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Comparison of Aluminum and Iron Electrodes for COD Reduction from Coffee Processing Wastewater by Electrocoagulation Process

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Authors' contributions

This work was carried out in collaboration between two authors GA and BMK. Author BMK wrote the protocol, reviewed and edited the final draft copy. Author GA designed the study, managed the literature searches, performed the laboratory studies, sample analysis, data interpretation and prepared first draft copy of the manuscript. Both the authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

In the present study, applicability of aluminum and iron electrodes to remove COD in the coffee processing wastewater is evaluated by electrocoagulation method. Optimum electrolysis duration using aluminum and iron electrodes are observed as 45 and 60 minutes respectively. The COD remaining after the electrolysis duration of 105 minutes is 0.265 Kg \ m³ and 0.732 Kg \ m³ with energy consumption of 3.61 kWh / Kg removal of COD and 40 kWh / Kg removal of COD using aluminum and iron electrodes respectively. A comparison of variations in the trends of COD removal using aluminum and iron electrodes by electrochemical process is observed. The study revealed that electrochemical treatment using aluminum electrode is better in comparison with iron electrode with satisfactory results of 97% and 89% COD removal efficiency and decolorization.

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1. INTRODUCTION

One among the beverages consumed throughout the world majorly is coffee. Coffee, belong to the species *Coffea* is a member of *Rubiaceae* family [1]. The outcome of primary processing of the coffee beans pollutes the hydrological basins where the production units are established [2].

Coffee is processed either by wet processing method or dry processing method. The later being widely used method to produce better quality of coffee. The wet coffee processing industry uses enormous amount of water concurrently generating large quantity of wastewater during mechanical separation of pulp [3]. The quantity of water required to produce one tonne of clean coffee is 80 m^3 for Arabica while it is 93 m^3 for Robusta adopting conventional methods [1] with the subsequent generation of huge quantity of wastewater i.e 1.5 to 23 m^3 .

Coffee processing wastewater has an elevated contaminating power as a result of its higher level of organic load, pH, color, complex compounds like caffeine, fat and peptic substances, macromolecules like lignins, tannins, humic acid which are highly structured and hence harder to degrade using conventional methods [4], pectin, protein and sugar [3,5,6] carbohydrates [2], suspended and dissolved organic solids [1] which demands the treatment ahead of disposing to the water bodies.

The major impact on the environment with the discharge of the coffee effluents arises due to the solid and liquid waste from the processing activities. The discharge of these wastes leads to the depletion of the dissolved oxygen which creates anaerobic condition in the receiving water bodies making it odorous and significantly effecting the aquatic environment.

Previously efforts have been made by various researchers to treat the coffee wastewater by conventional method like anaerobic treatment [2,7,8]. High maintenance costs, irregularity [3], fluctuations in the treatment level as the strength and volume of the effluents vary due to the seasonal nature of the coffee industry find it difficult to cope with the challenge of meeting the environmental demands.

Therefore to meet up the prescribed disposable limits, an attempt has been made in this study to

find an appropriate solution to reduce these organic loads and color including recalcitrant by combination of physico-chemical process. The selection of electrode material is a prime factor as it governs the generation of oxidant ions in solution. The aim behind this study is to compare the efficiency of electrochemical treatment in treating coffee processing wastewater using two different electrode materials like aluminum and iron.

2. MATERIALS AND METHODS

2.1 Wastewater Sample

The wastewater for the batch experiments was collected from pulping units of coffee estates located in and around Chikkamagalur and Mercara districts. For treating the coffee pulping wastewater, based on the previous literatures for treating high strength industrial wastewater, aluminum and iron was used as electrode materials for comparison. Previous researchers have tried electrochemical treatment of different high strength industrial wastewater with different type of electrodes with varying degree of pollutant removal. The samples collected were preserved in a refrigerator at 4°C to avoid initiation of microbial activity.

2.2 Electrochemical Reactor Setup

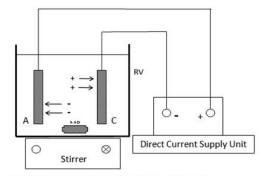
Electrolysis experiments were conducted in a glass beaker of 1000 ml capacity. The reactor operated under completely mixed was conditions, facilitated by a magnetic stirrer provided at the bottom of the beaker to avoid concentration gradients. The anode and cathode are positioned vertically and parallel to each other. The schematic diagram of experimental setup is shown in Fig. 1. Electrode assembly is the heart of the treatment facility. In the present investigation, studies were conducted to test the suitability of aluminum electrode and iron electrode for treatability of coffee pulping wastewater. The electrodes used and their dimensions are:

- Aluminum plates of dimension 7 cm x 7 cm
- Iron plates of dimension 7 cm x 7 cm

Before using the electrodes for experiments the aluminum electrodes were rubbed with sand paper and were dipped in 15% diluted hydrochloric acid for five minutes. Iron electrodes were dipped in 15% diluted hydrochloric acid

before the commencement of every trial to take out the layer of rust on the electrode. The instrument Testronix 35 D, dual DC regulated power supply was used to maintain current and voltage across the electrode system by means of copper wires.

electrochemical experiments The usina aluminum and iron electrodes were conducted in a glass beaker of constant working volume of 1 L. Fig. 1 shows the electrochemical setup made up of an electrolytic cell with one anode and cathode. Before the onset of electrolysis, aluminum electrodes were rubbed with sand paper and dipped in a 15% (W/V) hydrochloric acidic solution for about 5 minutes, rinsed with distilled water and dried in an incubator at 110°C. Similarly, Iron electrodes were dipped in 15% diluted hydrochloric acid before the start of every trial to remove the layer of rust on the electrodes. The instrument Testronix 35 D, dual DC regulated power supply was used to maintain 16 V current and voltage across the electrode system by means of copper wires. A magnetic stirrer was added into the reactor to maintain homogeneity. Aluminum and iron sheets of 7 cm x 7 cm were used as electrode materials. The gap of 1cm was maintained between the anode and cathode. The current of 16V was provided with a laboratory scale direct current power supply unit (Textronix 35D).



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

Fig. 1. Schematic diagram of electrochemical reactor setup

3. RESULTS AND DISCUSSION

Present study aims at comparing performance of aluminum and iron electrodes for COD removal and biodegradability under same operating conditions by electrocoagulation. Based on previous findings, the electrocoagulation is said to be strongly influenced by electrode material used [9,10]. Electrochemical reactor using aluminum and iron electrodes was operated for 120 minutes, in case of aluminum electrode; from Fig. 2 it can be observed that initially the COD concentration is 12840 mg/L and reduced to 8964 mg/L corresponding to 30% within 15 minutes of electrolysis. The COD removal rate is at increasing trend from the start of the electrolysis operation, tiny bubbles started evolving from the electrode providing larger surface area for particles to adhere each other hence increasing oxidation rate. After 30 minutes, the COD reduced to 3662 mg/L corresponding to 59.1% reduction. The possible reason for rapid destruction of contaminants at the onset of electrolysis time is possibly due to the generation of active chloro species at sacrificial anode like chlorine and hypochlorous acid or hypochlorite ion, which are highly oxidative in nature [10,11] and act as coagulants. Later nearing to 45 minutes, The COD was reduced to 1776 mg/L which corresponds to 52% removal. It is observed from the figure, that the reduction in the pollutant concentration in terms of COD is increasing with increase in operating time i.e after 60 minutes indicating that aluminum is oxidizing to aluminum hydroxide resulting in greater amount of precipitate for the removal of pollutants. The aluminum hydroxide flocs formed acts as adsorbents to trap metal ions so as to eliminate the same from the solution [12]. The COD reduced to 1084 mg/L corresponding to 38.6%. The probable reason for the decline in percentage removal is due to dissolution and formation of thin layer on the anode which might prevent electron transfer [13] changing its initial condition due to severe oxidation. The aforesaid variation in reduction of COD is due to decreased formation of flocs. With the significant destruction of COD, it was observed that BOD₅ was improving indicating that EC increases the biodegradability of wastewater [14]. At 75 minutes, though degradation of COD was noticed, but the percentage removal rate dropped significantly (12.1%). This may be attributed to the fact that the anode was corroding which led to passivation, a major effect on the reactor performance [13] and lessened evolution of H₂ from cathode, the bubble density decreased thereby reducing the pollution removal rate, these findings are in line with observation made by other researcher [12]. Further, at 90 minutes there was gradual improvement in the COD removal rate which may be due to the increase in the cell conductivity and OCI radicals, which in turn enhances biodegradability and destruction of organics present in wastewater. The COD reduced from 952 mg/L to 734 mg/L corresponding to 22.8%. Further after 105 minutes, COD reduced to 542 mg/L i.e. 26.1%. This improvement in the COD reduction rate is due to the scum floating and the settled sludge, which acts as attracting blanket for destabilized contaminants.

For comparison, experiments were conducted using iron electrodes with same operating After the start up, there was no conditions. change in the physical state of the solution in the reactor even after 60 minutes of electrolysis duration, and after analysis no positive removal of pollutants was noticed. Coffee pulping wastewater was diluted since it was concentrated and no changes appeared that happened with aluminum electrodes, hence it was decided to dilute the sample with 1:2 ratio. From Fig. 3, during initial hours of electrolysis, COD reduction was very fast i.e from 6536 mg/L to 1632 mg/L corresponding to 75% removal efficiency indicating that faster oxidation of organic contaminants as optimized dosage of NaCl was added as supporting electrolyte to speed up the reaction. However, to achieve more efficiency higher dose of electrolyte are added, which otherwise will increase the post treatment and energy cost [15].

The bubbles evolved clears the precipitate through the solution, resulting in coagulation by an entangle mechanism. Due to contact with coagulant and pollution particles compact aggregates are formed indicating high potential for pollutant removal. The bubbles formed were carried to the top through floatation, which was scooped off at the end of electrolysis. Later after 30 minutes though there was reduction continuously, removal rate was decreased. i.e 1632 mg/L to 1504 mg/L corresponding to 8% removal. The reason may be due to the evolution of bigger sized bubbles, which disturbed the scum, hence broke the continuity in the flow hindering the contact of coagulants and the sample. Simultaneously, the surface of the electrode appeared yellowish, this turned on to reddish brown in color due to the oxidation of Fe (II) to Fe (III) thereby coloring the effluent [14]. These observations are supported by the study made by various researchers. The solution appeared to be greenish in color [16,17]; the possible reason for this may be due to the

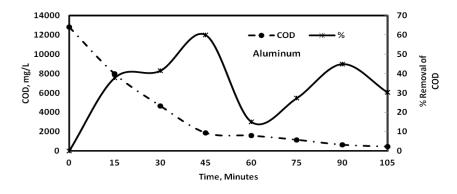


Fig. 2. Variation of COD using aluminum electrode

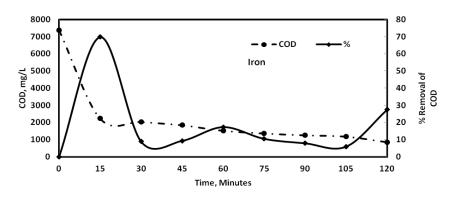


Fig. 3. Variation of COD using iron electrode

formation of rust. The corrosion of the electrode is the indication of the addition of coagulants into the solution. At 45 minutes, the COD concentration reduced from 1504 mg/L to 1484 mg/L which seems to be very less, possibly because the evolution of bubbles and thereby floc formation is lessened, leading to lesser formation of hydroxides. Thereafter, rapidly increasing trend was observed due to increase in conductivity and with the liberation of Cl₂ and OCI radicals, corresponding to higher COD removal rate in short span. This trend is in line with [18]. Similar findings are reported by [19] in their work. After 90 minutes, of electrolysis it was observed that due to severity in oxidation, the anode was corroded completely. Green layer of rust was noticeable which is the reason behind poison the electrode to treat further. Hence after 90 minutes, the COD removal rate was decreased.

3.1 Effect of Electrode Material

In the present work, batch studies were done using two different electrode materials i.e aluminum and iron, to treat coffee processing wastewater. The electrode potential was maintained constant at 16V at an inter electrode distance of 1 cm apart, the surface area of the electrodes used are 49 cm², the existing pH of the wastewater is 4.4.

From the Fig. 4 it is very clear that the destruction of organics is apparent using aluminum as electrode material since the $BOD_5 \setminus COD$ ratio increased from 0.03 to 3.26 at 105

minutes, with simultaneous destruction of contaminant in terms of COD. The COD reduced from 12144 mg/L to 256 mg/L corresponding to 97 % removal with subsequent increase in BOD 472 mg/L to 865 mg/L. The aluminum ions produced by the anode dissolution have larger surface area and hence as rapid adsorption capacity of organic compounds and other metal ions evolved [20]. These metal ions and compound gets settled down at a faster rate due to its higher density. Due to its coagulant property it traps all the colloidal particles and settles at the bottom of the solution by floatation [21].

From Fig. 5, it is seen that, in case of iron electrode, initially there was rapid COD reduction due to the higher quantity of ions generated from the electrodes. These ions which destabilize the pollutants and aggregates all the induced flocs simultaneous increase in hydrogen with evolution. This may be possibly due to increased current density, initiating higher COD removal i.e 151 Am⁻². Higher current density results in a significant decrease in current efficiency, which means there is excess anodic dissolution and wastage of electrical energy heating up the wastewater. Similar findings were observed by other researcher's in their study [11,22]. The improvement in the BOD₅ \ COD ratio from 0.09 to 1.25 indicates the destruction of the organics in the solution. The abatement of COD was significantly less as compared to aluminum electrode i.e 6884 mg/L to 732 mg/L in 105 corresponding to 89% removal minutes. efficiency.

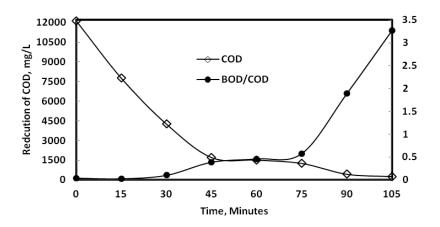


Fig. 4. Variation of BOD₅ to COD ratio with respect to COD reduction using aluminum electrodes

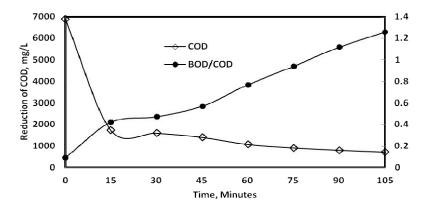


Fig. 5. Variation of BOD₅ to COD ratio with respect to COD reduction using iron electrodes

In case of iron electrodes, the gas bubbles that evolved at the anode carrying all the contaminants to the top of the treated solution where it can be easily collected and removed off for further treatment. Iron electrode destabilizes rapidly due to corrosion thereby leading to decrease in the removal rate. The current density increases rapidly upto 173 Am⁻² with slower abatement of COD thereby increase the energy requirement and cost of the treatment.

3.2 Instantaneous Current Efficiency (ICE) and Energy Consumption

For aluminum electrode, ICE value increased in the start of the reaction i.e during first 15 minutes signifying the increased removal efficiency due to the production of ions both at anode and cathode thereby increasing floc production. Current density varied from 0 to 97.95 A/m² (Fig. 6), energy consumption varied from 0 to 6.8 kWh / Kg COD (Fig. 7) removed from initiation of electrolysis till 105 minutes, it can be noticed that, the higher the current density maximum color removal was noticeable using aluminum electrodes which was not observed in case of iron electrodes [23] with less energy consumption.

While in case of iron electrode, current density varied from 0 to 246.93 A/m² (Fig. 8), energy consumption varied from 0 to 44.4 kWh / Kg COD removed (Fig. 9). The COD removal was gradual and continuous which indicated that during reduced COD removal rate, higher is the energy consumption. In comparison with aluminum and iron, iron requires more energy to abate the pollutants. As current increased, removal time decreased due to faster pollutant removal. This decreased the contact time between the coagulant and pollutant, which resulted in decreased coagulant efficiency. Though from the observation of graph values, it is very clear that initially COD removal was very efficient which later was not encouraging, time required to reduce the contamination level was more thereby increasing energy consumption, which is not economical. As current increases. both floating and separation rate constants increased due to additional coagulant generation. This faster removal is offset by decrease in coagulant efficiency.

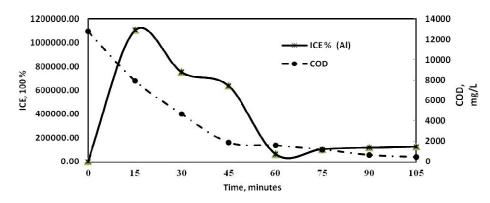


Fig. 6. Variation of COD and ICE using aluminum electrode

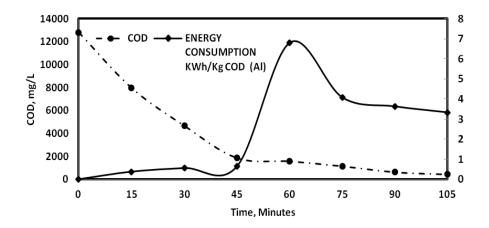


Fig. 7. Variation of COD and Energy consumption using aluminum electrode

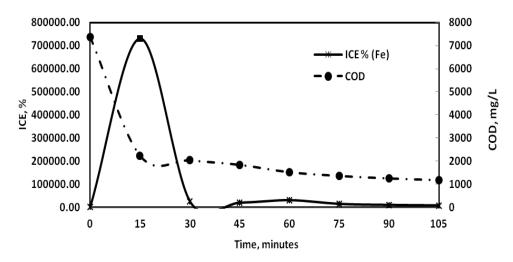


Fig. 8. Variation of COD and ICE using Iron electrode

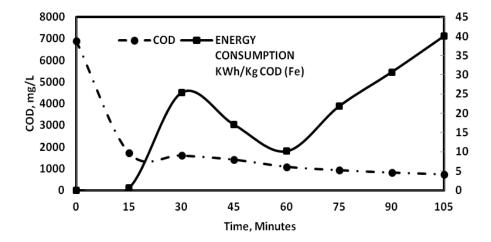


Fig. 9. Variation of COD and Energy consumption using Iron electrode

After 30 minutes in case of aluminum, gradual sudden dip in the graph can be observed, probably due to the short of liberation of ions to destabilize the contaminants, this was evident as there was less evolution of bubbles to the surface. While in case of iron electrode, rapid change in the trend is observed thereafter, which may be possibly due to the generation of oxygen bubbles at the bottom anode which might coalesce forming abnormal number of large bubbles. This in turn not only decreases the availability of the effective small bubbles, but also increases chances of breaking the previously formed flocs and disturbing the flotation efficiency.

In case of aluminum electrodes, later nearing to 45 minutes there was sudden rise in the graph possibly due to the increased aggregation of contaminants along with previously nondestabilized particles. While in case of iron electrodes the ICE is consistent. It can be seen from the graph that there was drastic reduction in COD up to 60 minutes of electrolysis, This inconsistency in the COD removal is dependent on the flocs formation which was evident during this interval, With such an drastic change, the initial condition was changed with severe oxidation, the reason for this may be due to the variation in energy consumption by the electrode material. Concurrently there was increase in current density which is in accordance with the Faraday's law which guotes that current density is directly proportional to COD reduction rate [24].

Later, after 90 minutes in case of aluminum, reduction rate was much better at lesser time span which shows that as the current density increases, the pollution removal rate could enhance rapidly, these results are similar to the findings of [11]. It can be noticed that, the higher the current density maximum color removal was noticeable using aluminum electrodes which was not observed in case of iron electrodes with less energy consumption, these findings are in line with the study of the other researcher [23]. The energy consumption was reduced to 3.6 kWh / Kg COD removed. While in case of iron electrode, after 90 minutes attributing to slower COD subsidence with simultaneous increase in electrical energy consumption, these findings are in line with the observation made by the other researcher [25]. As compared to aluminum electrode, the energy consumption by using iron electrode was significantly high, as much as 44.4 kWh / Kg COD removed.

4. CONCLUSIONS

- The removal efficiency of Aluminum electrodes with lower energy consumption is significantly high as compared to Iron electrodes.
- Complete decolorization and COD reduction was observed by using aluminum electrodes, while using iron electrode, the treated solution started turning cloudy with the progressing of electrolysis.
- After the electrolysis of 105 minutes using aluminum electrode and 120 minutes using iron electrode, it was observed that there was formation of white colored powder on aluminum electrode and yellow colored powder on iron electrode, from this physical change in the anode electrode it was evident that the reactor performance deteriorated rapidly with the decline in the life span of the anode.
- Electrochemical treatment of coffee processing wastewater using aluminum plates of size 7 cm x 7 cm at current density of 95.91 Am⁻² resulted in COD removal of 95 %, while using iron plates of size 7 cm x 7cm at current density of 173.46 Am⁻² resulting in COD removal of 89 % at an electric potential of 16V.
- Using aluminum as electrode material, energy consumption is 3.62 kWh/Kg removal of COD, while with iron electrode, it was 45.3 kWh/Kg removal of COD.
- The loss of electrode in case of aluminum was insignificant as compared to iron electrode, which was visible due to pitting corrosion and flake formation on the anode material.
- Aluminum was found better compared to iron as electrode material, as it produces clear and stable effluent. The drawback of iron electrode is that it renders green color to the wastewater, later to turbid yellow making it prone to polishing treatment for color removal.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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