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Effect of electrochemical treatment on the COD removal from biologically treated municipal wastewater

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ABSTRACT

This investigation observed the effect of electrolytic treatment time, current density, pH and supporting electrolyte on the removal efficiency of COD of secondarily treated sewage (STS). A glass chamber of 2 litre volume was used for the experiment with two electrode plates of Al, each having an area of 125 cm^2 and 2 cm distance apart from each other. The treatment showed that the removal efficiency of COD increased to 82.25% with the increase in current density (1.82–7.52 mA/cm^2), time (5–40 min) and pH (4–8) of STS. The electrode and energy consumption varied from 2.52×10^{-2} to 10.51×10^{-2} kg Al/m^3 and from 2.76 to 45.12 kWh/m^3. Under optimal operating conditions, the operating cost was 1.56 US $\$/m^3$. The addition of 0.5 g/L NaCl as a supporting electrolyte nominally increased the removal of COD (85.8%), and later, the observation is in contrast with previously published studies claiming greatly enhanced removal of COD in the presence of supporting electrolytes.

Keywords: Aluminum electrode; COD; Current density; Electrochemical treatment; Supporting electrolyte

1. Introduction

Sewage treatment consists of unwarranted impurities and toxins that deserve ample documentation due to environmental impact caused by such wastewater if directly discharged into receiving water bodies. In addition, due to an increase in the scarcity of clean water [1], there is an urgent need for proper management of available water resources. An important goal of the environmental protection and resource conservation concepts is reuse of treated wastewater, and if possible, of residues emanating there from, and other treatment by-products [2,3]. Therefore, the need to develop more efficient and cost-effective methods for the treatment of sewage cannot be over emphasized. It is well known that conventional treatment methods often induce chemical reactions through the use of coagulants, flocculants and other additives that aid in the removal or sedimentation of inorganic and organic contaminants present in wastewater. The role of electrochemistry in water and effluent treatment is relatively new and small, since conventional electrode materials achieve only low current efficiencies due to the water electrolysis side reactions and electrode passivation [4,5].

The "Electrolysis" literally means to break substances apart by using electricity. The process

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occurs in an electrolyte, an aqueous or a salt melting solution that gives a possibility to transfer the ions between two electrodes. The key process in electrolysis is the interchange of atoms and ions by the removal or addition of electrons from an external circuit. The anode is involved in rapid adsorption of soluble organic compounds and trapping of colloidal particles that can be easily separated from an aqueous medium by flotation [6,7]. In the electrolytic process for the treatment of secondarily treated sewage (STS), Al electrodes (anodes) are dissolved during electrolytic treatment to generate coagulating agents, and their hydroxides and polyhydroxides formed, thereby combine and subvert the organic and inorganic impurities present in STS.

In an electrolytic reactor, the Al^{3+} ions generated at anode immediately hydrolyse to produce corresponding hydroxides and/or polyhydroxides in adequate pH. The Al hydroxides and polyhydroxides produced by the electrochemical dissolution have been reported to have stronger affinity to capture the pollutants in the wastewater, causing more and better coagulation than those from the conventional Al coagulants such as alum. Additionally, the gas bubbles that evolve due to the water electrolysis can cause flotation of the pollutants and the coagulated materials. Therefore, electroflotation may also play an important part in an electrolytic cell. Although the $Al(OH)_3$ produced by the anodic Al dissolution is thought to be more active incoagulating the pollutants in wastewater, the passivation of Al anodes and impermeable film formed on cathodes may interfere with the performance of electrocoagulation and electroflotation [8].

The addition of sodium chloride to the electrolytic system leads to the decrease in power consumption because of increase in conductivity [9,10]. Vlyssides and Israilides [11] indicated that in the presence of chloride ions, the products of anodic discharge are Cl_2 and OCl^-; later is a strong oxidizer capable of oxidizing organic molecules present in wastewater. Lee and Pyun [10] specified that this was probably because of the NaCl which increases Cl^- anions that can destroy the passivation layer and increase the anodic dissolution rate of metal, either by the incorporation of Cl^- into the oxide film or by the participation of Cl^- in the metal dissolution reactions. This has motivated several groups to study the effect of sodium chloride on the electrolytic treatment of waste and contaminated water. For example, the effect of sodium chloride on the removal of pollutants in swine wastewater [6], the removal of arsenic from water [9] and decolorization/removal of crystal violet dye [12] have been studied. In swine wastewater [6] removal, efficiencies of NH4–N, soluble nitrogen (NH_4–N + NOx–N), soluble total organic carbon and colour were proportional up to 0.05% NaCl levels, but PO–P removal did not exhibit similar behaviour. However, the use of sodium chloride has been reported to greatly enhance COD removal efficiency in laundry wastewater [13] from 42 to 71%. In the present study, treatability of STS by electrolytic treatment at various operating conditions using Al electrodes and also after the addition of NaCl as a supporting electrolyte has been investigated for the removal of COD. We were able to achieve a significant reduction in COD to the extent of ~82% and in contrast to what has been reported, we did not observe any significant increase in COD removal after addition of NaCl. We also evaluated for the economic cost of the process including electrode and energy consumption during the electrolytic treatment.

2. Materials and methods

2.1. *Collection of STS samples*

The samples of STS were collected from the outlet of activated sludge process of the sewage treatment plant, Jagjeetpur, Haridwar (Uttarakhand), India and brought to the laboratory and subjected to electrolytic treatment using Al–Al electrode combination. The pH of STS was adjusted before the electrochemical process and was maintained by adding the required amount of H_2SO_4 (1 M) or NaOH (1 M). The characteristics of STS are shown in Table 1.

2.2. *Electrolytic experimental set-up*

The schematic arrangement of the experimental set-up is shown in Fig. 1. The experiments were carried out in a rectangular vessel having capacity to hold 2 L of STS. Al–Al electrode plates each having surface area of 125 cm^2 were connected to their respective anode and cathode leading to a DC power supply (LMC electronics, India 0–500 V and 0–2 A) and were energized for a required duration of time at different voltage and current values as required. The inter-electrode distance (2.5 cm) between two neighbouring

Table 1
Characteristics of STS

Parameters	Mean ± S.D
pH	7.54 ± 0.19
Conductivity (μS)	766.8 ± 18.09
TDS (mg/L)	527.5 ± 19.88
COD (mg/L)	106.69 ± 8.11

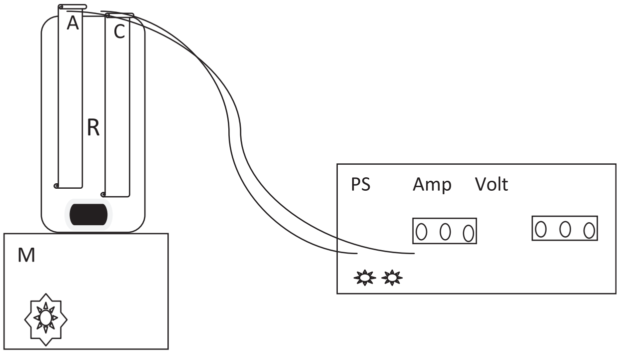

Fig. 1. Systematic design of experimental set-up. (A—anode; C—cathode; R—reactor; M—magnetic stirrer; PS-DC power supply; Amp—current and volt—voltage).

electrode plates was fixed. All the experiments were performed at room temperature (30 ± 2˚C) and at a constant stirring speed (100 rpm) to maintain the uniform mixing of STS during the electrolytic treatment. Before conducting an experiment, the electrodes were cleaned by dipped in dilute hydrochloric acid (HCl) (5% v/v) for 5 min and then were thoroughly washed with water and were finally rinsed twice with distilled water. Different quantities of NaCl (0.1, 0.3 and 0.5 g/L) were added to the electrochemical process as a supporting electrolyte to study the effect of chlorides on COD removal efficiency. After electrolytic treatment, the STS was allowed to stand for two hours and then sampled for COD analysis.

2.3. Analytical methods

The COD and pH of STS were determined before and after the electrolytic treatment following the Standard Methods [14]. The calculation of COD removal efficiency after electrolytic treatment was carried out using the following formula.

$$\mathrm{CR}\% = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 and C, respectively, are values for COD of STS before and after electrolysis.

3. Results and discussion

The results on COD removal efficiency of STS by electrolytic treatment at different operating conditions like current density, operating time, pH and supporting electrolyte are shown in Figs. 2–4.

3.1. Effect of current density and operating time

Current density is one of the most important parameters of electrolytic process that can affect the COD removal efficiency from STS. The rate of bubble generation increases and the bubble size decreases with increase in current density and both of these trends are beneficial in terms of high pollutant removal efficiency by H_2 flotation [15–17]. Zaroual et al. [18] reported that the efficiency of COD removal

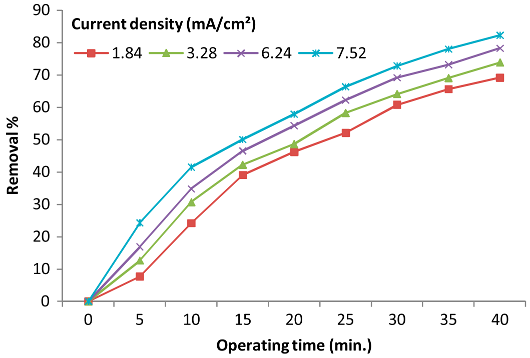

Fig. 2. Effect of current density and operating time on COD removal of STS.

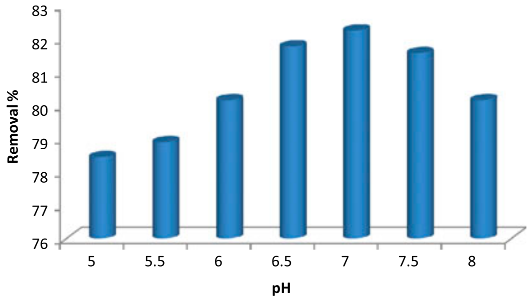

Fig. 3. Effect of pH on COD removal efficiency from STS (current density 7.52 mA/cm^2; operating time 40 min).

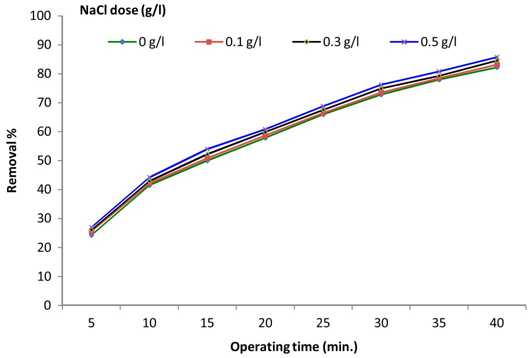

Fig. 4. Effect of supporting electrolyte (NaCl) g/L on COD removal efficiency of STS (current density 7.52 mA/cm^2; pH 7).

of textile effluent depended on the quantity of hydroxide flocs, which was bound with time and cell current of electrocoagulation. When one of the two parameters increased, the distribution of the coagulation agent density was more effective. The efficiency of ion production on the anode and cathode increased as the current density increased. Therefore, there was an increase in flocs production in the solution, and hence, there was an improvement in the efficiency of COD removal of baker yeast wastewater. It was also advisable to limit the current density in order to avoid excessive oxygen evolution as well as to eliminate other adverse effects like heat generation [19]. The COD and TOC removal efficiencies increased with increasing the current density while at high current densities can be attributed; the extent of anodic dissolution increased positively charged polymeric metal species resulting in increased COD and TOC removal efficiencies of paint manufacturing wastewater [20].

This study observed that the removal of COD from STS increased with the increase in current density and operating time of the electrolytic treatment. From this study, it was observed that the COD removal efficiency for the Al electrode increased from 69.17 to 82.25% with an increase in current density from 1.84 to 7.52 mA/cm^2, respectively (Fig. 2). This can be attributed to the fact that the current density determines the rate of metal oxidation resulting in a greater amount of precipitate being formed during the electrolytic treatment that increases the removal of pollutants from STS.

Operating time also influences the treatment efficiency of the electrolytic process. During the treatment, the anodic electrode dissolution leads to release the Al^{+3} ion into the STS and OH^- from the cathode leading to the formation of $Al(OH)_3$ and related oxidized products. The COD removal efficiency depends directly on the coagulant generated from the electrodes. It was revealed that the increase in time of electrolysis from 5 to 40 min yielded an increase in the COD removal efficiency from 7.69 to 82.24% for Al electrodes with different current densities (1.82 to 7.52 mA/cm^2) (Fig. 2). The present study indicated the removal efficiency of COD increased rapidly in the first 20 min of the electrolytic process. The maximum removal efficiency of COD was observed at 40 min, and highest current density was 7.52 mA/cm^2. This is due to the increase in concentration of aluminium and their hydroxides in the STS during electrolytic treatment. It has been reported that the increase in the electrolysis period resulted in a decrease in residual COD and BOD concentrations of distillery spentwash [21]. An increase in the operating time from 10 to 60 min in the treatment of the baker's yeast wastewater by electrocoagulation resulted in an increase in the removal efficiencies of COD, TOC and turbidity [19]. A study on the effect of operating time on STS showed that an increase in the operating time of electrolysis resulted in a corresponding increase in removal efficiency of TD, COD and BOD [22].

3.2. Effect of pH

The pH of electrolyte medium is an important contributing parameter that can influence the electrolytic process. The formation of $Al(OH)_3$ is due to the presence of generated Al^{3+} ions at the anode and OH^- at the cathode. In the present study, the effect of pH on COD removal efficiency with the different initial concentrations of pH (5–8) of STS was studied at optimum current density (5.72 mA/cm^2) and operating time (40 min). The removal efficiency of COD increased from 78.44 to 82.24% with increase in the pH from 5 to 7. However, an increase in pH above 7 decreased the removal efficiency of COD from 81.56 to 80.15% (Fig. 3). Gurses et al. [23] has reported an increase in the removal efficiency of colloidal particles in the pH range of 4–7 that leads to the formation of amorphous hydroxide precipitates and other aluminium hydroxide complexes with hydroxide ions and polymeric species. Zaied and Bellakhal [24] established that the increasing pH beyond 7 suppressed the COD removal most probably due to the formation of $Al(OH)_4^-$ which does not contribute to the reduction of COD.

Electrochemical-based electrolytic processes exhibit some buffering capacity because of the balance between the production and the consumption of OH^- and the need for charge neutralization before the final transformation of soluble Al compounds into $Al(OH)_3$ particles [19]. The Al^{3+} ions on hydrolysis may generate the aqueous complex species $Al(H2O)_6^{3+}$, which is predominant at pH < 4. Between pH 5 and 6, the predominant hydrolysis products are $Al(OH)^{2+}$ and $Al(OH)_2^+$; between pH 5.2 and 8.8, the solid $Al(OH)_3$ is more prevalent; and above pH 9, the soluble species $Al(OH)_4^-$ is the predominant and is the only species present above pH 10 [25].

3.3. Effect of supporting electrolyte

We studied the effect of supporting electrolyte (NaCl) on the COD removal efficiency in STS water at three concentrations of 0.1, 0.3 and 0.5 g/L. The results are shown graphically in Fig. 4. We did not observe any significant increase in the COD removal on addition of NaCl to the STS. We achieved a COD removal of 82.24% in the absence of any supporting electrolyte. There was nominal but consistent increase in COD removal on addition of NaCl, and highest COD removal of 85.76% was achieved in the presence of 0.05% NaCl (w/v). This is in complete disagreement with the observations of Wang et al. [13] who have reported a great enhancement in COD removal from ~40 to 71% after addition of NaCl to laundry wastewater. The addition of NaCl increases the ionic strength and current at same voltage, and the presence of chlorides leads to anodic discharge of Cl_2 and OCl^-. The OCl^- itself is a strong oxidant, which is capable of oxidizing organic molecules present in wastewater [9–13]. The addition of NaCl into the medium results in the following reactions taking place in the wastewater [15,26]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{2}$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \tag{3}$$

$$HOCl \rightarrow OCl^- + H^+ \tag{4}$$

Apparently, Cl_2 and OCl^- are better oxidizing agent for detergent impurities present in the laundry wastewater than for the sundry organic compounds present in STS. Consequently, addition of NaCl is not warranted for the removal of COD in STS. However, we still recommend the addition of supporting electrolyte for reducing the current consumption and in turn will lower the cost of the process making it economically more viable.

4. Operating cost

Electrical energy and electrode consumption are important economical parameters in EC process. In EC process, the operating cost includes material, mainly electrodes and electrical energy costs, as well as labour, maintenance, sludge dewatering and its disposal. In this study, energy and electrode material costs have been taken into account as major cost items in the calculation of the operating cost (US \$/m^3) as follows [12]:

$$\text{Operating cost} = aC_{\text{energy}} + bC_{\text{electrode}} \tag{5}$$

where C_{energy} (KWh/m^3) and $C_{\text{electrode}}$ (kg Al/ m^3) are the consumption quantities for the COD removal.

a—electrical energy price 0.1 US\$/ kWh; *b*—electrode material price 3.4 US\$ /kg for Al electrode. Cost due to electrical energy (KWh/m^3) is calculated as follows:

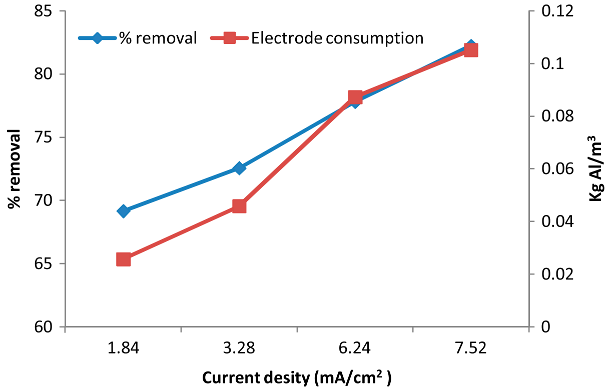

Fig. 5. Effect of current density on electrode consumption (kgAl/m^3) and COD removal efficiency from STS.

$$C_{\text{energy}} = \frac{U \times I \times t_{\text{EC}}}{v} \tag{6}$$

Cost for electrode (kg Al/m^3) was calculated as follows using the equation:

$$C_{\text{electrode}} = \frac{I \times t \times M_{\text{w}}}{z \times F \times v} \tag{7}$$

where U—cell voltage (V), I—current (A), $t_{\text{EC}-}$—time of electrolysis (s) and v—volume (m^3) of STS, M_{W}—molecular mass of aluminium (26.98 g/mol), z—No. of electrons transferred ($z = 3$) and F—Faraday's constant (96487C/mol).

It is evident from Figs. 5 and 6 that the COD removal increased from 69.17 to 82.24% with a corresponding increase in energy consumption from 2.76 to 45.12 kWh/m^3 with respect to an increase in current density from 1.82 to 7.52 mA/cm^2 that also resulted in an increase in the electrode consumption (2.52×10^{-2} to 10.51×10^{-2} kg/m^3). The operating cost of

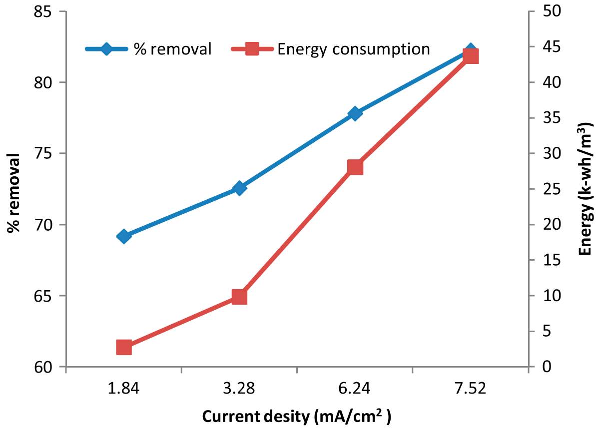

Fig. 6. Effect of current density on energy consumption (k-Wh/m^3) and COD removal efficiency from STS.

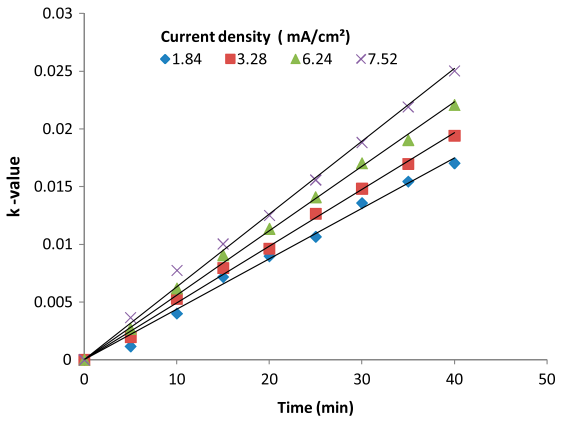

Fig. 7. Effect of current density on the rate constant versus. time.

electrolytic treatment was increased from 0.36 to 1.56 US$/m^3 due to increase in electrical energy as well as an electrode consumption in the electrolytic treatment.

4.1. Kinetic study

The rate of removal of COD is represented by the following first-order mechanism [27]:

$$\ln\left(\frac{C_0}{C_t}\right) = kt \tag{8}$$

where C_0—initial value of COD (mg/L), C_t—value of COD at time t, and t—time in minutes, and k isthe rate constant (min^{-1}) for electrolytic treatment with varying current density. The study indicated that the pseudo-first-order abatement kinetic was relatively fitted. Fig. 7 shows that an increase in current density from 1.84 to 7.52 mA/cm^2 increased the rate constant from 0.001159 to 0.025025 min^{-1} for Al–Al electrode system.

5. Conclusion

The removal efficiency of COD of STS for Al electrodes was found to be dependent on current density, operating time and initial pH throughout the electrolytic treatment. The optimal operating conditions of initial pH of 7, current density of 7.52 mA/cm^2, NaCl concentration of 0.5 g/L and operating time of 40 min yielded 86% removal of COD from the STS in the electrolytic cell. The kinetic rate constants for COD removal at various current densities indicated that pseudo-first-order kinetic is in good agreement with the experimental results.

However, the most surprising aspect of the present work was the observation that the addition of sodium chloride as a supporting electrolyte did not cause any significant increase in the removal of COD from STS. This is clearly at variance from the reported studies that have claimed greatly enhanced removal in the presence of sodium chloride.

The maximum electrode and electrical energy consumption was 10.51 × 10^{-2} kg/m^3 and 45.12 kWh/m^3 at the optimum conditions. The operating cost was found to be 4.87 US$/m^3 Thus, the electrolytic treatment can be used as an economical process for the removal of COD from STS.

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