COD Reduction of Anaerobically Digested Distillery Spentwash By Electro-Fenton Process

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Abstract- Advanced oxidation processes (AOPs) are powerful for degrading most organic and inorganic compounds, which led the way in the treatment of wastewater and so has attracted great attention. In present study shows, COD reduction efficiency of anaerobically digested distillery effluent by Electro-Fenton (EF) process, as it is one of the AOPs, evaluated in lab scale experiments. An electrochemical batch reactor furnished with two iron electrodes, connected parallel to each other and used to carried out the experiment. The E-Fenton process was studied for optimization of power consumption, agitation speed and the reaction time under different pH conditions (3.0, 5.0 and 7.0). In this process COD reduction up to 24.9 % was achieved at 18 W power consumption in acidic pH 3 with 500 rpm agitation speed and within 120 min reaction time. Electro-Fenton process can successfully apply for the treatment of ADSW having high organic content in the first stage only, because organic pollutants does not degrade completely and further treatment is necessary before discharging it into natural ecosystem.

Key words- Anaerobically digested distillery spentwash, AOP, Electro-Fenton process, COD reduction

1. INTRODUCTION

Distillery industry is one of the heavily polluting industry out of seventeen prescribed by Ministry of Environment, Forest and Climate Change (MoEFCC) Govt. Of India which is covered under central action plan [1]. The wastewater produced from distillation of fermented slop is very complex, caramelized and bulky agro industrial waste which is having temperature ranges between 70–80 ^{o}C, dark brown in color, acidic in nature (low pH), with high concentration of organic materials and solids. Pollution load of the distillery effluent depends on the purity of molasses, unit operation for handling of molasses and recovery of alcohols [2]. Most Indian distilleries exclusively use cane molasses as raw material for fermentation [3]. The residue of the fermented mash, which comes out as liquid waste, is termed as spent wash [4]. On an average 8–15 L of effluent is generated for every liter of alcohol produced [5]. Its complex nature is due to existence of the brown polymers, melanoidins, which formed by Maillard amino carbonyl reaction. These composites have antioxidant properties, which render to many toxic microorganisms especially those typically present in wastewater treatment processes [6]. In addition with melanoidins, the other recalcitrant complexes present in the distillery effluent are caramel, variety of sugar decomposition products, anthocyanins, tannins and dissimilar xenobiotic compounds [2]. Various treatment technologies have been explored for reducing the pollution load of distillery effluent i.e spentwash. Biological treatment used for distillery spent wash is either aerobic or anaerobic, but most of the distilleries in India use anaerobic treatment as pretreatment to the distillery spentwash. Anaerobic process is a very promising re-emerging technology which has stimulating advantages as compared to aerobic treatment. It has high capacity of degrading concentrated and robust substances. It produces small amount of sludge, needs less energy and can become profitable by cogeneration of valuable biogas [7]. The anaerobically digested distillery spentwash is necessary to cope up with environmental standards.

Table 1. Characteristics of anaerobically treated distillery effluent [8].

Parameters	Values
pH	7.5–8
BOD5 (mg L−1)	8000–10,000
COD (mg L−1)	45,000–52,000
Total solid (TS) (mg L−1)	70,000–75,000
Total volatile solid (TVS) (mg L−1)	68,000–70,000
Total suspended solid (TSS) (mg L−1)	38,000–42,000
Total dissolved solids (TDS) (mg L−1)	30,000–32,000
Chlorides (mg L−1)	7000–9000
Phenols (mg L−1)	7000–8000
Sulphate (mg L−1)	3000–5000
Phosphate (mg L−1)	1500–1700
Total nitrogen (mg L−1)	4000–4200

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 [9].

1.1. Advance Oxidation Process (AOP)

The main tool of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (OH•) are operative in destroying organic chemicals because they are reactive electrophiles (electron preferring) they react rapidly and non-selectively with almost all electron-rich organic compounds. AOPs are centered on the chemistry of hydroxyl radicals (OH•, E = 2.8V versus SHE). They have powerful technologies to treat wastewater containing recalcitrant organic compounds [10]. Hydroxyl radical reacts with pollutants in a non-selective

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way, the pollutant oxidized into mineral products, yielding CO2 and inorganic ions [11].

1.1.1. Electro-Fenton process

In presence of ferrous ions and in acidic aqueous medium the oxidation power will be enhanced due to the production of a very reactive one-electron oxidizing agent hydroxyl radical (•OH) from the Fenton reaction.

Compared to the conventional Fenton process, the electro-Fenton process has the benefit of allowing better control of the process and ducking the storing and transport of the H_2O_2. The kinetics of the electrochemical method are about 100-fold faster than biological oxidation methods [12]. Electrochemical techniques are beneficial as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost-effectiveness [13]. This electro-Fenton process can produce •OH radicals by the simultaneous electrochemical reduction of O_2 in the presence of catalytic amounts of ferrous ions [14].

The-most important factor for the E-Fenton process is pH. Generally, Fenton processes are conducted in acidic medium. Most of the studies reported that the optimum pH of Fenton process is around 3.00 [15, 16]. Acidic medium is the auspicious condition for the production of H_2O_2 [17]. Due to the revival of Fe^{2+}, through reaction between Fe^{3+} and H_2O_2, Fenton process becomes less effective at pH<3 [18]. At upper pH, the efficiency of E-Fenton process declines rapidly, especially pH>5. This happens because H_2O_2 is unstable in basic solution. H_2O_2 rapidly decomposes oxygen and water at neutral to high pH [19].

Efficiency of Electro-Fenton treatment assessed in laboratory scale experiment, which is one of the electrochemical treatment applications. The process includes the combined advantages of electrochemical and Fenton treatment methods.

2. MATERIAL AND METHODS

2.1. Material

Anaerobically Digested Spent Wash (ADSW) collected from M/s. Someshwar Sahakari Sakhar Karkhana Ltd (distillery unit) located in Maharashtra state of India. It was collected from outlet of Continuous stirred tank reactors (CSTR). The major physico-chemical characteristics of the ADSW at the time of collection were: pH: 7.3, COD: 24,800 mg/L, BOD: 6,200 mg/L, conductivity: 11 mS20/cm, color: dark-brown, odor: burnt sugar.

2.2. Methods

Laboratory scale experiment were performed in batch mode at room temperature and 0.5-liter capacity glass beaker arranged with iron electrode as cathode and an anode both at the distance of 4 cm from each other. The dimensions of electrode were ϕ 2 mm x 4 cm. The electrodes were situated vertically and fix at 4 cm away from each other. Both electrode were deepen in reactor with 0.3-liter working volume. The electrode was linked to a DC power supply provide power at 3, 9, 12, 15, 18 W electric current intensities measured throughout the experiment. The batch was stirred (100-500 rpm) with a magnetic bar (REMI make 2MLH magnetic stirrer) to ensure homogeneity and transport of reactants

toward/away from the electrodes. The effect of pH on electrochemical oxidation was studied at different pH (3.00, 5.00, 7.00). The pH of the reaction mixture was measured using a pH meter (EQUIPTRONICS, EQ. 661, India) and adjusted appropriately for every experiment using 0.1M H_2SO_4.

2.2.1. Electro-Fenton process

The electro-Fenton process was carried out with iron
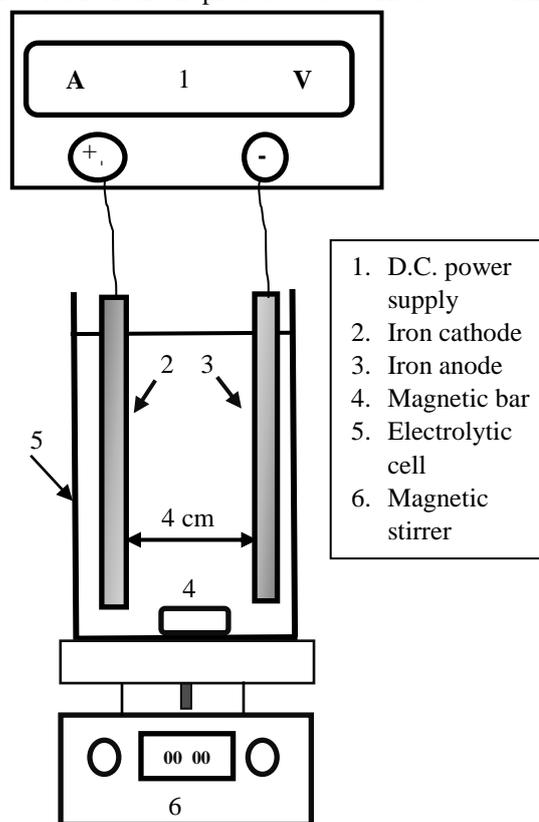
Figure 1: Electro-Fenton Experimental Setup
U. Kurt et. al, 2007 [20]

based electrode cathode and anode, the H_2O_2 is produced electrochemically via oxygen reduction; then addition of Fe^{2+} into the system generates analogously OH· radicals in the classical Fenton's reaction between Fe^{2+} and H_2O_2 [21]. Ferrous ions acts as coagulation materials in the electro-chemical treatment. On the other hand, ferrous ions create hydroxyl radicals and catalyze the Fenton reaction.

2.2.2. Analytical Procedures

Chemicals were obtained from Merck, India which has analytical reagent (AR) grade. The pH of the reaction mixture was measured by using a pH meter (EQUIPTRONICS, EQ.661, India) and adjusted appropriately for every experiment using 0.1M H2SO4. COD removal of ADSW after each treatment was check, by close reflux method (colorometric method) in accordance with standard methods of water and wastewater analysis standard methods in APHA AWWA.

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3. EXPERIMENTAL RESULT AND DISCUSSION

In this experiment, COD removal by E-Fenton process were studied with various impact causing parameters and results are discussed below in details.

3.1. Effect of pH

Figure 2: Effect of pH on COD removal
EF processes were perform for three different pH i.e.
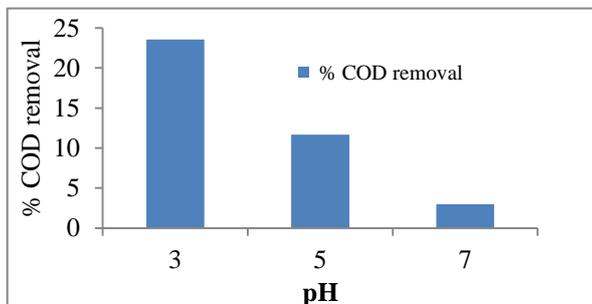
3.00, 5.00 and 7.00, and other parameter were fixed at each pH variation experiment. The agitation speed was set at 500 rpm for 120 min at 15 W current intensity. Fig. 2. shows that Removal of COD by E-Fenton process are more efficient in acidic medium than in neutral medium. In E-Fenton process maximum 23.55% COD observed at 3.00 pH. With increase in pH to neutral, the COD removal efficiency decreases. COD removal efficiency reduces up to 11.39% by increase in pH to 5.00 and at neutral pH (7.00) COD removal efficiency observed up to 2.98%. Most of the literature also reported optimum pH of E-Fenton process is 3.00.

3.2. Effect of treatment time
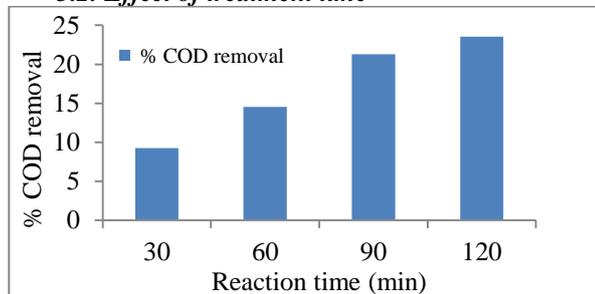
Figure 3: Effect of treatment time on COD removal
The effect of treatment time of E-Fenton process shown in fig. 3. E-Fenton experiment conducted at optimized pH 3.00, 15 W power supply with agitation speed of 500 rpm. To study the effect of treatment time process were conduct for 30, 60, 90 and 120 min interval in batch rector. COD removal efficiency 9.27%, 14.52%, 21.31% and 23.55% achieved at 30, 60, 90 and 120 min time respectively. COD removal efficiency gradually increase with increase in time and conquered constant after 120 min. COD reduction was observed till complete consumption of the Fenton's reagent that has been added to the system.

3.3. Effect of agitation speed
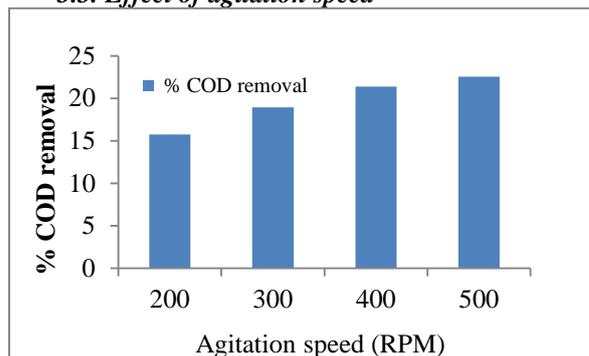
Figure 4: Effect of agitation speed on COD removal
E-Fenton process conducted at various agitation speed i.e. 200, 300, 400, and 500 rpm to evaluate the effect of agitation speed on COD removal at pH 3, 15 W power and 120 min treatment time. There was a
Steady increase in COD reduction efficiency from 15.73% to 22.55 % with an increase in agitation speed from 200 to 500 rpm. This is because, with an increase in agitation speed, the increase in movement of ADSW, which reacts more rapidly with electrodes and generate more ions. Increasing the agitation speed beyond 400-500 rpm doesn't shows major effect on the COD removal efficiency. At higher agitation speeds, the Fenton's reagent gets well mixed which results in increased oxidation of the organic pollutants [22].

3.4. Effect of current intensity
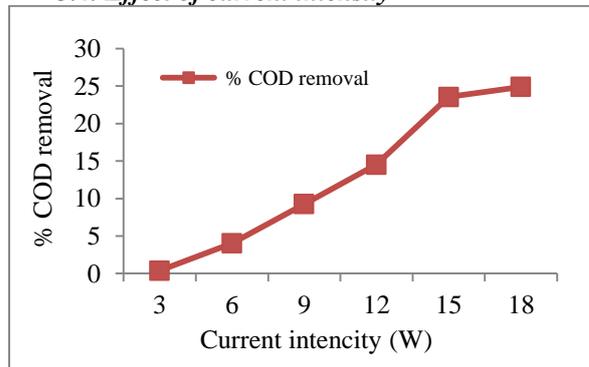
Figure 5: Effect of current intensity on COD removal
Current intensity is a significant parameter that exerts a large impact on the degradation rate of recalcitrant pollutants, which undergoes Fenton electrolysis. The electro-Fenton process based on the continuous electro-generation of Fe^{2+} ion. To study its effect, a sequence of electrolysis reaction were investigated with varying applied current intensity from 3 - 18 W to 300 ml ADSW at pH of 3.00 for 120 min with 500 rpm. Cumulative current intensity led to the rise in COD reduction efficiency. Higher current intensity increases the amount of H_2O_2 produced, thus increasing the number of •OH in the electrolyte, which are highly reactive and responsible for the degradation of recalcitrant pollutants. In addition, higher regeneration of ferrous ion from ferric ion with higher voltage increases the efficiency of reactions [23]. The rate of dissociation of iron electrode increased with an increase in current intensity. Initially at 3W COD reduction efficiency was 0.4% that increased by 1.3%, 9.27%, 14.52%, 23.55% and 24.9 % at 6, 9, 12, 15, and 18 W current intensity respectively, achieved in 120 min

of electrolysis time. After 15 W rate of COD, reduction efficiency goes down. However, the rate of COD reduction toughly depends on the current intensity and concentration of the organic matter present in ADSW.

4. CONCLUSION

In this study, the efficiency of COD reduction in ADSW was evaluate for different variables such as current intensity, pH, reaction time and solution agitation speed, which give rise to significant differences in the efficiency of the electro-Fenton process. For Electro-Fenton process, 24.9% ADSW COD reduction was attained using Fe-Fe electrode in electrolysis treatment. The COD removal efficiency found more at low pH (3.00), agitation speed 500 rpm, treatment time 120 min and power consumption 15 W and 18 W.

Acknowledgments

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