

Research Article

Reduction of Color and COD of Anaerobically Treated Distillery Wastewater by Electrochemical Method

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Abstract

Water pollution control is presently one of the major thrust areas of scientific research. While colored organic compounds generally impart only a minor fraction of the organic load to wastewaters, their color renders them aesthetically unacceptable. Stringent regulating measures are coaxing industries to treat their waste effluents to increasingly high standards. Various studies have been carried out here in reduction of color and COD from anaerobically treated distillery wastewater by electrochemical method which showed a good reduction in color (97-98%) and COD (70-72%). The optimized parameters for the process are Electrode distance 1cm, initial pH 4, current density 2 Amp/dm² for 3 hours and color and COD reduction observed are 97.8% and 68% respectively.

Keywords: Anaerobically treated distillery waste water, Electrocoagulation, spent wash, COD & Color reduction, color reduction, wastewater, COD reduction, Melanoidins.

Introduction

Presence of color and its causative compounds has always been undesirable in water used for either industrial or domestic needs. Color is a visible pollutant. Common man may not object to the discharge of colorless effluents laden with toxic and hazardous pollutants. Among all industries which incorporate color to water bodies is distillery industry. In India there are 285 distilleries, producing 2.71 billion litres of alcohol and generating 40 billion litres of wastewater annually. The wastewater generated from distillery units known as spent wash, is nearly 15 times the total alcohol production. Out of 285 distilleries in India, 129 have completed the construction of Biomethanation digesters for the primary treatment of the effluent, in 49 distilleries, it is under construction and the remaining is under planning stage. In the recent past, agro-based industries have emerged as the largest producer of alcohol.

Characteristics of Distillery Spent Wash

Distilleries are one of the most wastewater generating industries in India. The wastewater generated from this industry known as spent wash, which is produced as a result of fermentation and distillation of the molasses. Spent wash is characterized by its reddish brown color, high temperature, and low pH (4.2-4.5), high ash content and contains high percentage of dissolved organic and inorganic matter of which 50 % may be present as reducing sugars. It contains about 90-93 % water and 7-10

% solids; sugar being 2 – 20 % and protein 10 – 11 % in the dry spent wash. The metals present in spent wash are Fe, Mn, Zn, Cu, Cr, Cd and Co with electrical conductivity in the range of 15 - 23 deci siemens per meter (dS/m). The spent wash contains very high amounts of potassium, calcium, chloride, sulphate and BOD (40,000 - 50,000 mg/l) and COD (10,000-1, 25,000 mg/l).

Distillery wastewater poses a serious threat to water quality by lowering pH value of the stream, increasing organic load, depletion of oxygen content, destruction of aquatic life and bad smell. Groundwater contamination by effluent with high BOD and salt content near the lagoon sites in most of the distilleries has been reported widely. At places, the problem of groundwater pollution due to land disposal of distillery wastewater leads to provide separately the potable water to the surrounding villages. The use of spent wash for pre-sown treatment of agricultural land is being in practice for last few decades. Though it seems lucrative, this method is being discouraged.

Recognizing the problem of treating distillery effluent to a level suitable for disposal into the river/land, Minimum National Standards (MINAS) have been developed by CPCB, Ministry of Environment & Forests, through the Environment (Protection) Act 1986. Notification, dated January 8, 1990, specified effluent standards according to the disposal conditions, the BOD standards so specified are as follows: 30 mg/l for disposal into inland surface water; 100 mg/l for disposal on land for irrigation. The standards also include stipulations regarding net additional contribution to groundwater

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quality in terms of BOD not to exceed 3 mg/l and nitrate not to exceed 10 mg/l.

In 2003, CPCB constituted a task force on Corporate Responsibility for Environmental Protection (CREP). Under this task force, a road map has been developed to achieve zero discharge of spent wash into inland surface as per the following schedule.

A wide range of wastewater treatment techniques are known which includes biological processes for nitrification, denitrification and phosphorous removal; as well as a range of physico-chemical processes that require chemical additions. The commonly used physico-chemical treatment processes are filtration, air stripping, ion-exchange, chemical precipitation, chemical oxidation, carbon adsorption, ultra filtration, reverse osmosis, electro dialysis, volatilization and gas stripping.

In almost all distilleries demethanation process is adopted in order to treat spent wash which reduces pollutant concentration but still not in permissible limit to dispose into land or water bodies. Following table shows Characteristic of Sample used:

Table 1: Characteristic of Sample used:

Parameters	Values
pH	9.35
Color	Dark brown
BOD (mg/l)	2,085
COD (mg/l)	17,600
Ammonia (mg/l)	2,910.4
Chlorides (mg/l)	1,190
Solids (TD) (mg/l)	33,744
Conductivity (mS/cm)	30-32

The secondary spent wash produced by the anaerobically digested primary molasses spent wash (DMSW) effluent is darker in color, require huge volumes of water to dilute it and is currently used in irrigation water causing gradual soil darkening. The dark color of this molasses wastewater is caused by high molecular-weight organic compounds, from the non-enzymatic browning reaction between aldoses and amino-compounds, and the caramels which are produced by thermal degradation and condensation reactions of sugar these brown pigments collectively are known as 'melanoidins'.

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. During heat treatment, the Maillard reaction (non enzymatic reaction) takes place accompanied by formation of a class of compounds known as Maillard products. The reaction proceeds effectively at $>50^{\circ}\text{C}$ and it is favored at pH 4–7. Melanoidins are one of the final products of the Maillard reaction (M.P.Miranda et al 1996)

The empirical formula of melanoidin is $\text{C}_{17-18}\text{H}_{26-27}\text{O}_{10}\text{N}$. The molecular weight distribution is between 5000

and 40,000. It is acidic, polymeric and composed of highly dispersed colloids, which are negatively charged due to the dissociation of carboxylic acids and phenolic groups. When discharged to surface water, this melanoidin may cause reduction of sunlight penetration in rivers, lakes or lagoons which in turn decreases both photosynthetic activity and dissolved oxygen concentration there by severely affecting the aquatic life. Disposal on land is equally detrimental, causing inhibition of seed germination and depletion of vegetation by reducing the soil alkalinity and manganese availability. Recently, decolorization of molasses melanoidin has been attempted, but with limited success.

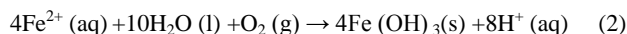
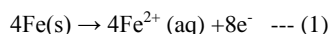
Conventional methods dealing with the treatment of distillery effluents consist of various combinations of biological, chemical and physical methods. Several methods viz., filtration using variety of filters, coagulation by added chemicals, reverse osmosis, adsorption, ion exchange process, dissolved air flotation method etc., are available for treating distillery effluents. Many of these methods are using more quantity of water and they are either pollutant specific, less efficient and more expensive than simple discharge without any effluent treatment. Hence, these methods become obsolete and new methods need to be sought. By observing the several advantages of electrochemical methods on other treatment techniques, some of color and COD reduction of distillery wastewater works carried out here.

Electrocoagulation process is characterized by an effective removal these of pollutants, compact size of the equipment, and simplicity in operation, low capital cost and operating cost. This process is more effective than other methods because of the subsequent electro flocculation. In electro flocculation, the pollutants are removed by the hydrogen bubbles, which are generated during Electrocoagulation. These bubbles uplift the coagulated/agglomerated pollutant particles to the surface, from where it could easily be removed. It is also reported that electrically added aluminum ions are more active than chemically added aluminum ions. This means that, less aluminum is required and Electrocoagulation could be used to treat a number of wastewaters, which could not be handled by chemical flocculants such as alum. This process is used to remove suspended (fine) solids and dissolved molecules. The suspended solids include bacteria, algae, clay and spores. The dissolved matters are organic matter (humes), dye molecules, detergent molecules and other materials.

General principle of Electrocoagulation with aluminum and iron as an electrode, Electrocoagulation is based on the in situ formation of the coagulant as the sacrificial anode (usually aluminum or iron cations) corrodes due to an applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. This technique combines three main interdependent processes, operating synergistically to remove pollutants: electrochemistry, coagulation and hydrodynamics. The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics

such as pH, particle size, and chemical constituent concentrations will also influence the Electrocoagulation process. According to Mollah et al., oxidation of iron in an electrolytic system produces iron hydroxide, $\text{Fe}(\text{OH})_n$, where $n = 2$ or 3 . Two mechanisms have been proposed for the production of $\text{Fe}(\text{OH})_n$; one of them was given below reactions (1)–(4) and more details have been given elsewhere by (Mollah et al 2001)

• Anode:



• Cathode:



• Overall:



The $\text{Fe}(\text{OH})_n(\text{s})$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation. (Mollah et al 2001).

Means and Method

The wastewater sample used for the work is brought from Distillery industry from Najangudu. And analyses of the characteristics were found out using Standard procedure.

From all physico-chemical treatment methods, electro coagulation (EC) was selected to check the color and COD reduction. Several attempts were already done in this area by using several electrodes and some electrolytes for better conduction with diluted samples. As characteristics of distillery wastewater used here had high conductivity (30-32 mS/cm), addition of external electrolytes was not required. Process was carried out without any dilution using aluminum and stainless steel as anode and cathode electrodes respectively. The process carried out in 250 ml beaker contains 200ml wastewater kept on mantle with magnetic stirrer. The electrode area covering 25cm^2 dipped and connected to (0-2 A; 0-30 V) DC-power supply. The cold water bath used to maintain temperature constant around 30°C throughout process.

First step Electrocoagulation processes were carried out with wastewater without any initial dilution at various current densities (2, 4, 8 Amp/dm^2) for one hour. After this experiment current density to be used further were determined. Then further processes are carried out to find the optimum condition by varying parameters like Electrode distance (from 1cm -3cm), initial pH(2pH – 10pH) and time(1hr - 6hrs). Some experiments are also carried out with 10% (v/v) diluted wastewater to check the effect by using the optimum condition determined by the above experiments.

COD analysis

The chemical oxygen demand (COD) was determined by the standard closed reflux titrimetric method. The COD removal was determined by the difference between the initial wastewater COD with added nutrients and the final COD after the treatment.

Color detection

Color elimination was determined as the decrease in optical density at an absorbance of 622nm for wastewater without any dilution, followed by filtration through a $0.45\mu\text{m}$ filter. The decolorization yield was expressed as the percentage of the decrease in absorbance at 622nm related to the initial absorbance at the same wavelength.

First step Electro coagulation processes were carried out with wastewater without any initial dilution at various current densities (2, 4, 8 Amp/dm^2) for one hour. Then further processes are carried out to find the optimum condition by varying parameters (electrode distance, initial pH, time).

Results and Discussion

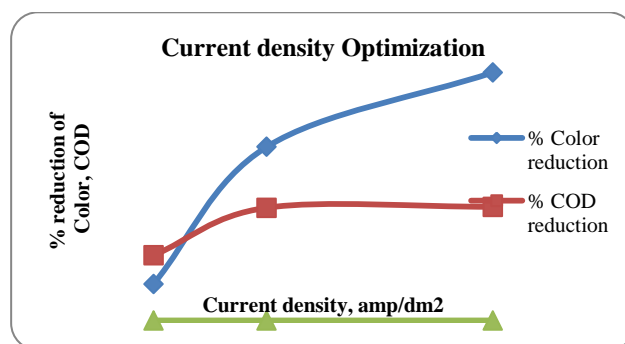


Fig.1. Current density optimization

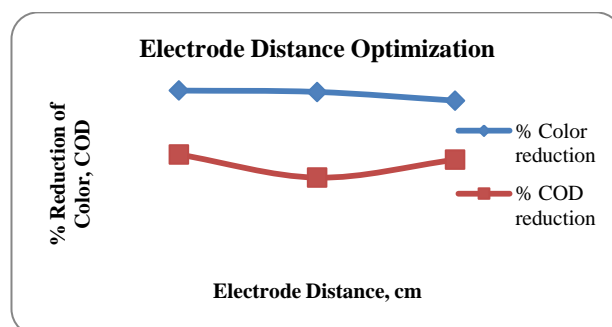


Fig.2. Electrode distance Optimization

As noted in characteristics of treated distillery wastewater, the conductivity of wastewater was good enough for better conduction and there was no need to add any external electrolyte to enhance the electro coagulation process.

Initially 200ml of anaerobically treated distillery wastewater was taken in a beaker, the electrode distance maintained was 1cm. the current densities were varied as 2,4,8 Amp/dm^2 for operating time of one hour. The initial and final pH was noted down. It was found that at high

current density (8 Amp/dm^2) the color removal was 80% and COD removal was 36.67%. At higher current density, the froth formation was more and temperature control was also difficult.

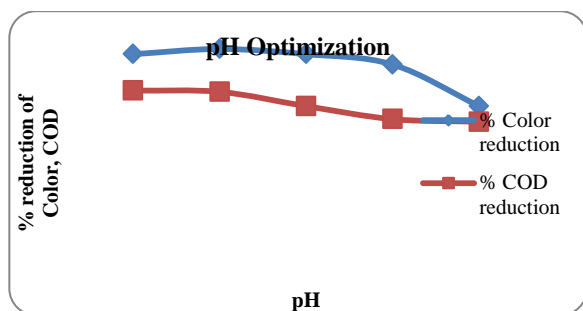


Fig.3. pH optimization

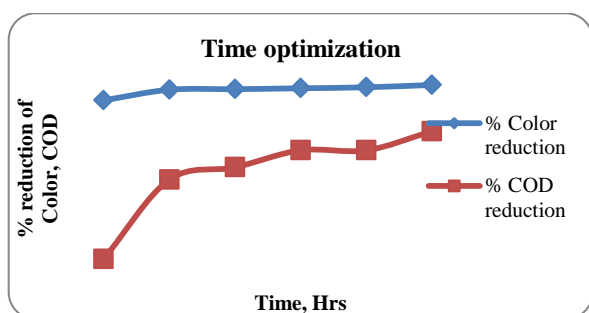


Fig.4. Time optimization

From literature it was found that the color reduction was favorable at lower pH. Experiments were carried out by varying the pH between 2 to 10 and to find the optimum pH value to get maximum removal of color and COD. This was done by using $1\text{N H}_2\text{SO}_4$ and 1N NaOH . The results obtained from this are shown in fig 2. An optimum of pH 4 was found and the color removal was 94% and COD removal was 77.5%.

Further experiments were carried out at initial pH 4, current density (CD) 4 Amp/dm^2 and for 2 hours to get better results at different electrode distance (ED) ranging from 1 to 3cm. The results are shown in fig 3. The optimum electrode distance was also found out to be **1cm** for maximum removal of color and COD i.e. 97.77% and 68.8% respectively.

So with these parameters $\text{CD} = 4 \text{ Amp/dm}^2$, $\text{ED} = 1\text{cm}$, and initial $\text{pH} = 4$, the results seemed to be good. With these parameters for 4hours, the removal percentage was maximum. The final results were as follows i.e. color reduction was 98.3% and COD was 67%.

The problem of temperature control for longer time duration is a draw back and the froth formation seems to be faster. To overcome these difficulties, experiments were carried out with further lower current density and at various times. The results obtained by this experiment showed (fig 4) maximum reduction of color (99.4 %) and COD (77.58%) at 6 hours. During this experiment it was observed that at the lower current density (2 Amp/dm^2) after 3 hrs the color (97.8%) and COD (60%) reduction

was as similar as what observed in high current density case.

Conclusion

In present study, the treated distillery wastewater has been subjected to Electrocoagulation treatment processes.

- Electrocoagulation processes carried out using aluminum and stainless steel as anode and cathode are capable of removing Color into almost colorless (97.77%) and reduce COD (70.0%) for 3 hours EC process and color (99.4%) and COD (77.58%) reduction observed for 6 hours EC process from treated distillery effluent without addition of any electrolytes.
- Several experiments carried out to find the optimum condition for the Color reduction processes. The optimum conditions for maximum Color and COD reduction are: electrode distance 1cm, current density 2 Amp/dm^2 , duration 3 hours, initial pH of wastewater 4. The pH adjustments for the processes were carried out using $1\text{N H}_2\text{SO}_4$.

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