

Advanced oxidation of catechol in reverse osmosis concentrate generated in leather wastewater by Cu-graphite electrode

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Abstract Reverse osmosis (RO) concentrate generated from tannery was treated by advanced electrochemical oxidation using graphite electrodes. Catechol was selected as model organic pollutant in the RO concentrate. The influence of applied current density, catechol concentration, pH, temperature and inner electrode space of electrodes was investigated in electrochemical oxidation system. The optimized conditions were found to be current density (j), 100 mA/cm²; electrolysis time (t_{eco}), 60 min; pH, 7.0; and temperature, 25 °C at an inner electrode space, 2 cm. The average mass transport coefficient for the removal of catechol as COD was found to be 3.0×10^{-5} m/s at optimum conditions. Faradic efficiency and specific energy consumption were also calculated for the applied current density. Further, the treatment of catechol was confirmed through Fourier transform infrared spectroscopy. Theoretical evaluation of current density suggested that the removal of catechol was controlled when supplied at above limiting applied current densities and mass transport controlled at lower of limiting current densities.

Keywords RO concentrate · Cu-graphite · Refractory organics · Electrolysis · Saline solution · Tannery

Introduction

Among the membrane separation processes, reverse osmosis (RO) is being widely applied for sea water desalination, production of potable water and in industrial tertiary wastewater treatment. Among the membrane processes, RO is being preferred for its modular construction and small footprint, which enables to combine with other treatment process sequences (Chelme-Ayala et al. 2009; Ahmet kaya et al. 2016). However, the concentrate stream generated from RO processes demands suitable treatment before being discharged into the environment (Mauguin and Corsin 2005).

Roberts et al. (2010) have reported an issue of ecological impacts on disposal of concentrate generated from sea water desalination. There are many laboratory-based experiments, toxicological investigations and manipulative field experiments reports on the potential impact on direct discharge of brines and their constituents to aquatic system. However, the RO processes simply compresses the solute constituents from feed stream to concentrate stream, which are normally found to be double or higher than the feed steam concentration (Chelme-Ayala et al. 2009). Conventionally, the brines are being discharged after diluted with power plant cooling waters, natural seawater or municipal wastewaters to reduce salinity (Einav and Lokiec 2003; Meneses et al. 2010). The disposal of diluted concentrates could severely affect the sensitive species of environment due to the refractory nature of organic pollutants present in concentrate (Meneses et al. 2010). There

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are other alternative methods of disposal of RO concentrate are being studied and reported, such as ozonation (Pophali et al. 2011), heterogeneous photocatalysis (UV/TiO₂) (Westerhoff et al. 2009; Mehmet et al. 2014a, b; Muhammad et al. 2015), sonolysis (Zhou et al. 2011a, b; Muneer et al. 2015). Recently, electrochemical advanced oxidation processes (EAOPs) have attracted considerable interests for the refractory organic removal from wastewater due to their simplicity and high efficiency by hydroxyl radical production (Hege et al. 2004; Dialynas et al. 2008; Perez et al. 2010; Chaplin et al. 2010; Zhou et al. 2011a, b; Boopathy and Sekaran 2014; Necip et al. 2015). The formation of hydroxyl radicals (OH) and secondary oxidizing agents (chlorine gas, hypochlorous acid) can effectively remove various refractory organic pollutants in the concentrate. There are reports on the electrochemical treatment of various wastewater using different anode materials, among which BDD and Ti/IrO₂-RuO₂ electrodes were found to be effective and dimensionally stable (Boopathy et al. 2012). The performance of electrochemical oxidation process is decided by the nature of anode material (active and non-active), and the mechanism of organic oxidation (direct and indirect) takes place during the electrochemical oxidation. Modern wastewater treatment process incorporates an integrated unit operation such as adsorption-cum-oxidation or adsorption-cum-disinfection for the minimization of time and land space. In this study, copper-coated graphite electrode was used for the treatment of prepared catechol containing RO concentrate with packed bed adsorption column for the removal of trihalomethanes. The application of tannin chemicals in leather processing generates a various by-products among which catechol was be primary end products. Hence, in this study catechol was selected as model organic compound in the tannery RO concentrate.

Materials and methods

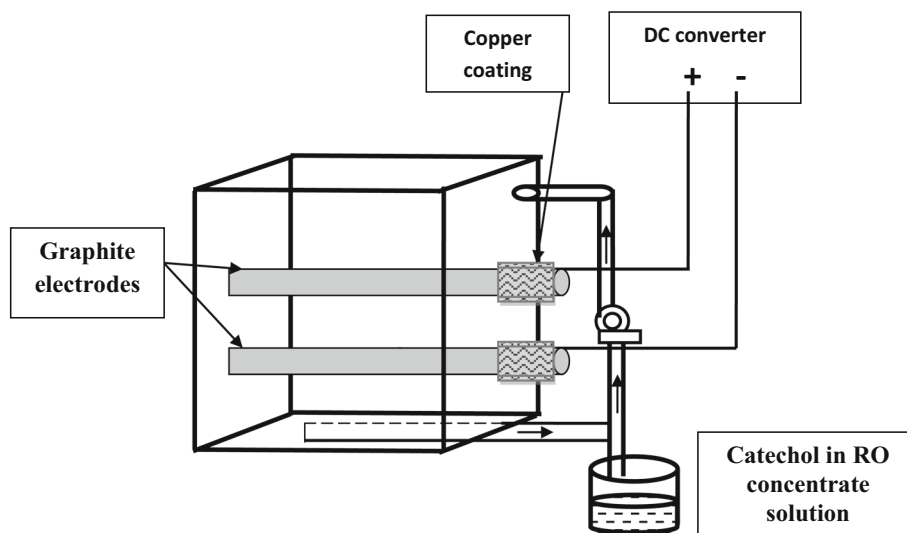
Preparation of catechol containing RO concentrate

Catechol containing RO concentrate was prepared by dissolving catechol (2.25, 4.5 and 9 mmol/L) at required experimental concentration in RO concentrate collected from a commercial CETP in Ranipet, Tamil Nadu, India (Murugananthan et al. 2005). All the above chemicals are procured from Merck India Ltd.

Reactor set-up and experimental procedure

A jacketed rectangular electrochemical cell (Fig. 1) (height 12 cm, width 10 cm and thickness 4.5 cm) was fabricated using 6-mm-thick acrylic plastic sheet for a working volume of 0.5 L. In this reactor, two graphite rods (diameter 2.5 cm and length 15 cm) were positioned horizontally with required experimental space (1, 2, 3, 4.5 and 6.5 cm) in a separate electrochemical cell. One end of the electrodes was initially coated with copper for a length of 3 cm (as shown in Fig. 1) for external lead to make electrical connection with DC power supplier. The used electrodes (exposed area) are allowed to soak in 1 % (v/v) (hydrochloric acid to remove any polarized salt particles and washed with distilled water twice. The washed graphite electrodes are dried in open atmosphere for next cycle of operation or wrapped using polythene plastic until any use (storage). The DC power supply (0–60 V and 0–5 A) was used to set a required current density and voltage for the electrochemical oxidation of catechol containing RO concentrate. The electrochemical cell was maintained at 25 °C by recirculation of externally temperature-controlled water pumping through jacketed medium during the experiments.

Fig. 1 Schematic diagram of electrochemical cell for the treatment of catechol containing RO concentrate



The performance of electrochemical oxidation of RO concentrate was evaluated for the applied current density (j) (100, 200 and 300 mA/cm²), catechol concentration (2.25, 4.5 and 9 mmol/L) and inner electrode spacing (1, 2, 3, 4.5 and 6.5 cm). Aliquot samples were drawn to estimate the residual solution COD value, and the corresponding decrease in sample volume during the sampling was corrected by adopting the methodology described by Choo et al. (2006).

Analyses

The catechol containing synthetic RO concentrate was characterized for various parameters according to standard methods (APHA 1999). The solution is found to be high content of chloride, which is known to affect the COD determination. Hence, the COD analysis was performed by adopting methodology (specific to high salt-containing liquid waste) described by Vyrides and Stuckey (2009). In this analysis, the digestion mixture was prepared by adding K₂Cr₂O₇, 3 g (which was previously dried at 103 °C for 2 h), to concentrated H₂SO₄, 167 mL and HgSO₄, 33 g and made up to 500 mL with deionized water. The mixture was then left to cool at room temperature before being diluted to 1000 mL. The sulphuric acid reagent (2.5 %, w/v) was prepared by dissolving Ag₂SO₄ in H₂SO₄, and the sampling and digestion were carried out in accordance with methodology described under the analysis of water and wastewater. Table 1 shows physico-chemical characteristics of reverse osmosis concentrate generated from leather industry

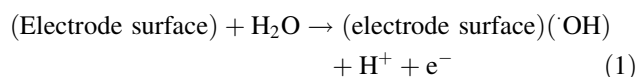
Table 1 Physico-chemical characteristics of reverse osmosis concentrate generated from leather industry

Sl. No.	Parameters	Mean value
1	pH ^a	6.42
2	Conductivity (mS/cm)	34.86
3	Total dissolved solids	15,240
4	Chemical oxygen demand	250
5	Total organic carbon	220
6	Total Kjeldahl nitrogen	46
7	Ammonia nitrogen	25
8	Calcium	1124
9	Magnesium	13.8
10	Chloride	9996
11	Sulphate	3020

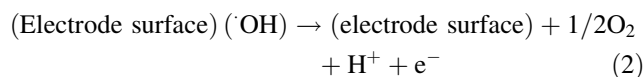
^a All the parameters are expressed in mg/L, except pH and conductivity

Theoretical approach

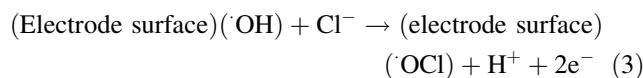
The mechanism of electrochemical oxidation of organic pollutants is a complex phenomenon involving the coupling of electron transfer reaction with a dissociate chemisorption step. Basically, two types of oxidative mechanism are observed with respect to the oxidant generation: Oxidation occurring at the electrode surface is called as direct electrolysis and oxidation occurring via the oxidant generated continuously on the anodic surface is called indirect electrolysis. In direct electrolysis, the rate of oxidation is depending on electrode activity, pollutants diffusion rate and applied current density. In direct electrolysis, first, H₂O is discharged at the anode to produce adsorbed hydroxyl radicals according to Eq. (1) given,



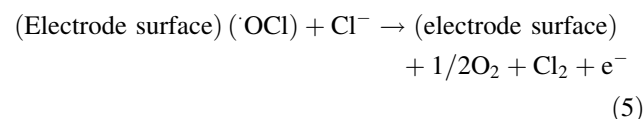
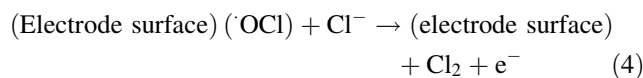
At the anode surface, active oxygen can be present in two states, either as physisorbed hydroxyl radicals ($\cdot\text{OH}$) and/or as chemisorbed (oxygen in the porous surface of the graphite electrode). In the absence of oxidizable organics, the active oxygen produces dioxygen according to Eq. (2):



In indirect oxidation, the addition of NaCl as supporting electrolyte favours the generation of OCl⁻ radicals according to Eq. (3) as given below,



Further, the OCl radicals combine with chloride ions generating the chlorine gas and thus responsible for the oxidation of organic pollutants in the bulk solution.



These sequential reactions will continue until the formation of carbon dioxide and water in the bulk solution during the electrochemical oxidation process (Bindu et al. 2000; Malpass and Motheo 2001). In direct oxidation, the rate of diffusion of organic compounds onto anode area controls the electrochemical oxidation reaction (Buso et al. 2000; Raghu and Basha 2007). On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect



electrolysis (Comminellis and Pulgarin 1999; Miwa et al. 2006; Malpass et al. 2007).

Results and discussion

Effect of current density on electrochemical oxidation of catechol

The influence of current density on the degradation of catechol containing RO concentrate was determined by varying the current density of 100, 200 and 300 mA/cm². The other conditions such as initial concentration of COD 680 mg/L (for the addition of 2.25 mmol/L of catechol), native pH and temperature 25 °C were kept constant for the batch experimentation. At regular interval of time, the samples were collected to analyse COD values for the organic removal load. Figure 2a shows that the increase in current density decreased the COD concentration in RO concentrate significantly. Figure 2b shows the variation in instantaneous current efficiency with time at different current density in the treatment of catechol containing RO concentrate solution.

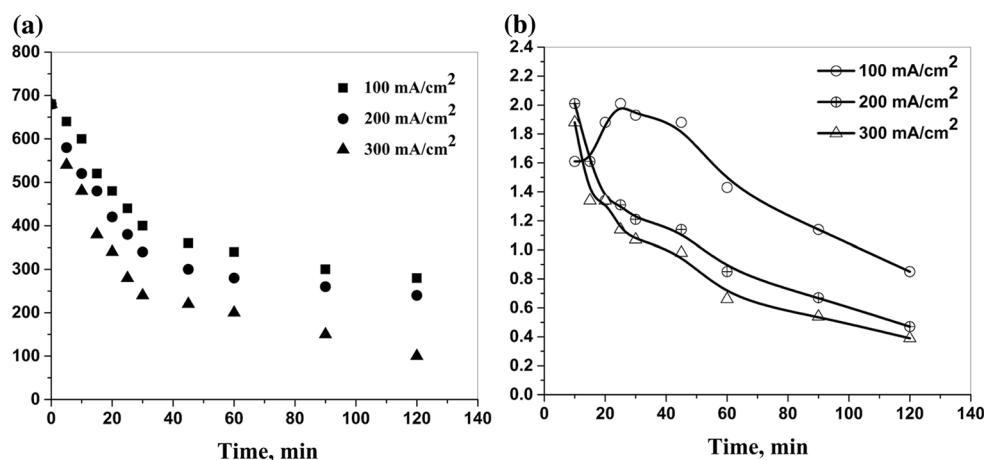
At initial stage of oxidation, graphite rod electrodes have exhibited the ICE values greater than 1.0. The high value of ICE at the beginning of electrochemical oxidation may be due to the fact that total applied current was completely utilized for the degradation of organic compound (catechol) present in RO concentrate solution. And thereafter, ICE starts to decrease beyond 30 min of electrochemical oxidation time (t_{eco}). The response suggested that beyond 30 min, the mechanism of organic oxidation is controlled by mass transfer diffusion. A similar kind of

mechanism was observed on oxidation of organics present in textile effluent (Bhaskar Raju et al. 2009). Further, the increase in applied current density (j) for the organic removal decreased the current efficiency of the process. This could be due to electrode polarization effect with increase in current density and thus reduces the active surface area of the electrode significantly. The current efficiency for the current densities (j) 100, 200 and 300 mA/cm² was found to be 0.67, 0.37 and 0.32 %, respectively. The maximum reduction in COD reduction was observed at current density of 300 mA/cm² and at electrochemical oxidation time (t_{eco}) of 120 min.

Effect of pH on electrochemical oxidation of catechol

The effect of initial pH of catechol containing RO concentrate solution was varied from 2.0 to 10.0 for the electrochemical treatment, and other experimental conditions such as j , 100 mA/cm²; temperature, 25 °C; initial COD, 680 mg/L; and t_{eco} , 60 min were fixed as constant. Figure 3 shows that the magnitude of percentage removal of COD increased significantly with the increase in solution pH of catechol containing RO concentrate solution from acidic to alkaline condition. There was an increase in removal of COD with the increase in pH from 2.0 to 8.0, and thereafter, for increase in pH up to 10.0, the removal rate remains constant (Nematollahi et al. 2009; Hadi et al. 2013; Roya and Davood 2011). The electrochemical oxidation was found to be highly significant at neutral pH range. Hence, the treatment of catechol containing RO concentrate can be taken between the pH range of 7.0–8.0.

Fig. 2 Electrochemical treatment of catechol containing RO concentrate solution. **a** Influence of applied current density (j) on COD removal. **b** Instantaneous current efficiency (conditions: pH 7.0; initial COD 680 mg/L and temperature 25 °C)



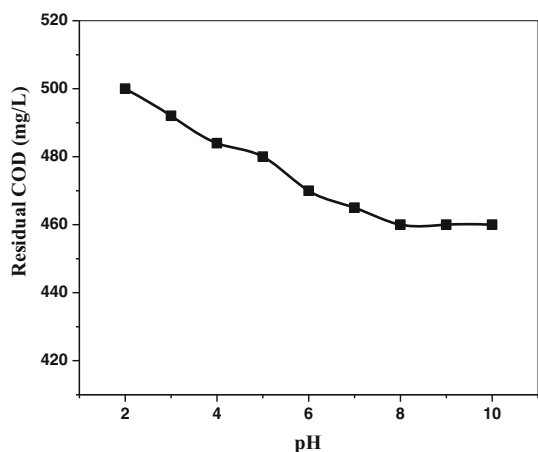


Fig. 3 Effect of initial pH on COD removal by electrochemical oxidation of catechol containing RO concentrate solution (conditions: t_{eco} , 60 min; temperature, 25 °C and j , 100 mA/cm²)

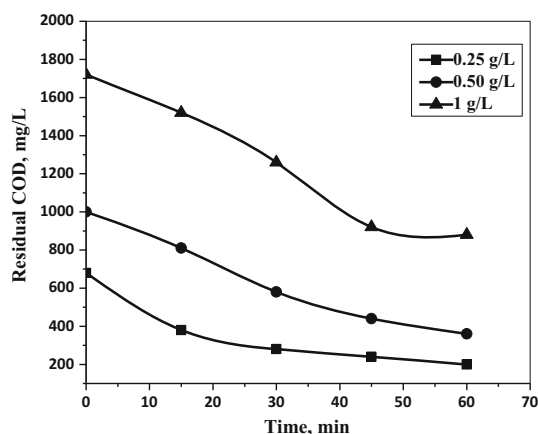


Fig. 4 Effect of catechol concentration on treatment of catechol containing RO concentrate solution (conditions: t_{eco} , 60 min; temperature, 25 °C and j , 100 mA/cm²)

Effect of catechol concentration in RO concentrate solution

The RO concentrate with different catechol concentration of 2.25, 4.5 and 9.0 mmol/L was prepared, and their respective initial COD values were found to be 680, 1000 and 1720 mg/L, respectively. The batch experiments were carried out at optimum j , 100 mA/cm²; t_{eco} , 60 min; pH, 7.0; and temperature, 25 °C. Figure 4 shows the COD removal pattern of synthetic RO concentrate solution by electrochemical oxidation.

Effect of temperature on electrochemical oxidation of catechol

The influence of solution temperature on the removal of COD from catechol containing RO concentrate solution

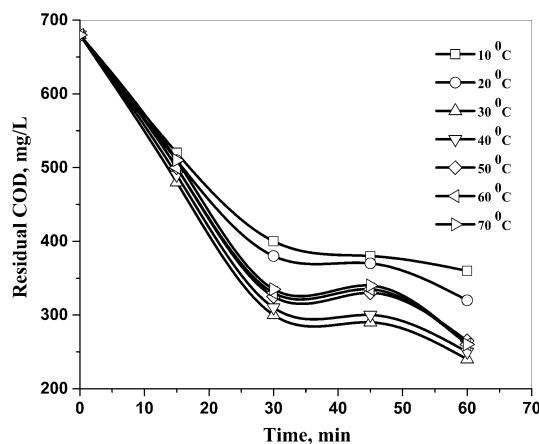


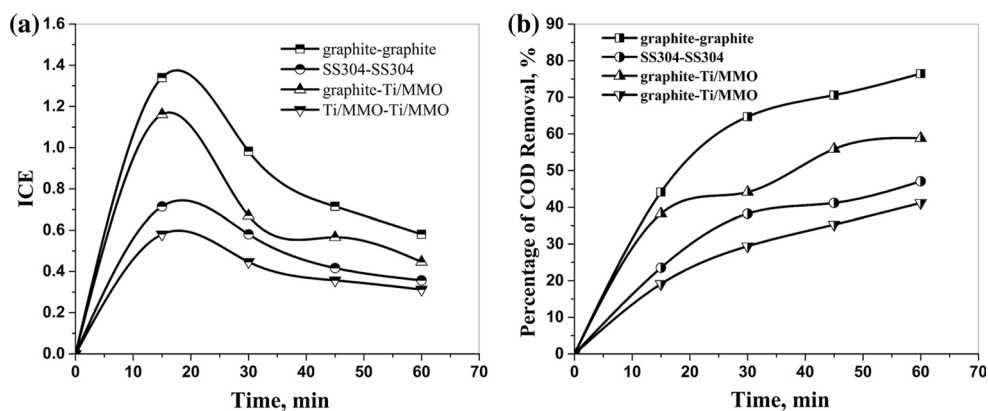
Fig. 5 Effect of solution temperature on treatment of catechol containing RO concentrate solution (conditions: t_{eco} , 60 min; j , 100 mA/cm² and initial COD, 680 mg/L)

was determined by varying the solution temperature from 10 to 70 °C. Jacketed electrochemical cell was used to maintain the required set temperature by circulating water from thermostatically controlled water bath. All the other electrochemical parameters such as j , 100 mA/cm²; t_{eco} , 60 min; concentration of catechol, 2.25 mmol/L; pH, 7.0; and COD, 680 mg/L were maintained constant. Figure 5 shows that the COD removal increased with the increase in temperature up to 30 °C and thereafter, the increase in temperature decreased the COD removal significantly. This may be due to increased molecular movement in bulk solution by the increased thermal radiation transport of organic molecules in the electrochemical cell which extends up to 30 °C. Further increase in temperature might reversed the reaction by rigorous molecular collision and also favoured the generation of undesirable products which could be the reason for the increase in COD over the initial concentration with increase in temperature. Hence, the optimum temperature in further experiments was kept at 25 °C.

Materials of selection for the electrochemical treatment of catechol containing RO concentrate solution

Anodes and cathodes of various materials of construction were changed to find the COD removal efficiency in electrochemical oxidation of catechol containing RO concentrate solution under batch experiment. The operating conditions were at j , 100 mA/cm²; t_{eco} , 60 min; applied potential, 4.5 V; COD, 680 mg/L; and temperature, 25 °C. Figure 6a, b shows that high percentage removal of COD was observed with graphite/graphite electrode system than other electrode systems.

Fig. 6 Selection of materials of construction of electrodes (anode–cathode) for electrochemical oxidation of catechol containing RO concentrate solution based on **a** ICE, **b** percentage of COD removal (conditions: t_{eco} , 60 min; temperature, 25 °C; j , 100 mA/cm² and applied potential, 4.5 V)



Kinetic studies on electrochemical oxidation of catechol containing RO concentrate solution

Kinetic study on the removal of catechol in terms of COD in catechol containing RO concentrate solution was analysed based on the limiting current density (j_{lim}) during the electrolysis for the graphite/graphite electrode system. The j_{lim} could be related to $[\text{COD}]_0$ by the mathematical expression

$$j_{\text{lim}} = nFk_m[\text{COD}]_0 \quad (6)$$

where j_{lim} is the limiting current density (mA/cm²) at the instant 't', n is the number of electrons transferred, F is the Faraday constant (96,487 C/mol), and $k_m(\text{COD})$ is the average mass transport coefficient (m/s) based on COD removal. Then, the COD removal rate (r) can be expressed as (Roberts et al. 2010),

$$r = \frac{j_{\text{lim}}}{nF} = k_m[\text{COD}] \quad (7)$$

From the mass balance of the whole system operating under batch mode, we get,

$$\frac{d[\text{COD}]}{dt} = -\frac{A}{v}r \quad (8)$$

where A is the electrode area (m²) and v is the total volume of the solution (m³) being processed on integration and simplification, and we get,

$$\ln\left(\frac{[\text{COD}]_t}{[\text{COD}]_0}\right) = -\frac{Ak_m t}{v} \quad (9)$$

The plot of $\ln(\text{COD}_t/\text{COD}_0)$ versus time shows that the degradation of catechol in RO concentrate solution followed the pseudo-first-order rate equation as given in Eq. (9).

From the slope of the plot of $\ln(\text{COD}_t/\text{COD}_0)$ versus time (Fig. 7), the values of mass transfer coefficient

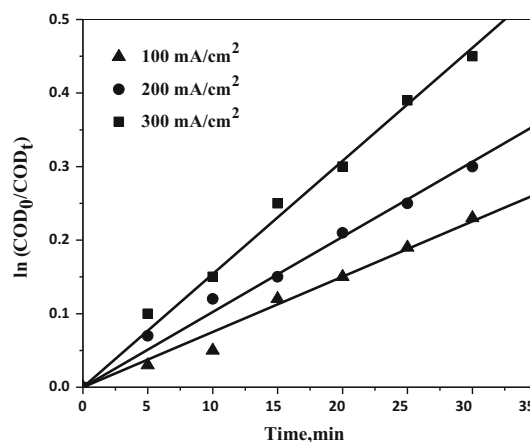


Fig. 7 Mass transfer coefficient for electrochemical oxidation of catechol containing RO concentrate solution (conditions: temperature, 25 °C; j and applied potential, 4.5 V)

Table 2 Evaluation of mass transfer coefficient, k_m , and limiting current density, j_{lim} , values at different current densities for the electrochemical oxidation of catechol containing RO concentrate solution (conditions: COD_0 , 680 mg/L; temperature, 25 °C and pH, 7.0)

Current density, j (mA/cm ²)	Mass transfer coefficient, k_m (m/s)	Limiting current density, j_{lim} (mA/cm ²)
100	3.01×10^{-5}	246.5
200	4.06×10^{-5}	333.5
300	6.19×10^{-5}	507.6

were calculated for the electrochemical oxidation of catechol containing RO concentrate solution. Table 2 shows that increase in current density increased the mass transfer coefficient significantly. The rate controlling mechanism for electrochemical oxidation was confirmed by evaluating the limiting current density using Eq. (7). The value of mass transfer coefficient

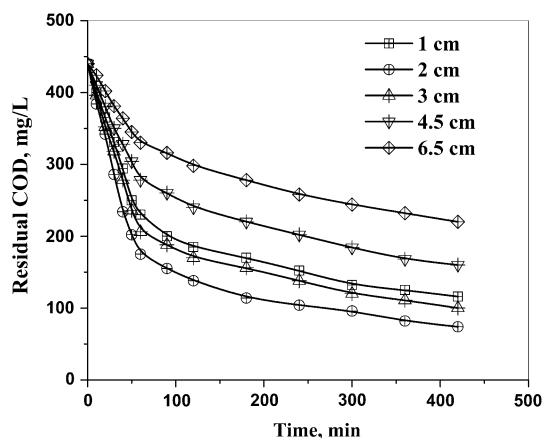


Fig. 8 Effect of inner electrode space for the treatment of catechol containing RO concentrate (conditions: current density, 300 mA/cm² and concentration, 2.25 mmol/L)

(k_m) was calculated from the slope of straight line. The value of k_m was found to be 3.00×10^{-5} m/s at optimum conditions j , 100 mA/cm²; t_{CCO} , 30 min; and temperature, 25 °C.

Effect of electrode spacing

The inner space between the anode and cathode electrode was varied from 1 to 6 cm for the evaluation of effective space for the electrochemical oxidation of catechol in RO concentrate solution. Figure 8 shows that the increase in electrode space from 1 to 2 cm increased the rate of COD removal (0.77–0.87 mg of COD/min) significantly and thereafter, increase in electrode space beyond 2–6.5 cm decreased the rate of COD removal from 0.87 to 0.52 mg of COD/min. The results revealed that the effective electrode spacing between the anode and cathode is 2 cm. Thus, the 2-cm electrode spacing is sufficient enough to diffuse generated oxidants in bulk solution for maximum destruction of catechol. Also, the increase in space between the electrodes increased working potential for applied current density and thus increased the ohmic resistance of the electrochemical oxidation process. The working potential for electrode space 2 and 6.5 cm was found to be 2.2 and 5.4 V for the applied current density of 300 mA/cm². The removal of COD during the 1 cm spacing was less, and this may be due to the generation of halogenated by-products. This halogenated by-products are more refractory in nature; hence, the overall removal of COD was observed to be less at 1 cm electrode space. The effective electrode space significantly reduces the cost of electricity by the low-voltage operation for the electrochemical oxidation than the conventionally following

Table 3 Apparent faradic efficiency and specific energy consumption for the treatment of catechol containing RO concentrate (conditions: catechol concentration, 2.25 mmol/L and inner electrode space, 2 cm)

Current density (mA/cm ²)	Apparent faradic efficiency (η_F , %)	Specific energy consumption (E_{SP} , kW/g of COD)
100	57.4	0.11
200	43.0	0.24
300	30.8	0.55

vertical electrode system. Also, the skill and maintenance required for the horizontally positioned electrodes are less than for the available electrochemical method.

Apparent faradic efficiency and specific energy consumption

The apparent faradic efficiency of COD removal was calculated using the following formula

$$\eta_F = \frac{(\Delta\text{COD} \times V \times F)}{8 \times I \times \Delta t} \quad (10)$$

where ΔCOD is the net COD removed (mg/L) after a treatment time t , V is the volume of treated solution (L), F is Faradays constant (96,487 C/equiv), 8 is the equivalent weight of oxygen, I is the applied current, and Δt is the treatment duration (s). The η_F for COD removal was found to be (Table 3) 57.4, 43.0 and 30.8 % at 0.1, 0.2 and 0.3 A, respectively.

Specific energy consumption (E_{SP}), the electric energy in kilowatt hours required to degrade a kilogram of a pollutant in water, was calculated using the formula for batch operation (Necip et al. 2015).

$$E_{SP} = \frac{P \times t \times 10^6}{V(C_0 - C_t)} \quad (11)$$

where P is the rated power (kW) of the reactor, V is the volume (L) of water treated in the time t (h), C_0 and C_t are the initial and final pollutant concentration in COD (mg/L), and the factor 10^6 converts mg to kg. The E_{SP} for the removal of COD during 2 h at 100, 200 and 300 mA/cm² was evaluated as 0.11, 0.24 and 0.55 kW/g of COD.

Instrumental analyses

Fourier transform infrared spectroscopy (FTIR) analysis

The catechol containing RO concentrate solution before and after electrochemical oxidation was characterized using FTIR spectroscopy. Figure 9a shows FTIR spectra of



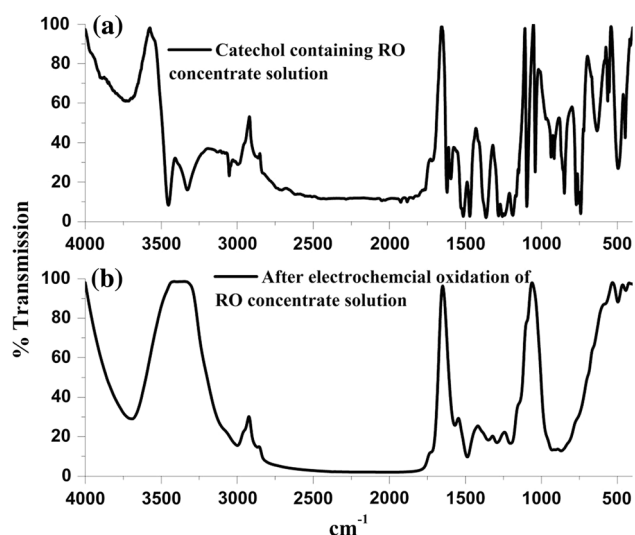


Fig. 9 FTIR spectra of **a** catechol containing synthetic RO concentrate solution, **b** solution after electrochemical oxidation of RO concentrate

catechol containing RO concentrate with broad stretching vibration peak observed at $1400\text{--}1600\text{ cm}^{-1}$, indicating the presence of aromatic $\text{C}=\text{C}$ functional groups, and medium stretching band at 3052 cm^{-1} confirms the presence of $\text{C}\text{--}\text{H}$ functional group of catechol in initial RO concentrate solution; further, the strong stretching band at $1670\text{--}1820\text{ cm}^{-1}$ illustrates the presence of $\text{C}=\text{O}$ functional group.

The solutions after electrochemical oxidations of catechol containing RO concentrate (Fig. 9b) showed that there was a significant reduction in multiple peaks observed in the initial solution at $1400\text{--}1600\text{ cm}^{-1}$. This clearly confirmed the oxidation of catechol compound from RO concentrate solution.

Conclusion

Electrochemical treatment of catechol containing RO concentrate was performed using graphite electrode. The optimized conditions were found to be current density (j), 100 mA/cm^2 ; electrochemical oxidation time (t_{eco}), 60 min; pH, 7.0; and temperature, $25\text{ }^\circ\text{C}$ at an inner electrode space, 2 cm. The average mass transport coefficient for the removal of catechol in terms of COD was found to be $3.0 \times 10^{-5}\text{ m/s}$ at optimum conditions. Fourier transform infrared spectroscopy analysis confirmed the removal of catechol by electrochemical oxidation using graphite as

electrodes. The results suggested that the removal of organic pollutants in electrochemical treatment was favoured by applied current density when the applied current is less than limiting current density and mass transport was controlling step when the applied current density is higher than the limiting current density.

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Abbreviations

RO	Reverse osmosis
COD	Chemical oxygen demand
AOP	Advanced oxidation process
EAOP	Electrochemical oxidation process
BDD	Boron-doped diamond
ETP	Effluent treatment plant
i_L	Limiting current density (mA/cm^2)
F	Faraday constant, $96,487\text{ C/mol}$
k_m	Average mass transport coefficient (m/s)
A	Electrode area (cm^2)
V	Volume of the solution (L)
k_{app}	Apparent oxidation rate constant ($\text{mg/m}^2\text{ s}$)
η_F	Apparent current efficiency
E_{sp}	Energy consumption (kW/g of COD)

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