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Anaerobically digested spentwash degradation by application of MW assisted O_3 and H_2O_2 process

Vivek Patil[1], Satish Patil[2]
Ph. D. Student[1], Professor and Head[2]
Department of Environmental Sciences,
Dr. Babasaheb Ambedkar Marathwada University, Aurangabad [1, 2]
Email: vivekppatil12@gmail.com[1], sushshrey1@gmail.com [2]

Abstract- Degradation and biodegradability enhancement of highly concentrated organic matter in the form of COD and color in ADSW treatment with microwave assisted ozone, and hydrogen peroxide was studied in laboratory scale experiment. The effects of corresponding effective factors, ozone (60 liter), H_2O_2 (1ml of H2O2/100 ml ADSW) dose, MW treatment time (3min) optimized and used in experiment. The performance of all the three treatments was compare and measured in terms of percentage color, COD and BOD variation. For ozone treatment at 60 liter dose, reduction of 37.01% COD, color 64.75% and increase in BOD 64.75% was observed. Ozone in combination with H_2O_2 remove 41.93% COD and color 70.28%. Alone MW treatment removes 19.35% COD remove and increase in BOD 20%. Combine ozone, H_2O_2 and MW treatment shows more reduction COD 49.19%, color 36%, and BOD increase up to 56%, which shows the enhancement in biodegradability of ADSW.

Keywords- Anaerobically digested distillery spenwash, Microwave, H_2O_2, ozone, Oxidation

1. INTRODUCTION

Alcohol distillery industry is one of agro-based industry, which play a vital role in rural India to generate various employment opportunities. Most of the distilleries in India uses sugarcane molasses as row material to produce alcohol or ethanol.

Distillery industry generates huge amount of wastewater i.e. spentwash, during the alcohol production, which an average of 10-15 lit of wastewater is released with the production of per lit of alcohol [1]. Spentwash contains various types of recalcitrant organic pollutants containing endocrine upsetting substances like phthalates are reported and it causes the hormonal imbalance and distract the reproductive fitness of living organism and ultimately leading to the carcinogenesis [2-3]. It is one of the most recalcitrant wastewater characterized by very high BOD, COD, SS, TDS, color and low in pH [4]. Several treatment technologies like physico-chemical treatments, incineration, drying, composting and biological treatment including aerobic and anaerobic have been studied for the treatment of spent wash. Many researchers have verified that anaerobic processes aiding recovery of biogas appear to be the most promising technology for the treatment of spent wash [5]. Most of the distilleries have installed anaerobic digester as it is cost effective and energy thus generated in the form of biogas is utilized for running steam boilers for the generation of electricity. The anaerobically digested distillery spentwash is necessary to be further cope with environmental standards. The COD, BOD of anaerobically treated spentwash ranges between 45,000 - 50,000 mg/L and 8,000 -10,000 mg/L, respectively [6]. These values are much higher than the permissible limits and effluent standards notified for molasses-based distilleries deserving maximum BOD level of 30 mg/lit for disposal to surface water and 100 mg/lit for disposal on land [7].

1.1 Advanced Oxidation Process (AOP)

AOP are grounded on the chemistry of hydroxyl radicals (•OH), which are non-selective reactive species, able to oxidize pollutants into mineral end-products, producing CO_2 and inorganic ions, They are powerful technologies to treat wastewater containing recalcitrant organic compounds [8]. Several technologies are included in the AOPs like Ozone, Fenton, Electro-Fenton, Photo-catalysis etc. and the main difference between them is the manner to form the radicals [9].

1.1.1 Ozone

Ozone is one of the most powerful oxidizing agent with oxidation potential of 2.08 eV. Fluorine and hydroxyl radicals only surpass it in oxidation power, as atomic oxygen is very much unstable [10]. Formation of the hydroxyl radical (HO•) and superoxide radical ($O2^-$ •) occurs when ozone introduces to water, through a complex series of reactions. The fragmentation rate of ozone in water is better at higher pH levels [11]. Oxidation by ozone could achieve 80% decolorization for anaerobically treated distillery wastewater with simultaneous 15-25% COD reduction. It also resulted in improved biodegradability of the effluent. However, ozone only transforms the chromophore groups but does not degrade the dark colored polymeric compounds from the effluent [12]. In the combined reaction, hydrogen peroxide decomposes in the presence of ozone or UV into Hydroxyl radicals. These hydroxyl radicals exist in solution a combination of ozone molecules in high oxidative state and free radical in very high oxidative state. Ozone and ultrasound as a pre-treatment step for the thermally pretreated spentwash for aerobic treatment through increasing the COD removal efficiency. Ozone was more efficient in COD removal with a 25-times increase in the rate of biodegradation of ozonated sample along with discoloration of the effluent sample [13]. Ozone is a powerful but highly selective oxidant, and the reaction rate constants between ozone and organic or inorganic contaminants are greatly varied [14]. Ozone is generally used for the decontamination and oxidation in drinking water and wastewater by a chain reaction to form OH• radicals [15]. The efficiency of the hydroxyl radical gives AOP the ability to reach oxidative destruction of compounds refractory to conventional H_2O_2 or O_3 oxidation.

1.2 Microwave (MW) irradiation treatment

Microwave (MW) irradiation has acquired a great deal of devotion in domestic, industrial and medical applications. MW has been used in various environmental applications including pyrolysis [16, 17]. The energy of MW is inadequate to disrupt the chemical bonds of several organic compounds. Therefore, MW has been combined with adsorbents, catalysts and AOPs for increasing the treatment efficiency of various pollutants and also to shorten the reaction time [18]. A variability of MW absorbing materials by high surface area and a wide series of pore size distribution were establish for enhancing the degradation of organic pollutants under MW [19]. MW in combination with AOP was studied to enhance the treatability of anaerobically digested distillery effluent.

2. MATERIAL AND METHODS

2.1 Material

Molasses based distillery pretreated effluent i.e. Anaerobically digested spentwash (ADSW) was brought from Shri Someshwar Sahakari Sakhar Karkhana Limited, situated near near Baramati, Maharasthra, India. Microwave treatment given in microwave oven (Model Life's Good (LG) 900 watt). Ozone was generated using oxygen feed ozone Generator (Model AM Amsons technologies, India) with 5g/hr output dry air flow and produced from ozone generator by principle of corona discharge method. Laboratory and Analytical reagent chemicals was used for the preparation of reagents, analytical methods and for experimental treatment. All reagents used as received without further purification.

2.2 Methodology

2.2.1 *Ozone treatment*

The Ozone studies were conduct by varying dose of ozone expose in ADSW. The ozone generator produced ozone through corona discharge method using the O_2 as feed gas (Model AM Amsons technologies, India). The diagram of the experimental arrangement is shown in Fig. 1. The studies were conducted at room temperature i.e. 26 ^oC. Ozone contact vessel (impingers) containing 100 ml of ADSW for maximum exploitation of ozone gas used as reaction vessel. The Ozone were passed in ADSW through 4mm silicon tube followed by bubbled through the aeration port of the ozone contact vessel with the help of air diffuser. Ozone trap with 100ml KI solution were attached at the end of ozone trail. Ozone flow was controlled using rotameter at 2lpm to enhance the reaction efficiency. The ozone dose were optimize by varying the ozone dose of 30, 60, 90 and 120 liter to ADSW. The samples collected after the experiments were analyzed for color, COD and BOD to check the treatability of Ozone treatment. Optimum Ozone dose of 60 liter (result given in fig. 3) used for further experiments in combination with hydrogen peroxide and microwave irradiation.

2.2.2 *Ozone in combination with H_2O_2*

To optimize the dose of H_2O_2, ADSW in presence of H_2O_2 alone was investigated under different percentage

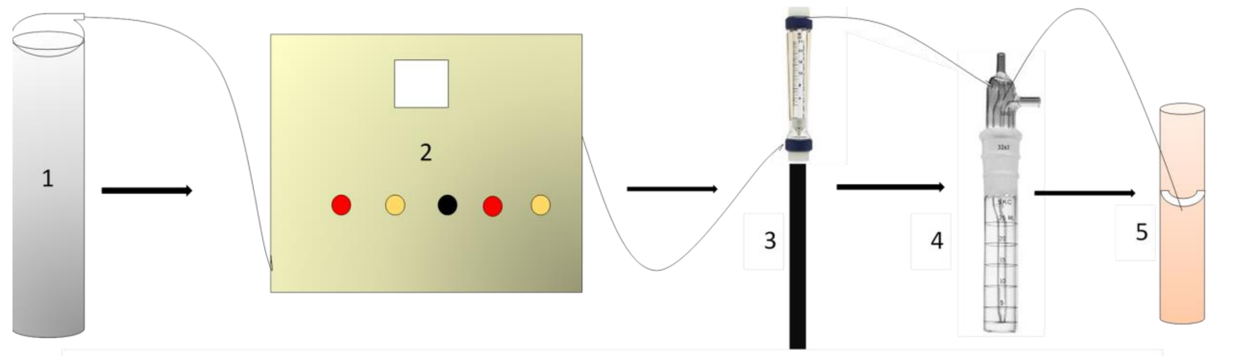
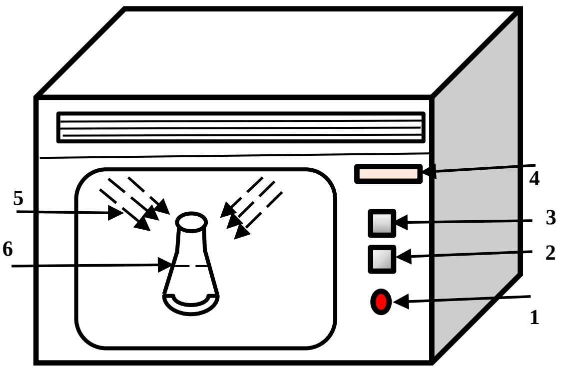


Fig. 1: Experimental Setup for Ozone treatment
1. Oxygen cylinder 2. Ozone generator 3. Rotameter 4. Ozone contact vessel 5. Ozone trap with KI

of H_2O_2 from 0.5 to 3%. The collected sample were analyze for COD which shows maximum COD reduction in combination with 1% H_2O_2 (30%, w/w, density 1.1). There for the 1% H_2O_2 in ADSW used for further experiments. Earlier optimize dose of H_2O_2 i.e. 1 ml of H_2O_2 per 100 ml ADSW sample and 60-liter ozone was passed through 100 ml ADSW. Final treated samples were then analyzed for COD, BOD and color and results are given in fig. 3.



2.2.3 MW- assisted ADSW degradation experiments

Figure 2: Microwave irradiation treatment setup
1. Power switch 2. Time adjuster 3. Power adjuster 4. Time and Power display 5. Microwave 6. Sample

In MW-assisted degradation experiments, ADSW degradation with MW alone was investigated. A close digestion system with an extreme output of 900W was use in this study. The system works at 2450 MHz and consists of dual sovereign magnetrons with a rotating microwave diffuser for homogeneous microwave distribution. The MW effects are mainly classified as thermal and non-thermal effects. The thermal properties result from MW heating, which may result in a different temperature command, whereas non thermal properties are specific effects resulting from non-thermal interaction between the substrate and MW [20]. The samples each with a total volume of 100 ml were subjected to microwave treatment. The heating time was set at 1, 2, 3, 4, 5 min for the optimize the MW dose. However, with a temperature increment setting of per minute the ramp times varied until the desired heating temperature was reach. After the MW treatment, samples were analyzed for COD to optimized MW treatment time. Maximum COD reduction achieved up to 19.35% (fig. 4) which shows that MW alone is insufficient for complex organic pollutants removal, which is also reported by several researchers in the past [21].

2.2.4 MW with Ozone and hydrogen peroxide

Experiment were conducted to evaluate the combine treatment of MW, ozone and H_2O_2 on ADSW. Ozone (60 liter) treatment given to the ADSW in combination H_2O_2 followed by MW treatment for the optimum time of 3min and treated sample was analyzed for Color, COD and BOD, results given in fig. 3.

2.2.5 Analytical Methods

Before and after treatment color were measured by ten time's diluted sample for measurement of Color reduction. The absorbance was measured using uv vis-spectroscopy at λ 475 using UV-spectrophotometer. The decolourization value was express as the percentage decrease in absorbance at λ 475 related to the initial absorbance at the same wavelength.
Degradation ability of ADSW after each treatment was checked, by means of Chemical Oxygen Demand (COD) by close reflux method (colorometric method) in accordance with standard methods of water and waste water analysis standard methods in APHA AWWA. Biological Oxygen Demand BOD was determined as 3 days BOD at 27 ^{o}C by 'Winkler's Iodometric' method given in APHA AWWA.

3. EXPERIMENTAL RESULTS

3.1 Ozone treatment

The effect of Ozone treatment to enhancement of degradation of distillery effluent (ADSW). The actual design of experiments and responses for color, COD and BOD removal by Ozone treatment optimization are presented in fig. 3. The increase in ozone dose shows increase in reduction of COD and Color. It was observed that COD and Color removal efficiencies

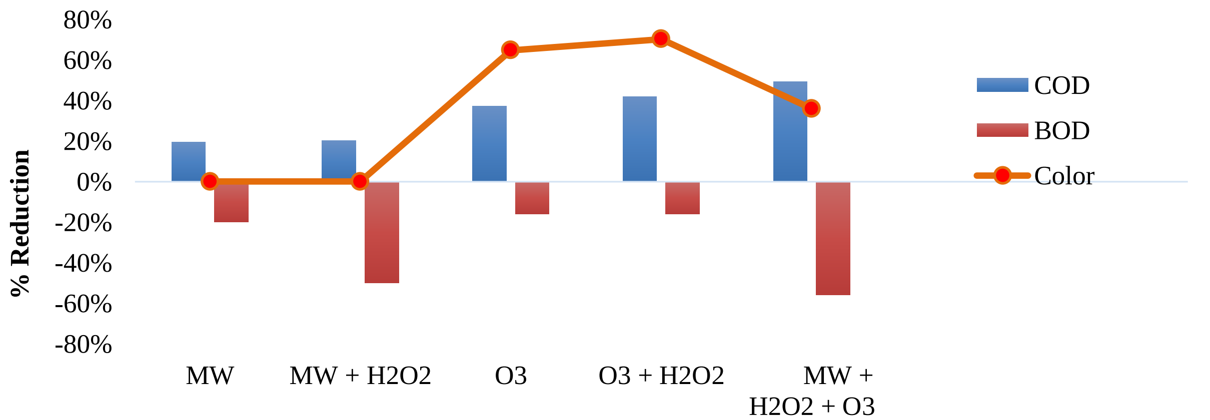


Figure 3 : Treatment on ADSW

increases but BOD removal efficiency decreases. Ozone dose of 60 liter were choose for combine treatment with H_2O_2 (1ml/100ml sample) and MW based on optimum ozone dose for COD and color removal efficiency.
Alone Ozone treatment removed 37.09 % COD, 64.75% Color and BOD increases by 16 %. Increase in BOD is a good indication in the enhancement of biodegradability in ADSW for further biological treatment.

3.2 Ozone in combination with H_2O_2

ADSW were treated with 60 liter of ozone dose in presence of H_2O_2 and outcome of the experiment is given in Fig 3. Ozone in combination with H_2O_2 gives color and COD reduction up to 70.28% and 41.93% respectively, it shows improved results than ozone alone. This is because H_2O_2 gets decompose in the presence of ozone into Hydroxyl radicals. They exist in solution in combination with ozone molecules at high oxidative state [22]. The combination is extremely reactive as the free radicals capable of removing atoms from oxidizable material.

3.3 MW irradiation treatment

MW treatment work on ADSW containing recalcitrant compounds. MW treatment given to ADSW for the period of 1,2,3,4 and 5 minutes to optimize the MW treatment. Maximum COD removal efficiency found at 3 min. In alone MW treatment, 19.35 % COD removal observed. It shows that MW alone is not more efficient as compare with ozone and combined ozone and H_2O_2 (1ml/100ml sample) treatment. Color removal efficiency also found very poor, but the increase in BOD up to 20% shows the enhancement in biodegradability. The detailed outcome of the experiment given in fig 3. The increase in the temperature of MW-reaction could have increased the rate of reaction. Moreover, its hypothesized that the stimulation energy required for COD removal could have minimized by many folds at the higher MW-reaction temperature.

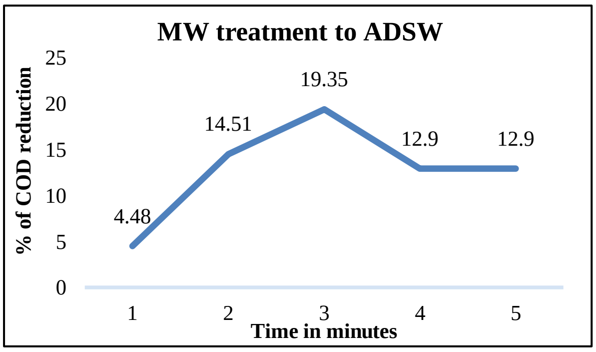


Figure 4. : Microwave treatment dose optimization

3.4 MW with Ozone and hydrogen peroxide

Treatment outcome for ADSW treated with ozone dose of 60 liter in presence of H_2O_2 (1ml/100ml sample) followed by MW irradiation is given in fig 3. In combination of MW with ozone and H_2O_2 shows more COD reduction i.e up to 49.19 % as compare to individual treatments due to the founding of stronger oxidizing agent. Color reduction found up to 36 % which is more as compare with MW treatment but less than ozone and H_2O_2 combination treatment. BOD also increases up to 56% that indicates the combined treatment is more efficient to enhance the biodegradability of ADSW. The more hydroxyl radicals produced by the special heating of MW potency will be utilized for fast breakdown of recalcitrant compound present in ADSW.

4. CONCLUSION

The present study demonstrate the treatability of microwave, ozone and H_2O_2 treatment on ADSW. The treatment outcome given in terms of percentage Color, COD and BOD evaluated. Optimization of input of ozone, H_2O_2 dose and MW treatment time for each individual process was perform. The significant outcome of the experiment given as follow. Individual ozone treatment reduces COD and Color but increase in BOD, the similar outcome observe in ozone and H_2O_2 combination. Alone MW treatment shows comparatively low efficient in reduction of color and COD but increase in BOD. Combined MW, ozone and H_2O_2 treatment shows more efficient in removal of Color, COD and increase in BOD that shows enhancement of biodegradability of ADSW.

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