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Combine Ozonation Treatment Followed by Biological Treatment to Anaerobically Digested Spentwash

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ABSTRACT: Experiments were conducted with Ozone, Ozone–UV, and H_2O_2 -UV radiation process. Ozone treatment (flow 0.3 m^3/hr for 30 min) reduces ADSW 47% COD and 62% color. Ozone with H_2O_2 obtained 61% COD and 85% color reduction. ADSW exposed to ozone together with H_2O_2 and UV radiation over all COD and color reduction observed was 68% and 88% respectively. Biodegradability (BOD $_{(3)}$) in the ADSW effluent increased by 17% when, treated with ozone and hydrogen peroxide. Maximum BOD enhances 25.6% by Ozone in combination with UV and H_2O_2 treatment. UV-Ozone alone treatment enhances 22% and 20% BOD. Increase in BOD indicates, recalcitrant organic material becomes biodegradable. Pretreated (ADSW) with Optimized combine Ozonation-H_2O_2-UV treatment was examined using aerobic treatment. Combine ozonation pre-treatment reduces 42% color and 67% COD. Without ozonation pre-treatment 15% color reduction and 31% COD reduction was observed.

KEYWORDS: Anaerobically digested spent wash, Ozonation, Hydrogen peroxide (H_2O_2), UV radiation

I. INTRODUCTION

Distillery effluent (spentwash) is considered to be among the highest-polluting industrial wastewater and approximately seven times more than that of the entire Indian population. Distillery spentwash contains enormous quantity of dissolved organic matter, dissolved solids, suspended solids; color along with other pollutants and pollution caused by it is one of the most critical environmental issues [9]. The recalcitrant nature of wastewater from sugarcane molasses is due to presence of large amount of a brown pigment which is biopolymeric colloidal materials that are negatively charged. The color is hardly degraded by the conventional treatments and can even be increased during anaerobic treatments, due to repolymerization of compounds. Phenolics (tannic and humic acids) from the feedstock, melanoidins from Maillard reaction of sugars (carbohydrates) with proteins (amino groups), caramels from overheated sugars, and furfurals from acid hydrolysis mainly contribute to the color of the effluent [8].

Several technologies have been explored for reducing the pollution load of sugarcane molasses spentwash wastewater. Aerobic and anaerobic biological treatments are well established and accepted practice. However, anaerobically treated effluent contains high concentrations of organic pollutants and as such cannot be discharged directly [10]. Physico-chemical treatment, viz. adsorption, coagulation/flocculation, oxidation processes, membrane treatment have been examined with particular emphasis on effluent decolorization. Majority of these methods decolorize the effluent by either concentrating the color into the sludge or by breaking down the colored molecules. Comprehensive combine treatment process for molasses distillery spentwash leading for effective removal of organics and color is not currently available. Thus, the use of alternative treatment technologies, aiming to mineralize or transform refractory molecules into other simpler or biodegradable form is essential. Advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing recalcitrant organic compounds and successfully used as pretreatment methods to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment.

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Ozone chemistry is composed of a single bond and one double bond. The single bonds are weak and this leads to easy formation of free radicals .The double bond of ozone is as strong as the double bond of oxygen and so nonreactive. According to Baratharaj, use of ozone in combination with peroxide, UV or reactions under high pH assist ozone in oxidation process. Whereas Hydrogen peroxide is an oxidant, UV is not, but when used with Ozone the breakdown of organics to CO_2 and H_2O is facilitated. The combination is highly reactive as the free radicals capable of withdrawing atoms (often hydrogen) from a substrate. The role of hydrogen peroxide in AOP is thought to make the pollutant more susceptible to ozone attack and also aid in the overall oxidation. UV light provides energy to break chemical bonds .This makes the remaining fragments more susceptible to ozone attack .UV light also converts H_2O_2 to the highly reactive hydroxyl radical and the generation of oxygen [4]. The combination of chemical and biological treatment is often the way to optimize the overall process of treating wastewaters [7]. Use of AOP as a pretreatment for the enhancement of biodegradability of recalcitrant or inhibitory compounds can be justified when the intermediate resulting from the reaction can be readily degraded by microorganism. Thus combination of advanced oxidation processes and biological treatment processes provide a best approach to treat recalcitrant waste.

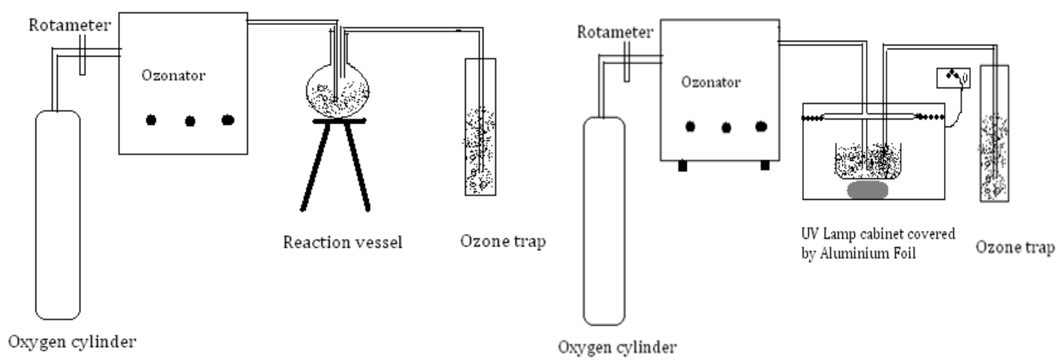
The objective of the research was to study treatability of ozone in combination with Hydrogen peroxide and UV radiation to ADSW. Treated ADSW with combine ozonation was further investigated for biological (Aerobic) treatment effect. Purpose of the biological treatment to coagulate, remove the non settleable colloidal solids and to stabilize the contained organic matter and reduce the concentration of organic and inorganic compound.

II. EXPERIMENTAL METHODS

Anaerobically digested spentwash (ADSW) was obtained from molasses based distillery Bhima Sahakari Sakhar Karkhana Limited, situated near Pune, Maharasthra, India. Hydrogen peroxide (Merck, India, 30%, w/w, density 1.1) used for experiment. Ozone gas was generated using Ozone Generator (Model AM Amsons ozonics, India) with 5g/hr output dry air flow and produced from ozone generator by corona discharge method using oxygen supplied by oxygen cylinder (Laboratory use oxygen cylinder). Analytical reagent chemicals were used for the preparation of reagents, experimental treatment and analytical methods.

1. Experimental Setup

Experiments were conducted in 250 ml round bottom flask with one cylindrical glass vessel as an ozone trap with 2% potassium iodide. Purpose of ozone trap is to collect unreacted ozone. Ozone gas was generated using Ozone Generator (Model AM Amsons ozonics, India) and produced from ozone generator by corona discharge method using oxygen supplied by oxygen cylinder (Laboratory use oxygen cylinder). Rota-meter was connected to Oxygen cylinder and generated ozone flow was measured. Ozone was supplied at the bottom of the flask by 2 mm glass tube. Reaction time was 30 min to each experiment. The schematic of experimental setup is shown in fig. 1.



(a) (b)

Fig 1: Experimental setup for (a) Ozone treatment, (b) UV-Ozone treatment

2. Ozone treatment

Experiment carried out by varying reaction time at room temperature. ADSW sample was filled in 250 ml round bottom glass flask which was attached to ozone trap. Both ozone traps contained 100ml % KI solution [12].

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The Ozone was passed (flow rate 0.3 m^3/hr) in ADSW sample through 2 mm glass tube. During the 30 min reaction time 20 ml sample was withdrawn at every 5 minutes time interval. Collected samples were then analyzed for COD, BOD and color.

3. Ozone with Hydrogen peroxide treatment

Previously optimize dose of H_2O_2 (30%, w/w, density 1.1) i.e. 1 ml of H_2O_2 per 100 ml ADSW sample. Constant Ozone flow rate 0.3m^3/h was passed through 250 ml ADSW. During the reaction time 20 mL sample were withdrawn at every 5 minutes time interval. The samples were then analyzed for COD, BOD and color.

4. Ozone with Hydrogen peroxide and UV radiation

ADSW of 250 ml treated with H_2O_2 (1ml of H_2O_2/100 ml ADSW) followed by ozone at flow 0.3 m^3/h in presence of UV light (254 nm). Sample was analyzed for COD, BOD and color after every 5 min time interval.

5. Aerobic biological treatment

Combine UV-H_2O_2-Ozone treatment was employed for aerobic biological treatment as it showed better reduction in COD, color and increases BOD value. Two acrylic reactors of 14 L capacity and two air pumps of 25 L/min were used to for aerobic treatment. Aerobic bioreactor was inoculated with activated sludge slurry collected from sewage treatment plant located in Mundhava at Pune. The collected slurry was taken 14% (w/v). Initial MLSS of the reactors was 2000 mg/L. During the stabilization (acclimatization) period carbon source i.e dextrose was added externally. The bioreactor was initially loaded with diluted ADSW containing an initial substrate concentration of 500 mg/L COD, and then the bioreactor was aerated and for 5 days. The same procedure was repeated with continuous additions of ADSW loads to the biomass, with increasing concentrations from 500-5000 mg/L COD with 0.5 L/day flow rate. Stabilization period was extended up to 25 day. Stabilization was considered to be achieved when a similar removal of substrate was obtained. At the end of stabilization MLSS was 5,000 mg/L. Once stabilization period over, combine UV-H_2O_2-Ozone treated sample was supply to aerobic reactor with 5 L/day flow rate for three days hydraulic retention time (HRT). During the experiment sample were withdraw at regular interval i.e. every day. The biologically post treated sample was filter in order to separate the biomass and to analyze sample for color and COD removal. One control reactor was set without feeding pretreated ADSW.

6. Analytical method

Parameters analyzed for ADSW were pH, TDS, TSS, COD, BOD, chlorides, suphate, Phosphate, Potassium. by standards methods given in *APHA AWWA WPCF*. All the chemicals used for these were laboratory grade. For color assay, ADSW effluent was centrifuge for 10,000 RPM for 10 min and supernatant was diluted 50 times with distilled water. The absorbances were recorded in spectrophotometer (166 Systronics)-at λ_{max} 475 nm [1]. Color reduction was measured as a decrease in OD at 475 nm of supernatant versus a blank. Results of the all experiments were mean of three replication of each experimental set.

III. EXPERIMENTAL RESULT

1. Effect of Ozone coupled with hydrogen peroxide on ADSW

Ozone with hydrogen peroxide process was found effective in biodegradability of initially non-biodegradable organic compounds. Figure 2(a) shows that COD reduced up to 61.4 %. Figure 2(b) shows that BOD comprises a good measure in the enhancement of biodegradability in ADSW effluent and the BOD $_{(3)}$ increased by 17%. A color reduction observed was 85.7%. Alone Ozone treatment removed 46.8 % COD, 80% color and BOD increases by 13.9 %. Figure 2 (a & c) depicts individual H_2O_2 treatment resulted in 13% reduction in COD and 59.5% color reduction. BOD value decreases in H_2O_2 treatment i.e. 26.5%.

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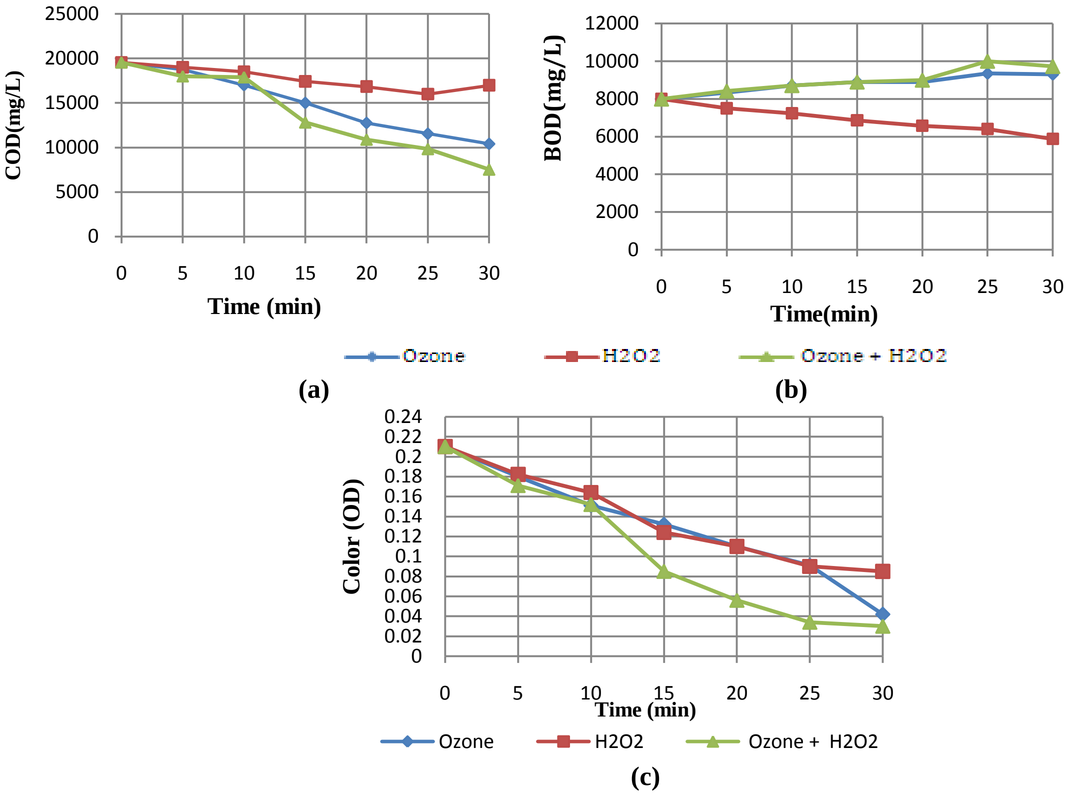

Fig 2: Effect of ozone coupled with H_2O_2 treatment (a): Effect on COD value (b) Effect on BOD value(c) Effect on color value

Use of ozone in combination with H_2O_2 shows much better result than H_2O_2 alone. This is because H_2O_2 decomposes in the presence of ozone into Hydroxyl radicals. They exist in solution in combination with ozone molecules at high oxidative state. The combination is highly reactive as the free radicals capable of withdrawing atoms (often hydrogen) from a substrate. The role of hydrogen peroxide in AOP is thought to make the pollutant more susceptible to ozone attack and also aid in the overall oxidation [4].

2. Effect of Ozone coupled with hydrogen peroxide and UV radiation

Fig 3 describes the efficiency of integrated ozone treatment along with hydrogen peroxide and UV radiation to treat high strength ADSW. Experiments carried out at constant ozone flow 0.3m^3/hr and H_2O_2 dosage (1ml/100ml ADSW sample), UV radiation of short wave length 254 nm. UV in combination with Ozone and H_2O_2 promotes the 68% COD and 88% color reduction fig 3 (a & c) due to the formation of stronger oxidizing agent. Ozone coupled with hydrogen peroxide and UV radiation enhances biodegradability in form of 25 % increase in BOD. UV radiation with ozone affect COD and color reduction by 43.7% and 76% as shown in fig 3 (a & C). BOD of the UV-Ozone reaction increases by 22 %. Collective effect of UV radiation and H_2O_2 has shown 39% COD and 57% color reduction. BOD value decreases in UV radiation and H_2O_2 treatment i.e. 37.5%. The major factor affecting the UV radiation in degradation is it provides energy to break chemical bonds .This makes the remaining fragments more susceptible to ozone attack. UV light also converts H_2O_2 to the highly reactive hydroxyl radical and the generation of oxygen. Effect of UV radiation and H_2O_2 has shown less reduction in COD and color compare to other H_2O_2 has poor UV absorption characteristics. Hence there is a poor ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical and water matrix there in waste absorbs a lot of UV light energy, single UV and ozone treatment was not very effective compared to combined effect of UV, Ozone and H_2O_2. The reason for poor reduction is UV-radiation alone would attack and decompose some organic molecules by bond cleavage and free radical generation, but usually it occurs at very slow rates. The combination of UV-light and various oxidants can decompose

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pollutants very effectively [5]. Figure 3 (a & c) depict UV alone and ozone oxidation alone attributed to 35% and 46.8 % COD decomposition respectively. Ozone treatment increases 20 % biodegradability in form of increase in BOD value where as UV radiation exposure has not shown any enhancement in BOD although 34.5% BOD reduced. The increment in BOD_3/COD from 0.4 to 1.75 after combine ozone (UV-H_2O_2 and O_3) treatment is an indicative of biodegradability improvement due to increase in contained organic matter proportion willing to bio-oxidation.

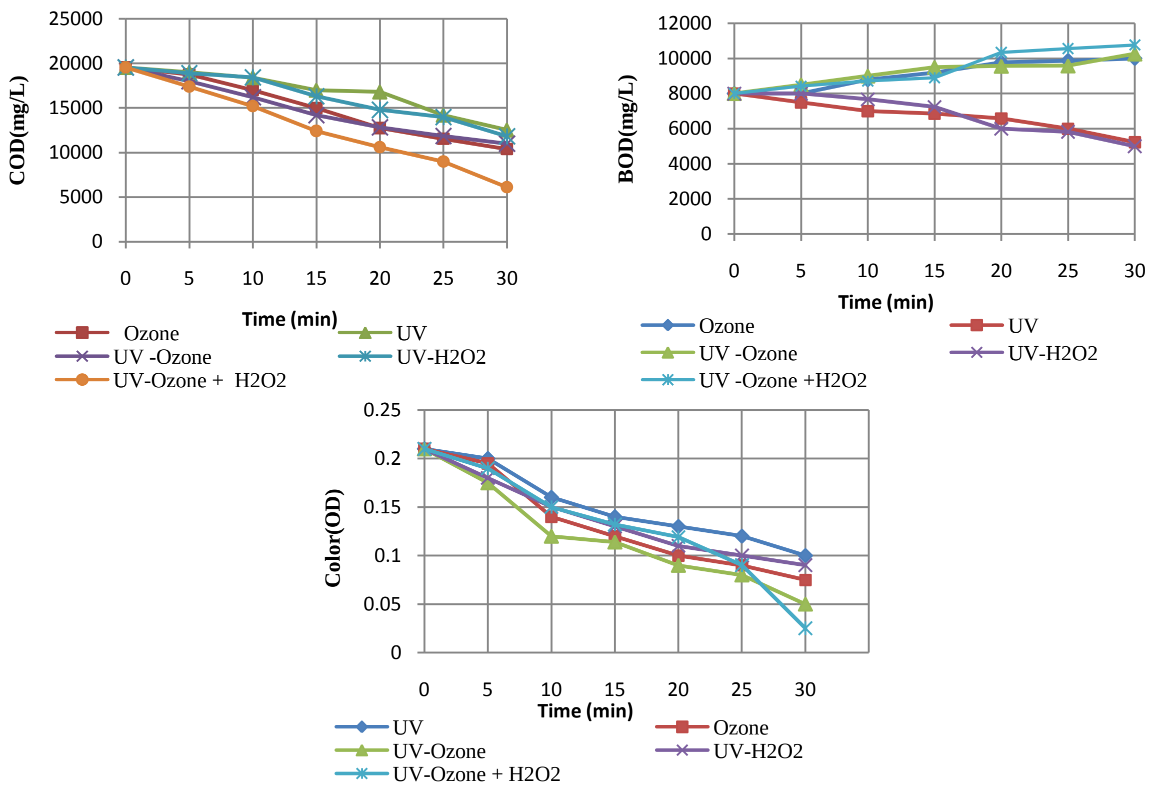

Fig 3: Effect of ozone coupled with H_2O_2 and UV radiation treatment (a): Effect on COD value (b) Effect on BOD value(c) Effect on color value

3. Aerobic biological treatment

Combine ozonated pre-treated ADSW with BOD_3/COD = 1.75 was used. This pre-treated ADSW was obtained from 30 min experimental time with initial concentrations 1ml /100ml ADSW H_2O_2 through short wavelength of UV 254 nm and O_3 dose 0.3m^3/hr. The pre-treated solution was fed to two different aerobic biological reactors. The bio- reactor was contained biomass acclimate to ADSW for 3 weeks.

COD and color removal with, without combine ozone pre-treatment and whole COD and color reduction in initial ADSW are shown in fig. 4 and table.1, respectively. Combine ozonation pre-treatment resulted 68.7% COD and 88% color reduction compared to the ADSW without ozonation pre-treatment that resulted to 31% and 29 % COD and color reduction respectively. Combine ozonation prior to aerobic biological treatment improved the biodegradability of the distillery wastewater. Color level increased after the aerobic treatment for ozonation pre-treatment. In ozone treatment O3 compound only transforms the chromophore groupsbut does not degrade the dark colored polymeric compounds in the effluent [2]. Therefore further increase in color level after few hours was observed. Reappearance of color was stopped up to some extend (20%) by adding 1g/250 ml of sodium sulphate (Na_2SO_4) immediately after treatment to stop the oxidation reaction.

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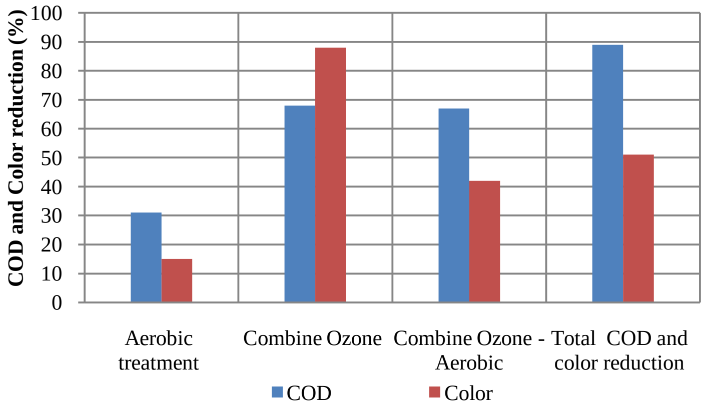

Fig 4: COD and color reduction (%) with and without combine ozonation followed by aerobic treatment

Table 1: Effect of Aerobic biological treatment on COD and color concentration

Days	Influent		Aerobic treatment		Influent		Combine ozonation (UV-H_2O_2-Ozone) and Aerobic treatment	
	COD (mg/L)	Color O.D	COD (mg/L)	Color O.D	COD (mg/L)	Color O. D	COD (mg/L)	Color O.D
1	19560	0.21	15820	0.188	6520	0.175	5040	0.154
2	19220	0.201	12540	0.158	6500	0.178	3500	0.138
3	18740	0.190	10500	0.1471	6120	0.171	2140	0.118

4. Role of microorganisms

The removal of carbonaceous BOD, the coagulation of non settleable colloidal solids, and the stabilization of organic matter are accomplished biologically using of microorganisms, principally bacteria. The microorganisms are used to convert the colloidal and dissolved carbonaceous organic matter into various gases and into cell tissue. Because cell tissue has specific gravity slightly greater than that of water the resulting cells can be removed easily from treated liquid by gravity settling [6].

IV. CONCLUSION

Ozonation in combination with other oxidizing agent as a pre-treatment enhances the biodegradability of ADSW. Ozone together with H_2O_2 and UV radiation over all COD and color reduction observed was 68% and 88% respectively. Biodegradability (BOD $_{(3)}$) in the ADSW effluent increased by 17% when, treated with ozone and hydrogen peroxide. Maximum BOD enhances 25.6% by Ozone in combination with UV and H_2O_2 treatment. UV-Ozone alone treatment enhances 22% and 20% BOD. Increase in BOD indicates, recalcitrant organic material becomes biodegradable. Pretreated (ADSW) with optimized combine Ozonation - H_2O_2 -UV treatment was examined using aerobic treatment. Combine ozonation pre-treatment reduces 42% color and 67% COD. Without ozonation pre-treatment 15% color reduction and 31% COD reduction was observed.

Study reveals that combine ozonation treatment to ADSW followed by aerobic treatment is better alternative treatment compared to an anaerobic treatment

V. ACKNOWLEDGEMENT

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