

Distillery Spent Wash Treatment: Model Degradation of Synthetic Melanoidin by In-Situ Chemical Oxidation

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Abstract

The ever-increasing generation of distillery spent wash in one hand and stringent legislative regulations of its disposal on the other has stimulated the need for developing new technologies to process this effluent efficiently and economically. The distillery generates large volumes of dark brown coloured, acidic wastewater called spent wash, which is highly acidic in nature and having recalcitrant coloring compound as melanoidin. In the present paper, detailed studies on the in situ chemical oxidation of melanoidin using persulfate as oxidizing agent and activation of it by heat was investigated. The effect of various operating parameters such as oxidant dosage, initial concentration of melanoidin and pH of solution on the degradation of melanoidin have been studied and optimized.

Keywords: In situ chemical oxidation, melanoidin, activated persulfate.

Introduction

One of the most important environmental problems faced by the world is management of wastewater^[1,36]. Industrial processes create a variety of wastewater pollutants which are difficult and costly to treat. Wastewater characteristics and levels of pollutants vary significantly from industry to industry. Now-a-days emphasis is laid on waste minimization and revenue generation through byproduct recovery^[19]. Pollution prevention focuses on preventing the generation of wastes, while waste minimization refers to reducing the volume or toxicity of hazardous wastes by water recycling and reuse and process modifications^[4].

Distillery spent wash refers to the effluent generated from alcohol distilleries^[1]. The alcohol distilleries are extensively growing due to widespread industrial applications of alcohol such as in pharmaceuticals, food, cosmetics, perfumery etc. It is also used as an alternate fuel. Distilleries are amongst the most water intensive industries, and have been ranked as heaviest polluter among 17 heavily polluting industries by the Ministry of Environment & Forests, India. There are 319 distilleries in India alone, producing 3.25 billion liters of alcohol and generating 40.4 billion liters of wastewaters annually^[2-4]. As 8-15 lit of effluent is generated for production of 1 lit alcohol. As per the Ministry of Environment and Forests (MoEF), alcohol distilleries are listed at the top in the “Red Category” industries^[1-3].

Approximately 88% of the raw material is converted in waste and released as wastewater^[2-37]. The high BOD, COD and TSS content in the distillery effluent makes it imperative to develop an elaborate treatment solution for attaining zero liquid discharge^[4]. The industry generates large volumes of dark brown coloured (black liquor), acidic wastewater called spentwash, which is highly acidic in nature and has a variety of recalcitrant coloring compounds as melanoidins, phenolics and metal sulfides. It contains nearly 2% of melanoidin, due to which it gains dark brown colour^[4-7] means approximately 0.808 billion liters of melanoidin is generated annually.

Distillery wastewater contains high organic load causing a large chemical oxygen demand (COD) ranging from 70,000 to 1,00,000 mg/L and a large amount of colored substances which give dark brown color, to the effluents^[14]. After the conventional biological treatment, quite of the organic load is removed but nevertheless the dark brown color still persists, it can even increase because of the polymerization of colored compounds^[14-15]. The main colored compounds are known as melanoidins formed via Maillard reaction which is initiated by the condensation of an amine with a carbonyl group, often from a reducing sugar^[5].

With government policies on pollution control becoming more and more stringent, distillery industries have been forced to look for more effective treatment technologies. Such technologies would not only be beneficial to environment, but also be cost effective^[3-4]. Central Pollution Control Board (CPCB), the national agency responsible for environmental compliance stipulated that, distilleries should achieve zero discharge in inland surface watercourses. Consequently, the wastewater needs to undergo extensive treatment in order to meet the stipulated environmental demands^[1-3].

Melanoidin is a recalcitrant polymer formed by maillard reaction, named after the French chemist Louis Maillard who first described such conversion reactions in 1912, but it was only in 1953 that the first coherent scheme was put forward by Hodge^[8-10]. The Maillard reaction, which is a non-enzymatic browning reaction, is a complex network of reactions involving carbonyl and amino compounds, such as reducing sugars and amino acids. It is the main reaction responsible for the transformation of precursors into colorants^[8].

The synthetic melanoidin solution can be prepared by refluxing the equimolar (1M) solution of sugar (glucose), amino acid (glycine) and 0.5 M sodium bicarbonate at 100°C for 7 h or at 90°C for 9 h^[11-13]. Croh proposed the proposed structure of melanoidin, having an empirical formula of $C_{17-18}H_{26-27}O_{10}N$ and molecular weight between 5000 and 40,000Da^[13-30] as shown in fig.1. Melanoidins are major pollutant when discharged into a water resource system, due to dark colour they impart, prevent the penetration of sunlight and affect the photosynthetic activity of aquatic plants^[16]. The high organic load of the effluent causes eutrophication. This will therefore create anaerobic conditions thereby killing most of the aerobic

aquatic fauna. When spread over soil, molasses wastewater acidifies soil and affects agricultural crops^[3-11].

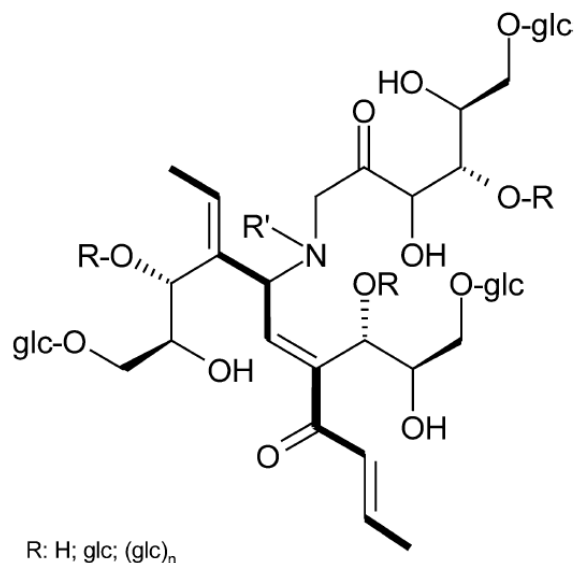


Fig.1: Structure of melanoidin proposed by Croh

As melanoidins are recalcitrant to biodegradation, the elimination of colored effluents in molasses-based distillery wastewater treatment system is mainly based on physic-chemical methods^[17-29] are not efficient for decolorisation^[37] and so advanced methods such as adsorption^[12-13], coagulation and flocculation^[18], oxidation^[14], electrochemical oxidation^[24] photo catalytic oxidation^[25], ultrasound^[34-35] and membrane techniques^[31-33] are efficient techniques. Although these methods are effective, however they suffer from some short coming such as requiring high reagent dosage, high cost, formation of hazardous byproducts and intensive energy consumption. These methods also generate large amount of sludge^[5].

In situ chemical oxidation, a form of advanced oxidation processes and advanced oxidation technology, is an environmental remediation technique used for soil and/or groundwater remediation to reduce the concentration of targeted environmental contaminants to acceptable levels^[7-19]. ISCO is accomplished by injecting or otherwise introducing strong chemical oxidizers directly into the contaminated medium may be in soil or groundwater to destroy chemical contaminants in place^[20]. It can be used to remediate a variety of organic compounds^[21-22], including some that are resistant to natural degradation. The main mechanism of AOPs function is the generation of highly reactive free radicals^[19-21]. Major oxidants used for this purpose are ozone^[27], potassium permanganate^[26], Fenton's reagent^[28] and persulfate^[20-21].

The use of persulfate has recently been the focus of attention for an alternative oxidant in the chemical oxidation of contaminants^[21-23]. In our present work we have used potassium persulfate. Technically this compound is the potassium salt of peroxydisulfate (K₂S₂O₈) and is a solid white powder at standard

temperature and pressure which decomposes under moisture conditions^[20]. It's one of the strongest oxidants known in aqueous solution. It has great capability for degrading numerous organic contaminants through free radicals ($\text{SO}_4^{\cdot-}$ and OH^{\cdot}) generated in the persulfate system. It offers some advantages over other oxidants: Ease of storage and transport, high stability, high aqueous solubility and relatively low cost^[22]. Base activation, UV-irradiation, thermal activation, metal activation, and soil mineral activation have been used for generation of sulfate radical (2.5- 3.1V), a stronger oxidant than persulfate (2.01 V) itself which is initiated as^[20-23]. For activation thermal activation is better as it produces two sulfate radicals, in other activations one radical and one anion gets formed^[38].



Materials and Methods

Materials

Aqueous melanoidin solutions were prepared in Milli Q water. Potassium Persulfate was used as an oxidizing agent for in situ chemical oxidation. Acetonitrile, acetic acid, Sodium acetate, methanol and De-ionized water (DI Water) was used for analysis of sample.

Analytical procedure

The concentration of melanoidin in the samples was monitored by high performance liquid chromatography fitted with a UV detector and a C-18 column. The mobile phase was 0.55 L DI water, 0.44 L acetonitrile, and 0.5 g sodium acetate. Flow rate of mobile phase was 1 ml/min. Column temperature was 35°C.

In situ chemical oxidation experiment

Oxidation of melanoidin was conducted in a batch process. This unit is configured with an annular cylindrical reactor (Fig. 2) kept on a heating element, one side of the reactor to house the thermometer ($T = 80^\circ\text{C}$), and another condenser was provided for cooling purpose. Cooling media (water) was circulated by condenser. For each set of experiments, 10 g/L solution of melanoidin was prepared. In prepared melanoidin solution Persulfate oxidizing agent mixed and shaken well. This mixture was charge into reactor for oxidation. Samples were periodically withdrawn and analyzed by TOC analyzer and melanoidin concentration, analyzed by High Performance Liquid Chromatography (HPLC) equipped with a C-18 column.

Results and Discussions

Effect of oxidant dosage

Oxidation treatments using $\text{K}_2\text{S}_2\text{O}_8$ in suspension were performed to know its influence on degradation of melanoidin: Main goals chased in this case were the comparison of oxidant dosage. In Fig 3, the melanoidin decay curves are shown for $\text{K}_2\text{S}_2\text{O}_8$ dosage, varying from 0.5 to 2.5 g/L. Degradation of Melanoidin increased with increasing $\text{K}_2\text{S}_2\text{O}_8$ loading in the range 0.5 to 2.5 g/L. Catalyst loading of 0.5

g/L $K_2S_2O_8$ showed slow degradation of melanoidin. Catalyst loading of 2 g/L and 2.5 g/L $K_2S_2O_8$ has similar degradation. After 60 min, degradation of melanoidin in case of 2 g/L oxidant dosage was more than 2.5g/L. The 2 g/L $K_2S_2O_8$ catalyst loading showed remarkable degradation as compared to 2.5 g/L. Based on the results, the optimum potassium persulfate concentration for degradation of melanoidin in aqueous solution are 2 g/L. Potassium persulfate is a strong oxidizing agent activated by thermal activation, metal activation and alkaline activation, which is generally ascribed to have a radical formation and initiation rate.

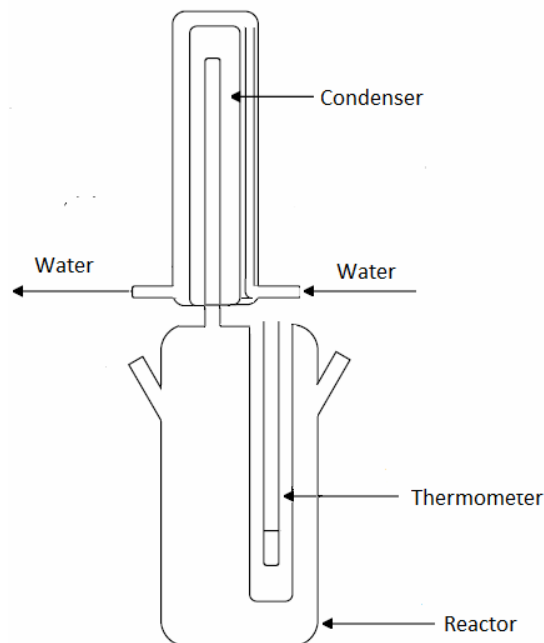


Fig.2: Reactor for in situ chemical oxidation

When $K_2S_2O_8$ concentration increases, more radical species are formed by oxidant, which in turn leads to higher concentrations of hydroxyl radicals and activated persulfate species which accelerate the degradation process. The increase in degradation with an increase in the catalyst concentration approaches a limiting value at high $K_2S_2O_8$ concentrations, and this limit depends on the solubility of the $K_2S_2O_8$ particles; when the oxidizing agent concentration is very high, saturation level opposes the further degradation.

Effect of Initial Concentrations of Melanoidin

Fig. 4 shows the effect of initial Melanoidin concentration on degradation at 2 g/L $K_2S_2O_8$. The degradation of Melanoidin at different initial concentration of 10,000 mg/L, 20,000 mg/L and 30,000 mg/L i.e. of 1%, 2% and 3% were studied. It was observed that near about 90% degradation of 10,000 mg/L of Melanoidin achieved at 120 min. The degradation rate depends on initial concentration of Melanoidin it decreases with increases in initial concentration of Melanoidin.

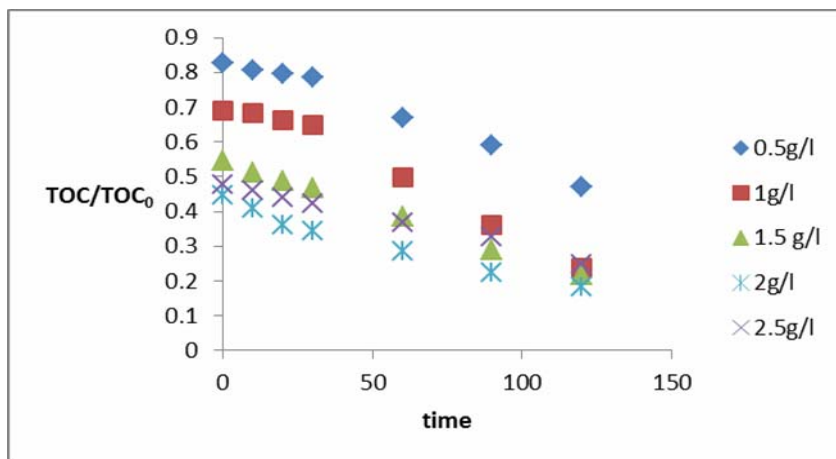


Fig.3: Effect of oxidant dosage

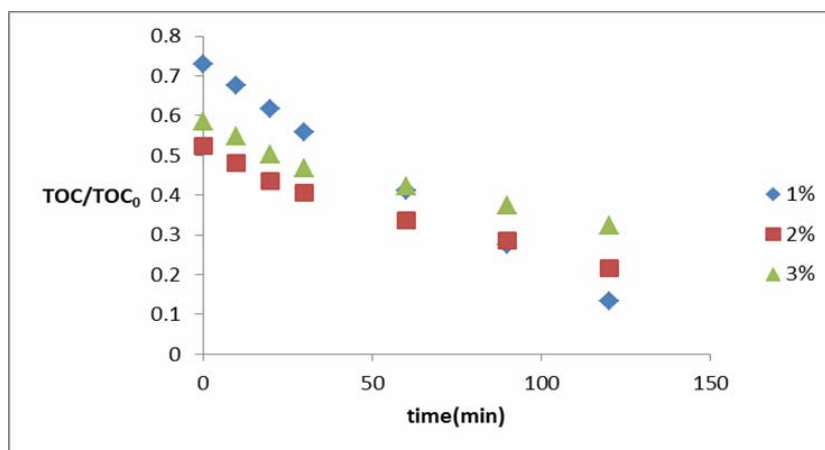


Fig.4: Effect of initial concentrations of Melanoidin

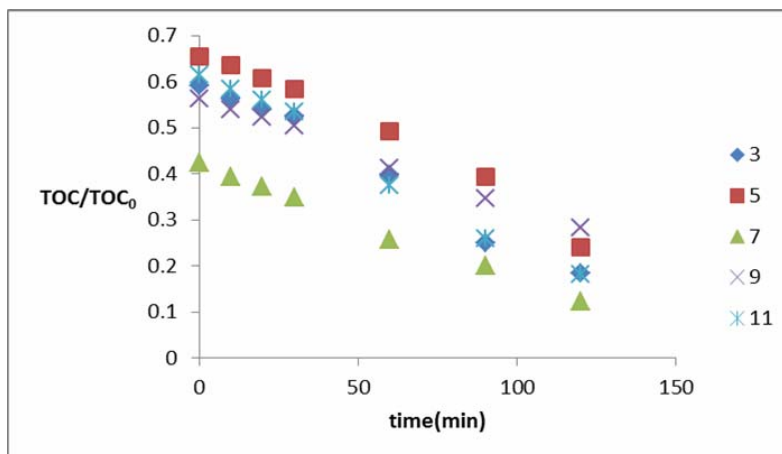


Fig.5: Effect of pH on degradation of Melanoidin

The degradation of Melanoidin were found 86%, 78% and 67% at initial concentration of Melanoidin 10,000 mg/L, 20,000 mg/L and 30,000 mg/L respectively at 120 min. It was reported in the

literature, that the oxidation reaction occurs between the contaminant substrate (Melanoidin) and OH^\bullet and $\text{SO}_4^{\bullet-}$ generated on $\text{K}_2\text{S}_2\text{O}_8$ surface. Thus although melanoidin concentration increases, the rate of degradation decreases due to a lower OH^\bullet and $\text{SO}_4^{\bullet-}$ to Melanoidin ratio.

Effect of Initial pH Value

The distillery spent wash have acidic pH and that of melanoidin have pH 5.3. pH of effluent water plays an important in degradation of pollutant, so effect of pH on degradation was studied. The pHs of melanoidin solution was changed from 3, 5, 7, 9 and 11. Fig. 5 shows the degradation of melanoidin at different pH with respect to time. In the alkaline range, the pH was varied using aqueous NaOH (1M), whereas in the acidic range, pH was varied using HCl (1M). Initial melanoidin concentration of 10,000 mg/L and 2 g/L oxidizing agent ($\text{K}_2\text{S}_2\text{O}_8$) concentration were used in all these experiments. It is observed that at neutral pH the degradation is highest and as pH moves towards alkaline or acidic it first decrease and then increase and higher at pH 11 and pH 3. As reported in the literature, from neutral to acidic solutions (pH 7–2) the formation of $\text{SO}_4^{\bullet-}$ is observed and in solutions with pH > 12 OH^\bullet is favored and at neutral pH both the radicals are generated.

Conclusions

Various advanced oxidation processes such as electrochemical, ozonation, $\text{H}_2\text{O}_2/\text{UV}$ oxidation, Fenton and electro-Fenton has been studied for removal of melanoidin from wastewater. In situ chemical oxidation technique was employed for degradation of melanoidin. The complete degradation of melanoidin was achieved using potassium persulfate as oxidant and activated by heat. The influences of dosage of $\text{K}_2\text{S}_2\text{O}_8$ on melanoidin degradation investigated. The selection of an optimal oxidant dosage is of paramount importance in order to avoid excess of oxidant and to ensure a total use of generated efficient radicals. The melanoidin degradation was obtained for optimum catalyst loading of 2 g/L. For the initial concentration of melanoidin, degradation of melanoidin decreased with increased concentration of melanoidin. It is observed that at neutral pH the degradation is highest and as pH moves towards alkaline or acidic it first decrease and then increase and moderate at pH 11 and pH 3.

Fig. 6 and 7 shows the effect of activated persulfate treatment, analyzed on the basis of peaks i.e. results obtained in HPLC as before treatment and after treatment respectively.

Table 1: HPLC result of standard melanoidin analysis (1% melanoidin) before degradation

No.	Retention Time (Min)	Peak Name	Height m AU	Area m AU*min	Area %
1	1.45	Melanoidin	9973200	132695720	100

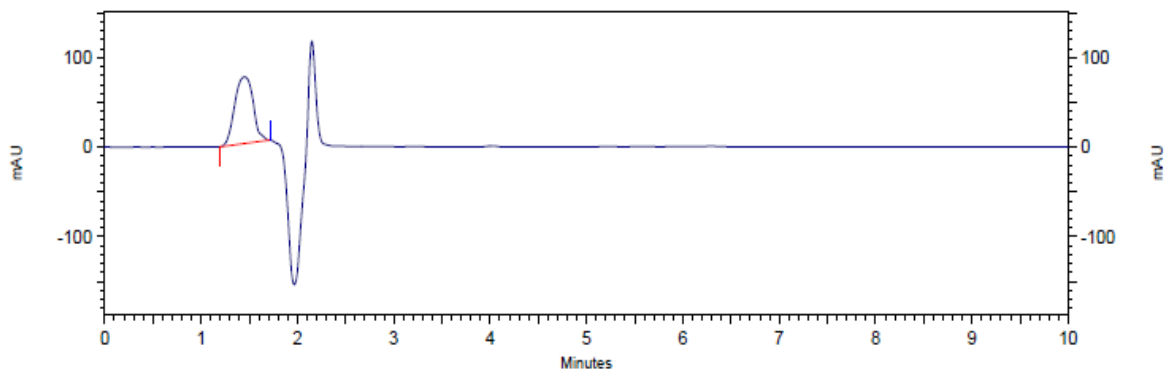


Fig.6: HPLC result before treatment

Table 2: HPLCResult of melanoidin analysis after degradation

No.	Retention Time(Min)	Peak Name	Height m AU	Area m AU*min	Area %
1	1.54	Melanoidin	254249	505239	100

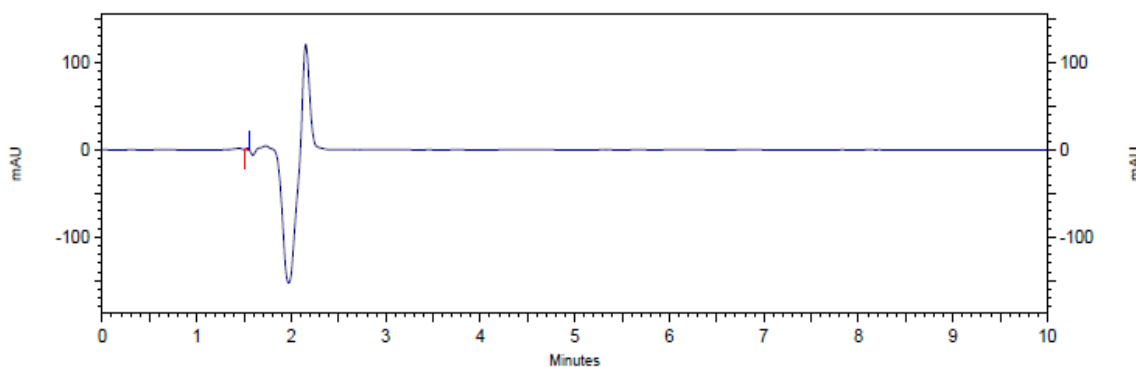


Fig.7: HPLC result after treatment

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