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Research Article

Color Removal from Bio-Digester Effluent (Bde) by Electrochemical Treatment with and Without Fenton Reagent

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Abstract

Advanced Oxidation Processes (AOPs) have led the way in the treatment of industrial waste and are rapidly becoming the chosen technology for many applications. Color of the distillery effluent is dark brown due to melanoidin pigment which is a serious problem concern in environmental point of view. In this paper, Color reduction potential of Bio-Digester effluent (BDE) by electrochemical treatment with and without Fenton reagent, as one of the AOPs, was experimentally evaluated. Treatment of the wastewater was carried out by an electrochemical batch reactor equipped with two aluminum electrodes, which were connected parallel to each other. The oxidation process was studied for optimization of Electro- duration, H_2O_2, Fe(II), pH and current density. In this process, maximum color removal was 94% for 140 min for Electrocoagulation without Fenton reagent at pH 7 at $0.03A/cm^2$ and 84.28% at optimum operating condition such as when pH = 7, Fe^{2+} = 400mg/L, H_2O_2 = 500mg/L , H_2O_2/Fe^{2+} mass ratio = 1.25 for 80 min at $0.03A/cm^2$. Thus, electrochemical treatment with and without Fenton reagent in color removal proves to be effective and efficient treatment technology.

Keywords: *AOP's; Electrocoagulation; Fenton reagent; Color removal; Aluminum electrodes.*

1. Introduction

Environmental concern. The distillery effluent contains a dark brown pigment Melanoidin. It is the product of non – enzymatic reactions between sugars and amino compounds (P. Manisankar et al, 2004). Dark brown color leads to obnoxious odor problem, they prevent sunlight penetration into aquatic system thereby dissolved oxygen concentration is depleted leading to the death of aquatic life. This wastewater has very high concentration of carbohydrates; reducing sugars, dissolved lignin, proteins, alcohols, waxes etc impart high COD and BOD to the distillery wastewater. Anaerobic digestion has very high efficiency of energy recovery in the form of methane rich gas with 70 – 80% BOD removal and 70% COD removal efficiency. However the effluent from anaerobic digestion plant (Bio-Digester effluent) still contains high BOD and COD. Due to the very stringent effluent discharge standards for COD and BOD, the BDE is to be treated further (P.K Chaudhari et al, 2008).

Biological methods of primary treatment are unable to degrade the coloring compounds. Many traditional processes are being modified and new treatment processes were developed for distillery effluents. This incorporates the addition of secondary chemicals to precipitate or reacts with primary pollutants in the effluent. The use of chemical doses to clean up an effluents often results in discharge which itself remains unacceptable .Considering the economics and scale of wastewater purification operations, electrochemical procedure has been found to be the most suitable one.

The present study focus on the pretreatment of distillery wastewater collected from the outlet of anaerobic digester of existing treatment plant for color removal using aluminum electrode with and without Fenton reagent. The operating parameters affecting the electrochemical degradation for color removal such as electrolysis duration, pH and current density are evaluated during this study.

2. Mechanism in Electrocoagulation-Fenton Treatment

Two electrochemical methods were investigated in this study to treat BDE: electro coagulation (EC) without fenton reagent and electrofenton (EF) i.e electrocoagulation with Fenton reagent . According to (Adhoum Nafaa et al, 2004) 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. Main reaction occurring are

At the anode:

$$Al \rightarrow Al^{3+} + 3e^- \qquad (a)$$

At the cathode:

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$3H_2O + 3 e^- \rightarrow 3/2 H_2 + 3 OH^-$ (b)

Al^{3+} and OH^- ions generated at electrode surface reaction the bulk wastewater to form aluminum hydroxide

$Al^{3+} + 3 OH^- \rightarrow Al(OH)_3$ (c)

Aluminum hydroxide flocs acts as adsorbents and traps the metal ions and eliminate them from the solution.

In the electro-Fenton process, H_2O_2 is formed by the reduction of the dissolved oxygen on the cathode surface (Eq.(1)). H_2O_2 can then react with the externally added Fe^{2+} to produce OH· (Eq.(2)), and this reaction is Fenton's reaction.

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (1)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot$ (2)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (3)

OH· has high oxidation potential that is only lower than fluorine, and must react with most organic pollutants completely and rapidly. Moreover, the regeneration of Fe^{2+} from the reduction of Fe^{3+} at the cathode (Eq.(3)) is crucial for the electro-Fenton process. The sum of reactions in Eqs.(1)~(3) gives the global reaction that takes place in the cathodic compartment (Eq.(4)). In the anodic compartment, the reaction that takes place is simply the oxidation of water (Eq.(5)). The overall reaction ((Eq.(6)) taking place in the electrolysis cell and leading to the production of hydroxyl radicals emphasizes the catalytic character of elector-Fenton process. Thus, the only reagents necessary for the production of OH· are oxygen and energy from the electrical generator (Jiang et al., 2007)

$O_2 + 3H^+ + 3e^- \rightarrow H_2O + OH\cdot$ (4)

$H_2O \rightarrow 12O_2 + 2H^+ + 2e^-$ (5)

$12O_2 + H_2O \rightarrow 2OH\cdot$ (6)

In fact, the regeneration of Fe^{2+} can also be achieved by the oxidation of an organic, by the reaction with H_2O_2 or by the reaction with hydroperoxyl radical as described below

$Fe^{3+} + R\cdot \rightarrow Fe^{2+} + R^+$ (7)

$Fe^{3+} + H_2O_2 \leftrightarrow [Fe\text{-}O_2H]^{2+} + H^+ \leftrightarrow Fe^{2+} + HO_2\cdot + H^+$ (8)

$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + H^+ + O_2.$ (9)

Thus AOP's treatment in pollutant removal involves all the above reaction mechanism.

3. Materials and Methods

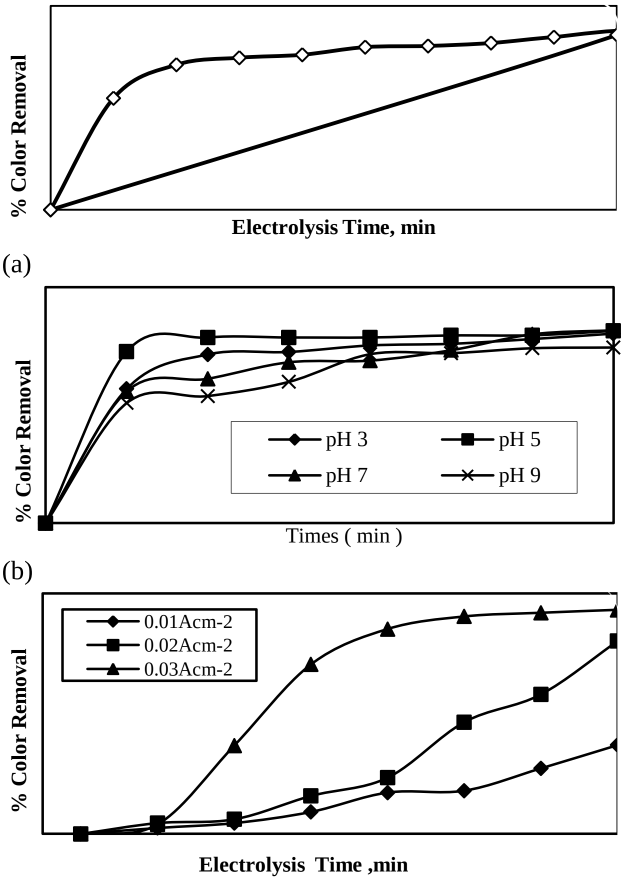
Biodigester Effluent (BDE) was obtained from the outlet of anaerobic digester from a local alcohol distillery plant. Physico-chemical characteristics of BDE used in the study are: pH 8.19, color dark brown, COD 4992-5760, BOD 594-860 and BOD/COD ratio 0.14.

3.1 Experimental Methodology with & without Fenton Reagent

Experiments were conducted in 1L capacity reactor. The aluminum plates of size 5cm X 5cm were used as both anode and cathode electrode. The anode and cathode were positioned vertically and parallel to each other with an fixed inter electrode gap of 1cm. A direct current dual power supply unit was used as power source to supply and maintain current and voltage across the electrode system by means of copper wires. The reactor content was kept under complete mixed condition facilitated by means of a magnetic stirrer to avoid concentration gradients. To follow the progress of the treatment, samples were periodically withdrawn from the reactor, then filtered and analyzed for various parameters. Whereas for Electrochemical treatment with Fenton reagent procedure starts with the addition of Fenton reagent in different quantities into the EC reactor and the power is switched on and the influence of various operating parameters are studied as a function of color removal. Samples were periodically withdrawn from the reactor, then filtered and analyzed. Color reduction was determined at 475 nm using spectrophotometer.

4. Results and Discussion

4.1. Electrochemical Treatment for Color removal without Fenton reagent

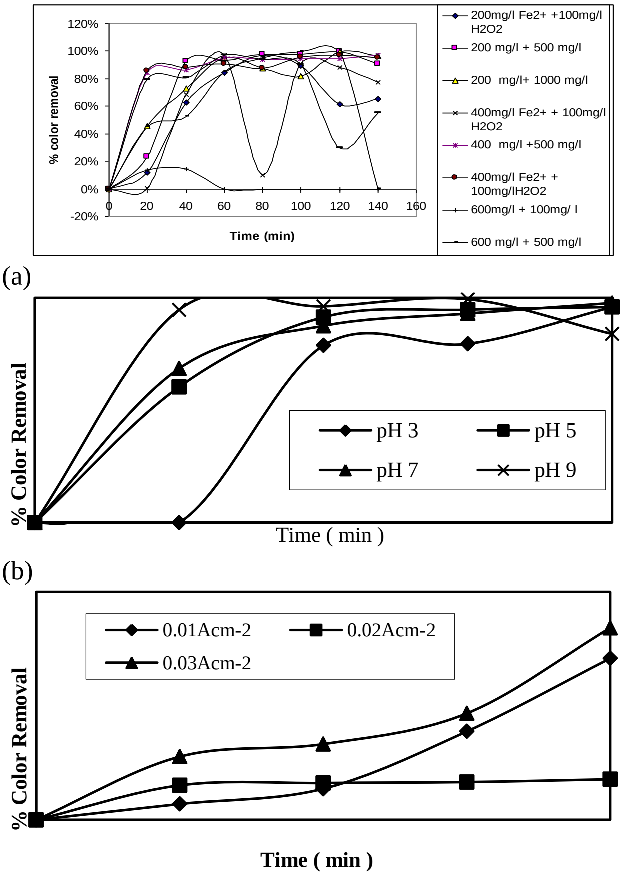


(c)

Fig 1 Effect of (a) Electrolysis Time (b) pH and (b) Current Density on Color removal without Fenton Reagent

Series of experiments were performed introducing the BDE into the electrocoagulation reactor cell, useful results could be obtained. Studies were carried out at different pH (3, 5, 7 and 9) and current densities (0.01, 0.02, and 0.03 A/cm^2) .As a result of the studies, after 180 min of electrocoagulation performed at the existing wastewater pH, color removal of 81.84% at 475 nm at 140 min of electrolysis duration as seen in Fig 1(a) could be achieved and the optimum electrolysis duration was fixed for 140min. The effect of pH of wastewater and current density is also studied by obtaining the desired pH by using 0.1N HCl and 0.1N NaOH and the role of pH in color removal is seen in Fig 1(b) where 98.14% color removal was achieved at the end of 140 min at pH 7. Color removal was 93.25 % at 140 min with pH 7 at 0.03A/cm^2 could be achieved at this optimum operating conditions as shown in Fig 1(c). Thus from the curves Fig 1(a), it is also observed that @ 475nm color removal increased from 54.75% to 81.84% at 140 minutes, indicating the increase in destabilization of colloidal particles with increasing in electrolysis duration (N. Daneshvar et al , 2004). Thus decolorisation occurs indirectly in the solution bulk due to the reaction between the generated chlorine / hypochlorite and the coloring material (E-S .Z El. Ashtoukhy et al, 2009) with an increase in electrolysis duration. Percentage of absorbance reduction indicates the complete destruction of organic coloring matter present in the effluent.

4.2. Electrochemical Treatment for Color removal with Fenton reagent



(a)

(b)

(c)

Fig 2 Effect of Fenton dosage on (a) Electrolysis Time (b) pH and (c) Current Density

Electrochemical treatment with Fenton process was found very effective in the color degradation studies carried out by many researchers previously. The removal efficiencies of this method can be explained by the fact that oxidation reactions are coupled to coagulation occurring due to the presence of ferrous/ferric cations, thus these metallic ions play a double role as a catalyst and a coagulant in the process. In the present study a series of experiments were carried out with varying Fe^{2+} and H_2O_2 concentrations to determine the effective electrolysis duration, optimum Fenton dosage, pH and current density. The result of the usage of Fenton in ECT in color removal is as seen in Fig 2(a), it was observed that at 400mg/L of Fe^{2+} and 500mg/L of H_2O_2 concentration with 1.25 H_2O_2/Fe^{2+} mass ratio ,the maximum color removal was found to be 95% at existing wastewater pH for 60 min of electrolysis. Further to study the effect of controlled pH on color removal the experiments was carried out and curves in Fig 2(b) shows , color removal of 97.76% at pH 7 and thus pH 7 was considered to be optimum pH for further studies . The current density determines not only the coagulant dosage rate, but also the bubble production rate and size. It was previously shown that the bubble size decreases with increasing current density, which is profitable to the separation process. Thus, this parameter should have a significant impact on pollutant removal efficiencies. In ordered to study the effect of current density on color removal, experiments were conducted for 0.01, 0.02 and 0.03A/cm^2 and results are shown in Fig 2(c). The maximum color removal was 84.28% at 0.03A/cm^2 which was optimum.

5. Conclusions

The results of the present study suggest that the Biodigester effluent can be effectively treated by electrochemical oxidation methods with and without Fenton reagent and final effluent with substantially reduced pollutant load can be obtained along with Color removal. Maximum color removal with and without Fenton reagent was 94% and 84.28% at 140min and 80 min of electrolysis duration at pH 7 with corresponding current density of 0.03A/cm^2. Thus AOP's i.e electrochemical treatment with and without Fenton reagent using aluminum electrodes proved to be an effective and efficient technique in color removal.

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