IMPROVEMENT OF BOD₅/COD RATIO INPRE-TREATED DISTILLERY WASTE WATER BY ELECTROCHEMICAL TREATMENT METHOD

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ABSTRACT

Electrochemical oxidation of low (BOD₅/COD) ratio post-methanation distillery wastewater was investigated. The effects of operating parameters like pH, electrolysis duration and current density on COD removal were studied. At a current density of 0.03 Ampere/cm² and at pH 3 the COD removal was found to be 72%. The BOD₅/COD ratio of pretreated distillery wastewater was 0.145 and increased to 0.686 for an optimum of 120 minutes electrolysis duration indicating improvement of biodegradability of wastewater. The TOC reduction is 8.77% at 180 minutes of electrolysis duration. The maximum anodic efficiency observed was 21.58 kg COD h⁻¹A⁻¹m⁻² and the minimum energy consumption observed was 84.16 wh kg⁻¹ COD. The kinetic study reveals that reaction rate (k) decreases with increase in pH and increases with increase in current density.

Key Words : Electrochemical, Treatment, Distillery, Wastewater, Aluminum, Electrode.

INTRODUCTION

Distillery waste in the form of "spent wash" is amongst the worst pollutants produced by distilleries both in magnitude and strength. The wastewater characterized by high BOD, high COD and high recalcitrant organics with dark in color. Most of these organics are known to persist in nature[1]. Various secondary treatment techniques have been attempted by several researchers for the removal of organic and recalcitrant pollutants and anaerobic digestion has gained wide acceptability due to methane recovery in the anaerobic step of the treatment. Pathade, (2002)[2] found that anaerobic treatment results in 60-85% of the BOD reduction, but still substantial amount of recalcitrant organic pollutants are left behind which requires post treatment. Research work has also been carried out in the past to evaluate alternate options for abating the pollution potential of post-digested distillery effluent. They include physico-chemical treatment[3] and bioremediation[4].

The BOD_5/COD ratios values depend on the nature of the wastewater namely, whether is municipal or industrial oriented and vary considerably with the degree of treatment the wastewater has undergone. The BOD_5/COD ratio value for municipal raw wastewater in general is in the range of 0.4 to 0.8, whereas for some industrial raw wastewater it will be

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less than 0.4. In general this ratio is used to indicate the biodegradability of wastewater. If BOD_5/COD ratio is greater than 0.5, then the waste is amenable for biodegradation and if it is less than 0.5, then it is not amenable for biodegradation by the microorganisms, because of the presence of recalcitrant material in wastewater. Recalcitrant materials are highly complex materials, which are not easily biodegradable by the microorganisms. After improvement in BOD_5/COD ratio of wastewater by electrochemical methods it can treated further by biological methods.

Normally BOD_5/COD ratio of pretreated distillery wastewater is very low, further treatment by biological methods is very difficult. Many researchers have made attempts to use electrochemical methods for the treatment of high strength wastewater. The electrochemical treatment is an emerging technology used for the destruction of recalcitrant organics from different wastewaters[5-10]. Several researchers have reported the mechanism and application of electrochemical process for treatment of different industrial wastewater[11-13].

Studies have also been done on electrochemical treatment of anaerobically digested distillery effluents. Among them Manisankar et al., (2003)[14] have studied electrochemical treatment in a static electrochemical cell employing two different kinds of anodes viz., graphite and titanium anodes and stainless steel cathode under varying conditions of current density. Jegan et al, (2002)[15] have conducted experiment on distillery wastewater using triple oxide coated titanium as anode and stainless steel as cathode in a batch recirculation electrochemical cell. Piya-areetham et al., (2006)[16] also conducted experiment on distillery wastewater using graphite particles and titanium sponge as voluminous anodes and cathode made from Ti/RuO_2.

It is evident from the above discussion that, the treatability studies of the pretreated effluent in terms of enhancing BOD_5/COD ratio have not been studied. Hence the main objective of the present study is to investigate the applicability of electrochemical treatment for the improvement in BOD5/COD ratio of post-methanation distillery wastewater. Furthermore, the effect of operating factors such as electrolysis duration, pH and current density on COD removal and improvement in (BOD_5/COD) ratio were also evaluated in this study.

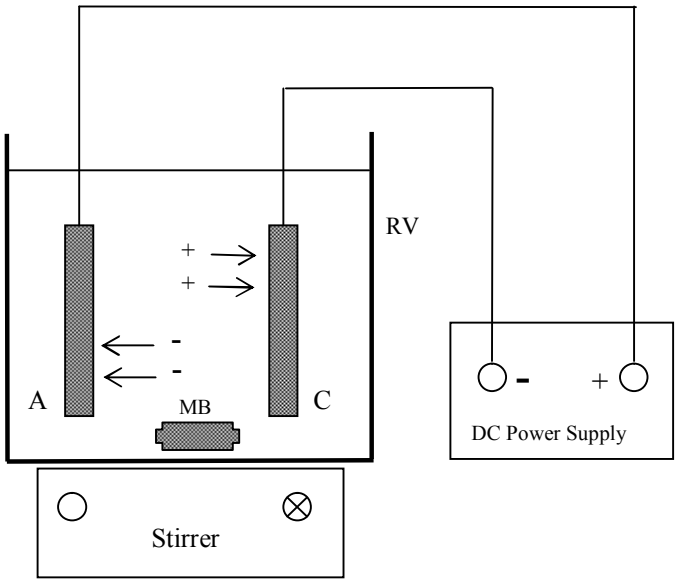
MATERIAL AND METHODS

For this study post-methanation distillery wastewater was collected from the anaerobic lagoon of distillery effluent treatment plant. The wastewater was analyzed for various parameters and is characterized by high COD in the range of 42240-46440 mg/L, BOD of 6757-8600 mg/L, chlorides ranging from 6300-7200 mg/L and pH varying between 7.7-7.95, which indicates that the wastewater contains high amount of organics. The initial (BOD_5/COD) ratio was found to be very low in the range of 0.159 to 0.185, which suggests that there is a presence of recalcitrant nature of organics in the wastewater.

Electrochemical Reactor setup

A plexi-glass laboratory scale batch reactor of working volume 1.5 litres with dimensions 13.5 cm x 19 cm x 14.5 cm was used for electrochemical oxidation experiments. The aluminum plates of size 5 cm x 5 cm was used as both anode and cathode electrode which were placed at a

fixed distance of 2 cm apart. The experimental setup is shown in **Fig. 1**. A direct current power supply unit (Textronix-35D, 0-10A, 1-15V) was used for current supply. The samples were collected at pre-assigned regular time interval from the sampling port provided in the reactor and the samples were analyzed for various parameters. All the analytical procedures followed the standard methods for examination of water and wastewater[17].



A-Anode, C-Cathode, MB-Magnetic Bit, RV-Reactor Vessel

Fig. 1 : Electrochemical batch reactor setup

The first batch studies conducted were to find the optimum electrolysis duration at the existing pH of the post-methanation distillery wastewater. At the optimum electrolysis duration, further experimental runs were conducted pH of 3, 5 and 7. The optimum pH, which resulted in maximum COD removal, was fixed up for further experiments with varying current densities. Thus all the experimental conditions such as duration of electrolysis, pH and current density were optimized on the basis of maximum percent COD removal efficiency.

RESULTS AND DISCUSSION

Effect of Electrolysis Duration

The initial experiments were conducted at the existing wastewater pH of 7.9. **Fig. 2** shows the variation in percent COD removal along with BOD_5/COD ratio. The maximum of 48.76 % COD reduction has been achieved in 120 minutes of electrolysis duration. The experiment was continued further and there was slight decline in COD removal, which may be due to the exhaustion of hypochlorite ($HClO_3^-$) and free chlorine generation in-situ in the reactor (indirect oxidation). It was observed that BOD_5/COD ratio increased from 0.178 to 0.583 at 120 minutes of optimum electrolysis duration, suggesting increase in biodegradability. The increase in BOD concentration is attributed to the fact that

some of the organics have broken down into smaller fragments, which are more biodegradable than parent compounds[18].

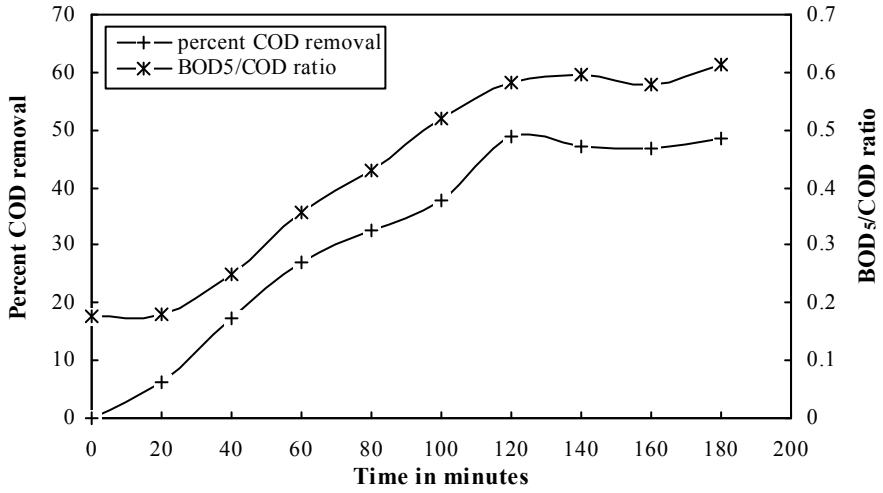


Fig. 2 : Variation of COD removal efficiency and BOD_5/COD with electrolysis duration

Effect of pH

Individual experiments were conducted at varying wastewater pH of 3, 5 and 7. Based on the previous experiment the electrolysis duration was fixed at 120 minutes. The pH of wastewater was adjusted using NaOH or H_2SO_4 to get the desired pH throughout each run. From **Fig. 3** the maximum COD reduction of 70.51% was observed at wastewater pH while at pH of 7 and 5, the COD removal rate was 53.42% and 66.71% respectively. This shows that acidic condition is more favorable for the treatment of distillery wastewater. The BOD_5/COD ratio exhibited an analogous optimum increase from 0.192 to 0.684 at pH 3 as shown in **Fig. 4**. The decrease in COD removal rate and BOD_5/COD ratio with increase in pH is may be due to the decreased production of chlorine/ hypochlorite at higher pH condition, because of the formation of chlorate and perchlorate as a side reaction[19].

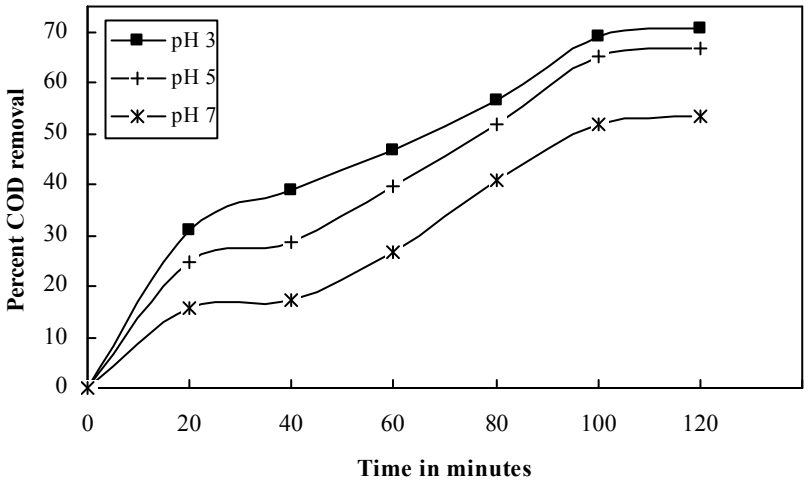


Fig. 3 : Effect of pH on COD removal

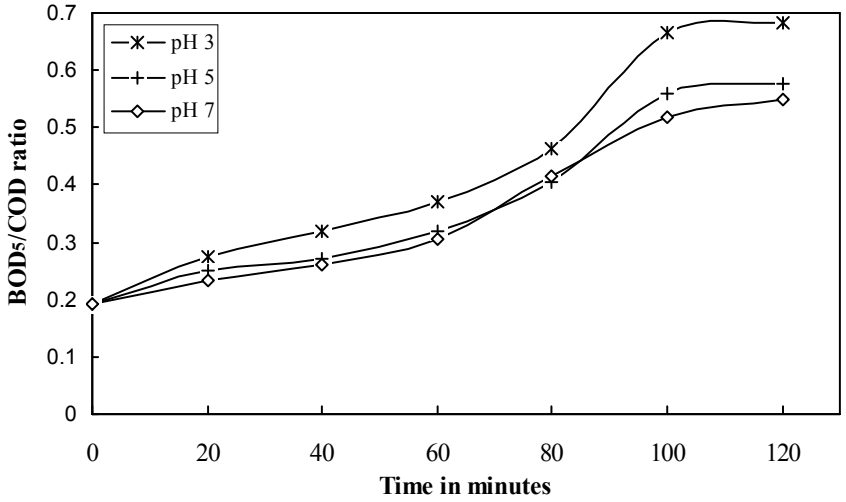


Fig. 4 : Effect of pH on BOD_5/COD ratio

Effect of Current Density

Once the optimum electrolysis duration and pH were found further experiments were done at different current density of 0.01, 0.02 and 0.03 A/cm^2 (amounting to a current of 0.25, 0.5, 0.75 Amperes respectively). The experiment was conducted for 120 minutes keeping constant electrode surface area and constant pH of 3. From **Fig. 5** it can be seen that the maximum COD removal of 72% was observed at an applied current density of 0.03 A/cm^2. At current density of 0.01 A/cm^2 and 0.02 A/cm^2 the COD removal was gradual and at the end of electrolysis duration it was 38.7% and 54.5% respectively. Increasing current density led to the increase in COD reduction following Faraday's law[20], because of the increased production of chlorine/ hypochlorite at higher current densities. From **Fig. 6** it is observed there was increase in BOD_5/COD ratio from 0.145 to 0.686 at current density of 0.03 A/cm^2. The reason is that increasing current density, increases the over potential required for the generation of chlorine/hypochlorite, as similar observation were made by Rajkumar et al., (2007)[19].

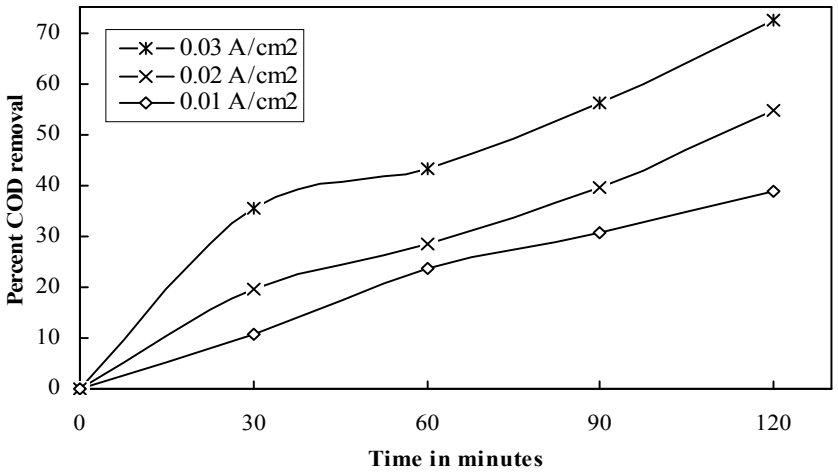


Fig. 5 : Effect of current density on COD removal

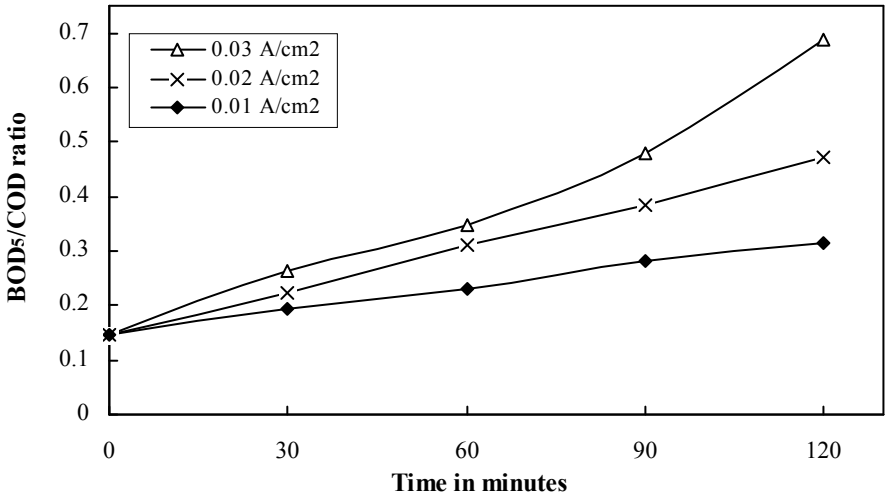


Fig. 6 : Effect of current density on BOD_5/COD ratio

Behavior of TOC under different operating conditions

Apart from the removal of COD, the removal of TOC is also of great importance during the electrochemical degradation of wastewater containing organic pollutants, because it indicates the extent of mineralization[21]. In the present study the TOC reduction has been discussed under three experimental conditions viz; during batch studies to determine optimum electrolysis duration (ED), under controlled pH conditions and finally under varying current densities. The variation of TOC reduction with respect to the ED has been graphically presented in **Fig. 7**. It can be observed that TOC removal was 8.77 % for 180 minutes electrolysis duration without adjusting pH and current density. **Fig. 8** shows the removal of TOC as a function of pH. It was observed that acidic conditions favored the TOC reduction analogous to the observation (pH 2.6-4.6) made by Lei and Maekawa (2007)[22]. **Fig. 9** shows percent reduction of TOC with varying current density at controlled pH 3. It reveals an increase in percent TOC removal with a concurrent increase in current density

On observing the behavior of TOC reduction under three sets of experiments and on reviewing the literature, it reveals that the change of TOC is very slow, indicating the presence of aromatic ring compound of organic compounds, which at given operating conditions, are not further degraded by the electrochemical process. The drop of TOC values could be attributed to the formation of CO_2 along with other organic compounds. The observed decrease in TOC can also be explained by a second probable explanation based on the decline of aromatic structures and formation of lower molecular weight aliphatic structures with carboxylic (-COOH), hydroxyl (-OH), and aldehyde (-CHO) functional groups. The TOC removal followed a more gradual removal of organic compounds, which may increase with increasing time of electrolysis. This trend is expected based on the greater ability of the anodic electro catalytic surface sites to mineralize or at least partially

oxidize; difficult to oxidize organic compounds to carbon dioxide[19].

Though the removal of TOC was less, it was observed that the COD/TOC ratio decreased from 1.01 to 0.308 during the course of electrolysis. It has to be noted that the maximum reduction in COD/TOC ratio was observed at optimum pH 3 and current density of 0.03 A/cm^2. Literature reports have shown reduction of this ratio from 2.3 to 0.25 (Piya-Areetham et al.,2006)[16] and from 3.3 to 1.7 (Ribordy et al., 1997)[23].

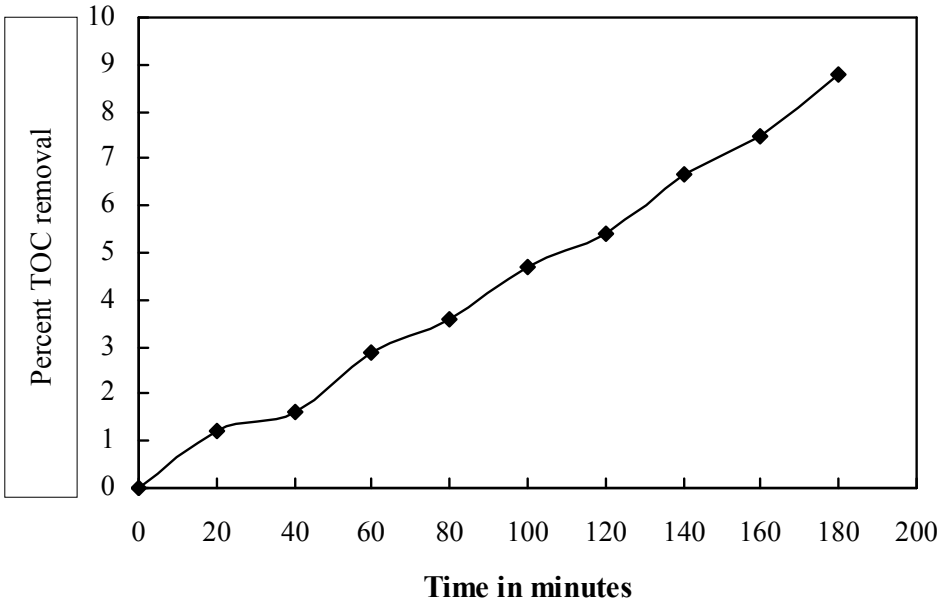


Fig. 7 : Variation of TOC removal efficiency v/s electrolysis duration

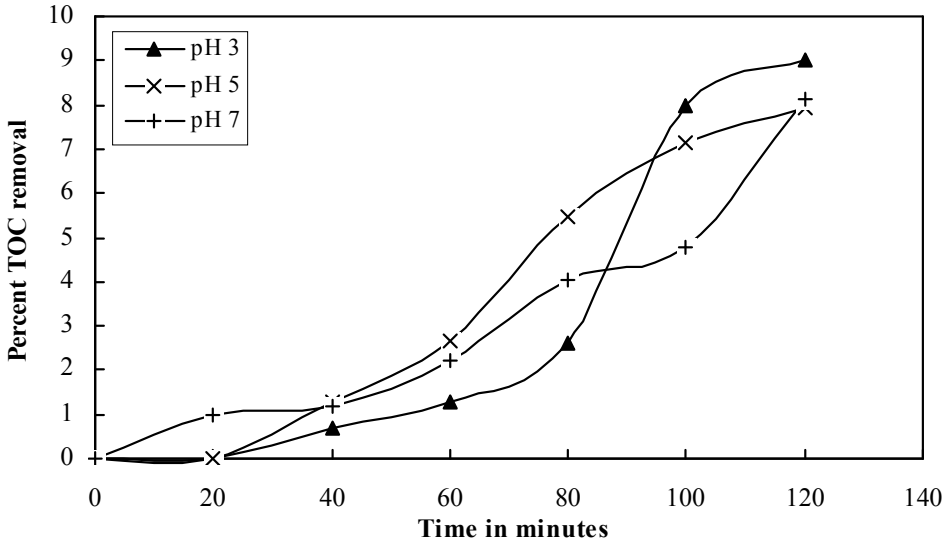


Fig. 8 : Variation of TOC removal efficiency v/s time as function of controlled pH

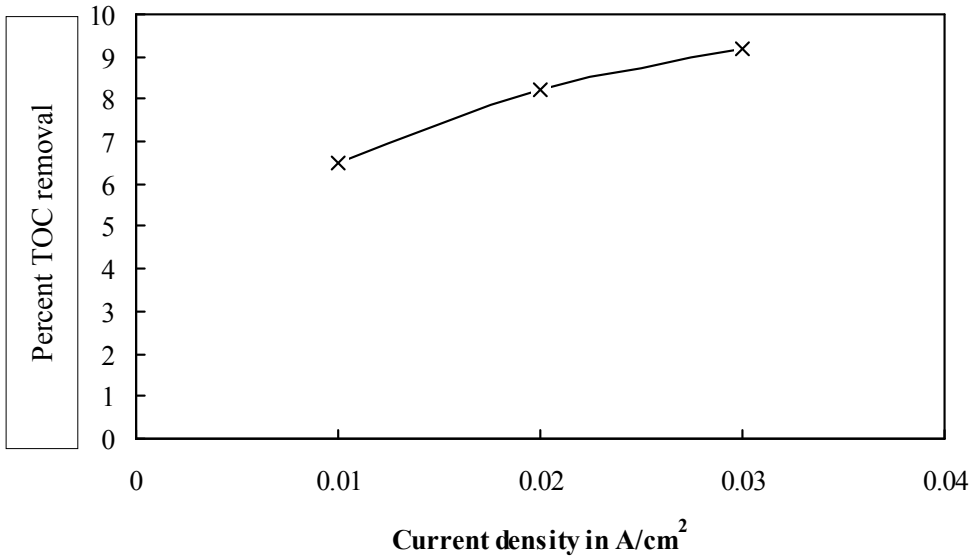


Fig. 9 : TOC removal efficiency with varying current density at controlled pH 3

Anodic efficiency and energy consumption

The anodic efficiency of electrochemical treatment has been determined in terms of kg COD removed per hour per ampere per square meter area of electrode (kg COD $h^{-1}A^{-1}m^{-2}$) and the energy consumption in terms of watt hour per kg of COD removed (wh kg^{-1}COD). At the wastewater pH of 3 the maximum anodic efficiency of 21.58 kg COD $h^{-1}A^{-1}$ m^{-2} and the minimum energy consumption of 84.16 wh kg^{-1} COD removal was observed with applied current of 0.25A. The anodic efficiency at 0.25 A is 1.6 times more than that at a current of 0.75A. Under similar conditions, the energy consumption increased 3.8 times with increase in current from 0.25A to 0.75A. This is in comparison with the studies made by Deshpande et al., (2005)[18]. It is evident that increase in current density has actually resulted in decrease in anodic efficiency and increase in energy consumption.

Kinetic studies

The pseudo first order reaction kinetics was reported for most of the organic pollutants with chloride as supporting electrolyte. In indirect electrochemical oxidation process, the COD removal rate is proportional to the concentration of organic compound and also to the chlorine/hypochlorite concentration because the indirect oxidation is mediated by chlorine/hypochlorite. Therefore the kinetics for COD removal has been done based on Rajkumar, et al., (2003)[21].

The pseudo first order plots of ln $[COD_t/COD_0]$ versus time for different wastewater pH and different current density are presented in **Fig. 10** and **Fig. 11** respectively. From the **Fig. 10**, it is observed that as the pH increases from 3 to 7, the reaction rate (k) decreases from 0.011 to 0.0065 (min^{-1}) gradually. The maximum reaction rate (k) was observed at acidic pH of 3 and minimum at pH 7. The reaction rate data reveal that distillery wastewater degrade easily at acidic pH than at higher pH values. **Fig. 11** It is observed that the

reaction rate (k) increases from 0.0035 to 0.0102 (min^{-1}) as the current density increases from 0.01 to 0.03 $A.cm^{-2}$. The maximum reaction rate was observed at current density of 0.03 $A.cm^{-2}$ and minimum at 0.01 $A.cm^{-2}$. The coefficients of determination (R^2) values obtained are above 0.95. It shows that higher current density strongly influences on faster degradation of distillery waste. Chiang et al., (1995)[9] found that the chlorine/ ypochlorite production rate is improved by increasing current density during electrolysis. Therefore enhancing effect of current density is attributed to the improvement of chlorine/hypochlorite production rate that enhances the indirect oxidation effect during the electrolysis.

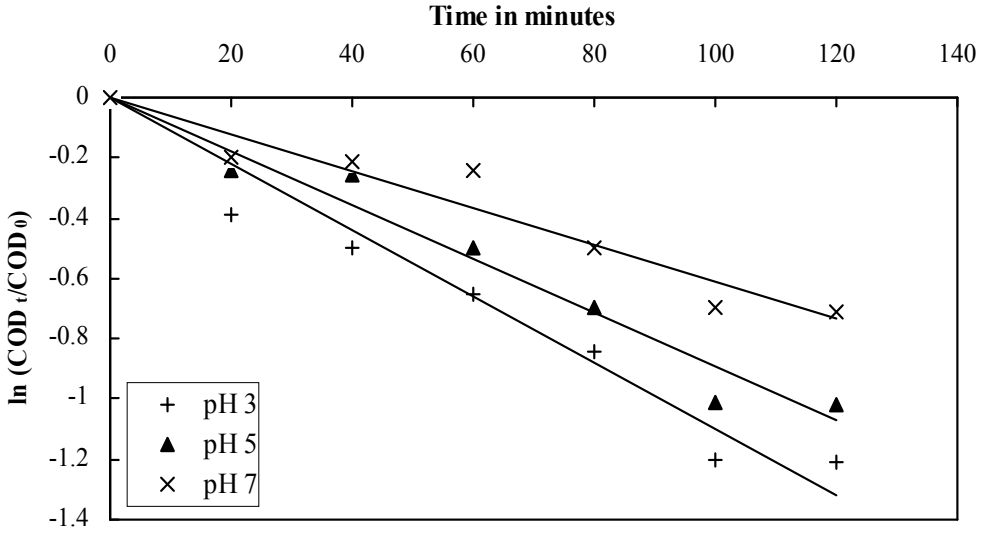


Fig.10 : Effect of pH on reaction rate

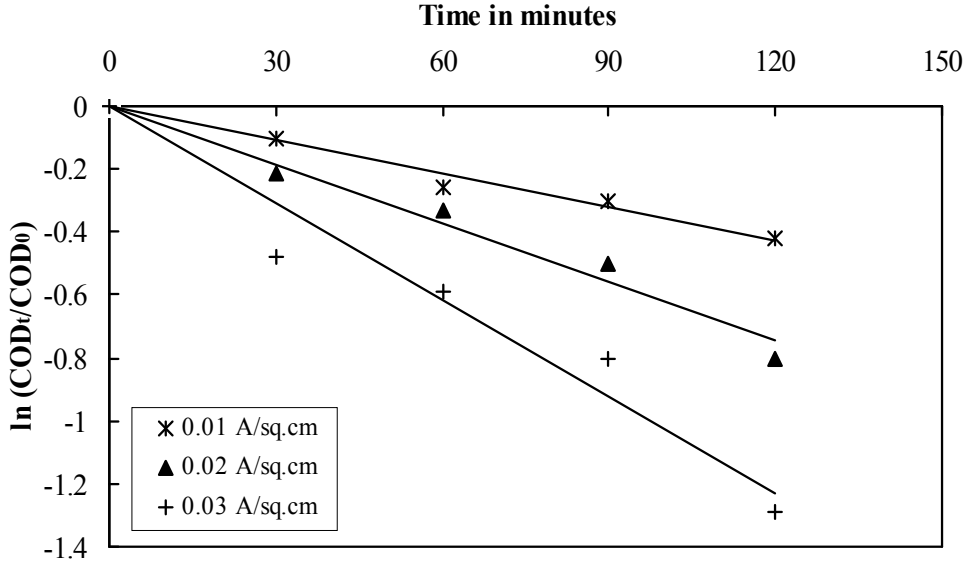


Fig. 11 : Effect of current density on reaction rate

CONCLUSION

Based on the findings of this study, the electrochemical technique can be effectively used for the pretreatment of distillery effluent using aluminum electrode. The efficiency of aluminum electrode in terms of COD removal was 72 % at 120 minutes of electrolysis duration, at a current density of 0.03 A/cm^2 and wastewater pH of 3. There was an improvement in biodegradability of wastewater with BOD/COD ratio increase from 0.145 to 0.686. The maximum anodic efficacy of aluminum electrode for COD removal observed was 21.58 kg COD $h^{-1}A^{-1}m^{-2}$ and the minimum energy consumption observed was 84.16 $whkg^{-1}$ COD removed. The TOC reduction is 8.77% at 180 minutes of electrolysis duration. The COD/TOC ratio reduced from 0.987 to 0.547 at pH 3 and from 1.01 to 0.308 at a current density of 0.3 A.cm^{-2}. Although all organic contaminants of wastewater were significantly reduced during this study still COD and BOD were found to be high. It was found that the one step treatment by electrochemical process was not sufficient and further treatment by appropriate methods is required to bring down the pollutant concentration within the statutory limits of effluent disposal.

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