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Research Article

Treatment of Composite Reverse Osmosis (RO) Reject Water for Chemical Oxygen Demand (COD) Reduction

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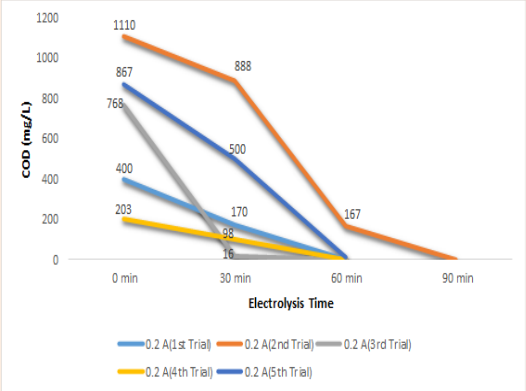
Abstract

This paper depicts the performance of electrochemical oxidation (EO), an advanced oxidation process (AOP) for water/wastewater treatment and which is highly advantageous in saline effluents due to their conductivity. The sample composite reverse osmosis (RO) reject water taken here has salinity of more than 2.7% and hence the conductivity varies from 45000 to 50000 μS. In EO, the effects of parameters like current density, pH, time and temperature were studied. The best reduction in chemical oxygen demand (COD) of up to 100% was found to be at a native pH of RO reject, i.e., around 10, current of 0.2A, current density of 0.0035A/cm^2, electrolysis time of 1 hour and at an ambient temperature of around 30°C. The power consumption was found to be 0.2 kWh, i.e., Rs.1 per m^3 of reject (considering 1 unit (kWh) = Rs. 5/-).

The EO treatment was carried out in lab scale with a capacity varying from 500 mL to 1000 mL.



Keywords: Electrochemical oxidation, wastewater treatment, COD, power consumption

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Introduction

Saline wastewater is generated from many industrial sectors like textile, petroleum, petrochemical, leather etc. All these sectors generate very large amount of saline wastewater, rich in both salt (NaCl) and organic matter. When this wastewater is discharged into the environment without prior treatment, it can cause severe damage to the aquatic life, water potability and agriculture by contamination of soil, surface and groundwater [1]. Biological treatment of saline wastewater results in poor removal of chemical oxygen demand (COD) due to the inhibition by high salt content [2-5]. Due to high conductivity in saline wastewater with the presence of anions and cations, EO treatment might be a favorable route [6]. Several studies have been carried out on the EO of different organic compounds and anode materials [7, 8]. This method also has been successfully applied for the treatment of saline wastewater in textile industry, tannery, distillery, domestic sewage and landfill leachate [9-16].

Graphite electrodes have been widely used recently, for organic removal because of its low cost. It has large surface area and high current efficiency compared to other electrodes [10]. In graphite electrodes, oxidation is dominated mainly by physisorbed active oxygen hydroxyl radicals. These hydroxyl radicals cause the complete destruction of organic matters. However, the relatively poor service life due to surface corrosion especially when the EO is conducted at high potential is the notable short-coming of graphite electrode. But here since the potential for the operation is optimized to 3 - 4V only, this short-coming is nullified.

In the EO, organic pollutants are removed by electro-generated oxidizing agents like chlorine and hypochlorite [17]. In general, the following reaction takes place during EO using graphite electrodes in the presence of sodium chloride, magnesium chloride, calcium chloride and ammonium chloride.

At the anode:

$2Cl^- \rightarrow Cl_2 + 2e^-$ (1)

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ (2)

At the cathode:

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

In the undivided cell, chlorine formed at the anode and hydroxides formed at the cathode react to form chloride and hypo chlorites. Both the hypochlorite and free chlorine are chemically reactive and oxidize the organic pollutants in the effluent to carbon dioxide and water [14, 18].

HOCl is then formed.

$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$ (4)

The HOCl dissociates into OCl^- and H^+ ions.

$HOCl \leftrightarrow H^+ + OCl^-$ (5)

These hypochlorite ions act as the main oxidizing agent in the organic degradation.

The overall desired reaction of electrolysis is:

Organic matter + $OCl^- \rightarrow$ Intermediates (6)

Intermediates $\rightarrow CO_2 + Cl^- + H_2O$ (7)

The other important products of electrolysis include Cl_2, ClO_2, O_3, $OH^\cdot$, $O^\cdot$, $ClOH^\cdot$, H_2O_2, O_2, H_2 and CO_2. Due to the high oxidation potential of the radicals, they may undergo decomposition to produce other oxidants which may oxidize the organic compounds. This process is called direct oxidation. The primary (Cl_2 and O_2) and secondary (ClO_2, O_3 and H_2O_2) oxidants have long life. They are capable of diffusing into the areas away from the electrodes and continue to oxidize the pollutants [19]. The objective is to analyze the performance of EO treatment of a composite RO reject water sample and optimize the operational parameters for the same in a large scale basis.

Experimental

Electro-oxidation cell

The setup comprises of: 2 electrodes.

- Anode: Graphite. Cathode: Stainless Steel (OD = 1cm) Area: 56.27cm^2
- AC to DC convertor power source equipped with current-voltage monitoring
- Cylindrical vessel
- Polystyrene covered vessel (1L) to conduct temperature studies if COD reduction at ambient temperature is not found satisfactory
- In both the types, a possible route for aeration also helps for COD reduction substantially, though may not be mandatory.
- Source to maintain the temperature inside the vessel as low as 5 °C or less. Here, ice cubes were used.
- Accessories: Copper wire and tape

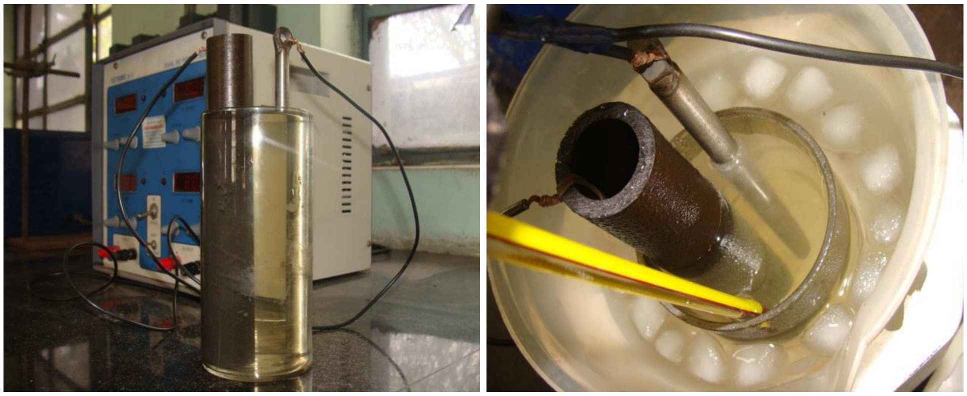

Figure 1 Electro-oxidation setup and other components

Results and Discussion

The process of standardization of EO of sample RO reject was carried out by studying the effects of voltage, current, pH, concentration of the organic matter, temperature and time.

Variations in parameters and its effects

Voltage variation depends on the current input, which again is dependent on the resistance of the RO reject sample. The current variation was varied from 0.05 A to 0.5 A requiring a voltage of 2.3 V to 4.1 V. The more important parameter than current is the current density, which ranges from 0.001 A/cm^2 to 0.01 A/cm^2. The anode material graphite's immersed length was kept at 14.95 cm and its ID was 21.08 mm and OD 31.28 mm; this surface area of the hollow graphite tube was used for the current density measurement. However, after 40-days trial runs, corrosion was noted in the graphite electrode, which is obvious since it acts as an anode. But being cheap and readily available, its replacement, when necessary, should not be much of an issue [20].

Figure 2 Corrosion of graphite electrode

Graphite Tube OD = 3.128 cm (Before trial runs), Graphite Tube OD = 3.120 cm (After 40-day trial runs)
Difference in OD = 0.08 mm

Variation in current

As shown in Table 1, current ranging from 0.3 A to 0.5 A, effective reduction in COD was noticed but there may be wastage of power due to overtime in effective electrolysis for COD reduction. Current needs to be optimized in such a way that no power loss or wastage occurs and that power is consumed only for COD reduction and nothing else. If more power is supplied, then excess hypo/free radicals are produced and competitive electrolysis of water takes place after effective oxidation of organic pollutants, which is undesirable and not only it increases power consumption but also disturbs COD analysis. At higher current, effective COD reduction may happen but its analysis is disturbed due to the presence of excess hypo (OCl^-) as shown in **Figure 3**.

From around 50 to 60 trial runs taken, it was found that 0.2 A, i.e., 0.0035 A/cm^2 gives the best results in the COD

Table 1 Effect of current and electrolysis time on COD reduction

Current (A)	Voltage (V)	Electrolysis Time (hr)	Initial COD (mg/L)	Final COD (mg/L)	Power Consumption for 250 m^3 per day (kWh)
0.5	4.1	1	332	Nil	167
0.5	3.6	3	373	290	2294
0.4	3.3	1	912	124	56
0.3	3	1	1200	320	35
0.2	3	1	400	Nil	45
0.2	3.1	1.5	1110	Nil	25
0.2	3.1	0.5	768	16	12
0.2	3.1	0.5	203	Nil	44
0.2	3.1	1	867	12	11
0.1	2.8	0.5	902	430	4
0.1	2.6	0.5	705	41	6
0.1	2.6	2	256	51	73
0.1	2.7	1.5	184	Nil	63
0.1	2.7	1	593	327	34
0.05	2.3	0.5	999	560	4

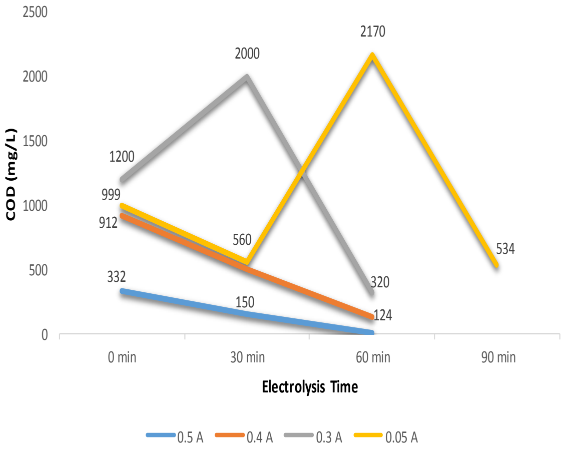

Figure 3 COD variation at 0.5A, 04A, 0.3A and 0.05A

remediation of the sample RO reject water taken here as shown in Fig.4. 0.1 A current depicts good reduction too, but cannot breakdown complex organics (cyclic, aromatic, cross-linked) at the later stage, due to its low rate of electron transfer, i.e., free radical/oxidizing agents release and therefore, is suitable only for low initial COD with linear organics (aliphatic)[1]. 0.2A current has the best rate of electron transfer and optimum oxidizing power for the given sample which can be verified from the successful results of up to 0 mg/L of COD achieved in some cases as shown in Table 1 and Figure 4. 0.05A is favorable only for a low COD and linear organics.

Figure 4 depicts the dominance of 0.2A current or 0.0035 A/cm^2. The erroneous COD values in **Figure 3** are mainly due to excess hypo generation. It interferes with COD analytical solution and gets oxidized to other oxidizing agents like ClO_2^-, ClO_3^- and ClO_4^-. These oxidation answers in the COD analysis and therefore, gives higher value than the actual.

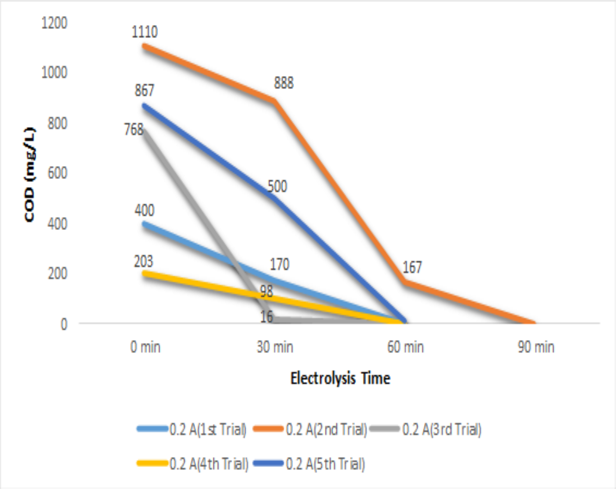

Figure 4 COD variation at 0.2 A

Excess hypo may be produced in two cases:

- All the organics are killed or oxidized/ no presence of organics.
- The organics are more powerful than hypo itself and cannot be oxidized by it.

Variation in pH

The pH of sample RO reject is alkaline (around 10) which is favorable for EO here and therefore no change in pH is required. With an alkaline pH, the equilibrium shifts towards the forward direction in reaction 5.

Variation in Temperature

EO at lower temperatures produced excess hypo not only at the optimum current of 0.2A but also at other current ranges of 0.05 A and 0.1 A. Even if there is a desirable COD reduction taking place, it cannot be correctly analyzed or measured, due to this excess hypo content. Therefore, low temperature studies were discontinued.

Variation in electrolysis time

For the optimized current of 0.2A, a high COD up to 1300 mg/L requires 1.5 hours and for a low COD, 1 hour of electrolysis time is sufficient as shown in fig. 4. Also, the anode efficiency, total current efficiency and energy consumption were found to be the most desirable for 0.2 A; since these parameters are directly proportional with the amount of COD reduced. For 0.2A current, anode efficiency and total current efficiency peaked at 0.628 kg/hAm^2 and 11.84 % respectively with energy consumption the least at 0.88 kWh/kg of COD for 0.2A as shown in Figures 5, 6 and 7 respectively.

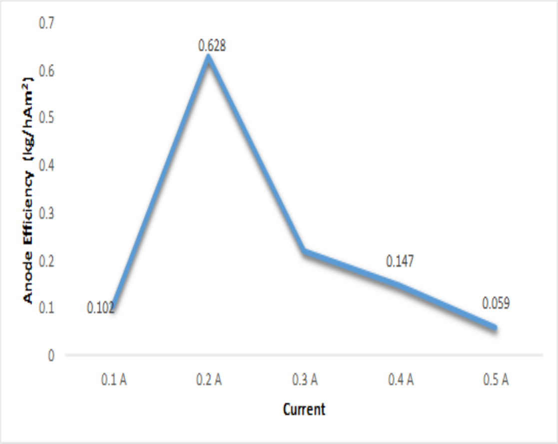

Figure 5 Effect of current on anode efficiency

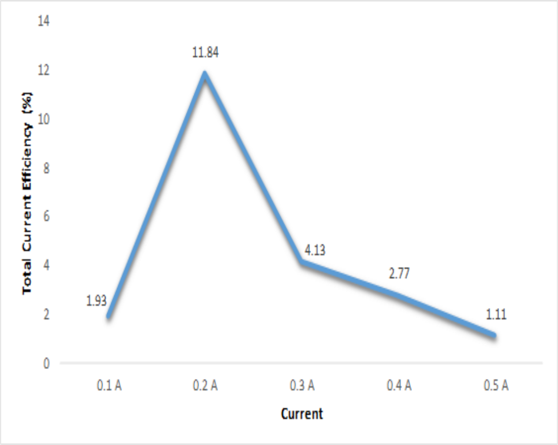

Figure 6 Effect of current on total current efficiency

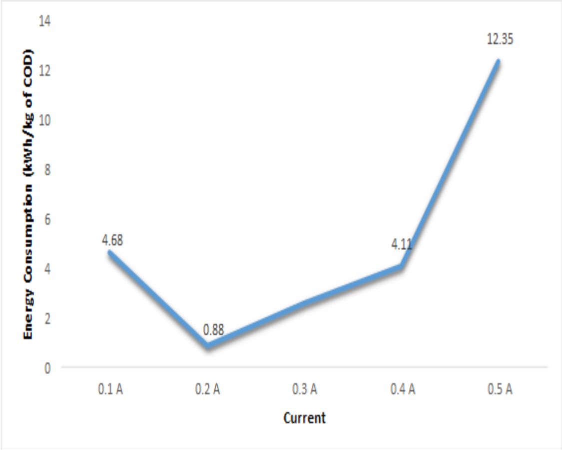

Figure 7 Effect of current on energy consumption

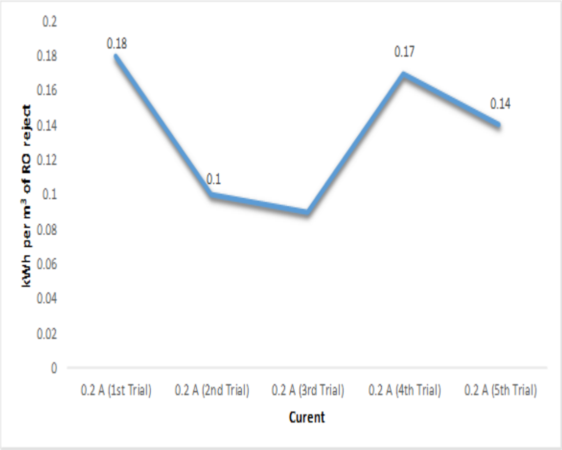

Figure 8 Energy consumption per m^3 of RO reject

The maximum energy consumption per m^3 of RO reject as shown in Fig. 8 is 0.18 kWh, which is at 0.2 A.

Basis for pilot plant

Electrode plates are preferable for higher capacity since it provides higher surface area and therefore, minimizing the power consumption with less voltage requirement. The dimensions of the plates and current were estimated from the optimized parameters at lab-scale. Considering a sample RO reject containing COD to a maximum of 1300 mg/L, i.e., 1.3 kg. Therefore, for a 1m^3 capacity, a 1m^2 surface area of electrode plates with a current flow of 3.5A to 4A for 1.2h to 1.5h will give the desired current density with the anode efficiency being 0.3 kg/hAm^2. If the anode efficiency is found to be better than the lab scale, then lesser current is required and hence, power consumption can be further reduced. Table 2 shows the details.

Table 2 Parameters for 1m^3 pilot-study

Average Anode Efficiency = 0.3 kg/hAm^2			
COD reduced (kg)	**Electrolysis Time (h)**	**Current (A)**	**Immersed Surface Area (m^2)**
0.3	1	1	1
1.05	1	3.7	1
1.26	1.2	3.7	1

The temperature and pH will not be altered from the native condition. As far as voltage is concerned, it depends upon RO reject's conductivity, which varies from 45000 – 55000 μS and can be optimized and predicted only after the pilot study is conducted.

Conclusions

In this investigation, EO of organic content in a sample composite RO reject water was studied. Graphite material was selected as the anode material due to its stability in a saline environment. COD measurement was done using the standard open reflux colorimetric method. The various parameters, after trials, were optimized for the sample as follows: pH: native; Temperature: Ambient; Potential: 3.1V; Current: 0.2A and electrolysis time: 90 minutes. Total current efficiency (TCE), Anode efficiency (AE) and Energy consumption (EC) were also found favourable at these optimized conditions. These factors are required to be considered for setting up or designing EO cell at a higher scale. In a commercial setup, a safe passage for chlorine and hydrogen gases, which may arise in minimal amount, must also be provided.

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