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Removal of Recalcitrant Carbon from an Industrial Wastewater Using Electrocoagulation

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Abstract Manufacturing industries synthesize new chemical products every day, which eventually find their way into domestic and industrial wastewaters. As a result, wastewater is becoming increasingly more complex in nature. The emerging pollutants escape the treatment systems and appear in the receiving water bodies. Wastewater treatment plants in India still report effluent parameters in terms of biological oxygen demand (BOD) and chemical oxygen demand (COD) at the ppm level, whereas these emerging pollutants, many of whom are non-biodegradable, can be toxic and carcinogenic at the ppb level. Therefore, it is imperative to look for alternatives or upgrade the existing systems which safely remove these harmful compounds from wastewater. In this research, efficiency of electrocoagulation process was assessed in a laboratory-scale setup in removing recalcitrant carbon from a real wastewater. The wastewater was collected from an effluent treatment plant that receives domestic wastewater and industrial effluents from chemical, bulk drugs and allied industries, for treatment. In this study, the wastewater sample was analyzed for total dissolved solids (TDS) and total organic carbon (TOC), and then treated biologically in a respirometer using aerobic microorganisms. After the oxygen uptake curve plateaued, indicating a cessation of biological process, the sample was analyzed for TDS and TOC and put in a lab-scale electrocoagulation setup. Iron and Aluminium electrodes were used in the study and efficiency

of the system in removing the recalcitrant/residual carbon and TDS was studied with respect to the reaction time. The results showed that electrocoagulation can be a potential post-biological treatment system for removal of recalcitrant carbon from wastewaters.

Keywords Electrocoagulation · Recalcitrant carbon · TDS

1 Introduction

Manufacturing industries are synthesizing new chemical products every day, which eventually find their way into domestic and industrial wastewaters. As a result, wastewater, both industrial and domestic, is becoming increasingly more complex in nature. Existing biological wastewater treatment plants in India are not adequately equipped to treat the emerging pollutants; as a result, these emerging pollutants escape the treatment systems and appear in the receiving water bodies. Wastewater treatment plants in India still report influent and effluent parameters in terms of biological oxygen demand (BOD) and chemical oxygen demand (COD) at the ppm level, whereas these emerging pollutants, many of whom are non-biodegradable, can be toxic, mutagenic and carcinogenic at the ppb level. Although COD and BOD are important pollution parameters, Total Organic Carbon (TOC) has gained more importance in recent years because of the accuracy and reliability. Organic chemicals that are recalcitrant to biodegradation are common in effluents emerging from chemical industries. Many recalcitrant chemicals pose challenges to successful implementation of biological treatment processes, as these chemicals cannot serve as carbon and energy sources for microbial growth. Rather, these

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chemicals may be treated by physio-chemical methods like Electrocoagulation.

Electrochemical method was found to be a promising method due to its higher treatment efficiency and lower cost. This method has also been applied to clay for removal of lead in recent studies. Electrocoagulation technology is based on electrochemical production of destabilizing agents that remove different compounds by charge neutralization, adsorption and precipitation or flotation. Usually aluminum or iron electrodes are used for anode and cathode [1–3]. Electrocoagulation is a complex process involving multiple of mechanisms that operate simultaneously. Anodic oxidation occurs on a sacrificial anode that generates adsorbents like ferric hydroxides or aluminum hydroxides. At the same time, cathodic reaction results in the evolution of hydrogen gas, which makes the adsorbents float [4]. Electrocoagulation works mainly on principles of electrochemistry, coagulation and hydrodynamics. Reactions occurring at anode and cathode are as follows:

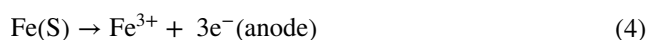
For Aluminum:



Aluminum (Al^{3+}) and hydroxide (OH^{-}) ions generated in the above reactions react in wastewater to produce aluminum hydroxides.



For Iron:



The hydroxides or polyhydroxide particles, thus formed, are more active and effective than conventional coagulants [3, 4]. Organic pollutants can be removed by electrostatic attraction or by surface complexation where pollutant acts as a ligand to bind a hydrous ion [5]. The sludge, formed during the process, can be removed using tube settlers at the industrial scale, thereby reducing the footprint [6]. Electrocoagulation has been applied successfully on various wastewaters from industries like textile, paper mill, dairy, distillery, palm oil, for removal of color, COD, oil and grease [7–15]. COD removal efficiencies found in dairy wastewaters were around 98 and 61% using aluminium electrodes [7–9]. Removal efficiency of COD in distillery wastewaters was 81.3 and 50.5% with aluminium and iron electrodes, respectively [10, 11]. Optimum operating conditions like initial pH, reaction time and current density were investigated for maximizing removal of COD in the paper and pulp industries. COD removal efficiencies were

90 and 98% at following conditions of ($\text{pH}=7$, $t=30$ min & current density = 15 mA/cm^2) and ($\text{pH}=7$, $t=50$ min & current density = 14 mA/cm^2) respectively [12, 13]. However, COD removal was found to be only 42.94% in palm oil mill effluent [14]. In textile wastewater, color and COD removal was found to be 100 and 84%, respectively, at 3 min reaction time and at 60 mV [15]. COD removal efficiency depends on the complexity of wastewaters and contributors of COD. Apart from these, electrocoagulation has been applied for removal of inorganic ions like chromium, arsenic, fluoride, cadmium, boron, nitrate and phosphates. These ions contribute to total dissolved solids (TDS) [16–23].

The objective of this work is to study the efficiency of an electrocoagulation process in removing residual/recalcitrant carbon from a biologically (aerobic) treated industrial wastewater that contains dye and intermediates, bulk drugs and allied products. These recalcitrant compounds are usually toxic because of their molecular structure, size and possess very stable bonds [24]. The efficiency of the process in removing TDS from the effluent was also studied. Aluminum and iron electrodes were selected. Efficiency of the system as a function of time at a constant current density was investigated.

2 Experimental Procedure

2.1 Sampling of the Wastewater

The wastewater used in this study was sampled at the inlet of a wastewater treatment plant (WWTP). The WWTP has adopted activated sludge process for treating wastewater. The wastewater was collected from an equalization tank located upstream of the biological treatment and kept at 4°C until use. Return activated sludge was also collected from the secondary clarifier. Prior to the laboratory test, the collected wastewater was uniformly mixed. Total organic carbon (TOC), Chemical Oxygen Demand (COD) and Total Dissolved Solids (TDS) were tested.

2.2 Experimental Setup

2.2.1 Respirometric Study

Study on biodegradation of the wastewater under aerobic condition was conducted using a batch type respirometer setup. The experimental setup was made as presented in Fig. 1 using a head space gas respirometer (RSA-PF-8000). 3–500 ml test bottles were filled with wastewater and return activated sludge in 4:1 ratio. Two controls were set up using ethanol as the sole substrate. Nutrients and buffer solutions were also added. Seeded test bottles were kept in

Fig. 1 Head space respirometer setup



an orbital shaker operated at 150 RPM. The temperature was maintained at 25 °C. The test reactors were connected to an oxygen cylinder via a flow control module (PF-8000) and a pressure control module (PR5010). The flow control module, which acts as a flow meter, was connected to a computer fitted with a data-logging system. Carbon dioxide, generated in the headspace, was removed using a sodium hydroxide scrubber fitted into the reactors. A negative pressure, thus created, forced oxygen into the reactors from the cylinder. The flow of oxygen was measured by the flow control module and recorded in the computer.

Oxygen uptake was measured and the experiment was continued till the oxygen uptake curves plateaued, indicating complete oxidation of the biodegradable organics in the sample. At the end of the run, the mixed liquor in the bottles was centrifuged to separate liquid from solids. The liquid samples were then analyzed for TOC, filtered COD, and TDS. Afterward, liquid was put through the electrocoagulation test for recalcitrant carbon removal.

2.2.2 Electrocoagulation Setup

Electrocoagulation is a complex process and is affected by several operating parameters such as initial pH, pollutant levels, electric potential (voltage), reaction time, electrode geometry, and type of electrodes. In this study, the effect of the type of electrodes and the reaction time of removal of recalcitrant carbon and TDS from a biologically treated wastewater were evaluated. Experiments were performed in a batch reactor, as presented in Fig. 2. Voltage, electrode spacing, and electrode geometry were kept constant for all the electrocoagulation test runs. Voltage was adjusted to 20

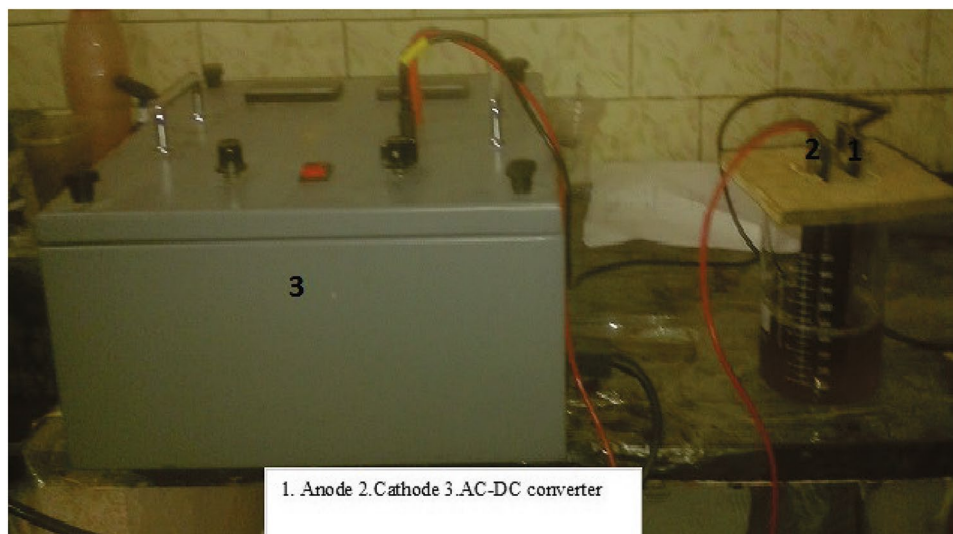
volts and electrode geometry was kept same for both the runs with iron and aluminum electrodes. The internal size of the cell was 10.9 × 12.5 cm (dia × height). The effective volume was 400 ml. The active area of each electrode was 4 × 5 cm. The distance between electrodes was 2 cm. Power supply pack had an input voltage of 250 V and a variable output of 0–220 V (20 V for this study). The experiment was performed using aluminum and iron electrodes having above-mentioned active area. At regular time intervals (10 min), 15 ml of treated sample was collected and filtered. The samples were then analyzed for TOC and TDS. The electrocoagulation experiment was conducted for 40 min.

2.3 Analytical Methods

The Total Solids, Volatile solids, Total Dissolved solids, COD, and pH were determined following Standard Methods (APHA, 20th edition). Total organic carbon (TOC) was determined by a total organic carbon analyzer TOC (Shimadzu-TOCL-CPN).

3 Results and Discussions

Characteristics of the raw wastewater The characteristics of the influent are given in Table 1. pH of raw wastewater was 8 indicating its alkalinity. The wastewater sample was dark brown in color, and had a moderately high level of COD and TDS. Characterization of wastewater after respirometric study is also presented in Table 1.

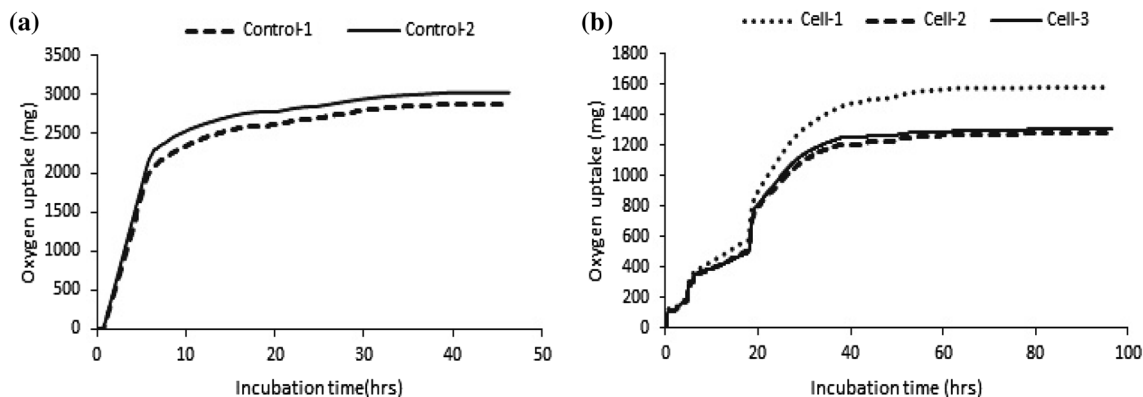
Fig. 2 Electrocoagulation setup**Table 1** Initial and post respirometer characterization of wastewater sample

Parameter	Initial value	Post respirometer study
pH	8	9
Color	Dark brown	Light yellow
TDS (ppm)	4214	3104
Filtered COD (ppm)	4953	800
TOC (ppm)	1847	177

3.1 Respirometric Study

Respirometric study was conducted under aerobic condition. Oxygen uptake indicates the amenability of a wastewater to biological treatment [25]. The experiment was conducted to examine the extent of aerobic biodegradation of the wastewater and also to make sure that only recalcitrant portion is available for electrocoagulation. Oxygen

uptake of the two controls and the three test reactors is shown in Fig. 3a, b, respectively. The graph indicates that the readily biodegradable matter was completely oxidized within 40 and 60 h from the beginning of the test for the controls and the wastewater, respectively. The controls showed a cumulative oxygen uptake of 3027 mg of O_2 at the end of the test run. Oxygen uptake was about 1389 mg of O_2 on an average for the wastewater bottles. The final COD in the control reactors indicated 95% removal of COD, whereas COD removal in the samples was found to be 83%. The extent of biodegradation in control was observed to be greater than in samples. Fluctuations in the oxygen uptake rate were observed till 20 h from the beginning of the study in the wastewater reactors. This phase indicates the initial phase of acclimatization of biomass with the wastewater. This may also indicate a period of hydrolysis or transformation of the waste, outside or within the cells, before respiration picked up. For the controls, this phase was observed to be too short. A steep linear curve

**Fig. 3** **a** Oxygen uptake (mg) for control; **b** oxygen uptake (mg) for wastewater samples

for the control bottles indicates a log phase when respiration proceeded at a maximum possible rate [25]. Aerobic biodegradation of the wastewater resulted in reduction of color, a TDS removal of 28%, and a TOC removal of 90%. pH, TDS, filtered COD, and TOC, were analyzed after the end of the test and presented in Table 1.

3.2 Electrocoagulation Study

3.2.1 Effect of Reaction Time with Aluminum Electrodes (Case-1)

The time dependence of the TOC and TDS removal of Aluminum electrodes in electrocoagulation process is shown in Fig. 4. It can be seen that for the applied voltage, TOC removal efficiency reached a maximum of 90% at 40 min from the beginning of the test, whereas TDS removal was around 20% during the entire run. TOC like COD comprises biodegradable and non-biodegradable portions. However, at this stage TOC comprises only non-biodegradable portion. TOC removal could be due to the precipitation of organic molecules, electrochemical oxidation, or adsorption by electrostatic attraction [24, 26]. The removal of TDS was much less as compared to the removal of the TOC. Dissolved ions like fluoride, nitrate, and phosphate usually destabilize at higher voltage [3, 17–19]. A low applied voltage of 20 V, which was maintained in this experiment, might be a possible reason for such a low removal of TDS. Al^{3+} and OH^- ions generated by electrode reactions (2) and (3) react to form many monomeric and polymeric forms which finally transform into $\text{Al}(\text{OH})_3$. Precipitation and adsorption mechanisms occur at different pH ranges. Precipitation occurs at a low pH range and adsorption usually occurs at a high pH range ($\text{pH} > 6.5$). In this case, the pH was observed to be 9. This indicates the possibility of removal of the TOC by adsorption. The freshly formed flocs of $\text{Al}(\text{OH})_3$ have large surface areas

which are beneficial for rapid adsorption of organic materials [27].

3.2.2 Effect of Reaction Time with Iron Electrodes (Case-2)

Electrically generated ferric ions may form monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species, depending on the pH range. These complexes transform finally into $\text{Fe}(\text{OH})_3$. The polymeric metal hydroxide neutralizes the negatively charged particles, after this they bind together to form flocs. These flocs containing oxides, hydroxides, and oxy-hydroxides form active surfaces for adsorption of organic pollutants [27–29]. The time dependence of TOC and TDS removal of Iron electrodes in the electrocoagulation process is shown in Fig. 5. It can be seen from the figure that for the applied voltage of 20 V, TOC removal efficiency increased up to 82% in 30 min from the beginning of the experiment. Removal efficiency decreased after 30 min, possibly due to the desorption of TOC from the flocs or possible formation of soluble compounds when organic compounds usually acids react with Fe^{+2} [3, 24]. A maximum TDS removal of 35% was observed at 20 min reaction time. For all other times, the TDS removal was observed to be around 2580 ppm with an average removal efficiency of 17% which possibly could be due to desorption. Effluent disposal is an important part of wastewater treatment. Table 2 shows the effluent quality at highest removals after the electrocoagulation process for both the electrodes. The values were compared with the discharge limits set by the Central Pollution Control Board of India (CPCBI) for industrial effluents. As per the guidelines, TOC is not a measure of discharge limits of organic content. The effluent COD, which can be measured by multiplying TOC by a factor ($=2.67$), was estimated to be below 100 ppm. This values are well below the discharge criteria set by CPCBI for organic content ($=250$ ppm) [30]. It can be observed from Table 2 that the TDS value

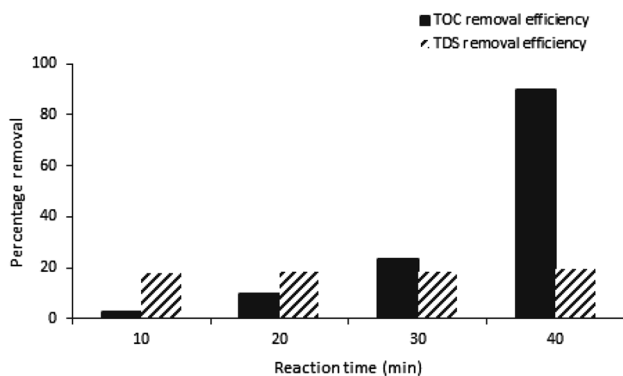


Fig. 4 Removal efficiencies using aluminum electrodes

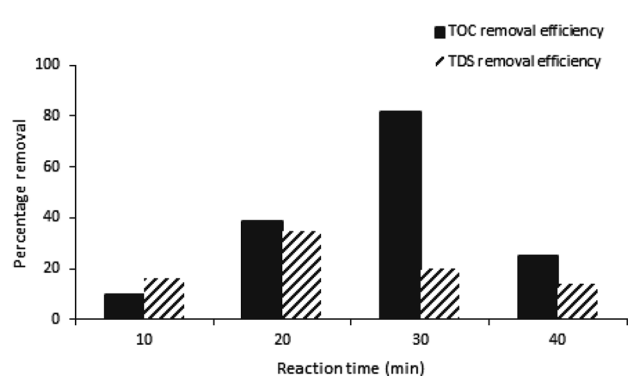


Fig. 5 Removal efficiencies using iron electrodes

Table 2 Characterization of wastewater sample after electrocoagulation

Parameter	Value	Discharge limit (as per CPCBI)
Aluminum electrodes		
pH	9	5.5–9.0
TDS (ppm)	2448	2100
TOC (ppm)	18.4	
Iron electrodes		
pH	9	5.5–9.0
TDS (ppm)	2031	2100
TOC (ppm)	32.8	

obtained in case 2 was within the limit, whereas in case 1, TDS exceeded the limit. The TDS removal efficiency can be enhanced by increasing the applied voltage potential.

4 Conclusions

The current research was a preliminary study on application of electrocoagulation technology as a post-biological treatment for removal of non-biodegradable organic content of wastewater. The results were encouraging. Iron and aluminium electrodes showed comparable efficiency in removal of TOC and TDS. Removal efficiency was higher in the case of aluminium electrodes. However, peak removal efficiency was achieved at a lesser reaction time with iron electrodes which results in lesser electrode dissolution, lesser electrical consumption, and faster treatment. The cost of aluminium electrodes is 4–5 times higher than iron electrode. Disposal of aluminium-laden sludge can be problematic. Therefore, this study suggests using iron electrodes for removing recalcitrant carbon from industrial wastewaters, which would be technically and economically feasible. Further studies are required for optimizing electrocoagulation process in terms of operating parameters like voltage, inter-electrode spacing, initial pH, etc.

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