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Electrochemical Treatment of Evaporated Residue of Reverse Osmosis Concentrate Generated from Leather Industry

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Abstract

Reverse Osmosis (RO) concentrate generated from leather industry is evaporated through solar pans/multiple effect evaporators as a disposal technique. The evaporated residue (ER) majorly consists of chloride and sulphate ions along with partially oxidized/a fresh organic compounds. Earlier studies from us concluded that, chloride and sulphate ions could be successfully separated by selective ion precipitation technique from the saturated solution of ER. In the present investigation organic compounds present in ER solution was attempted to treat by electrochemical oxidation using three different electrode systems: Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite. Amongst the studied electrode systems Cu-graphite/Cu-graphite and Ti-MMO/Cu-graphite electrode systems were found to be effective destruction of organic compounds from ER solution than SS304/Cu-graphite system at current density of 50 mA/cm^2. The calculated specific energy consumption for the selected electrode system was found to be in the order of Cu-graphite/Cu-graphite>Ti-MMO/Cu-graphite>SS304/Cu-graphite at 50 mA/cm^2 for ER treatment. Furthermore the hazardous total trihalomethanes (TTHMs) generated in electrochemical oxidation was removed by adsorption through mesoporous activated carbon packed bed (MACPB) column. The results revealed that the electrochemically oxidized solution could satisfy the discharge limit after passed through MACPB column.

Keywords: Evaporated residue; Reverse Osmosis concentrate; Electrochemical oxidation; graphite electrode; Leather industry, mesoporous activated carbon.

Abbreviations

RO Reverse Osmosis

ER Evaporated residue

MMO Mixed metal oxide

TTHMs Total trihalomethanes

MACPB Mesoporous activated carbon packed bed

DSA Dimensionally stable anode

COD_0, COD_{cr}, initial chemical oxygen demand, Critical chemical oxygen demand, mg/L

TKN Total kjeldhal nitrogen, mg/L

j, j_{lim}, Current density, limiting current density, mA/cm^2

t_{eco}, Electrochemical oxidation time, min

ETP Effluent treatment plant

APHA American public health association

AC, DC Alternating current, Direct current

DPD N,N-diethyl P-phenlendiamine

λ Wavelength

EEM Excitation and emission matrix

MAC Mesoporous activated carbon

W Specific energy consumption, kWh/m^3

V Cell potential, V

I, Current, A

S_v Volume of ER, L

ΔCOD, ΔTKN Difference in COD and TKN in time t, mg/L

Introduction

In recent decades, reverse osmosis (RO) concentrate is being widely generated from water reclamation system used in wastewater treatment plants in leather, chemical, food, pharmaceutical, and other industries.[1-3] The integrated conventional wastewater treatment plant with RO generates concentrate of 5–25% of feed stream volume and its solute concentration was found to be increased by about 20 times than the feed stream concentration.[4] In addition, RO concentrates contain biological materials (i.e., bacteria, viruses, and cell fragments) and organic molecules that also represent a potential environmental hazard on direct disposal in surface water. The direct discharges of such concentrate stream severely affect the aquatic life, water potability and agriculture produce. The sources of organic pollutants in RO concentrate maybe from natural water sources, refractory chemicals used in the product manufacturing processes, and residual chemicals from wastewater treatment processes (e.g., soluble microbial products, partially biodegraded organics, anti-scaling chemicals). Management and treatment of such RO concentrate shall become a key component for reducing the environmental impact of wastewater treatment plant equipped with zero liquid discharge option. There are reports on separation of inorganic salts from RO concentrate stream.[5] Recovery of valuables from RO concentrate would be the alternative treatment option, as it overcomes the environmental issues with RO concentrate disposal, and as the economic profitability of desalination process. Earlier from us concluded that inorganic salts such as sodium chloride and calcium sulphate could be recovered by applying common ion precipitation technique.[6,7] RO concentrate stream after the removal of sodium chloride and calcium sulphate contained anthropogenic organics much higher than discharging limit.[8] The wise environmental practices demand the treatment of organic pollutants present in RO concentrate before it is released and diluted into the environment. In many cases, biological treatment processes are unsuitable and inefficient for RO concentrate because of the presence of high TDS and low organic pollutants.

Several methods, such as coagulation, activated carbon adsorption,[10] ozonation,[8] combined O_3 with activated carbon,[9] and photocatalysis[10,11] as well as electrochemical oxidation[12,13] have been investigated for the treatment of RO concentrate.

In recent years, electrochemical oxidation processes for RO concentrate treatment is being received greater attention due to several perceived advantages such as efficient control of reaction conditions, no chemical requirements, simplicity and robustness of operation at ambient conditions.[15, 12, 14] A number of different anode materials including thin film oxides (e.g. PbO_2, SnO_2), noble metals (e.g. Pt, Pd), and dimensionally stable anodes (DSA) such as Titanium base metal covered by metal oxides (e.g. RhOX, RuO_2, IrO_2) or mixed metal oxide (MMO) such as Ru-IrO_2 and Pt-IrO_2 have been investigated in recent years for the treatment of tannery wastewater, landfill leachate, petroleum processing wastewater and other bio-refractory organic waste streams.[15,16] The advantage of electrochemical oxidation for its in-situ generation of active chlorine species (i.e. Cl_2, HOCl and OCl^-) from chloride ions present in the RO concentrate, which facilitates oxidation of organic compounds in waste stream.[17,18] However, this potential also leads to formation of hazardous chlorinated organic molecules such as total trihalomethanes (TTHMs).[19] Hence it is important to find best electrode system and operating conditions for the treatment of ER solution to avoid the formation of TTHMs.

In the present investigation three different electrode systems (Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite) were selected for electrochemical oxidation of ER solution after recovery of sodium chloride and calcium sulphate from RO concentrate of leather industry.[6,7] The performance of the selected electrode systems was evaluated based on the maximum removal of organic pollutants in terms of COD & TKN and minimum formation of hazardous by-product of TTHMs. Furthermore, the removal of TTHMs was assessed by adsorption technique using mesoporous activated carbon packed bed (MACPB) column.

The selected process parameters for the destruction of organic compounds by electrochemical oxidation were: current density, j (25, 50 and 75 mA/cm^2), and electrochemical oxidation time, t_{eco} (60, 120 and 180 min). In Recent years the optimization of two or more parameters is being performed using multivariate experimental design. Since, it is easier, statistically correct and more functional; such kind of multivariate analysis for parameter optimization will be done and incorporate in our future work.

MATERIALS AND METHODS

Source of Evaporated residue and preparation of saturated solution of ER

The ER was collected from a solar evaporation pan in an Effluent Treatment Plant (ETP) of a commercial tannery in Ranipet, Tamil Nadu, India and stored under packed condition in the laboratory for further studies. The saturated solution of ER was prepared by dissolving 600 g in 1litre of deionised water under stirring.[6] The undissolved sand, grit and floating solids were separated by filtration through whatman 1 filter paper. The filtered saturated ER solution was characterized (Table.1) for pH, total dissolved solids, COD, TKN, ammonical-nitrogen, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} by following the methods of APHA.[20] The detailed preparation and characterization of saturated ER solution were reported elsewhere.[6]

Chemicals

The concentrated hydrochloric acid, sodium hydroxide, calcium hydroxide and calcium sulphate dihydrate used in this investigation were purchased from Merck chemicals (India) Pvt. Ltd.

Experimental setup for separation of chloride, sulphate ions and electrochemical oxidation of ER

A known volume of saturated solution of ER was taken in the reactor vessel for the selective precipitation of sodium chloride. At optimized conditions such as pH, 8.0; temperature, 40°C; and concentration of ER, 60 % (w/v) was maintained to separate NaCl from saturated solution of ER using hydrogen chloride gas at an injection rate of 2.06 g/min. The supernatant solution was transferred to the evaporative crystallization reactor to furthermore crystallize out NaCl. Then, the residual solution of ER was pumped to a neutralization reactor for the precipitation of calcium sulphate using calcium hydroxide. The neutralized ER solution was taken into the electrolysis cell for destruction of organic pollutants. The electrolysis cell is rectangular in shape with water jacketed medium made of glass (length, 15cm; width, 3.5cm and height, 15cm). Graphite electrodes (length, 15cm and diameter, 1cm) were positioned parallel in the electrolysis cell with an equal distance of 1 cm. The electrodes were mounted onto the reactor walls horizontally and extended outside the reactor for the electrical connection as shown in Fig. 1. In order to reduce the ohmic resistance and to ensure good electrical connectivity, the graphite electrodes were coated with metallic copper across its length of 2 cm in either one end and named as Cu-graphite (See supporting document for copper coating procedure). Similarly, two more electrochemical cells with the same dimensions were fabricated using Ti-MMO & SS304 as anode materials while Cu-graphite was chosen as a cathode material. The AC to DC rectifier (0-60 V and 0-5 A) was used to supply predetermined current density and voltage for the batch experiments. The required bulk solution temperature of the electrochemical cell system was maintained by water recirculation in external jacket provided in the electrolysis cell using cryostat (Labnet, India). The required oxygen for the oxidation of organic pollutants was supplied in the form of compressed air using compressor at a pressure 2 kg/cm^2. The compressed air was distributed at the bottom of the electrolysis cell as fine bubble using air spargers.

The electrolyzed ER solution was finally passed into the mesoporous activated carbon packed bed (MACPB) column (diameter, 50 mm and length, 300 mm, bed height, 200 mm, weight of mesoporous activated carbon, 150 g) (see supporting document for preparation and characterization of mesoporous activated carbon) for the removal of chlorinated organic molecule (TTHMs) for high current electrochemical oxidation batch experiments.

Analytical methods

The ER solution was filtered through glass microfiber filter paper of pore size 0.45 µm. Chemical oxygen demand (COD) was determined in accordance with procedure illustrated by Vlysides et. al., (2000), to overcome the interference due to chloride.[21] The concentration of TKN and ammonium-nitrogen were determined as per APHA method.

Total free chlorine generation during the electrochemical oxidation process was analysed through color development with DPD (N, N diethyl-p-phenlenediamine) followed by absorbance measurement in spectrophotometer at λ, 550 nm. The concentration of hydrogen peroxide was determined by following the methodology of APHA (1999).[20] The formation of total trihalomethane (TTHMs) in electrochemical oxidation process was estimated by solvent extraction and detected using Gas chromatographic techniques.

The Excitation-Emission image matrix (EEM) was carried out for detection of organic molecules in the solution by fluorescence spectrophotometer (Cary Eclipse). The system made up of Xenon arc lamp as a radiation source, excitation and emission gratings, and a sample chamber for quartz cuvettes (10×10 mm) and red-sensitive photo-multiplier tube was used as the detector. EEMs were recorded in the excitation wavelength range of (λ_{ex}) 200–400 nm with a step width of 5 nm and in the emission wavelength range of (λ_{em}) 250–600 nm with a step width of 5 nm.

Results and Discussion

Separation of sodium chloride from ER solution

From our previous report, sodium chloride was successfully separated from ER solution by selective ionic precipitation process using hydrogen chloride gas.[6] The ionic chemical precipitation technique removed 27 g of NaCl and by evaporative crystallization process 5.5 g of NaCl from 100 mL of ER solution. The sodium chloride was precipitated first and settled at the bottom of the reactor while purging HCl gas. Furthermore the removal of water molecules from the supernatant of ER solution after NaCl precipitation by evaporation induced the crystallization of NaCl and thus increased the yield of NaCl crystals. The cumulative yield of NaCl from reactive precipitation and evaporative crystallization was found to be 32.5 g per 100 mL of ER solution, i.e. the overall percentage recovery of NaCl from ER solution was 98.7 % (w/v). The recovered NaCl was washed with pure saturated sodium chloride solution to get pure sodium chloride.

Separation of calcium sulphate from ER solution

The residual solution after NaCl recovery still contained sulphate ions along with trace amounts of other inorganic and organic salts. The sulphate ions from the residual solution were separated by reactive precipitation by the addition of neutralizing agent, calcium hydroxide. About 99.5 % (w/w) of sulphate ions was precipitated as calcium sulphate with the addition of $Ca(OH)_2$ 132 g/L, along with rise in solution pH.[7] Then the neutralized ER solution was characterized (Table 1) and electrochemical oxidation was carried out for the removal of organic compounds.

Electrochemical oxidation of neutralized ER solution using Cu-graphite, Ti-MMO and SS304 as anode material

The performance of electrochemical oxidation is decided by the nature of the anode material used and operating conditions.[22,23] In the present investigation Cu-graphite, Ti-MMO and SS304 were selected as anode material (Cu-graphite as cathode material for all the three electrochemical cell) for the evaluation of organic pollutants removal from the neutralized ER solution in batch experiment.

The parameters such as pH, COD and TKN were observed and assessed for the electrolysis of neutralized ER solution and the results are presented in Fig. 2 for the three selected electrode systems. The conditions for the above experiment were operated for different electrochemical oxidation time (t_{eco}) at temperature, 25°C; COD_0, 1780 mg/L and TKN_0, 180 mg/L. The percentage removal of COD and TKN were found to be 89 % and 86 %; 88 % and 82 % and 56 % and 55 % for Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite electrode systems respectively at t_{eco} of 3 hr. Amongst the selected electrode systems, SS304 anode electrode in SS304/Cu-graphite system was rapidly corroded and large amount of iron precipitate was observed. But, Cu-graphite electrode as anode was found to exhibit significantly less amount of electrode mass loss than with SS304 and no loss of mass was noticed on Ti-MMO as anode material. This implies that the high oxygen evolution potential at SS304 anode electrode etched the surface and led to precipitation of iron. The mass percentage loss of anodic electrodes SS304, Cu-graphite and Ti-MMO were recorded as 1.67, 0.007 and 0.00001 % (w/w) respectively for the t_{eco} of 3 hr. The pH of electrolyzed ER solution was decreased from 7.5 to 3.44, 3.9 and 4 for SS304, Cu-graphite and Ti-MMO as anodic electrode systems respectively. This maybe attributed to the liberation of H^+ ions at the cathode during the oxygen generation at the anodic electrode surface by water molecules dissociation. However, Cu-graphite and Ti-MMO anodic electrode systems were found to be dimensionally stable at this acidic pH and also at all the tested experiments. Hence, the Cu-graphite and Ti-MMO electrode systems were considered as ideal anode electrode materials over SS304 for the electrochemical oxidation of neutralized ER solution.[24]

The efficiency of electrochemical oxidation depends on the rate of generation of oxidants, diffusion of oxidants from electrode surface into bulk solution, solution temperature and solution pH.[25] The reduction of oxygen at cathode surface generates hydrogen peroxide at anode electrode surface in electrochemical process in presence of hydrogen ion.[26] The quantified concentration of H_2O_2 generated in the electrolyzed ER solution was found to be 162 mg/L, 154 mg/L and 34 mg/L respectively for the Cu-graphite, Ti-MMO and SS304 anodic systems. The oxidation of organic pollutants in neutralized ER solution maybe explained by generation of hydrogen peroxide under electrolytic acidic conditions. The higher concentration of hydrogen peroxide was observed in Cu-graphite and Ti-MMO anodic systems than SS304 material as anode system. This could be explained as, high active surface area of the graphite material and presence of large functional sites in Ti-MMO material (owing to the porous structure) responsible for the generation of hydrogen peroxide than SS304 electrode material. The elimination of TKN concentration in neutralized ER solution was achieved by generation of hypochlorous acid, that converts nitrogen containing organic pollutants into chloramine and then into molecular nitrogen. Thus, there was a significant reduction in COD and TKN of neutralized ER solution by electrochemical oxidation using Cu-graphite/Cu-graphite and Ti-MMO/Cu-graphite electrode systems than SS304/Cu-graphite system.

Effect of current density on removal of organic pollutants in neutralized ER solution

The influence of operating current densities (j) for the reduction of COD and TKN concentration from neutralized ER solution was studied at 10, 20, 50 and 100 mA/cm^2 as shown in Fig. 3a-f. The reduction of COD and TKN were evaluated and they were reduced from 1780 mg/L to 180 mg/L, 200 mg/L and 780 mg/L & TKN from 180 mg/L to 24 mg/L, 32 mg/L and 80 mg/L respectively for Cu-graphite, Ti-MMO and SS304 as anodic systems at operating current density, 50 mA/cm^2 and t_{eco}, 120 min. The increase in current density beyond 50 mA/cm^2 did not oxidize the organic pollutants significantly with all the electrode systems. The results indicate that the available concentration of oxidants in the electrochemical oxidation system was sufficient enough to oxidize the pollutants in the neutralized ER solution at 50 mA/cm^2. However, too high operating current density was not practiced in the present study for the electrochemical oxidation of organic pollutants present in the neutralized ER solution, to avoid the formation of halogenated organic compounds. Since, there are reports on the prevention of chloro and bromo organic compounds formed by operating at low current density.[27]

The increase in electrochemical oxidation time (t_{eco}) increased the elimination of COD and TKN from neutralized ER solution for three selected electrode systems (Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite), and the evaluated equilibrium electrochemical oxidation time was found to be 120 min for the studied operating current densities. Furthermore, Fig 3 shows that the rate of COD and TKN removal was (17.6 & 1.67, 16 & 1.26 and 15.5 & 0.6 mg COD/min & mg TKN/min for the Cu-graphite, Ti-MMO and SS304 anodic electrolysis system) found to be high in the initial period of 30 min and then the rate of organic pollutant removal was decreased (9.3 & 1.3, 9.1 & 1.1 and 5.1 & 0.2 mg COD/min & mg TKN/min) and reached equilibrium at 120 min. The residual inorganic salt in neutralized ER solution was responsible for the electrical conductance for all the applied current densities; thereby the required t_{eco} was also decreased for the electrochemical oxidation of neutralized ER solution.[28] Moreover, the increase in electrochemical oxidation time stimulated the generation of secondary oxidant such as hypochlorite which was responsible for indirect oxidation of organic compounds in neutralized ER solution. Moreover, the increase in t_{eco} may act as a driving force for the movement of ionic solute in the electrochemical oxidation system by its electrical conductance.[29, 10]

There are reports on the external addition of NaCl to remove color through the generation of hypochlorous acid and to increase the electrical conductivity in electrochemical oxidation of industrial dye effluents.[30, 31] The neutralized ER solution itself contained residual inorganic salt and thus responsible for high electrical conductance and ease of current flow were observed in the electrochemical oxidation of neutralized ER solution. The increase in solution conductance resulted in the reduction of applied cell voltage and thus substantially decreased the electrical energy consumption.[32]

Formation of free chlorine in electrolysis cell

The generation of free chlorine gas during the electrochemical oxidation of neutralized ER solution was estimated for the evaluation of efficiency and their removal of excess concentration. The chlorine gas generated at the anodic surface is converted into hypochlorous acid (HOCl) and hypochlorite ion as indicated in equations (2) and (3). The algebraic sum of dissolved chlorine gas, hypochlorous acid and hypochlorite is termed as free chlorine. Hypochlorite ion is the major component of free chlorine in the normal pH range of waste water (≥7.5).

$$2Cl^{-} \rightarrow Cl_2 + 2e^{-} \tag{1}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (3)$$

Fig. 4a, b, c shows the evolution of free chlorine concentration for the electrochemical oxidation system of Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite electrode systems. The results revealed that the increase in current density increased the free chlorine concentration significantly with all the three selected electrode system. The maximum concentration of free chlorine was found to be 38, 21, 32 mg/L for the anodic systems of SS304, Ti-MMO and Cu-graphite at current density, 100 mA/cm^2 and t$_{eco}$, 120 min. As expected, the increase in operating current density and electrochemical oxidation time increased the concentration of free chlorine in the electrochemical oxidation of ER solution. The free chlorine gas generated was responsible for the indirect oxidation of organic pollutants present in the neutralized ER solution.[33,34] Ammonia oxidation took place due to an indirect oxidation with electro-generated hypochlorous acid, according to a mechanism analogous to the breakpoint chlorination reactions.[35-37]

There are many reports on the probability of formation of halogenated organic compounds (TTHMs) with free chlorine gas. The direct surface discharge of TTHMs are harmful to aquatic organisms.[38,39] To evaluate the formation of halogenated organic compounds as TTHMs, the electrolyzed ER solution was eluted (dialysed) after adsorption onto C18 column using n-hexane. The solvent extracted compound was analyzed through Gas Chromatography. Figure 5a shows the evaluated concentration of total trihalomethanes (TTHMs) with respect to the applied current densities for t$_{eco}$ of 120 min. The results revealed that the increase in current densities increased the formation of TTHMs concentration significantly. Among the selected electrode systems, SS304/Cu-graphite system generated TTHMs by 120 μg/L and the other systems such as Cu-graphite/Cu-graphite and Ti-MMO/Cu-graphite generated considerably lower concentration (32 μg/L and 38 μg/L) of TTHMs than the permissible limit (100 μg/L).

The problem of excess free chlorine and TTHMs discharge can be minimized by adsorbing the electrolyzed products onto activated carbon material. Hence, in this present investigation, TTHMs and excess free chlorine concentrations were reduced by-passing through a column packed with mesoporous activated carbon (MAC). The concentration of free chlorine in the electrolyzed ER solutions and after passed through a MACPB column is illustrated in Fig. 5b. The results revealed that, the concentration of TTHMs concentration after passing through MACPB column was evaluated to be negligible with Cu-graphite and Ti-MMO anodic electrode systems, and for the SS304 anodic system the maximum concentration of TTHMs was found to be 11 μg/L. However, the concentration of liberated TTHMs was within the permissible limit (100 μg/L). Hence, the integrated MACPB column and electrochemical oxidation system can be considered as a viable technique for the removal of organic pollutants without generating hazardous products in the presence of high inorganic salt concentration in ER solution.

Specific energy consumption (W)

The specific energy consumption for the electrochemical oxidation of neutralized ER solution on COD and TKN removal for Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite systems were evaluated using the Eq (4) and (5).

$$W, kWhm^{-3} = \frac{(tVI)/(S_v)/(1\times 10^3)}{\Delta COD/(1\times 10^6)} \tag{4}$$

$$W, kWhm^{-3} = \frac{(tVI)/(S_v)/(1\times 10^3)}{\Delta TKN/(1\times 10^6)} \tag{5}$$

Where ‘t’ is the time of electrochemical oxidation in hours, V is the average cell potential, I is current (A), S_v is the sample volume in litres and; ΔCOD and ΔTKN are the difference in COD and TKN in time “t” in mg/L.

Fig. 6a,b shows the cumulative specific energy consumption for the specific removal of COD and TKN of the operating current densities (j). The increase in operating current density increased the specific energy consumption for the removal of both COD and TKN in neutralized ER solution for three selected electrode systems. The specific energy consumption for the selected electrode systems was in the order to be Cu-graphite/Cu-graphite< Ti-MMO/Cu-graphite< SS304/Cu-graphite.

Kinetic model study

Kinetic study on the removal of COD and TKN from neutralized ER solution was based on the applied limiting current density in electrolysis for Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite systems. The limiting current density could be related to $[COD]_0$ by the mathematical expression

$$j_L = nFk_{m(COD)}[COD]_0 \tag{6}$$

where j_L is the limiting current density (mA/cm^2) at the instant *t*, n is the number of electrons transferred, *F* is the Faraday constant (96487 C/mol), $k_{m(COD)}$ the average mass transport coefficient (m/s) based on COD removal. Then, the rate of COD removal (*r*) can be expressed as [30]

$$r = \frac{j_L}{nF} = k_{m(COD)}[COD] \tag{7}$$

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

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

Where A is the electrode area (m^2) and v is the total volume of the solution (m^3) being processed. Integration and simplification yield

$$\ln(\frac{[COD]_t}{[COD]_0} = -\frac{Ak_{m(COD)}}{v} t \qquad (9)$$

Similarly the removal of TKN in neutralized ER solution is

$$\ln(\frac{[TKN]_t}{[TKN]_0}) = -\frac{Ak_{m(TKN)}}{v} t \qquad (10)$$

The calculated mass transfer coefficient (k_m) for the removal of COD was found to be 6.34×10^{-5} ms^{-1}; 5.86×10^{-5} ms^{-1} and 2.1×10^{-5} ms^{-1} respectively for Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite electrode systems. In the case of TKN removal, the K_m were 5.13×10^{-5} ms^{-1}; 4.4×10^{-5} ms^{-1} and 2.06×10^{-5} ms^{-1} respectively for Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite electrode systems.

The mass transport coefficient obtained from Eq (9 & 10) was used to calculate the critical COD (COD_{cr}):

$$COD_{cr} = \frac{1}{4AFk_m} \qquad (11)$$

COD_{cr} maybe regarded as the COD below which organic pollutants in the neutralized ER solution were oxidized with mass transfer limitation. The calculated COD_{cr} was found to be 104, 112 and 314 mg/L for Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite electrode systems. Thus, the COD_{cr} indicated that the removal of COD from the ER solution was limited by kinetic control.

The limiting current density, j_{lim} predicts the stoichiometric requirement of current density for the electrochemical oxidation of neutralized ER solution and it was calculated by using the following equation

$$j_{\lim} = 4Fk_m COD_0 \tag{12}$$

the calculated j_{lim}, were found to be 43.52, 40.25 and 14.43 mA/cm^2 respectively for Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite electrolysis systems. Hence, the required optimum current density for the treatment of neutralized ER solution was found to be 50 mA/cm^2. It is justified that, slightly higher amount of applied current density was required for effective removal of COD to overcome the system resistance in electrolysis.

Fluorescence spectroscopy analysis on electrochemical oxidation of neutralized ER solution

The composition and structure of fluorophores in wastewater are variable and essentially unknown. Hence, researchers have tended to favour simple techniques for the evaluation of treatment of fluorophores in wastewater. This can be done by comparing visual identification of fluorescence peaks in effluent before and after electrochemical oxidation of treatment process.[40,41]

The excitation emission matrixes (EEM) of the neutralized ER solution, solution after electrochemical oxidation and solution after passed through MACPB column were evaluated to validate the performance on organic pollutant removal. Fig. 7a shows a peak at 275-400/350-550nm due to the presence of humic like organic substances in the neutralized ER solution. The neutralized ER solution after electrochemical oxidation showed a significant reduction in fluorescence intensity (Fig 7b). A green to blue color shift is associated with a decrease in the number of aromatic rings, elimination of fewer conjugated bonds in a chain structure of ER solution. Also, a shift in color indicates the conversion of a linear system to a non-linear systems or/and elimination of particular functional groups including carbonyl, hydroxyl, and amine groups.[42,43] This maybe due to generated chlorine gas oxidized organic pollutants in the ER solution and shifted to shorter emission wavelengths. Moreover, it can be explained by electrochemical oxidation processes succeeded in breaking chromophoretic groups within the structure, and thus reduced the fluorescence intensity.

It is reported that natural organic substances of humic and fulvic acids are the two major precursors for the formation of TTHMs.[44] In order to confirm the elimination of TTHMs, electrolyzed ER solution was passed into the MACPB column and recorded for its fluorescence intensity. Fig. 7c shows complete elimination of fluorescence intensity beyond 400 nm emission wavelength. Thus the proposed integrated electrochemical oxidation with MACPB column was successfully removed organic pollutants and the formed hazardous products was eliminated by MACPB column to meet the standards for surface water discharge of ER solution.

Conclusions

Separation of inorganic salts and treatment of organic compounds from evaporated residue of reverse osmosis concentrate generated from leather industry was carried out for environmental sustainability. In our earlier studies, the separation of chloride and sulphate ions was achieved by selective ion precipitation technique. In the present investigation destruction of organic compounds was achieved by electrochemical oxidation using three different (Cu-graphite/Cu-graphite, Ti-MMO/Cu-graphite and SS304/Cu-graphite) electrode systems. Furthermore, the generation of halogenated organic compounds was successfully eliminated by passing through a packed bed mesoporous activated carbon column reactor. Thus, the present investigation elucidated the integrated electrochemical oxidation and MACPB column could be a viable option for the treatment of organic pollutants and its surface discharge.

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Tables

Table 1: Characteristics of saturated ER solution and neutralized ER solution

Parameters	Saturated ER solution	Neutralized ER solution
pH	8.67	7.52
Total dissolved solids	474.2	371.58
Chemical Oxygen Demand	1.78	1.78
Total kjeldhal nitrogen	0.18	0.18
Ammonical-nitrogen	0.03	0.03
Chloride	215.94	235.95
Sulphate	127.15	0.03
Sodium	125.92	3.27
Calcium	1.44	130
Magnesium	0.51	0.51

* All the values except pH are expressed in g/L