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Physico-chemical Methods for Colour Removal of Waste Water in molasses-based alcohol distilleries: A Review

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Abstract:

The effluent from molasses based distilleries contains high organic content & also contains nutrients in the form of nitrogen, phosphorus & potassium & colour causing melanoidin that can lead to eutrophication of water bodies. Also hinders photosynthesis by blocking sunlight & is therefore deleterious to aquatic life. Different processes including anaerobic, aerobic as well as physicochemical methods have been employed to treat this effluent. Further treatment to reduce residual organic constituents & Colour includes: i) Biological methods employing different fungi, bacteria & algae, & ii) physicochemical methods such as adsorption, coagulation/ precipitation, oxidation & membrane filtration.

This review paper presents the effect of melanoidin, existing status & advances in physiochemical methods applied to the treatment of molasses based distillery wastewater for Colour (i. e. melanoidin) removal.

Keywords: Molasses, Distillery, Spentwash, Decolourisation, Melanoidin , Effluent.

Introduction:

The manufacture of ethanol from molasses generates large volumes of high strength wastewater as alcohol distilleries generating an average of 8-15 litres of effluent per litre of alcohol produced (Saha et al., 2005, S. Mohana., 2009). The production & characteristics of spentwash is highly variable & dependent on feedstocks & various aspects of the ethanol production process (Durate et al .,1997). This effluent is characterized by extremely high chemical oxygen demand (COD) (80,000 -100,000 mg /l) & biochemical oxygen demand (BOD) (40,000-50,000 mg / l) , apart from low pH , strong odour & dark brown colour . The distillery wastewater contains high organic content & also contains nutrients in the form of nitrogen (1660-4200 mg/l), phosphorus (225-3038 mg/l) & potassium (9600-17,475mg/l) that can lead to eutrophication of water bodies (Mahimairaja & Bolan, 2004) . The reason is due to the presence of water soluble recalcitrant colouring compound called melanoidin (Evershed et al., 1997). Further, it's dark colour hinders photosynthesis by blocking sunlight & is therefore deleterious to aquatic life. The colour is due to the presence of brown polymers melanoidins, which are formed by Maillard amino carbonyl reaction (Kumar et al .,1997, Plavsic et al.,2006). Since conventional methods can accomplish only low degradation of melanoidins, it is necessary to explore additional treatments to remove colour from molasses effluent & prevent serious environmental problems that coloured waste water scan promote in river courses such as reduction of photosynthetic activity & dissolved oxygen concentration. Mellanoidins can be removed by physicochemical treatments, but these methods require high reagent dosages & generate large amount of sludge (Pena et al., 2003). Studies on water quality of a river contaminated with distillery effluent displayed high BOD values of 1600-21000mg/l within a 8 km radius. Adequate treatment is therefore imperative before the effluent is discharged.

From earlier review on this subject, workers Wilkie et al. (2000) have examined characteristics & anaerobic treatment of effluent obtained from different feedstock used for ethanol manufacture. This review focuses on advances in molasses-based distillery wastewater treaement for colour removal & emerging technologies in this area.

Physico-chemical Characteristics of wastewater generated:

The main source of waste water generation is the distillation step where the large volumes of dark brown effluent i.e. spentwash is generated (Patil et al . 2003 ,Y. Satyawali, 2008.). The distillery spentwash is hot, highly coloured & acidic with strong & objectionable odour that presents significant disposal or treatment problem.(R. Agarwal, 2010). The characteristics of the spentwash depend on the raw materials used, also estimated that 88% of the molasses constituents end up as waste. Molasses spentwash has very high levels of BOD, COD, COD/BOD ratio as well as high potassium , phosphorus & sulphate content (Table 1) in addition , sugar cane molasses spentwash contains low molecular weight compounds such as lactic acid , glycerol, ethanol, & acetic acid. Sugarcane molasses also contains 2% of a dark brown pigment melanoidins that impart colour to the spentwash. Melanoidins are low & high molecular weight polymers formed as final products of Maillard reaction. (Martins & van Boekel,2004) The structure of melanoidins is still not well known . Due to their structural complexity , dark colour & offensive order, these pose to serious threat to soil & aquatic ecosystem that release of melanoidin cause increased load of recalcitrant organic material to natural water bodies. This then causes the problem, like reduction of sunlight penetration, decreased photosynthetic activity & dissolved oxygen concentration whereas on land, it causes reduction in soil alkalinity & inhibition of seed germination (R. Agarwal, 2010). Melanoidins have antioxidant properties & are toxic to many microorganisms involved in wastewater treatment. Further due to the possibility of complaxation reaction of introduced melanoidin with metal ions, they could influence the biogeochemical cycle of many constituents in natural water (Chandra et al, 2008), which are highly resistant to microbial attack. Apart from melanoidins, spentwash contains other colourants such as phenolics, caramel & melanin. Phenolics are mainly presents in cane molasses wastewater & melanoidin is significant in beet molasses. (Y. Satyawali, 2008) . Hence the wastewater requires pretreatment before it's safe disposal in to the environment (Kumar & Chandra, 2006., Mohana et al.,2007).

Physiochemical Treatments:

After biological treatment the effluent still retains the dark colour., as the multistage biological treatment reduces the organic load but intensifies the colour due to repolymerisation of coloured compounds (Pena et al .,2003 ;Y. Satyawali 2008). Conventional anaerobic & aerobic treatment can accomplish degradation of melanoidin upto only 6-7%. Therefore it is necessary to study about additional treatments required to decolourise distillery effluent (Pena et al .,2003) Thus for colour removal Various physico-chemical treatment options have been explored .

Coagulation & flocculation:

The decolourisation by coagulation is effective with the help of agent like lime. The optimum dosage of lime was found to be 10g/l resulting in 67.6% reduction in colour in a 30 min period. Migo et al.(1993) who used a commercial polymer of ferric hydroxyl sulphate $[Fe_2(OH)_n(SO_4)_{3-n/2}]_m$ for the treatment of molasses wastewater which resulted in 87% decolourisation for biodigested effluents.

$FeCl_3$ & $AlCl_3$ together also effective in decolourisation of biodigested effluent & showed similar colour removal efficiencies. About 93% decolourisation when either $FeCl_3$ or $AlCl_3$ was used alone. The process was independent of chloride & sulphate ion concentration but adversely affected by high fluoride concentration (Sowmeyan and Swaminathan, 2008)

The complete decolourisation almost 98% of biologically treated distillery spent wash is possible with conventional coagulants such as ferrous sulphate, ferric sulphate & alum under alkaline conditions (Pandey et al.2003) The 99% decolourisation were done by using Percol 47 , a commercial organic anionic polyelectrolyte , in combination with ferrous sulphate & lime. (Mandal et al. 2003) . Also the iron pickling waste water gave 98 % colour removal.

Adsorption:

Bernardo et al ., 1997 were reported the decolourisation of synthetic melanoidin using commercially available activated carbon as well as activated carbon produced from sugarcane bagasse .

Chemicaly modified bagasse using 2-diethylaminoethyl chloride hydrochloride & 3-chloro-2-hydroxypropyltrimethylammonium chloride was capable of decolourising diluted spentwash (Mane et al. 2006). 0.6g of chemically modified bagasse in contact with 100ml 1:4 (v/v) spentwash: water solution resulted in 50% decolorisation after 4 hrs contact with intermittent swirling. (Y. Satyawali, 2008) . Adsorption by commercially available powdered activated carbons resulted in 18% colour removal, whereas combined treatment using coagulation – flocculation with polyelectrolyte followed by adsorption resulted in almost complete decolourisation (Sekar, Murthy 1998). The treatment of distillery wastewater by using chitosan (as an anion exchanger) at an optimum dosage of 10g/l & 30min contact time, 98% colour removal was observed. The Chitosan is natural carbohydrate polymer derived from exoskeleton of crustaceans (Lalvo et al. 2000).

Bagasse flyash & activated carbon the low cost adsorbent has high carbon content . 58% colour removal was reported with 30g/l bagasse fly ash & 80.7% with 20g/l of commercial activated carbon. (Mall & Kumar 1997).

Oxidation Process:

Wet air oxidation process & oxidation with the help of ozone has been successfully used for colour removal.

Almost ozone has been applied for treatment of dyes, phenolics, pesticides, etc. as it destroys hazardous organic contaminants (Pena et al., 2003). Both ozone & hydroxyl radicals are stong oxidants & are capable of oxidizing a number of compounds (Bes-Pia et al.,2003). It has been observed that oxidation by ozone could achieve 80% colour removal for biologically treated spentwash. However, ozone only transforms the chromophore groups but does not degrade the dark coloured polymeric compounds in the effluent (Alfafara et al. 2000). Fenton's reagent ,which involves homogeneous reaction & is environmentaly acceptable , is a mixture of hydrogen peroxide & iron salts which produces hydroxyl radicals which ultimately leads to decolourisation of the effluent (Pala and Erden, 2005). 97% colour removal was observed after oxidation of effluent with chlorine, but colour reappeared after a few days (Mandal et al, 2003).

Wet air oxidation process has been recommended as part of a combined process scheme for treating anaerobicaly digested spent wash (Dhale & Mahajani, 2000). The post anaerobic effluent was thermally pretreated at 150 ^{0}C under pressure in the absence of air. This was followed by soda lime treatment, after which the effluent underwent 2hrs wet oxidation at 225^{0}C, 95% colour removal was obtained in this process.

Conclusion:

The review indicates that the use of an individual process alone may not treat the waste water completely. A combination of these processes is necessary to achieve the desirable norms.

After Biological treatments the distillery spent wash still retains the dark brown colour due to presence of melanoidin. The properties of colour causing melanoidin are not fully understood. Physico-chemical treatment methods especially coagulation & flocculation, adsorption and oxidation are effective after biological treatments, for both colour and organic load reduction. So it is essential to identify the limitations of existing methods & to develop effective and commercial treatment processes which can provide the complete remedy for colour removal of distillery spent wash.

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Table No. 1: Characteristics of spentwash generated from various feedstock (Pathade, 1999; Wilkie et al, 2000 ; Y.Satyawali 2008)

Sr. No.	Characteristics	Feedstock	
		Cane molasses Pathade (1999)	Beet molasses Wilkie et al. (2000)
1	COD (mg/l)	65,000-130,000	91,100
2	BOD (mg/l)	30,000-70,000	44,900
3	COD/BOD ratio	2.49	1.95
4	Total solids (mg/l)	30,000-100,000	-
5	Total suspended solids (mg/l)	350	-
6	Total dissolved solids (mg/l)	80,000	-
7	Total nitrogen (mg/l)	1000-2000	3569
8	Total Phosphorus (mg/l)	800-1200	163
9	Potassium (mg/l)	8000-12,000	10,030
10	Sulphur as SO4	2000-6000	3716
11	pH	3-5.4	5.35