of anaerobically treated spent wash implemented to decolurization and removal of chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Number of microorganisms such as bacteria like Saccromyes cerevisiae and Saccharomyces pombe bacteria, fungi, yeast.

Fungal Treatment

Ohmomo et al., (1987) [60] , Miranda et al., (1996) [61] , Shayegan et al., (2004) [62], suggested that one of the highly recommended fungus having potential to degrade and decolourize distillery spent wash is Aspergillus such as Aspergillus fumigates G – 2- 6 , Aspergillus Niger, Aspergillus Niveus, Aspergillus fumigates UB260 gave an average of 69 – 75 % decolourization along with 70 – 90 % COD reduction. Watanabe et al., (1982)[63], had brought into notice that Coriolus sp no 20 in class basidomycetes was the first strain for the application of its ability to remove melanoidine from molasses waste water. [61], went through Aspergillus Niger and concluded that under optimum nutrient condition 83 % of total colour removal was gained due to biodegradation of the organism and 17% by adsorption on the mycelium. Ohmomo et al., (1988)[64], studied Aspergillus oryzae Y -2 -32 that the thermophilic strain adsorbed lower molecular weight fractions of melanoidin and required sugars for growth. 75% colour was removed.

Benito et al., (1997) [23], revealed that using mycelium fungi 82 % decolourization is obtained anaerobically and 12.5% aerobically.

Ohmomo et al., (1988) [64], studied that microorganism having the inherent capacity to metabolize a variety of complex compounds, therefore, used in the degradation of recalcitrant, a toxic and complex compound present in different types of industrial wastes. Dahiya et al., (2001) [65] , discovered that Pseudomonas fluorescence decolurized melanoidine effluent up to 76% under non sterile conditions and up to 90 % in sterile sample this difference was because of the fact that melanoidin in spent wash stability varies with pH and temperature. Sirianuntapiboon et al., (1995) [66], state that under experimental conditions Rhizoctonia sp. D 90 decoloured molasses melanoidins medium and a synthetic melanoidin medium by 87.5% and 84.5% respectively. Shweta et al., (2012) [67] , suggested that microorganisms play the key role in the process of bioremediation and biodegradation because of their great metabolic diversity, which includes the ability to metabolize these pollutants. As per Kumar et al., (1988)[68], increasing attention has been focused towards utilizing fungal activity for decolourization of distillery spent wash. Hence fungal treatment is preferred to treat distillery spent wash.

Table VI Fungi employed to treat distillery effluent [Modified table of Mohana et al., (2009)][4], Yadav et al., (2012)[21]

Sr. No	Name of fungi	Comments	% Colour Removal	References
1	Trametes Versicolor	COD and N–NH4 removal observed in the presence of sucrose and KH_2PO4 as a nutrient source	82	23
2	Coriolus Hirsutus	A large amount of glucose was required for colour removal, but the addition of peptone reduced the decolourizing ability of the fungus	80	69
3	Mycelia Sterilia	Organism required glucose for the decolourizing activity	93	70
4	Aspergillus Niger UM2	Decolourization was more by immobilized fungus and it was able to decolourize up to 50% of initial effluent concentrations	80	71
5	Rhizoctonia sp. D-90	Mechanism of decolourization of melanoidin involved absorption of the melanoidin pigment by the cells as a macromolecule and its Intracellular accumulation in the cytoplasm and around the cell membrane as a melanoidin complex, which was then gradually decolourized by intracellular enzymes	90	66
6	Aspergillus Oryzae Y-2-32	The thermophilic strain adsorbed lower molecular weight fractions of melanoidin and required sugars for growth	75	64
7	Phanerochaete Chrysosporium	Both cultures decolorized to reduce the COD of effluent in presence of (3- 5 %) glucose and 01. % Yeast extract.	53.5	72
8	Pseudomonas aeruginosa (MTCC 2474)	Anaerobic digestion efficiently achieved decolourization	47.6	55
9	Pseudomonas Aeruginosa (MTCC 2642) Acetobacter aceti (MTCC 3246)	0.5 gm of glucose as carbon source and decolourization occurs on 9th day	55.30 46.95	54

Table VII White Rot Fungi Employed for Treatment of Distillery Effluent (Modified Mohona et (2009) [4]; Yadav et al., (2012) [21])

Culture	Treatment	COD removal	Color removal	Reference
Coriolus No.20	Synthetic melanoidin solution was decolourized by the fungus free cells as well as Ca alginate immobilized cells decolorized the distillery effluent.	NR NR	80% 85% 59%	63 80
Trametes versicolor	Anaerobically treated distillery effluent supplemented with sucrose and inorganic N sources was decolorize by the culture in shake flask studies	75%	80%	23
Phanerochaete chrysosporium	Both the cultures decolorized to reduced the COD of effluent in presence of (3-5%) glucose and 0.1%yeast extract	73%	53.5%	68
Coriolus hirsutus	Synthetic as well as wastewater melanoidin was decolorized by the fungus in a medium containing glucose and peptone.	NR	80%	73,74
Coriolus hirsutus IF044917	The fungal culture was immobilized on PUF and used for decolourization of melanoidins present in heat treated liquor	NR	45%	75
Flavodon flavus	Distillery effluent was decolorized using this marine basidiomycetes in presence of 5% glucose.	NR	80%	76,77
Coriolus versicolor	The cultures were incubated along with cotton stalks in vinasses, media in static condition. No synthetic carbon or nitrogen sources were used.	49%	63	75
Phanerochaete chrysosporium ATCC 24775	The fungus was immobilized on different support materials such s PUF and scouring wet and the decolorization was carried out in a RBC	48%	55%	77
P. chrysosporium NCIM 1073	The cultures were employed to study the decolourization of molasses in medium containing 2% w/w glucose in static as well as submerged conditions.	Nil	Nil	77
Aspergillus Fumigates G-26	Thermophilic strain tried for molasses wastewater Decolourization but colouring compounds hardly Degraded	Nil	56	60
Mycelia Sterilia	Organism required glucose for the decolourizing Activity	Nil	93	70
Aspergillus Oryzae Y-2-32	The thermophilic strain absorbed lower molecular Weight fractions of melanoidin and required sugars For growth	Nil	75	64

Rhizoctonia sp. D-90	Mechanism of decolourizatin of melanoidin involved Absorption of the melanoidin pigment by the cells as a macromolecule and its intracellular accumulation in the cytoplasm and around the cell Membrane as a melanoidin complex, which was then gradually decolourized by intracellular enzymes	Nil	90	66
Coriolus hirsutus	A large amount of glucose was required for colour removal but addition of peptone reduced the decolourization ability of the fungus	Nil	80	73
Phanerochaete Chrysosporium JAG-40	This organisms decolourization synthetic and natural melanoidins when the medium was supplemented with glucose and peptone	Nil	80	65
Aspergillus niger UM2	Decolourization was more by immobilized fungus and it was able to decolorize up to 50% of initial effluent concentrations	Nil	80	65
Flavodon fiavus	MSW was decolourization using a marine basidiomycete fungus.It aiso removed 68% benzon (a)pyrene,PAH found in MSW	Nil	80	77
Planerochaete Chrysosporium	Sugar refinery effluent was treated in a RBC using Polyurethane foam and scouring web as support	Nil	55	79

Chemical oxygen demand and biochemical oxygen demand of distillery spent wash can be treated by investigating phsico-chemical method and biological method; biogas recovery can be achieved extensively by implementing anaerobic treatment. Anaerobic treatment is the primary and basic treatment accepted by several distilleries. Aerobic treatment is the secondary treatment to treat the distillery effluent, while required more energy to transfer oxygen, so economy is not achieved [2]. Biomethanation process reduces organic load and bring down BOD value up to 80-90 %. Post methanated distillery spent wash cannot be disposal directly for irrigation purpose, as effluent contains high BOD and more water is required to dilute this parameter below 100 mg/l as per CPCB rule and regulation. Anaerobic lagoon process produces odour but still using in India. Anaerobic process is slow process and time consuming. Decolourization of distillery spent wash is not only remaining unsolved but also become more serious since melanoidin pigment get accelerated under anaerobic condition [50].Several distillery industries in India reported that use of diluted biodigested effluent cause soil brown darken [68]. In a biomethanation process molasses is used for alcohol manufacturing is diluted 3 – 4 times thus large quantity of water is consuming for the fermentation process, and generating 8 – 15 l spent wash during 1 lit of alcohol manufacturing. Physico chemical treatment such as adsorption, coagulation, electro coagulation, flocculation, oxidation, membrane technology, evaporation and combustion methods are implemented for decolourization and to reduce organic load. These methods are more effective for colour removal as well as reduction in organic loading, but sludge is generated on large scale and another method is required for disposal of sludge. For removal of COD, BOD, SS, and colour coagulation and flocculation methods are more effective.

Drawback of coagulation flocculation the generation of sludge, and its disposal. By adding polyelectrolyte large quantity sludge can be reduced by using small amount of sludge. Ozonation is the clean treatment technology because ozone is more powerful oxidizing agent for COD and colour removal. Limitation of ozone treatment is very high capital and operating cost. Decolourization is faster for alkaline as compare to acidic condition. Fentons reagent and electrochemical oxidation are more powerful and achieving good efficiency of removing COD and colour from distillery spent wash, fenton reagent is powerful in acid condition to remove COD and colour due to reactive hydroxyl radical [1]. Composting process is use on large scale due to zero pollution, high product value, no odour easy to handle only drawback is continuous use of compost make the land infertile. Combustion - incineration with energy recovery would be an ideal solution available for complete treatment of spent wash apparently this method is not viable because of the large quantity of auxiliary fuel is required for combustion [80, 81].

III CONCLUSIONS

On a large scale anaerobic, aerobic physic-chemical and biological methods are invented for decolourization and removal of chemical oxygen demand (COD) of distillery effluent but still no any method is more effective on a large scale and ecofriendly. So following point are mention which indicate there is gap between the literature reviews

- Anaerobic treatment to distillery spent wash was implemented successfully by recovering methane gas. There is scope to use number of advance techniques to be adopt.
- Implement the technique that can treat without diluting spent wash and less hydraulic retention time (HRT).
- Post methanated distillery effluent can be treated by using combination of electro-coagulation with aeration , due to aeration rate of oxidation will be accelerate and effective decolourization can be possible.
- Electro-coagulation is more effective to treat spent wash, only problem is secondary sludge is generated during the process. This limitation can be overcome by using combination of ozone treatment and electro-coagulation method, as ozone is powerful oxidizing reagent, clean method and less time consuming.
- The structure and characteristics of brown dark colour causing reagent melanoidin is still not fully understood. By using different methods such as (SEM) Scanning Electron microscopy , X ray diffraction (XRD) , Fourier transform infrared spectroscopy(FTIR) basic composition of melanoidin can understand and help to investigate proper method to treat such spent wash.

Biological method was revealed by number of researcher and scientist and effectively implemented for decolourization and COD removal, while limitation of this method is biodegradation and decomposition rate is very slow and time consuming, secondary sludge is generated on a large scale. This limitation can be overcome by investigating pure culture aerobic system, which can treat both COD and colour

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