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Waste Water Treatment of Distillery By Photochemical Process

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ABSTRACT

Conventional oxidation processes are used in water treatment to disinfect water, to reduce toxins, odour and colour or to reduce manganese and iron levels in potable water. These processes may not destroy all toxins and have the potential to create dangerous disinfection by-products (DBPs). Advanced oxidation process (AOP) utilises the strong oxidising power of hydroxyl radicals that can reduce organic compounds to harmless end products such as carbon dioxide and water.

The hydroxyl radicals can be generated by different oxidation processes, such as ozone (O3), ultraviolet (UV), Hydrogen peroxide combined with ultraviolet radiation (H_2O_2/UV), Fenton reagent ($Fe^{2+/}H_2O_2$) photo- Fenton process (Pignatello,1992), O3/UV , O_3/H_2O_2 and heterogeneous photo catalysis using semiconductors such as zinc oxide (ZnO) but mainly titanium dioxide (TiO_2) - TiO_2/UV and (H_2O_2/UV) process Ultrasonic technology as an innovative technology may be used for water and wastewater treatment for pollution removal. This technology acts as an advanced oxidation process.

Application of this technology leads to the decomposition of many complex organic compounds to much simpler compounds during physical and chemical compounds during cavitation process. Advanced Oxidation Processes (AOP) using ozone, H_2O_2, ultrasound (US), ultraviolet radiation (UV), Fenton's reagent (FeII+H_2O_2) alone or in combination involving hydroxyl radicals are considered as possible methods of clean and ecologically safe remedial treatment for the degradation of organics.

Advanced Oxidation Processes (AOP) involving hydroxyl radicals, which are one of the strongest inorganic oxidants next to elemental fluorine, have been extremely effective in the destruction of organic pollutants. These advanced oxidation process (AOP) generally use a combination of oxidation agents (such as H_2O_2 or O_3), irradiation (such as UV or ultrasound), catalysts (such as metal ions or photo catalysts) and radiolysis (such as gamma irradiation or electron beam) as a means to generate hydroxyl radicals .

Keywords

Advanced oxidation process, Ultrasonic, wastewater Treatment, Oxidising, Catalysts, Fenton reagent.

1. INTRODUCTION

Sugarcane molasses is the byproduct of sugar industry which generated during sugar production, sugarcane molasses contain 50 % fermentable sugar and about 4 to 10 kg of molasses which is required for 1 l of alcohol production. Molasses is the dark brown, putrid, viscous liquid. Sugar molasses is the most common feed stock for industrial fermentation processes, molasses are diluted 1- 3 fold for effective fermentation process and purification of spirit. Spent wash is highly acidic, having strong odor, variety of recalcitrant coloring pigment as melanoidins, metal sulfides and phenolics are responsible for dark brown color of spent wash. Along all these characteristics spent wash is daily generated with huge quantity, so during the ethanol production around 8 – 15 l of spent wash generated. Melanoidin having high molecular weight nitrogenous brown polymer form by Maillard reaction between the amino acid and sugar. Due to rapid growth of population and industrialization the requirement of water increase but the natural source of water which is useful for the domestic and industrial uses is very limited. From the industrial process the large amount of waste water is coming out treatment of this waste is necessary to protection of environment and human being from harmful effect.

Necessity of wastewater treatment

- Protection Of the Environment from pollution.
- Protection Of Human Health by harmful effect.
- Avoid Shortage Of the Water for Domestic as well as Industrial use.
- Save the Earth life.
- Increasing awareness about the environment.

Treatment Technology for distillery Spent Wash There is a need of modernization and scientific revolution as the tremendous changes occur in the surrounding area of distillery industry and environmental crises problem also terrestrial and aquatic land badly affected due to these industries. To minimize and economical disposal of waste water problem in 21st century number of techniques are developing to treat the distillery spent wash indirectly reduce the overburden pollution of the environment. Today modern and huge numbers of technologies are explored to reduce pollution load of distillery spent wash.

2. TREATMENT PROCESS

There are three major treatment option of treatment of process industry

- Onsite treatment on factory waste water treatment plant-

Onsite treatment method of waste water treatment is requires waste water treatment plant. This type of method of treatment is economical and environmentally physible.

Most of processes industries are prefer this method for waste water treatment. The quality and quantity of handling is greater in this method and the water can be reuse for the process which avoids the shortage of process water, protection of environment from waste and also protection of human health.

- Discharge to the nearby sewage treatment plant-

In this type of treatment method if process industry which don't have any own waste water treatment plant. The need is to find the waste water treatment plant and Discharge of the waste water in to the plant. This method is less economic.

The quality and quantity of handling is lower than the first method and the water can be reuse for the process which avoids the shortage of process water, protection of environment from waste and also protection of human health.

- The site removal of semisolid and special wastes by waste disposal contractors-

The quality and quantity of handling is very lower compare with first two methods and the water can be reuse for the irrigation purpose for protection of environment from waste and also protection of human health.

Last two options arecontinuously impacted by increasing costs, while the control of allowable levels of SS, BOD and COD in discharged wastewaters are also becoming more stringent. So the First option is better comparing with other two options on point of cost and the handling purpose. The quality and quantity of handling is greater in first method and the water can be reuse for the process which avoids the shortage of process water, protection of environment from waste and also protection of human health.

Irreversible damages to the environment due to the wastewater and also contributes to the reduction of fresh water reserves, creating threats to the next generation. Reduction of water resources cause many industries which consume fresh water and exhaust as a wastewater. According to the water standard wastewater should be treated properly to reduce or indicate the pollutants and achieve the permissible limit for its reutilization in the industrial and agriculture process to promote sustainability. For security of environment there is a need of more cost-effective methods to purify a wide range of polluted water on-site, and with minimal additives that are required for sustainable water management. Innovative technology as electrolytic treatment of wastewater in which a sacrificial metal anode and cathode produce electrically active coagulants and tiny bubbles of hydrogen and oxygen in water.

Major concern with the hospital wastewater is that, it is been discharged into the sewage network without any primary treatment or there is no any conventional wastewater treatment facility provided for the treatment of collected wastewater is not able to meet Wastewater originate from domestic, industrial, commercial, agriculture activity may create threat to human life. Waste water which generated from the Municipal and hospital usually conveyed in combined sewer or sanitary landfill and treated at wastewater treatment plant. This type of human activity may create heavy load to the wastewater treatment units.

Waste which generated from the contains solids, toxic pollutants, metal oxides, hazardous liquid waste from various units, pharmaceuticals, radioactive waste, bacteria, viruses, blood, and fluid which has high BOD and COD are due to presence of solids and bacterial in it and think if not treated properly, it may create threat to human life as well as environment. So there is necessity to treat wastewater before discharge in to natural stream.

The followings are the various goals of waste water treatment

- To control pollution
- Prevention of infectious, chronic and hazardous diseases
- Protecting environment
- Reusing water for gardening and agriculture purpose.
- Increase the water resources

Presently there arevarious (processes) conventional methods are available for the treatment of waste water like, ion exchange, adsorption, coagulation flocculation, chemical oxidation, reverse osmosis, filtration, ultra filtration etc. these are expensive methods. Electrocoagulation method is highly accepted for the treatment of water and wastewater which is used for the treatment of water and wastewater.

Hydroxyl radicalsare one of the strongest inorganic oxidants next to elemental fluorine, have been extremely effective in the destruction of organic pollutants in waste water treatment by Advanced Oxidation Process and which generally use a combination of oxidation agents (such as H_2O_2 or O_3), irradiation (such as UV or ultrasound), catalysts (such as metal ions or photo catalysts) and radiolysis (such as gamma irradiation or electron beam) as a means to generate hydroxyl radicals.

H_2O_2 can be used for such diverse applications is the different ways in which its selectivity can function. There are no problems of gaseous release or chemical residues that are associated with other chemical oxidants and adjusting the conditions of the reaction (e.g., pH, temperature, dose, reaction time, and/or catalyst addition), H_2O_2 can often be made to oxidize one pollutant over another, or even to favor different oxidation products from the same pollutant.

The most polluting industries generating large volumes of high strength wastewater which is distillery and containing highly colored, COD, BOD, TDS and other organic matter. Treatment of effluent is must before letting out to the environment and by the various studies has been carried out on the treatment of distilleries wastewater. Presently the various methods are use as biological flocculation, Nano filtration, activated carbons), bio electrochemical process, ozonation-based process electro-oxidation, membrane-based Nano filtration and reverse osmosis.

Most common feed stock for industrial fermentation processes which is molasses and molasses are diluted 1- 3 fold for effective fermentation process and purification of spirit. Pretreatment method in an integrated system these advanced oxidation processes can be use and also able to enhance the biodegradability of contaminants through converting recalcitrant contaminants into smaller and consequently more biodegradable intermediates.

There are much of AOPs adopted for the treatment of industrial effluent, but limited studies have been focused on distillery effluent treatment. Our study focuses the depolarization and degradation of distillery effluent and some studies shows the depolarization and degradation studies using These processes are the energy efficient process has been identified for the high color and COD removal of the distillery effluent as comparing to other processes and oxidative degradation through their reactions with valence bond holes, hydroxyl and peroxide radicals as well as reductive cleavage through their reactions with electrons.The degradation of surfactant has been attempted by Ozonation. UV + Fenton's reagent (Fe II + H_2O_2) and UV + H_2O_2 heterogeneous and homogeneous photochemical reactions ultrasonic irradiation combined sono chemical and photochemical techniques with variable results. Extensive studies on the Photo-Fenton and TiO_2- mediated photo catalytic degradation of several surfactants using solar energy has been reported. Previous studies reveal information on the different advanced oxidation processes for the degradation of SDS and LAS at concentration levels of 1,000 mg/L-1,600mg/L.

Most of the reports about surfactant degradation are related to pure surfactants like SDS, LAS namely Sodium Dodecyl

Benzene Sulphonate (SDBS) but very few reports are available on the degradation of mixtures of surfactants present in the commercial detergent products which are discharged into wastewaters.

2.1 Types of AOP

Table 1. Types of AOP

Non Photochemical	Photochemical
Homogeneous processes	
Alkaline media ozonation (O_3/HO^-)	Vacuum ultraviolet (VUV)
Ozonation with Hydrogen peroxide ($O3/H_2O_2$)	UV/H_2O_2
Fenton (Fe^{2+} or Fe^{3+}/H_2O_2)	UV/O_3
Electro-oxidation	$UV/O_3/H_2O_2$
Electro hydraulic discharge - ultrasound	Photo-Fenton (Fe2+ or Fe3+/H2O2/UV)
Wet air oxidation (WAO)	
Supercritical water oxidation (SCWO)	
Heterogeneous processes	
Catalytic wet air oxidation (CWAO)	ZnO/UV, SnO_2/UV, TiO_2/UV, TiO_2/H_2O_2/ UV

3. TITANIUM DIOXIDE/UV LIGHT PROCESS

Hydroxyl radical generate in TiO_2/UV light process by titanium peroxide semiconductor absorbs UV light and during UV illumination of TiO_2, conduction band electrons and valence band holes are initially yielded.

Interaction of the band electron on surface adsorbed molecular oxygen to yield superoxide radical anions, while band holes interact with water to produce hydroxyl radical.

TiO_2 + UV light $\rightarrow e + h^+$

$e + O_2 \rightarrow O_2^-$

$h^+ + H_2O \rightarrow H^+ + HO\bullet$

.

Advantages

- TiO_2 is a cheap.
- Readily available material.
- The photogenerated holes are highly oxidizing.
- Capable for oxidation of a wide range of organic compounds into harmless compounds such as CO_2 and H_2O.

Factors affecting

- Initial organic load.
- Amount of catalyst.
- UV irradiation time.
- Reactor's design.
- UV irradiation time.
- Temperature, solution's pH, light intensity and presence of ionic species.

3.1. Hydrogen peroxide/UV light process

Hydrogen Peroxide / UV light process includes H_2O_2 injection and mixing followed by a reactor that is equipped with UV light (200 to 280 nm). Use of ultraviolet radiation is to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical.

Followings are the various reactions describing UV/H_2O_2 process

H_2O_2+ UV Light $\rightarrow 2\ HO^\bullet$

$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O$

$H_2O_2 + HO_2^\bullet \rightarrow HO^\bullet + H_2O + O_2$

$2HO^\bullet \rightarrow H_2O_2$

$2\ HO_2^\bullet \rightarrow H_2O_2 + O_2$

$HO^\bullet + HO^{2\bullet} \rightarrow H_2O + O_2$

Higher initial hydrogen peroxide concentration produces higher hydroxyl radical concentration, which decomposes more target compound and optimal hydrogen peroxide concentration exists because overdosing of hydrogen peroxide would lead to reaction with hydroxyl radical and formation of $HO_2^\bullet$.UV/H_2O_2process is efficient in mineralizing organic pollutants. This process is that it cannot utilize solar light as the source of UV light due to the fact that the required UV energy for the photolysis of the oxidizer is not available in the solar spectrum.

In this waste treatment process H_2O_2has poor UV absorption characteristics and if the water matrix absorbs a lot of UV light energy, then most of the light input to the reactor will be wasted. Reactor design is special for UV illumination is required, while residual H_2O_2 should be addressed. Kinetic rate constant for the degradation process is inversely proportional to the initial concentration of the pollutant and waste water dilution should be done at an optimum level.

Efficiency of UV/H_2O_2 and $US/UV/H_2O_2$processes on the removal of malachite green as a model contaminant from textile industry was investigated. $US/UV/H_2O_2$was the most effective process for the degradation of malachite green as the use of ultrasound contributed together with photolysis to the scission of $H_2O_2$and the reaction rate increased with increasing temperature (294 to 307 K), power density (0.049 to 1.163 W ml) and decreasing initial concentration of the target compound (10 to 2 mg/l).

For the degradation of Phenolic compounds that are detected in olive mill waste water UV/H_2O_2 process are used. In degradation of Phenolic compound effect of hydrogen peroxide dosage, pH, UV and natural sunlight on the depolarization and removal of organic carbon and phenols from olive mill waste water.

The major factors affecting

- Initial concentration of the target compound.
- Amount of H_2O_2 used
- Wastewater pH.
- Presence of bicarbonate.
- Reaction time.
- UV light.

3.2 Fenton's reactions/H_2O_2

Mixture of ferrous iron (catalyst) and hydrogen peroxide (oxidizing agent), has been known as a powerful oxidant for organic contaminants and the $Fe^+$is called as Fenton's reagent.

Reactions are carried out in Fenton process

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet}$

$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^-$

$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet}$

$R^{\bullet} + Fe^{3+} \rightarrow R+ + Fe^{2+}$

Factors affecting Fenton process

- pH
- Amount of ferrous ion
- Concentration of H_2O_2
- Initial concentration of the pollutant
- Presence of other ions.

For Fenton's reagent processes ranges of optimum value of pH from 2 to 4 and higher than 4, the Fe2+ ions are unstable and they are easily transformed to Fe3+ ions, forming complexes with hydroxyl. H_2O_2 loses its oxidative power due to its breakdown to oxygen and water in alkaline solution. Wastewater pH adjustment is usually needed before treatment with Fenton processes and increase of ferrous ions and H_2O_2 concentration results to an increase of degradation rate.
The toxicity of H_2O_2 to several microorganisms and the use of excess amounts of H_2O_2 could possibly deteriorate overall degradation efficiency forcases that Fenton process is followed by biological oxidation. Organic compounds are inhibited by phosphate, sulfate, fluoride, bromide and chloride ions in Fenton's process.
Inhibition of Fenton's process by following

- Precipitation of iron
- Scavenging of HO•
- Coordination to dissolved Fe(III) to form a less reactive complex.

Electrochemical reactions include in Electro-Fenton methods situ generation of their agents used for the Fenton reaction and generated reagents depend on solution conditions, cell potential and nature of electrodes. Production of Ferrous ions oxidative dissolution of anodes such as iron metal or by reduction of ferric ions at an inert cathode such as platinum and H_2O_2 may be produced by dioxygen reduction at the cathode.

4. PHOTO-FENTON PROCESS (PHOTOCHEMICAL PROCESS)

The production of iron sludge can be reduced. Photo-Fenton reaction does not produce new pollutants and only small amount of iron salt is needed. The radiation sources of the Photo-Fenton process Using UV or solar light can increase the mineralization degree and make dark Fenton process more efficient by the photoreduction of $Fe(OH)^{2+}$ which leads to additional ·OH production and continuous regeneration of Fe^{2+}.

4.1 UV-A light

UV-A wavelength is between 315 and 400 nm. Experiments with UV-A light have been made to determine the best conditions for ethylenediaminetetraacetic acid (EDTA) photochemical removal by photo-Fenton and photo Fenton-like reactions. EDTA is a common chelating agent used in the photographic and metal industry, in textile and paper manufacturing, but it may cause harmful effects on the environment. Influence of UV-A on EDTA degradation was tested, using Fenton and photo Fenton-like reactions in the presence of Fe2+, Fe3+, Cu2+ and mixtures of Fe2+/Cu2+ and Fe3+/Cu2+ ions. Results show that the removal of TOC and EDTA degradation was efficient under irradiation.

4 .2 UV-CS light

UV-C wavelength is between 100-280 nm. Using UV-C light as a radiation source in the photo-Fenton process has not been tested enough yet, but there are some studies that show very promising results. UV-C light has been used in photo-Fenton oxidation of methyl parathion.
According to the research, methyl parathion was quickly destroyed because of the ·OH generated from Fenton's reaction and the UV-C irradiation.Presence of UV-C light in photo-Fenton process gives a faster oxidation as a result of the higher quantum yields.

4.2.1 Sunlight

In the recent years, using radiation of sunlight for the treatment of wastewater has drawn a lot of attention. Experiments with solar photo-Fenton were performed to achieve degradation of alachlor. Solar pilot-plant consisted of a reservoir tank, a recirculation pump, compound parabolic collectors exposed to sunlight and connecting tubing.
Experiments were made as follows: alachlor was homogeneously dissolved in the pilot-plant with the parabolic collectors while the pH was adjusted to 2.7 with sulphuric acid. According to the results, alachlor was completely degraded, mineralization of chloride and 85-95% mineralization of dissolved organic carbon (DOC) was achieved.

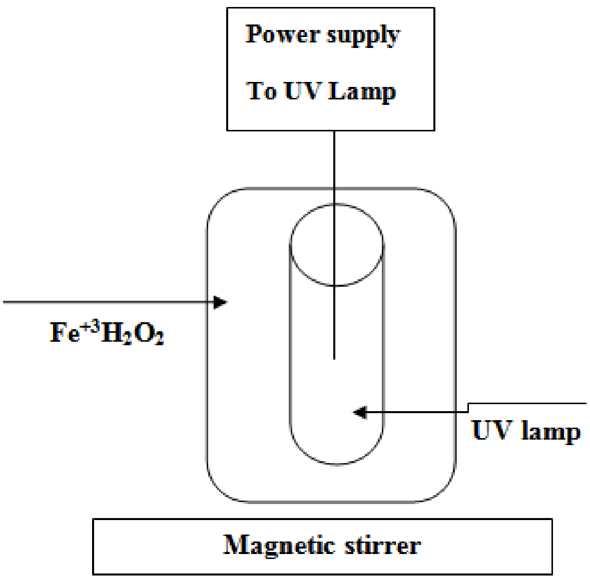

Fig.1 Photo Fenton process shows in the schematic diagram

Photo Fenton process shows in the schematic diagram
Consist of following parts

- UV Lamp with Cylinder
- Cylindrical cell or Reaction Vessel

- Power supply
- Magnetic Stirrer
- Inlet and Outlet for Waste water and Solutions.

Formation of hydroxyl radical also occurs by the following reactions.

H_2O_2+ UV → OH• + OH•

Fe^{3+} + H_2O + UV → OH• + Fe^{2+} + H^+

This process is combination of Fenton process and UV light could be an interesting allied in dye decolorization due to its capacity to influence the direct formation of •OH radicals. Pollutant degradation could be increased by irradiation of Fenton with UV light (photo-Fenton process).
In this process UV light leads not only to the formation of additional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe^{3+}. Concentration of Fe^{2+} is increased and the overall reaction is accelerated.
The oxidation using Fenton's reagent and photo-Fenton's reagent has been found to be a promising and attractive treatment method for the effective depolarization and degradation of dyes. The removal rate is strongly dependent on the initial concentration of the dye, Fe^{2+} and H_2O_2.

5 PARAMETERS TO BE ANALYSED

5.1 Physical Characteristics

- **Color:**This property of effluent can normally be detected by naked eye and color of the effluent mainly depends on some specific industrial waste depending on the operation of the industry.
- **Odor:**As waste water contains less oxygen in it then it starts omitting offensive odors, especially if it contains the gases like hydrogen sulphide.
- **Temperature:**The solubility of gases in the effluent is affected by temperature in addition it also affects the viscosity which in turn affects the sedimentation process of the effluent.
- **Turbidity:** If the effluent contains untreated matter or any other suspended matter the turbidity is more and turbidity can be measured by using turbid meters.

5.2 Chemical Characteristics

This is the important characteristics of the effluents is the main factors which decides its impact on stream and extent and the type of treatment required for its safe disposal and it manly contains the properties like total dissolve solids, pH value, chemical oxygen demand, bio-chemical oxygen demand etc.

- **Total Solids:**The solids presents in the effluent such as untreated matter dissolved substance etc are called the total solids.
- **pH value:** pH value of the effluent indicates the negative log of hydrogen ion concentration present in the effluent and indicates the alkalinity of effluent. If the pH value is less than 7 the effluent is acidic and if it is more than 7 the effluent is alkaline.
- **Chemical Oxygen Demand (C.O.D):**COD is measure the organic matter present in the effluent and the amount of oxygen used for oxidizing the organic matter present in the effluent.
- **Bio-chemical Oxygen Demand (B.O.D):**Oxygen required by the effluent for its biological decomposition called as BOD.

5.3. Characteristics of Pre-Treated Distillery Waste Water

Table 2. Characteristics of Pre-treated distillery waste water

Parameter	Value
pH	3.67
Total Solids	66,980 mg/l
Total Dissolved Solids (TDS)	14,660 mg/l
Chemical Oxygen Demand (COD)	34000 mg/l

6 Result

6.1 Experiment with 0.5:1 proportions of H_2O_2:Fenton's Reagent (450:900 mg/l)

After collecting the samples of waste water and giving treatment from all the three methods for every 15 minutes interval following are results obtained for all the parameters values.

Table 3 Experiment with 0.5:1 proportions of H_2O_2: Fenton's Reagent (450:900 mg/l)

Time (Min)	% Reduction COD	% Reduction Color
15	23	25
30	32	35
45	48	50
60	59	60
75	63	64
90	68	72
105	68	72

6.2 Experiment with 1:1 proportions of H_2O_2: Fenton's Reagent (900:900 mg/l)

After collecting the samples of waste water and giving treatment from all the three methods for every 15 minutes interval following are results obtained for all the parameters values.

Table 4 Experiment with 1:1 proportions of H_2O_2: Fenton's Reagent (900:900 mg

Time (Min)	% Reduction COD	% Reduction Color
15	28	30
30	42	44
45	67	68
60	78	80
75	87	88
90	92	94
105	92	94

CONCLUSION

- There is complete mineralization of organic matter.
- There is no need for any processing units on the surface.
- This process reduces organic loading in terms of chemical oxygen demand and done the removal of recalcitrant and toxic pollutants thus allowing for further conventional biological treatment.
- Fenton process is a relatively economical method since it requires no additional energy when compared to many other AOPs and both iron and hydrogen peroxide are relatively cheap and safe.
- The reactions are efficient at low pH-levels (<6) - which is difficult to maintain.
- In some cases chemical oxidation may even lead to increased toxicity due to the formation of even more toxic oxidation by-products.
- The Fenton Process for waste water treatment shows better results over the conventional method.
- The Fenton Process can be used as a tertiary treatment to waste water.
- The other parameters such as TDS, COD, BOD shows effective changes over conventional method.
- Waste water samples are collected from industry after giving primary and secondary treatment and Fenton Process with any convectional method gives better results.

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