

## International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

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Vol. 7, Issue 1, January 2018

# Decolourisation of Distillery Spent Wash on the Background of Various Bio-remediation Strategies: A Review

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**ABSTRACT:** India is the fourth largest producer of ethanol in the world and second largest in Asia. The distilleries using Molasses for the production of alcohol, is considered as one of the most polluting industries. Different technologies covering anaerobic, aerobic, composting, concentration and incineration with energy recovery, reverse osmosis etc. have been followed by Indian distilleries to treat spent wash to achieve a complete solution. But no system or strategy till date is ideal to deliver a complete solution with respect to zero discharge, as well as return on investment and water conservation associated with the processes.

Looking into that angle, this paper is being presented as a review of the problems associated with different treatment strategies and prospect of decolourisation by capillary seepage system through immobilized whole cells incorporated in artificial soil bed with a designed novel system which would deliver zero discharge with good ROI through crop cultivation.

**KEYWORDS:** Decolourisation; Distillery; Spent wash; Melanoidin; ROI (Return on Investment); BOD (Biological Oxygen Demand).

### I. INTRODUCTION

India produces about 3.25 million kiloliters (KL) of alcohol annually from 319 distilleries, generate approximately 404 million KL waste water (Uppal, 2004). Due to increasing demand of potable alcohol and the use of alcohol as blend in motor fuel (gasohol) there will be drastic increase in demand for ethanol which could overcome the existing unutilized capacity and hence creating an excess demand. Distillery spent wash is a potential water pollutant in two ways: First, it has a high organic and inorganic load which would result in eutrophication of contaminated water sources (Fitz Gibbon et al., 1998). Second, it has dark chocolate colour after biomethanation which can block out sunlight from rivers and streams thus reducing oxygenation of water by photosynthesis and hence becomes detrimental to aquatic life. Moreover, it also contaminates the ground water level through percolation as a result tube well water in villages become unfit for drinking. In addition to pollution, increasing stringent environmental regulations are forcing distilleries to find out a complete solution that cannot be provided by existing spent wash treatment options of effluent management. Moreover, Indian distilleries are bound to achieve zero discharge of spent wash as well as water conservation.

This review article focuses on the advances in distillery waste water treatment in the last two and half decades and the emerging technologies in this field. However, there are limitations posed by these technologies for full compliance. Many physico-chemical and biological methods for the decolourisation of distillery waste water tried, but an efficient

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treatment system which would be cost effective and would ensure zero discharge with some ROI through crop cultivation is still need of the hour.

### II. GROWTH OF INDIAN DISTILLERIES

The first distillery was set up at Crwnpore (Kanpur) in 1805 by Carew & Co. Ltd., for manufacture of Rum for the army. The technique of fermentation, distillation and blending of the alcoholic beverage was developed in India on the lines of practices adopted overseas particularly in Europe. Distilleries manufacture rectified spirit and extra neutral alcohol for human consumption and denatured spirit for industrial purpose.

The distillery industry today consists the industrial alcohol and potable liquor. The potable distillery producing Indian made Foreign Liquor (IMFL) and country liquor has a growth rate of about 7-10 percent per annum whereas the industrial alcohol industry on the other hand is showing a declining trend because of high price of molasses. The alcohol produced is now being utilized in the ratio of approximately 52 percent for potable and the balance 48 percent for industrial use. Apart from its use as beverage, medicinal, pharmaceutical and flavouring, alcohol constitute the feedstock of large number of organic chemicals which are used in manufacturing a wide variety of intermediates like drug, rubber, pesticides, solvents etc. (Mall, 1995). With the advent of ethanol blending with petrol/motor fuel, the requirement of ethanol/industrial alcohol has increased manifold in the country to the extent that in case 5% blending, if made mandatory all over the country, the sugar factory molasses available in the country shall not be adequate for meeting the total requirements of ethanol including its use for potable liquor and other industrial uses.

However, the notification no. G.S.R 705 (E) dated 27<sup>th</sup> October, 2004, Ministry of petroleum and Natural Gas, Government of India, mandates that 5% ethanol blended petrol (E5), conforming to bureau of Indian standards specifications, shall be sold in the following ten states viz. Andhra Pradesh (except Chittoor and Nelloor districts); Goa; Gujrat; Haryana; Karnataka; Maharashtra; Punjab; Tamil Nadu (only in districts of Coimbatore, Dindigul, Erode, Kanyakumari, Nillgiri, Ramanathapuram, Tirunelveli, Tuticorn and Virudhnagar); Uttar Pradesh and Uttaranchal and the following three Union territories viz. Daman and Diu; Dadra and Nagar Haveli; and Chandigarh. It is also stipulated that government may extend above notification to all states and Union territories in phase 2, and enhance the percentage of ethanol in the ethanol blended petrol from 5% to 10% in phase 3 (MoPNG, 2004). Due to government promoting ethanol to mix in petrol there will be drastic demand for ethanol, which could overcome the existing unutilized capacity and thus creating an excess demand. For example, according to the estimates prepared by the Ministry of Petroleum and Natural Gas, about 410 million liters of anhydrous ethanol (conforming to IS 321: 1964) shall be required to implement 5% blending in the above mentioned 10 notified states (Ethanol India, 2008). Looking to its wide use, it can be inferred that the demand for alcohol is likely to increase in the country. All India Distillers Association (AIDA) and Ethanol India predicting the birth of many new distilleries along with the major expansion in capacity of existing distilleries (AIDA, 2008; Ethanol India, 2008).

### III. WASTEWATER (SPENT WASH) FROM DISTILLERY

Distilleries generate (i) Spent wash from the bottom of the analyser column (ii) Spent lees from the bottom of the rectification column after separation of alcohol and column after separation of alcohol and (iii) waste water generated from bottling, fermentation tank cooling, washing and utility section of the plant. Among these, spent wash is of major environmental concern due to its quantity and quality. About 10-15 litre of spent wash is generated for every litre of alcohol produced and is characterized by high percentage of dissolved organic (BOD: 52,000-58,000 mg/L; COD: 90,000-1,20,000 mg/L) and inorganic matter (1,660-4,200 mg/L form of nitrogen, 225-3,038 mg/L of phosphorous, 9,600-17,475 mg/L potassium, 400-1,500 mg/L sodium, 2,000-6,000 mg/L Calcium, 5,000-7,500 mg/L chlorides and 4,000-8,500 mg/L sulphates), dark brown colour (2,38,000-2,52,00 Pt-Co units), high temperature (70-100<sup>o</sup>C) and low pH (4.5-5.5). About 50% of the organic and inorganic matter are present as reducing sugars. The properties of Spent wash being dependent on the quality of molasses, fermentation process and operating conditions, could be the main reason for the significant variability. Spent wash is toxic to aquatic organisms as LC50 value for distillery spent wash is found to be 0.5% for fresh water fish like *Cyprinus carpio* var. *communis* (Gupta, 2007). If disposed untreated on the soil, it reduces alkalinity of the soil, and crops may be destroyed. Moreover, the colour problem in groundwater is so

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acute that distilleries have to provide potable water in the nearby villages. It behaves much more hazardous when disposed into water bodies, because of complete depletion of dissolved oxygen as a result aquatic life is destroyed (Kumar, 1991). Anaerobic treatment of spent wash has been favoured over aerobic treatment because of various advantages. Biomethanation plants which generates biogas (methane 60-65% v/v), is used to run boilers for power generation, reduces power consumption of sugar factory remarkably. The payback period of most of the plant is less than 3 years. Therefore, almost all Indian distilleries have adopted it as the best available technology at the first step.

The effluent standards notified by Ministry of Environment & Forest (MOEF), Govt. of India vide GSR 176(E), April 2, 1996, require that the effluent should have pH between 5.5-9, suspended solids 100mg/L, and maximum BOD level of 30mg/L for disposal into water courses and 100mg/L for disposal in land. It is suggested that all efforts must be done to remove colour and unpleasant odour, as far as possible. If land application is envisaged as secondary treatment, BOD is allowed upto 500-1000mg/L. However, the drainage water from the land after such treatment has to satisfy BOD limit of 30mg/L and nitrate as nitrogen should not be more than 10mg/L. Further, the underlying groundwater should not have a BOD more than 3mg/L and 10mg/L nitrate (CPCB, 2002).

To make and ensure the environment most cleaner and eco-friendly CPCB/MOEF issued "Charter of corporate Responsibility for Environment Protection (CREP)" for each of the 17 highly polluting industries. Accordingly, existing molasses based noncompliance distilleries are required to furnish bank guarantee and action plan to concerned state boards to ensure compliance with any or combination of the following measures:

- Compost making with press-mud / agricultural residue / municipal waste.
- Concentration and drying / Incineration.
- Treatment of spent wash through bio-methanation followed by two stage secondary treatment and dilution of treated effluent with process water for irrigation as per norms prescribed by CPCB/MOEF.
- Treatment of spent wash through bio-methanation followed by secondary treatment (BOD<2500 mg/L) for controlled discharge into the sea through a proper submerged marine outfall at a point permitted by SPCB/CPCB in consultation with National Institute of Oceanography (NIO), so that the dissolved oxygen in the mixing zone does not deplete, less than 4 mg/L.
- For taking decision on the feasibility of one-time controlled land application of treated effluent a study will be undertaken within three months.

The road map for the utilization of spent wash by distilleries to achieve zero discharge in inland surface water courses will be as below:

- 50% utilization of spent wash: By March 2004.
- 75% utilization of spent wash: By March 2005.
- 100% utilization of spent wash: By December 2005.

Till 100% utilization of spent wash is achieved, controlled and restricted discharge of treated effluent from lined lagoons during rainy seasons will be allowed by SPCB/CPCB in such a way that the perceptible colouring of river water bodies does not occur. Moreover, the task force consisting of CPCB, SPCB, experts and industry shall be constituted for monitoring and implementation of action plan. For new distilleries and expansion of existing distilleries (molasses based), the proposal without achieving zero discharge in surface water/ ground water will not be considered by MOEF/SPCB (CPCB, 2008).

## IV. TREATMENT OPTIONS: RELATED PROBLEMS

### 1. Biomethanation followed by irrigation

Biomethanation is a well-established process and is the best possible technical option for the treatment at the first step. This is capable of treating spent wash having BOD in the range of (55,000-58,000) with an efficiency of 90-95%, thus producing an effluent having a BOD equal to 5,000-5,800 mg/L. The treatment systems produce gas at the rate of 0.4-0.5m<sup>3</sup>/kg COD removed having a composition of 55-65% (v/v) methane, 35-45% (v/v) carbon-dioxide and 1-1.5% (v/v) hydrogen sulphide. The gas is used as a source of energy by

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the industry for generating steam. Comparing the effluent quality with the prescribed effluent standards it is seen that the treated effluent must be diluted if it has to be used for irrigation. In order to meet the standard of 100mg/L BOD, the required dilution would be about 45-50 times the effluent volume. The rate of dilution would also result in lowering the inorganic dissolved salts concentration to an acceptable level. Considering the large requirement of dilution water, such an alternative cannot be acceptable. Further in most cases there would also be a restriction of the availability of suitable land area.

## 2. Bio-methanation and secondary treatment followed by irrigation or disposal in surface water

In order to reduce the requirement of dilution water to meet the prescribed standards, a secondary biological treatment process is used.

The activated sludge process, trickling filters, extended aeration etc. are the most commonly used secondary treatment systems adopted. But such systems are capable of reducing the BOD level to about 500-800mg/L. Moreover, the process is energy intensive with no return on investment. Power requirement for the aeration process is directly proportional to the BOD removed.

Assuming the BOD of the final effluent from the aerobic treatment as 500-700mg/L, it will be diluted in the ratio to 1:5-7 for BOD, for application in land for irrigation. In case the water is to be disposed in inland surface water, effort should be made to treat the effluent a BOD level of at least 300-500 mg/L. In such a case, the required dilution would be 10 to 15 times to meet the standard of 30mg/L BOD.

Even if 30 mg/L BOD is achieved by dilution, the problem of colour would still persist.

## 3. Composting, after or without Bio-methanation

The composting process consists of converting the spent wash into useful manure. This is done with the help of specialized microbial culture or using fresh compost as seed for the microorganisms. The raw materials required for composting are spent wash, bacterial culture and filler material. The most common filler material is press-mud obtained from sugar factories. Other options are agricultural residue such as bagasse, segregated municipal waste and ash.

Composting should be carried out on an impervious floor and lined pits. The composting and storage area should be raised or protected by bunds so that the surface run off during rainy season does not wash off any of the spent wash and lead to any contamination of ground water and surface drains.

Success of the process is dependent on the availability of press mud from sugar factories or any other suitable filler material. For a 30KLPD distillery generating 400-450 KLPD spent wash, about 180 T press mud would be required. In general, press mud produced in a sugar mill is about 4% of sugarcane crushed and the capacity of the mill would be 4500T of sugarcane per day.

Since the operation of sugar mills is seasonal (5-6 months) and distilleries run on an average 300 days per year, arrangements for alternative source of filler material or an alternate spent wash treatment is required. Availability of bagasse as an alternate source of filler material does not arise on the basis of net energy balance compared to cogeneration. On the other hand, installation of single or multiple stage reboilers to concentrate spent wash is not a wise proposition on the basis of energy consumption. Moreover, land availability for composting is another problem.

## 4. Concentration and incineration with energy recovery

Concentration or drying the spentwash and burning it with auxiliary fuel (bagasse and coal), with energy recovery in the form of steam, is the most attractive alternative as it leaves a small amount of residue which could also be used as fertilizer. However, experience with continuously operating full scale plant is not yet available (CPCB, 2002). Moreover, economics for evaporation plus drying of spent wash shows a net burden of more than 53 percent of total revenue generation per liter of alcohol production for a 60 KLPD distillery capacity generating power by cogeneration (Bandyopadhyay, 2004). The problems associated with this system are:

- Corrosion and scaling of evaporator surfaces are very acute.
- The fly ash poses serious problems mainly itching and health hazards like respiratory disease.

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- Loss of alcohol production due to stoppage of boiler for 4 hr./day for cleaning the evaporator.
- Combustion process needs attention in terms of quality spray, air injection, mixing pattern, temperature, profile, pressure drop, the handling of heavy ash etc. (Venkateshwaran, 1987; Panda and Panda, 1991).

So, after critical and thorough analysis of different options practiced for the treatment of spent wash the various problems which are still remaining are as follows:

- Treated spent wash does not meet BOD level as per CPCB norms.
- To attain that norm, huge amount of dilution water is required. Hence, possibility of ground water depletion.
- Does not focus on water conservation.
- Besides biomethanation all other secondary and tertiary treatment plant are energy extensive and no return on investment.
- Possibility of ground water contamination in case of composting and surface disposal.
- Land requirement is high.
- Problem of colour still persisting.

Therefore, decolourisation of anaerobically digested spent wash (ADSW) is the ultimate solution to overcome all these problems mentioned above.

Biological and physicochemical methods are the two main approaches for colour removal of spent wash. Physicochemical processes have many disadvantages, such as:

- Economic constraints.
- Technical reasons of process scale up in case of electrocoagulation, electrode system and sonication.
- Enormous chemical consumption in case of precipitation.
- Low colour removal efficiency is very common in many cases with high volume of solid waste left behind (in adsorption) leading to secondary pollutant generation.
- Operational stability.

Whereas, biological treatment with microbial biodegradation/decolourisation methods are advantageous and becoming attractive because of following reasons:

- They are environment friendly.
- Non-specific.
- Wide range of operation and they are cost competitive alternatives to chemical methods (Mossvi et al., 2005; Nwuche and Ugoji et al., 2010).

Therefore, biological treatment is preferable.

## V. COLOUR REMOVAL OF SPENT WASH BY BIOLOGICAL SYSTEM

### 1. Colourants in spent wash

Spent wash has dark brown colour and objectionable odour. The dark brown colour becomes darker (like chocolate colour) after biomethanation followed by secondary treatment. This dark colour is due to the presence of brown polymers called melanoidins which are formed by the Maillard amino carbonyl reaction taking place between the amino and carbonyl groups in organic substances (Wedzicha and Kaputo, 1992). Spent wash is believed to resemble humic acid in its properties (Ivarson and Benzing-purdie, 1987). These compounds are highly recalcitrant and have antioxidant properties, which render them toxic to many microorganisms, typically present in wastewater treatment processes (Kitts et al., 1993).



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Phenolics (tannic and humic acid from the feedstock), melanoidins from maillard reaction of sugars (carbohydrates) with proteins (amino groups), caramels from overheating sugars and furfurals from acid hydrolysis mainly contribute to the dark brown colour of spent wash (Kort, 1979). During heat treatment, the maillard reaction (non-enzymatic reaction) takes place accompanied by formation of a class of compounds, known as Maillard products. The reaction proceeds effectively at less than 50°C and is favoured at a pH 4 to 7 (Morales and Jimnez-perez, 2001). Melanoidins are one of the final products of the maillard reaction. They are complex compounds with their structure not fully understood. The basic structure of melanoidins is presented in fig.-1.

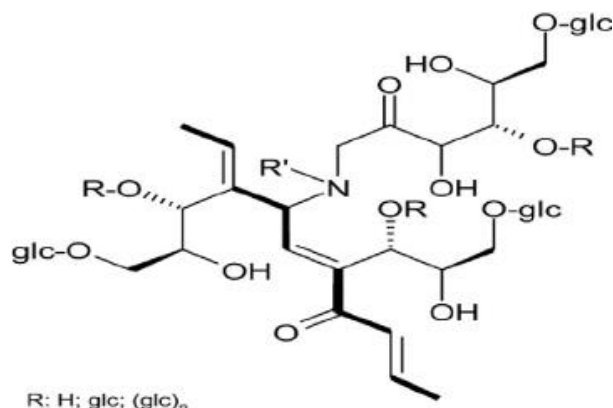


Fig.1 Basic structure of melanoidin.

The molecular weight distribution is between 5000 and 40,000. It consists of acidic, polymeric and highly dispersed colloids, which are negatively charged due to the dissociation of carboxylic acids and phenolic groups (Manishankar, Rani and Vishwanathan, 2004).

Caramel is formed by Caramelization process. Caramelization occurs when sugars are heated in the absence of nitrogen containing compounds. During a Caramelization reaction, the sugar first undergoes dehydration and then condensation or polymerization into complex molecules. Lightly coloured, pleasant tasting caramel flavors are produced during initial stages, but as the reaction continues, higher molecular weight bodies are produced which are more bitter (Yaylyan and Kaminsky, 1998).

### 2. Microbial decolourisation

Microbial degradation and decolourisation of industrial wastes is an environment friendly and cost competitive alternative to chemical decomposition process of waste minimization (Mohana et al., 2007; Pant and Adholeya, 2007). The degradation of various toxic and recalcitrant compounds present in industrial waste is measured in terms of decrease in absorbance at a particular wavelength corresponding to the compounds, bacterial growth, increase in biomass and reduction in colour intensity. However, the waste water released from distilleries is highly acidic in nature and has a variety of recalcitrant colouring compounds as melanoidins, phenolics and metal sulphides responsible for the dark colour having high inhibitory and anti-microbial activity (Dahiya et al., 2001b), slow down the anaerobic digestion process of distillery spent wash. The pH of spent wash increases from 4.8 to 8.0 during anaerobic treatment process. Many workers have isolated several aerobic, anaerobic, and facultative bacterial strains and studied the degradation and decolourisation of anaerobically treated spent wash by these organisms in terms of decrease in absorbance at 475 nm, growth at 620nm, increase in mass and reduction in colour intensity (Ramesh Kumar et al., 2017; Santal et al., 2016, Sankaran et. al., 2015; Mohana et al., 2007, Adikane et al., 2006; Kumar and Chandra, 2006). Kumar and Viswanathan (1991) had isolated some bacterial strains from sewage and acclimatized on increasing

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concentration of distillery waste, which were able to reduce COD by 80% in 4-5 days without aeration and the major products left after the degradation process were biomass, carbon dioxide and volatile acids. *Pseudomonas fluorescence* decolourised melanoidin present in wastewater upto 76% under non-sterile conditions and upto 90% in sterile samples (Dahiya et al., 2001a) and this difference in decolourisation might be due to the fact that melanoidin stability varies with pH and temperature and at higher temperature during sterilization melanoidins decompose to low molecular weight compounds (Ohomomo et al., 1987). Sirianuntapiboon et al., 2004 used an acetogenic bacterium to obtain a decolourisation yield of 76.4 % under optimal nutrient condition. Ghosh et al., (2004) have also isolated bacterial strains capable of degrading recalcitrant compounds from soil of effluent discharge site which were *Pseudomonas*, *Enterobacter*, *Stenotrophomonas*, *Aeromonas*, *Acinetobacter* and *Klebsiella*, all of which could carry out degradation of biomethanated spentwash and maximum 44% COD reduction was achieved using these bacterial strains either singly or collectively.

Several types of fungi have been used for the decolourisation of melanoidins in connection with colour removal of waste water from the distilleries (Thakkar et al., 2006; Raghukumar et al., 2004; Angayarkanni et al., 2003; Raghukumar et al., 2001; Kumar et al., 1998; Miranda et al., 1996). The larger molecular weight fractions of melanoidin were decolourised rapidly, while the smaller molecular weight fractions remained in solution and metabolized slowly. The decolourisation was less in sterilized spent wash than in non-sterile condition. The decrease in colour removal efficiency might be due to the fact that the effluent taken for the study was alkaline (pH 8.5) and melanoidins responsible for colour were more soluble in the alkaline pH. In the acidic pH, the melanoidins might be precipitated and removed easily. It was suggested that decolourisation by fungi takes place due to the destruction of coloured molecules and partially because of sorption phenomena. Microbial decolourisation of melanoidins is due to two decomposition mechanisms, in the first, the smaller molecular weight melanoidins are attacked and in the second, the larger molecular weight melanoidins are attacked (Ohomomo et al., 1985b). Under nutrient limiting conditions, fungal cells generally cannot remain active during a long-term cultivation. Therefore, the continuous culture method is not practical, and the semi batch method can be an alternative for long-term cultivation.

### 3. Role of enzymes in melanoidin degradation

The enzymatic system related to decolourisation of melanoidins is yet to be completely understood and it seems greatly connected with fungal ligninolytic mechanisms. Several studies regarding degradation of melanoidins, humic acid and related compounds using basidiomycetes have also suggested the participation of different categories of enzymes as Watanabe et al., (1982) have reported. The enzymatic degradation of melanoidins by *Coriolus sp.* No. 20 having an intracellular enzyme required oxygen molecules and sugars in reaction mixture. The enzyme was later identified as Sorbose oxidase. The purified enzyme aerobically decolourised the melanoidin pigments in presence of glucose, sorbose, galactose, xylose and maltose. But maximum activity was observed with sorbose as well as glucose. Melanoidins were suggested to be decolourised by the active oxygen ( $O_2^{\cdot-}$ ,  $H_2O_2$ ) species produced by the reactions catalyzed by enzymes probably oxidases because the reactions with pure enzyme was accompanied by the oxidation of glucose into gluconic acid.

Aoshima et al., (1985) reported that melanoidins decolourisation activity of *Coriolus versicolor Ps4a* was mainly due to intracellular enzyme that are induced by melanoidins. The induced enzymes consisted of two components, namely sugar dependent enzymes forming two third part and other sugar independent part constituting one third part of system. The sugar dependent enzyme might be same as that of sorbose oxidase as reported by Watanbe et al., (1982) or a same type of sugar oxidase and this was the first report about the existence of sugar independent enzyme decolourising melanoidins. Ohomomo et al., (1985a) used *C. versicolor Ps4a*, which decolourised molasses waste water 80% in darkness under optimum conditions. Decolourisation activity involved two types of intracellular enzymes, sugar dependent and sugar independent. One of these enzymes required no sugar and oxygen for appearance of activity and could decolourise molasses wastewater upto 20% darkness and 14-17% of synthetic melanoidins. Thus, the participation of these  $H_2O_2$  producing enzymes as part of the complex enzymatic system for melanoidins degradation by fungi should be taken into account while designing any treatment strategy. Colour removal of synthetic melanoidins by *Coriolus hirsutus* involves the participation of peroxidases (MnP and MIP) and the extracellular  $H_2O_2$  produced by glucose oxidase without disregard of a partial participation of fungal laccase.

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The magnesium peroxidase (MnP) has also been reported in bacteria as extracellular enzyme for decolourisation of melanoidin (Bhargava et al., 2009).

One of the more complete enzymatic studies regarding melanoidin degradation was reported using pallets of *Coriolus hirsutus* by Miyata et al., (1998). They used the *C. Hirsutus* pallets to decolourise a melanoidin containing medium. It was elucidated that extracellular H<sub>2</sub>O<sub>2</sub>, and two extracellular peroxidases, a manganese-independent peroxidases (MIP) and manganese-peroxidase (MnP) were involved in decolourising activity. But the detail role of MnP and laccase in bacteria for decolourisation has not been fully investigated.

The MnP and laccase activity in the bacterial culture supernatant decreases with the increase in the duration and further bacterial incubation showed gradual decrease of both enzyme activities. The enzymes activity has direct correlation with melanoidin decolourisation. The initiation of MnP activity in culture supernatant starts at 48 hr. of bacterial growth and remains active for 192 hr, whereas the laccase induction starts at 96 hr. and its activity decreased after 192 hr. This resulted in the initial role of MnP in melanoidin degradation (Yadav et al., 2012). The melanoidin decolourisation has also been reported by enzyme laccase in bacteria (Bhargava et al., 2009).

The white rot basidiomycetes fungus *F. flavous* produces extracellular enzymes, manganese dependent peroxidases (MNP), lignin peroxidases (LIP) and laccase which decolourises a number of synthetic dyes like Poly R and remazol brilliant blue R etc. (Raghu Kumar et al., 1999). They propose that hydrogen peroxide produced as a result of glucose oxidase activity acts as a bleaching agent on biometanated spent wash which has been further confirmed that in the absence of glucose the decolorization of MSW is lesser. With the addition of the starch to the medium, amylase activity stimulates and releasing reducing sugars, which are oxidized by glucose oxidase producing peroxide as a by-product results in greater decolourisation of biometanated spentwash (Raghu Kumar et al., 1999).

After considering the wholestic approach of the problem it is clear that treated spent wash doesn't meet Central Pollution Control Board (CPCB) standard of discharge into streams or land application. Moreover, groundwater colourisation is a standing problem for areas nearer to distilleries. So, microbial decolourisation of spent wash is the only solution which can be exploited to develop a technology that will not only be cost effective, eco-friendly with water conservation but also would meet CPCB discharge norm as well as zero discharge. Therefore, simultaneous decolourisation and crop cultivation in immobilized artificial soil might be the complete solution of these unsolved and persistent problems (Bandyopadhyay and Paul, 2013, 2015, 2017).

### VI. SIMULTANEOUS DECOLORIZATION AND CROP CULTIVATION IN IMMOBILIZED ARTIFICIAL SOIL BED

Technologies available in the present-day market to treat biometanated spent wash to the level of MOEF/CPCB discharge norms are highly energy intensive, expensive, land oriented, prone to ground water contamination and no return on investment. So, there is a need of the hour to develop a cost-effective technology to attain zero discharge with ROI (Bandyopadhyay and Paul, 2013 & 2015). The filed patent (Bandyopadhyay and Paul, 2013) has provided a solution to it by suggesting a physicochemical biosystem comprising consortium of bacteria immobilized in artificial soil for the decolourisation of industrial effluents along with its novel composition and method of preparation. This artificial soil would decolourise the effluent by degrading melanoidin present in it during the process of operation. Cultivation of seasonal crops (like sunflower, cane and paddy) was carried out on the top of the bed by irrigating decolourised effluent (pastel colour- fig.-2) without additional inputs of conventional fertilizer and groundwater. The system would restrict ground water contamination because of recycling of decolourised effluent (collected in pits) to the plant and hence zero discharge is attained.



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Fig. 2 Samples of raw and decolourised effluent.

All these claims were demonstrated in 10KLPD pilot plant (fig.-3) for simultaneous decolourisation and crop cultivation in immobilized artificial soil bed (Bandyopadhyay and Paul, 2017). The pilot plant was operated continuously on 0.155 acre (625m<sup>2</sup>) of land in eastern U.P. using biomethanated spent wash having input COD in the range of 20,000-23,000 mg/l for a period of 3-4 months. The schematic diagram of the pilot plant is presented in fig.-2.

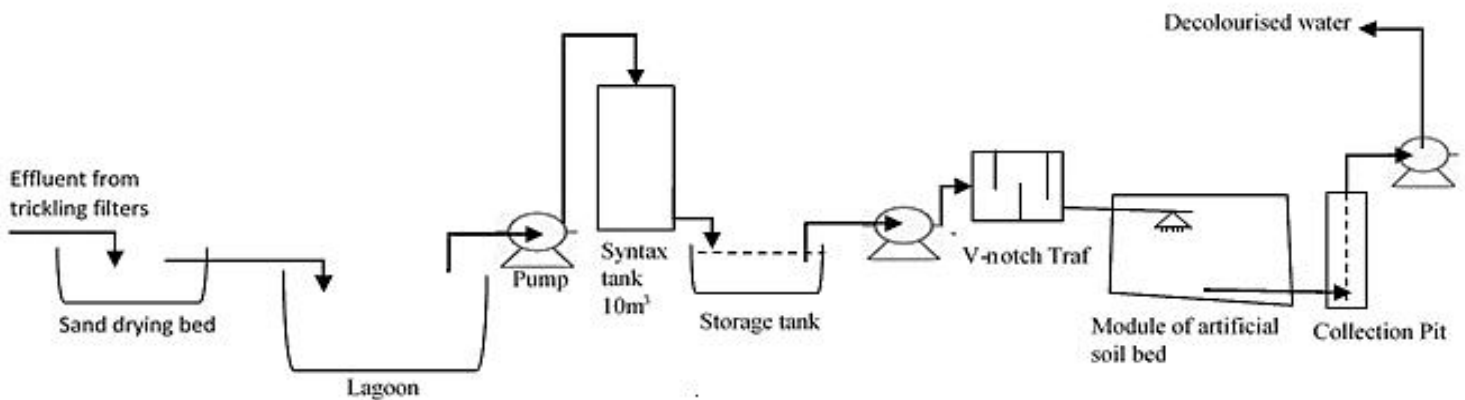


Fig. 3 Schematic flow diagram of 10KLPD pilot plant for simultaneous decolourisation and crop cultivation.

The artificial soil formulation, having desirable flow properties like critical hydraulic velocity, seepage velocity, soil bed compaction factor, porosity and conductivity etc. is lighter than natural soil. The hydraulic retention time and COD loading (200-220 kg/day) are manipulated by suitable pipe line distribution system comprising specially designed network of coils to provide required seepage velocity to optimize melanoidin degradation which in turn would reduce COD and colour to the tune of 96-98% and 98-99% respectively. The physico-chemico-biosystem increases the fertility of the soil by arresting various micronutrient of the effluent during the process (Bandyopadhyay and Paul, 2015). So far as the fertility of the artificial soil is concerned, it is normal with medium organic carbon (C) and very high in available phosphorous (P) and potassium (K) as compared to normal soil with low carbon and minimum amount of available phosphorous (P) and

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potassium (K). The decolourised effluent (Pastel colour, COD: 800-1000mg/l and BOD >25 mg/l) collected in the pits was used for irrigating the bed for the cultivation of crops. The crop productivity increases more than 2 folds (fig.4).

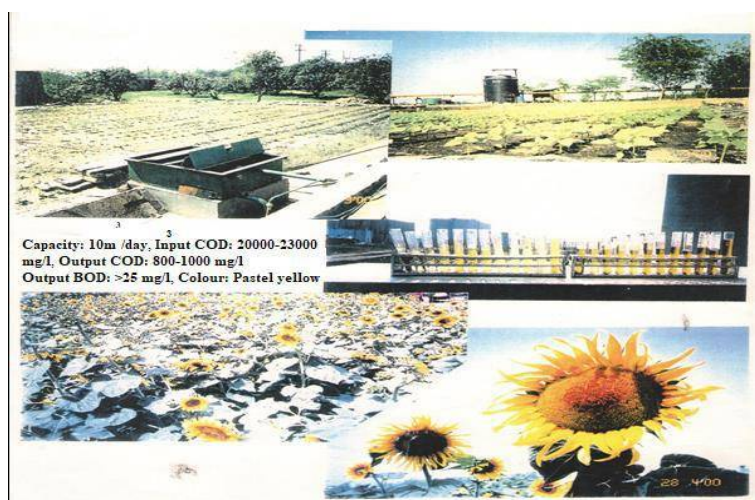


Fig. 4 Pilot plant studies on Simultaneous decolourisation and crop cultivation in Immobilized soil bed.

### Advantages of the process:

- The pilot plant is capable to degrade COD and decolourise to the tune of 96-98% and 98-99% respectively. The final COD level would be in the range of 800-1000 mg/l and BOD less than 25 ppm
- Decolourised effluent meet CPCB norms.
- The plant attains zero discharge (CPCB 2008).
- No ground water contamination.
- Higher soil fertility.
- Good ROI because of increase in crop yield more than two-fold and also by selling soil of the bed for terrace and kitchen garden.
- Water conservation is achieved by recycling the decolourised water for irrigation of crops.
- Generation of rural employment.

## VII. CONCLUSION

This review article is presented with the consideration of the need of distillery industry. Different treatment strategies available today to treat spent wash are unable to meet the target of zero discharge. Considering ROI, biomethanation coupled with decolourisation and crop cultivation in artificial soil bed is the best option and can be exploited to develop a cost effective eco-friendly technology for the treatment of spent wash. Operational stability of the system can be met by supplementing wasted molasses as carbon source and oxygen with sparged air through low cost sparger to make the system cost effective and promising.

### Acknowledgement

Authors express their deep sense of gratitude to founder President, Dr. Ashok K. Chauhan, Amity University, U.P. for his continuous encouragement in writing this manuscript. We are also indebted to Balrampur Chini Mills, Balrampur, U.P. for their help and assistance.

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