Chapter VII

Advanced oxidation treatment processes for the destruction of organic compounds in the neutralized RAS solution

7.1. Introduction

Electrochemical oxidation is a very efficient alternative for the treatment of wastewater containing non-biodegradable organics and ammonium compounds [106]. Generally electrochemical processes are performed at ambient conditions and without addition of chemicals in contrary to other non-electrochemical processes. Electrochemical treatment processes require compact reactors and simple equipments to control and operate the process. The process is relatively non-specific and applicable to a variety of contaminants but capable of preventing the production of unwanted side-products. Hence, in recent years there has been an increasing interest in the treatment of industrial effluents by electrochemical methods as an alternative to conventional biological treatment systems [107, 108]. However, no report claims the treatment of RAE, generated from Leather industry, by electrochemical oxidation.

Generally, destruction of organic pollutants in the electrochemical process was achieved by direct and indirect oxidations. In direct anodic oxidation, the organic pollutants are adsorbed onto the anodic surface, and destroyed by anodic electron transfer reactions, whereas in indirect oxidation the secondary oxidants such as chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide oxidize the
organic pollutants in wastewater [68]. The generation of secondary oxidants such as chlorine and hypochlorite for the removal of organics and ammonium ions becomes more probable and thus the electrochemical oxidation was preferred over other technologies for the management of RAE in Leather sector.

7.2. Materials and methods

7.2.1. Electro chemical oxidation of neutralized RAS (nRAS) solution

7.2.1.1. Experimental set-up for electro chemical oxidation of nRAS solution

A glass jacketed electrochemical cell (length, 15; width, 3.5 and height, 15cm) with a working volume of 500 mL was fabricated using poly acrylate material and used for the electro chemical oxidation of nRAS solution by batch experiments. Three numbers of graphite electrodes (length, 15cm and diameter, 2.5cm) were positioned parallel to each other with an equidistance of 1 cm between the successive electrodes in the electrochemical cell. The electrodes were mounted onto the reactor walls horizontally and extended outside the reactor for the electrical connection as shown in Fig. 7.1. In order to reduce the electrical contact resistance and to ensure better connectivity, the graphite electrodes across their length were coated with metallic copper for a distance of 2 cm at one end to act as terminals for electrical connection. Similarly, another electrochemical cell with the same dimensions was fabricated with SS304 as anode and graphite as cathode materials. The AC to DC rectifier (0-60 V and 0-5A) was used to supply predetermined current density and voltage for the
experiments. The required bulk solution temperature of the electrochemical cell was maintained through water circulation in external jacket provided to the reactor/electrochemical cell using cryostat (Labnet, India). The oxygen required for the oxidation of organics in nRAS solution was supplied in the form of air using air compressor at pressure 2 kg/cm$^2$. Air was distributed at the bottom of the electrochemical cell through fine bubble spargers.

Aliquots of samples of volume 10 mL were withdrawn from the electrochemical cell at regular time intervals for the characterization of pH, COD and TKN.

Fig. 7.1 Schematic diagram of electrochemical cell used for the treatment of nRAS solution
7.2.1.2. Method of copper coating on graphite electrodes

1) The graphite electrode surfaces were cleaned with mild sodium hydroxide, 0.4 % (w/v) to remove the dust and stains.

2) The electrode surfaces were sensitized (Step1 electrode) by dipping in a bath solution containing stannous chloride (SnCl₂·2H₂O), 10 g/L and concentrated hydrochloric acid (37 %, Sp. gr. 1.18), 40 mL/L.

3) Step 2: processed electrodes were then dipped in a solution mixture, consisting of silver nitrate (A) and formaldehyde (B) at the ratio of 5:1 (A: B). The concentrations of silver nitrate (A) and formaldehyde (B) were 120 g/L and 40 % (v/v) respectively.

4) Step 3: processed electrodes were initially dipped in the bath solution containing copper sulphate (CuSO₄·5H₂O), 75 g/L and concentrated sulphuric acid, 2.5 g/L. Then, the electrodes were placed in the electro chemical cell (Potential, 5 V; Current, 1 A) containing copper sulphate (CuSO₄·5H₂O), 250 g/L and concentrated sulphuric acid, 40g/L.
7.2.1.3. Parameters under investigation by RSM

The COD was determined by following the methodology (specific to high salt containing liquid waste) as described by Vyrides (2009) [66]. In accordance with the procedure, the digestion mixture was prepared by adding K$_2$Cr$_2$O$_7$, 3g (which was previously dried at 103°C for 2 h), to conc H$_2$SO$_4$, 167 mL and HgSO$_4$, 33g and made upto 500 mL with distilled water. The mixture was cooled to room temperature before it was diluted to 1000 mL. The sulphuric acid reagent (2.5 %, w/v) was prepared by dissolving Ag$_2$SO$_4$ in H$_2$SO$_4$. The sampling of wastewater and digestion of the sample were carried out in accordance with the methodology described under the analysis of water and wastewater. Total free chlorine was determined by DPD (N, N Diphenyl p-phenylene diamine) using spectrophotometer at $\lambda_{\text{max}}$515 nm and hydrogen peroxide concentration was estimated according to the standard methods. The electrochemical analyser (Model CHI 660 D, Sinsil India Ltd) was used for the spectral run of linear sweep voltammetry (reference electrode, Ag/AgCl; counter electrode, Pt wire) to determine the working potential of the electrodes.
7.2.1.4. Response surface methodology (RSM) for process optimization by electrochemical oxidation

The central composite design (CCD) is an effective design for sequential experimentation and allows a reasonable amount of information for testing interaction of selected parameters by RSM [109, 110]. In the optimization process, the responses can be simply related to the chosen factors by linear or quadratic models. A quadratic model, which also includes the linear and interaction terms, is shown in Eqn (7.1),

\[
Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{j<i=2}^{n} \sum_{j<i}^{n} \beta_{ij} x_i x_j + e_i \quad (7.1)
\]

where \(Y\) is the response, \(x_i\) and \(x_j\) are the variables (\(i\) and \(j\)=1 to \(k\)), \(\beta_0\) is the constant coefficient, \(\beta_i\), \(\beta_{ii}\) and \(\beta_{ij}\) are interaction coefficients of linear, quadratic (second order) and interaction terms, respectively, \(n\) is the number of independent parameters and \(e_i\) is the error. The physical significance of the second order term is to determine the real function of the selected independent variable and the interaction terms are used to evaluate the interaction between the two selected independent variables. In this study, total dissolved solids (TDS) of nRAS solution [the required TDS was achieved by dilution], current density, \(j\) (mA/cm\(^2\)) and electrochemical oxidation time, \(t_{eco}\) (min) were selected as the operational (independent) variables for the removal of organic compounds from neutralized RAS solution. The electro chemical treatment efficiency of nRAS solution was evaluated based on COD\(_t\)/COD\(_0\) and TKN\(_t\)/TKN\(_0\) (dependent variables) using graphite/graphite electrode system.
7.3. Results and discussion

7.3.1. Advanced oxidation process for treatment of nRAS solution

Advanced oxidation methods such as Heterogeneous Fenton oxidation, ammonium persulphate oxidation and sodium hypochlorite treatment were carried out for the removal of organic compounds in nRAS solution. Fig. 7.2 shows that, the removal of organic compounds was found to be very less. This may be due to the presence of high inorganic salt concentration that retarded the reactive oxidizing agents, which are responsible for the removal of organic compounds in nRAS solution. Hence, all the above mentioned treatment methods were not viable for the removal of organic compounds in nRAS solution. Electro chemical oxidation of organics in nRAS solution may be a viable process. The viability of electrochemical oxidation of organics was tested with model organic compounds such as catechol and pyrogallol. The same procedure was followed to nRAS solution

Fig. 7.2 Selection of advanced oxidation process for the treatment of nRAS solution
7.4. Electro chemical oxidation of catechol containing synthetic neutralized RAS solution (nsyn-RAS-cat)

7.4.1. Effect of current density on electro chemical oxidation of catechol

The influence of current density on the degradation of catechol containing neutralized synthetic RAS (nsyn-RAS-cat) solution was carried out by varying the current density of 100, 200 and 300 mA/cm$^2$. The other conditions such as initial concentration of COD 680 mg/L, 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. Fig. 7.3a shows that the increase in current density increased the organic removal rate significantly. Fig. 7.3b shows the variation in instantaneous current efficiency with time at different current density in the treatment of nsyn-RAS-cat solution.

Fig. 7.3 Electro chemical treatment of nsyn-RAS-cat solution (a) Influence of applied current density (j) on COD removal (b) Instantaneous current efficiency (Conditions: pH, 6.4; initial COD, 680mg/L and temperature, 25°C).
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 electro chemical oxidation may be due to the fact that, total applied current was completely utilized for the degradation of organic compounds present in the nsyn-RAS-cat solution. And thereafter ICE starts to decrease beyond 30 min of electrolysis time ($t_{eco}$). The response suggested that, beyond 30 min of electrolysis time, the mechanism of organic oxidation majorly followed by mass diffusion effect. A similar kind of oxidation response was observed for the removal of organics from textile effluent [111]. Further, the increase in applied current density ($j$) decreased the current efficiency of the process. This could be due to electrode polarization observed with increase in current density and thus reduced the active surface area of the electrode significantly. The current efficiency for the current densities ($j$) 100, 200 & 300 mA/cm$^2$ was found to be 0.67, 0.37, and 0.32 % respectively. The maximum reduction of COD reduction was observed at current density of 300 mA/cm$^2$ and at electro chemical oxidation time ($t_{eco}$) of 120 min.

7.4.2. Effect of pH on electro chemical oxidation of catechol

The effect of initial pH of nsyn-RAS-cat solution on removal of catechol compound during electro chemical treatment was varied from 2.0 to 10.0 under experimental conditions such as $j$, 100 mA/cm$^2$; temperature, 25°C; initial COD, 680 mg/L and $t_{eco}$, 60 min. Fig. 7.4 shows the magnitude of percentage removal of COD increased considerably with increase in pH of nsyn-RAS-cat solution from acidic to alkaline condition. There was a steady removal of COD in the pH range from 2 to 8 and
remains constant up to pH 10.0. The electrochemical oxidation was highly significant at neutral pH range than at acidic pH.

![Residual COD (mg/L) vs pH](image)

**Fig. 7.4** Effect of initial pH on COD removal by electrochemical oxidation of nsyn-RAS-cat solution (Conditions: $t_{\text{eco}}$, 60 min; temperature, $25^\circ\text{C}$ and $j$, 100 mA/cm$^2$).

### 7.4.3. Effect of catechol concentration in nsyn-RAS-cat solution

The catechol concentration of 0.25, 0.5 and 1 g/L in the nsyn-RAS-cat solution were prepared and their 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/cm$^2$, $t_{\text{eco}}$, 60 min; pH, 7.0 and temperature, $25^\circ\text{C}$. Fig. 7.5 shows the COD removal pattern of nsyn-RAS-cat solution by electrochemical oxidation.
Fig 7.5 Effect of initial catechol concentration on COD removal from nsyn-RAS-cat solution (Conditions: $t_{\text{eco}}$, 60 min; temperature, 25$^\circ$C and $j$, 100 mA/cm$^2$)

7.4.4. Effect of temperature on electro chemical oxidation of catechol

The influence of solution temperature on the removal of COD from nsyn-RAS-cat solution was determined by varying the solution temperature from 10$^\circ$ to 70$^\circ$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/cm$^2$; $t_{\text{eco}}$, 60 min; concentration of catechol, 0.25 g/L; pH, 7.0 and COD, 680 mg/L were maintained constant. Fig. 7.6 shows that the COD removal increased with increase in temperature upto 30$^\circ$C and thereafter the increase in temperature decreased the COD removal significantly. This may be due to transport of organic molecules from bulk solution in the electrochemical
cell are enhanced up to 30°C. Further increase in temperature might be reversed the reaction and favoured the generation of undesirable products which could be the reason for increase in COD over the initial concentration with increase in temperature. Hence, the optimum temperature in further experiments was kept at 25°C.

![Graph showing the effect of solution temperature on COD removal from synthetic neutralized RAS solution containing catechol as a model organic compound.](image)

**Fig 7.6** Effect of solution temperature on COD removal from synthetic neutralized RAS solution containing catechol as a model organic compound

(Conditions: $t_{eco}$, 60 min; $j$, 100 mA/cm$^2$ and initial COD, 680 mg/L)

7.4.5. Selection of electrode system for the electro chemical oxidation of nsyn-RAS-cat solution

Anodes and cathodes of various materials of construction were changed to find the COD removal efficiency in electro chemical oxidation of nsyn-RAS-cat solution under batch experiment. The operating conditions were at: $j$, 100 mA/cm$^2$; $t_{eco}$, 60 min; applied potential, 4.5 V; COD, 680 mg/L and temperature, 25°C. Fig. 7.7 shows that
high percentage removal of COD was observed with graphite/graphite electrode system than the other electrode systems.

Fig. 7.7 Selection of materials of construction of electrodes (Anode-Cathode) for electro chemical oxidation of nsyn-RAS-cat solution based on (a) ICE (b) percentage of COD removal nsyn-RAS-cat solution (Conditions: t_{eco}, 60 min; temperature, 25°C; j, 100 mA/cm^2 and applied potential, 4.5 V)

7.4.6. Kinetic studies on electro chemical oxidation of nsyn-RAS-cat solution

Kinetic study on the removal of COD in nsyn-RAS-cat solution was analyzed based on the limiting current density (j_{lim}) during the electrolysis for the graphite/graphite electrode system. The j_{lim} could be related to [COD]_0 by the mathematical expression

\[ j_{lim} = nFk_m[COD]_0 \]  

(7.2)
where \( j_{\text{lim}} \) 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 COD removal rate \( (r) \) can be expressed as [30],

\[
 r = \frac{j_{\text{lim}}}{nF} = k_m[COD] \tag{7.3}
\]

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

\[
 \frac{d[COD]}{dt} = -\frac{A}{v}r \tag{7.4}
\]

Where \( A \) is the electrode area (m\(^2\)) and \( v \) is the total volume of the solution (m\(^3\)) being processed. On integration and simplification, we get,

\[
 \ln\left(\frac{[COD]_t}{[COD]_0}\right) = -\frac{A k_m}{v}t \tag{7.5}
\]

The plot of \( \ln (\text{COD}_t/\text{COD}_0) \) versus time shows the degradation of organic compounds in nsyn-RAS-cat solution followed the pseudo first order rate equation as given in Eqn.(7.5).
Fig. 7.8 Mass transfer coefficient for electrochemical oxidation of nsyn-RAS-cat solution (Conditions: temperature, 25°C; j, and applied potential, 4.5 V)

From the slope of the plot of ln (COD<sub>0</sub>/COD<sub>t</sub>) versus time, the values of mass transfer coefficient were calculated for the electro chemical oxidation of nsyn-RAS-cat solution. Table 7.1 shows that increase in current density increased the mass transfer coefficient significantly. The rate controlling mechanism for electro chemical oxidation was confirmed by evaluating the limiting current density using Eqn (7.2). The value of mass transfer coefficient (k<sub>m</sub>) was calculated from the slope of straight line. The value of k<sub>m</sub> was found to be 3.00x10<sup>-5</sup> m/s at optimum conditions, j, 100 mA/cm<sup>2</sup>; t<sub>eco</sub>, 30 min; temperature, 25°C.
Table 7.1 Evaluation of mass transfer coefficient, $k_m$ and limiting current density, $j_{\text{lim}}$ values at different current densities for the electro chemical oxidation of nsyn-RAS-cat solution (Conditions: COD$_0$, 680 mg/L; temperature, 25°C and pH, 6.4)

<table>
<thead>
<tr>
<th>Current density, $j$ (mA/cm$^2$)</th>
<th>Mass transfer coefficient, $k_m$ (m/s)</th>
<th>Limiting current density, $j_{\text{lim}}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>$3.01 \times 10^{-5}$</td>
<td>246.5</td>
</tr>
<tr>
<td>200</td>
<td>$4.06 \times 10^{-5}$</td>
<td>333.5</td>
</tr>
<tr>
<td>300</td>
<td>$6.19 \times 10^{-5}$</td>
<td>507.6</td>
</tr>
</tbody>
</table>

7.4.7. Instrumental Analyses

7.4.7.1. Fourier transform infrared spectroscopy (FT-IR) analysis

The nsyn-RAS-cat solution before and after electro chemical oxidation were characterised using FT-IR spectroscopy. Fig. 7.9a shows a broad peak at 1400-1600 cm$^{-1}$, indicates the presence of aromatic C=C functional groups and medium stretching band at 3052 cm$^{-1}$ confirms the presence of C-H functional group in the initial synthetic solution further, the strong stretching band at 1670-1820 cm$^{-1}$ illustrates the presence of C=O functional group.

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After electro chemical oxidation of nsyn-RAS-cat solution (Fig. 7.9b) shows absence of broad multiple peaks at 1400-1600 cm\(^{-1}\) were absent. Thus, it confirmed the removal of catechol compound from nsyn-RAS-cat solution.

![FT-IR spectra](image)

Fig 7.9 FT-IR spectra of (a) nsyn-RAS-cat solution (b) after electro chemical oxidation of nsyn-RAS-cat solution.

7.5. Electro chemical oxidation of Pyrogallol containing neutralized synthetic RAS (nsyn-RAS-pyr ) solution

7.5.1. Effect of applied current density on electro chemical oxidation of pyrogallol

The effect of applied current density on electro chemical oxidation of nsyn-RAS-pyr solution was determined at current densities (j) 100, 200 and 300 mA/cm\(^2\). Batch experiments were carried out at experimental conditions, temperature, 25°C;
initial pyrogallol concentration, 0.35 g/L (COD, 680 mg/L) and $t_{\text{eco}}$, 120 min. Aliquot of samples were withdrawn for the analysis of COD. Fig. 7.10a shows the increase in current density ($j$) increased the removal of organic compound significantly. The maximum reduction of COD (80 %) was observed for the applied current density ($j$) at 300 mA/cm$^2$ and electrochemical oxidation time ($t_{\text{eco}}$), of 120 min.

The effect of applied current density on ICE is shown in Fig. 7.10b. The increase in current density decreased the efficiency significantly. The ICE values were found to be 0.47, 0.47, and 0.23 for the applied current densities ($j$) 100, 200 and 300 mA/cm$^2$ respectively. This may be due to the increase in applied current may polarize the surface of electrode used in the electro chemical oxidation. Hence, the performance may decrease with increase in applied current density. A similar kind of response was observed on treatment of textile effluent using mild steel as anode material [111].

Fig 7.10 Effect of applied current density for the electro chemical oxidation of nsyn-RAS-pyr solution (a) on COD removal (b) ICE (Conditions: COD$_0$, 680 mg/L; pH, 6.4(native pH), temperature, 25°C and $t_{\text{eco}}$, 120 min).
7.5.2. Effect of initial solution pH on electro chemical oxidation of pyrogallol

The effect of initial solution pH on electrochemical oxidation of nsyn-RAS-pyr solution was studied by varying the pH from 2.0 to 10.0 in batch experiment at j, 100 mA/cm²; COD₀, 680 mg/L; tₑₒ, 60 min; applied potential, 4.5 V. Fig. 7.11 shows the increase in solution pH decreased the removal of COD upto pH 4.0. Thereafter the increase in pH beyond 4.0 increased the removal of COD significantly. The nsyn-RAS-pyr solution also performed well at neutral and alkaline pH similar to oxidation of nsyn-RAS-cat solution. Similar kind of observation was recorded by Weiqing et al., (2011) in the electro chemical oxidation of isothiazolin containing wastewater [112].

Fig. 7.11 Effect of solution pH on electro chemical oxidation of nsyn-RAS-pyr solution (Conditions: tₑₒ, 60 min; temperature, 25°C; j, 100 mA/cm² and COD₀, 680 mg/L)
7.5.3. Effect of pyrogallol concentration on electro chemical oxidation

The concentration of pyrogallol was varied as 0.35, 0.7 or 1 g/L in nsyn-RAS-pyr solution for the electro chemical oxidation by graphite/graphite system. The corresponding initial COD were found to be 680, 1320, 1440 mg/L for the concentration of Pyrogallol 0.35, 0.7 and 1g/L respectively. The experiment was carried out at the optimum current density (j), 100 mA/cm$^2$ and $t_{\text{eco}}$, 60 min. Fig. 7.12 shows that the degradation of Pyrogallol decreased with increase in Pyrogallol concentration in nsyn-RAS-pyr solution. This may be due to the increase in concentration limits the diffusion coefficient of organic molecules during electro chemical oxidation.

![Graph showing the effect of Pyrogallol concentration on COD removal](image)

**Fig. 7.12** Effect of Pyrogallol concentration in nsyn-RAS-pyr solution on COD removal (Conditions: $t_{\text{eco}}$, 60 min; temperature, 25°C and j, 100 mA/cm$^2$)
7.5.4. Effect of temperature on electro chemical oxidation of pyrogallol

The effect of solution temperature on COD removal was carried out by varying the temperature from 10° to 70°C by electro chemical oxidation using graphite/graphite electrode system. The other operating conditions such as \( j \), 100 mA/cm\(^2\); \( t_{\text{eco}} \), 60 min, applied potential, 4.5 V; \( \text{COD}_0 \), 680 mg/L and pH, 6.7 were maintained constant. Fig. 7.13 shows that the COD removal from the nsyn-RAS-pyr solution was increased with increase in solution temperature upto 30°C and thereafter decreased with increase in solution temperature. Hence, the optimum temperature was observed to be 25°C for the electro chemical oxidation of nsyn-RAS-pyr solution.

![Graph showing effect of solution temperature on electro chemical oxidation of nsyn-RAS-pyr solution](image)

Fig. 7.13 Effect of solution temperature on electro chemical oxidation of nsyn-RAS-pyr solution (operating conditions: \( \text{COD}_0 \), 680 mg/L; \( t_{\text{eco}} \), 60 min and \( j \), 100 mA/cm\(^2\))
7.5.5. Selection of material of construction of electrodes (anode-cathode) for the electro chemical treatment of nsyn-RAS-pyr solution

In the present investigation different construction of electrode materials such as graphite, SS 304 and Ti-MMO were used to evaluate the electrochemical oxidation of nsyn-RAS-pyr solution. A batch experiment was carried out under the conditions j, 100 mA/cm$^2$; t$_{eco}$, 60 min; temperature, 25°C; potential, 4.5 V; COD$_0$, 680 mg/L. Amongst the selected electrode systems (Fig. 7.14) the graphite/graphite was found to be efficient enough to oxidize the organic compounds in nsyn-RAS-pyr solution. The maximum percentage COD removal (76 %) was achieved for the graphite/graphite electrode system.

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**Fig. 7.14** Selection of material of construction of electrode material for the electro chemical oxidation of nsyn-RAS-pyr solution (a) ICE (b) Percentage of COD removal (Conditions: COD$_0$, 680 mg/L; t$_{eco}$, 60 min; temperature, 25°C; j, 100 mA/cm$^2$ and applied potential, 4.5 V)
7.5.6. Kinetic studies on electro chemical oxidation of nsyn-RAS-pyr solution

Kinetic study on the removal of COD from nsyn-RAS-pyr solution was analysed based on the limiting current density \( j_{\text{lim}} \) during the electro chemical oxidation using graphite/graphite electrode system as derived in the section 7.4.6.

The plot of \( \ln \left( \frac{\text{COD}_t}{\text{COD}_0} \right) \) versus time shows the degradation of nsyn-RAS-pyr solution followed pseudo first order rate as expressed in Eqn (7.5).

![Graph showing mass transfer coefficient (k_m) for electrochemical oxidation of nsyn-RAS-pyr solution](image)

**Fig. 7.15** Mass transfer coefficient \( k_m \) for electrochemical oxidation of nsyn-RAS-pyr solution (Conditions: temperature, 25°C and applied potential, 4.5 V)

The slope of the plot of \( \ln(\text{COD}_t/\text{COD}_0) \) versus time was used to calculate mass transfer coefficient \( k_m \) for the electro chemical oxidation of nsyn-RAS-pyr solution. Table 7.2 shows that mass transfer coefficient \( k_m \) decreased with increase in current density \( j \). The rate controlling mechanism for electro chemical oxidation was confirmed by evaluating the limiting current density using Eqn (7.2). The value of mass...
transfer coefficient ($k_m$) was calculated from slope of straight line as illustrated in Fig. 7.15. The value of $k_m$ was found to be $1.23 \times 10^{-5}$ m/s for the optimum current density 100 mA/cm$^2$.

Table 7.2 Evaluation of mass transfer coefficient ($k_m$) and limiting current density ($j_{\text{lim}}$) values at different current densities (Conditions: pH, 6.7; temperature, 25°C and COD$_0$, 680 mg/L).

<table>
<thead>
<tr>
<th>Applied Current density, $j$ (mA/cm$^2$)</th>
<th>Mass transfer coefficient, $k_m$(m/s)</th>
<th>Limiting current density, $j_{\text{lim}}$ (mA/cm$^2$)</th>
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</thead>
<tbody>
<tr>
<td>100</td>
<td>$1.24 \times 10^{-5}$</td>
<td>89.5</td>
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<td>200</td>
<td>$3.01 \times 10^{-5}$</td>
<td>217.5</td>
</tr>
<tr>
<td>300</td>
<td>$4.07 \times 10^{-5}$</td>
<td>294.3</td>
</tr>
</tbody>
</table>

7.5.7. Instrumental analyses

7.5.7.1. Fourier transform-Infrared spectroscopy (FT-IR)

Fig. 7.16a shows the FT-IR spectrum of nsyn-RAS-pyr solution with multiple peaks at region 1400-1600 cm$^{-1}$, indicates the presence of aromatic C=C functional group and medium stretching band at 3052 cm$^{-1}$ correlates with the presence of C-H functional group in the nsyn-RAS-pyr solution. Further, the strong stretching band at 1670-1820 cm$^{-1}$ shows the presence of C=O functional group.
Fig. 7.16b shows FT-IR spectrum of nsyn-RAS-pyr solution after electrochemical oxidation. The disappearance of multiple peaks at 1400-1600 cm\(^{-1}\) indicates the elimination of Pyrogallol compound from the nsyn-RAS-pyr solution after electrochemical oxidation with graphite/graphite electrode system.

Fig. 7.16 FT-IR spectra of (a) nsyn-RAS-pyr solution (b) after electrochemical oxidation of nsyn-RAS-pyr solution

7.6. Electro chemical oxidation of neutralized RAS (nRAS) solution

7.6.1. Selection of anode material for the destruction of organic compounds in neutralized RAS solution

The efficiency of electrochemical oxidation of organic pollutants in wastewater is strongly dependent on the nature of anodic material [41]. Graphite/graphite and
SS 304/graphite systems were employed in the present investigation for the evaluation of dimensionally stable electrodes in electrochemical oxidation of nRAS solution. The experiment was conducted at a constant current density of 50 mA/cm².

The residual pH, COD and TKN of nRAS solution recorded at different electrochemical oxidation time (t_{eco}) for graphite/graphite and SS304/graphite electrode systems at experimental conditions temperature, 25°C; COD₀, 2870 mg/L and TKN₀, 310 mg/L are presented in Fig. 7.17. The COD and TKN were removed by 93 % & 87 % and 76 % & 70 % respectively for graphite/graphite and SS 304/graphite system at t_{eco}, 4 hr. In SS 304/graphite system, pitting corrosion on SS 304 electrode and large amount of iron precipitate was observed, while there was no appreciable amount of material loss was observed during electrochemical oxidation of nRAS solution using graphite as anodic material. The percentage loss in mass of SS 304 and graphite was found to be 1.98 and 0.008 % (w/w) respectively for the electro chemical oxidation time of 4 hr. This may be attributed to the evolution of excess oxygen at the SS 304 electrode surface. The solution pH was decreased from 7.85 to 3.45; this may be due to the generation of H⁺ ions during the dissociation of hypochlorous acid to hypochlorite ion as illustrated in Eqn.(7.8).

However, graphite/graphite electrode system retained their dimensional stability at this acidic pH and also at all the tested conditions. Hence, the graphite electrode was considered as an ideal electrode material over SS 304 for the electrochemical oxidation of nRAS solution.
The efficiency of indirect oxidation depends on the rate of generation of oxidants, diffusion of oxidants into the bulk solution, solution temperature and solution pH. The indirect oxidation of organic compounds in nRAS solution may be due to the generation of hydrogen peroxide under acidic conditions and hypochlorous acid from the chlorides of neutralized RAS solution.

\[ 2Cl^- \rightarrow Cl_2 + 2e^- \]  \hspace{1cm} (7.6)

\[ Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \]  \hspace{1cm} (7.7)

\[ HOCl \rightarrow H^+ + OCl^- \]  \hspace{1cm} (7.8)

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (7.9)

\[ H_2 + O_2 \rightarrow H_2O_2 \]  \hspace{1cm} (7.10)

The hydrogen peroxide was electrochemically produced by reducing oxygen at the cathode surface in the presence of hydrogen ion [113]. The concentration of \( H_2O_2 \) in the analyte was determined and they were found to be 134 mg/L and 34 mg/L respectively with graphite/graphite and SS 304/graphite systems. The higher concentration of hydrogen peroxide observed in graphite/graphite system may be attributed to the presence of high active surface area (owing to the porous structure) than with SS304/graphite system. Further, the generation of hypochlorous acid, as indicated by Eqn. (7.8), was responsible for the elimination of TKN content, probably by converting it into chloramine and then into nitrogen as described in Eqn. (7.11 & 7.12) [114].
\[ \text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{N}_2 + \text{HCl} \]  

(7.11)

\[ \text{NH}_2\text{Cl} + \text{HCl}_2 + \text{HOCl} \rightarrow \text{N}_2\text{O} + 4\text{HCl} \]  

(7.12)

Thus, there was a substantial reduction in COD and TKN of nRAS solution during electrochemical oxidation using graphite/graphite electrode system.

![Graph showing pH, COD, and TKN over time](image)

Fig. 7.17 Electro chemical oxidation of nRAS solution profile (a) pH, (b) COD and (c) TKN using graphite/graphite and SS 304/graphite electrode systems (Conditions: j, 50 mA/cm², COD₀, 2480 mg/L; TKN₀, 310 mg/L and temperature, 25°C).
7.6.2. Experimental design and optimization by response surface methodology (RSM)

The Central Composite Design (CCD) with three parameters at three levels was applied to optimise the process parameters using Design-Expert® 8.0.7.1. In this study, concentration of organic load of nRAS solution by dilution [nRAS solution: deionised water (v/v)], current density, and electro chemical oxidation time were selected as independent variables for the electrochemical treatment of nRAS solution using graphite/graphite system. Each independent variable was coded at three levels between −1 and +1 with an alpha value of 1 by face centered design as shown in Table 7.3. The type of electrode system can also be considered as a dependent variable, however, graphite/graphite system was found to be effective over SS 304/graphite system (from the results and discussion of section 7.6.1). Hence, the optimised conditions were evaluated by response surface methodology (RSM) for graphite/graphite system alone in the present investigation.

**Table 7.3 Selection of range and levels for the electro chemical oxidation of nRAS solution**

<table>
<thead>
<tr>
<th>Independent variables</th>
<th>Notation</th>
<th>Design variables</th>
<th>Range and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dissolved solids</td>
<td>TDS</td>
<td>A</td>
<td>-1  0  1</td>
</tr>
<tr>
<td>Current density (mA/cm²)</td>
<td>j</td>
<td>B</td>
<td>30  45  60</td>
</tr>
<tr>
<td>Electro chemical oxidation time (min)</td>
<td>t_eco</td>
<td>C</td>
<td>25  50  75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60  120 180</td>
</tr>
</tbody>
</table>

Table 7.3 Selection of range and levels for the electro chemical oxidation of nRAS solution
The total number of experiments with three parameters were obtained as 20
\((=2^k+2k + 6)\), where \(k\) is the number of selected factors (=3). Fourteen experiments were
augmented with six replicates at the design center points to evaluate the pure error and
were carried out in randomised order as required in many design procedures.
Performance of the process was evaluated with respect to removal of COD and TKN
from the nRAS solution using graphite/graphite system.

The quality of the fit of polynomial model was expressed by the coefficient of
variance determination, \(R^2\) and \(R^2_{\text{adj}}\). And the statistical significance was checked by the
\(F\)-test in the program during the statistical analysis. For optimization, a module in
Design-Expert software searched for a combination of factor levels that simultaneously
satisfy the requirement placed on each of the responses and factors. The desired goals
were selected based on the maximum reduction in COD and TKN. In Design-Expert
program, goal settings were designated with plus (+) symbols and corresponding
importance of goals were selected (+++++) for the highest in the program for all of the
dependent & independent variables. These individual goals were combined into an
overall desirability function by Design-Expert software for maximization to find the
best operating conditions for the treatment of nRAS solution by electrochemical
oxidation using graphite/graphite electrode system.
### Table 7.4 Analysis of variance for electrochemical oxidation of nRAS solution using graphite/graphite electrode system

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Means square</th>
<th>F-value</th>
<th>P&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD removal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>0.36</td>
<td>9</td>
<td>0.04</td>
<td>4.87</td>
<td>&lt;0.0001(Significant)</td>
</tr>
<tr>
<td>Residual</td>
<td>0.081</td>
<td>10</td>
<td>8.12x10^-3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>0.08</td>
<td>5</td>
<td>0.016</td>
<td>63.53</td>
<td>0.002(significant)</td>
</tr>
<tr>
<td>Pure Error</td>
<td>0.00126</td>
<td>5</td>
<td>0.00025</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TKN removal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>0.26</td>
<td>9</td>
<td>0.029</td>
<td>12.39</td>
<td>&lt;0.0003(Significant)</td>
</tr>
<tr>
<td>Residual</td>
<td>0.024</td>
<td>10</td>
<td>2.39x10^-3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>0.024</td>
<td>5</td>
<td>4.73x10^-3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure Error</td>
<td>0.0001</td>
<td>5</td>
<td>0.0001</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

#### 7.6.3. Optimization of operational parameters

The experimental results were evaluated by Design Expert software using approximating functions of dependent variables for the response to COD and TKN removal. The approximating response function of COD/\text{COD}_0 and TKN/\text{TKN}_0 are employed in Eqn. (7.13 and 7.14). In this study, most effective operating variables were preferred in the range of Total dissolved solids (TDS), 30, 45 and 60 (w/v) [the required TDS of nRAS was achieved by dilution]; current density (j), 25-75 mA/cm² and
electrochemical oxidation time (t\textsubscript{eco}), 0-180 min to effectively handle the neutralized RAS solution.

\[
\text{COD}\textsubscript{t}/\text{COD}\textsubscript{0}, (Y_1) = 0.996 - 0.023 (\text{TDS}) + 0.0105 (j) - 7.98 \times 10^{-3} (t) - 2.89 \times 10^{-4} (\text{TDS})(j)
\]
\[
- 2.62 \times 10^{-5} (\text{TDS}) (t\textsubscript{eco}) + 8.02 \times 10^{-6} (j) (t\textsubscript{eco}) + 4.22 \times 10^{-4} (\text{TDS})^2
\]
\[
+ 2.39 \times 10^{-5} (j)^2 + 3.38 \times 10^{-5} (t\textsubscript{eco})^2
\]

\[
\text{TKN}\textsubscript{t}/\text{TKN}\textsubscript{0}, (Y_2) = 0.987 - 2.46 \times 10^{-3} (\text{TDS}) - 1.65 \times 10^{-3} (j) - 0.011 (t) - 4.39 \times 10^{-5} (\text{TDS})(j)
\]
\[
+ 3.59 \times 10^{-5} (\text{TDS}) (t\textsubscript{eco}) - 2.59 \times 10^{-5} (j)(t\textsubscript{eco}) + 1.55 \times 10^{-5} (\text{TDS})^2
\]
\[
+ 5.76 \times 10^{-5} (j)^2 + 3.77 \times 10^{-5} (t\textsubscript{eco})^2
\]

Fig. 7.18a & b depict the interaction of total dissolved solids of nRAS solution by dilution and electrochemical oxidation time (t\textsubscript{eco}) on organic removal at constant current density (j) of 50 mA/cm\textsuperscript{2}. The increase in t\textsubscript{eco} increased the elimination of COD and TKN from nRAS solution, and they were removed by 93 % and 87 % respectively at t\textsubscript{eco} of 120 minutes and total dissolved solids of 60 % (w/v). The response showed that the initial rate of electrochemical oxidation (decrease in ΔCOD/t\textsubscript{eco}, mg/min) was high and reached the equilibrium condition within 120 minutes. The presence of inorganic salt, NaCl, increased the electrical conductance significantly at constant current density; thereby the required t\textsubscript{eco} was also decreased for the electrochemical oxidation. The increase in t\textsubscript{eco} stimulated the generation of secondary oxidants such as chlorine gas and hypochlorite which are involved in indirect oxidation. Moreover, the increase in t\textsubscript{eco}
enhanced the diffusion of oxidants from the electrode surface to bulk solution to oxidise the organic pollutants.

Fig. 7.18c &d show the response surface plot on the effect of current density (j) and t_{eco} on COD/tCOD and TKN/TKN in nRAS solution at total dissolved solids of 60 % (w/v). Fig. 7.18c &5.7d illustrate that there was a substantial increase in COD and TKN removal efficiency by 93 % and 87 % respectively at current densities upto 50 mA/cm^2 for t_{eco} of 120 min. The increase in current density beyond 50 mA/cm^2 recorded only a marginal increase in removal efficiency (COD and TKN removal at 75 mA/cm^2 were 94 % and 88 % respectively). This may be due to the concentration of oxidants available with graphite/graphite electrode system was sufficient enough to oxidise the pollutants in the nRAS solution at 50 mA/cm^2. However, too high current density was not applied in the present study for the electro chemical oxidation of organics in nRAS solution, to avoid the formation of chloro and bromo organic compounds. Because, the formation of chloro and bromo organic compounds are inhibited, when operating at low current densities [115].
Fig. 7.18 Response surface plot of electrochemical oxidation of nRAS solution using graphite/graphite system at temperature, 25°C (Conditions: j, 50 mA/cm² (a & b); TDS of nRAS 45 % (w/v) (c & d); t_eco, 120 min (e & f)).
Fig. 7.18e & f show the interaction effect of total dissolved solids (TDS) on nRAS solution dilution and current density (j) at $t_{eco}$, 120 min. Fig. 7.18e & f illustrate, the increase TDS in nRAS solution upto 60 % (w/v) increased the removal efficiency of COD and TKN (93 % and 87 % respectively) and thereafter the removal efficiency was decreased with increase in TDS of nRAS solution. The increase in TDS of nRAS solution increased the initial organic content [expressed in terms of high initial COD and TKN value]. Hence, the TDS of nRAS solution was maintained at 45 % (w/v) in the rest of the studies. Addition of NaCl has been under practice to remove color through the generation of hypochlorous acid and to increase the current flow efficiency in electrochemical oxidation of industrial dye effluents [116]. The nRAS solution itself contained high amount of chloride ions and thus high electrical conductance was regarded as an advantage. Hence, no external addition of salt was envisaged in the present investigation. The increase in solution conductivity resulted in the reduction of cell voltage and thus substantial decrease in specific electrical energy consumption was recorded [117].

7.6.4. Formation of free chlorine gas

The electro generation of free chlorine gas during the electrochemical oxidation was estimated for the evaluation of COD & TKN removal. The chlorine gas generated at the anodic surface was converted into hypochlorous acid (HOCl) and hypochlorite ion as indicated in Eqn. (7.7) and (7.8). 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 water ($\geq$7.5).
Fig. 7.19a shows the maximum evolution of free chlorine gas concentration was found to be 7.0, 12.5 and 14.0 mg/L at current densities 25, 50 and 75 mA/cm$^2$ respectively for the $t_{\text{eco}}$, 120 min. As expected, the increase in current density and electro chemical oxidation time ($t_{\text{eco}}$) increased the concentration of free chlorine in the bulk solution. The observed working potential for the selected current density (25 to 75 mA/cm$^2$) was found to vary from 2.5 to 4.2 V. This was found to be lower than the reported values for other non-active electrodes. Generally, smaller the applied working potential and lesser the generation of free chlorine gas for the same current density. The free chlorine gas generated was responsible for the indirect oxidation of organic compounds present in the nRAS solution [118].

**Fig. 7.19** Electro chemical oxidation of nRAS solution by graphite/graphite electrode system (a) formation of free chlorine gas (b) FT-IR spectral analysis for electro chemical oxidized nRAS solution (inner graph for the scale of 900 to 400 cm$^{-1}$)
There are many reports on the probability of formation of chloro and bromo organic compounds with free chlorine gas [119, 120]. This was confirmed from the selective elution of the electro chemical oxidized nRAS (EnRAS) solution (dialysed) after adsorption onto C18 column using n-hexane and ethanol. The solvent extracted compounds (before and after electro chemical oxidation) showed the same $r_f$ values in Thin Layer Chromatography. The solvent eluted compounds were analysed with FT-IR spectroscopy. The spectral analysis revealed that (Fig 5.8b), there was no peak corresponding to C-Cl and C-Br stretchings at around 750-850 cm$^{-1}$ and 650-485 cm$^{-1}$ in EnRAS solution [121]. However, the formation of trace quantities of chloro and bromo organic compounds cannot be ruled out. This can be effectively removed by adsorption using activated carbon.

7.6.5. Generation of by-products in electrochemical treatment of nRAS solution

During the electrochemical oxidation of nRAS solution, the formation of chloro and bromo organic compounds were more probable with generated free chlorine gas [122, 123]. This was confirmed from the selective elution of the EnRAS solution (dialysed) after adsorption onto C18 column using n-hexane and ethanol as eluting solvents. The compounds extracted with solvents (before and after electro chemical oxidation) were analysed through Gas chromatography. The results (Fig. 7.20a) depict that low or nil formation of organic halide was identified at low applied current densities ($j$) (5, 10 and 20 mA/cm$^2$). But, there was a considerable amount of total trihalomethane (TTHM) concentration (Fig. 7.20a) was detected at the applied current
density above 50 mA/cm\(^2\). However, the detected concentration of TTHMs was within the permissible concentration standard for drinking water (100 μg/L). Hence, it is very important to optimize the current density to be applied in order to increase the process efficiency and reduce the formation of TTHMs.

![Graph showing TTHMs concentration profile at different current densities](image)

**Fig. 7.20** Total trihalomethane (TTHMs) concentration profile at different current densities (a) after electro chemical oxidation of nRAS (EnRAS) solution (b) EnRAS solution after passed through packed bed adsorption column

The formed halogenated organic compounds could be effectively removed by adsorption using activated carbon [124]. Hence, CSAC packed bed column was used to remove the halogenated organic compounds from EnRAS solution at current density beyond 50 mA/cm\(^2\). The results suggest that the concentration of THMs was found to be below detectable limit for the EnRAS solution after passed through packed bed adsorption column. Hence, the integrated electrochemical oxidation and CSAC packed bed column would be an effective system for the treatment of nRAS solution.
7.6.6. Specific energy consumption on electro chemical oxidation

The specific energy consumption (W) for the electro chemical oxidation of nRAS solution on COD and TKN removal was evaluated using Eqn. (7.15) and (7.16).

\[
W, kWh/m^3 = \frac{(tPI)/(V)/(1 \times 10^3)}{\Delta COD/(1 \times 10^6)} \quad \text{(7.15)}
\]

\[
W, kWh/m^3 = \frac{(tPI)/(V)/(1 \times 10^3)}{\Delta TKN/(1 \times 10^6)} \quad \text{(7.16)}
\]

Where ‘t_{eco}’ is the electro chemical oxidation period in hours, P is the average cell potential (V), I is current (A), V is the sample volume in litres and; ΔCOD and ΔTKN are the decrease in COD and TKN in mg/L during electrochemical oxidation period “t_{eco}”.

![Variation of Specific energy consumption (W) for the electrochemical oxidation of nRAS solution using graphite/graphite electrode system.](image)

Fig. 7.21 Variation of Specific energy consumption (W) for the electrochemical oxidation of nRAS solution using graphite/graphite electrode system.
Fig. 7.21 shows the cumulative specific energy consumption for the removal of COD and TKN for all the studied current densities. The increase in applied current density increased the specific energy consumption for the removal of both COD and TKN in nRAS solution. The calculated specific energy consumption for the removal of COD at 25, 50 and 75 mA/cm$^2$ was 0.17, 0.41 and 0.71 kWh m$^{-3}$ respectively. The specific energy consumption for the removal of TKN was 1.03, 2.57 and 4.31 kWh m$^{-3}$ at current densities 25, 50 and 75 mA/cm$^2$ respectively.

### 7.6.7. Kinetic model study on electro chemical treatment of nRAS solution

Kinetic study on the removal of COD and TKN from nRAS solution was analysed based on the limiting current density ($j_{lim}$) during the electro chemical oxidation for the graphite/graphite and SS304/graphite system.

\[
\ln\left(\frac{[COD]_t}{[COD]_0}\right) = -\frac{A k_m(COD)}{v} t \tag{7.17}
\]

Similarly for the removal of TKN in neutralized RAS solution is,

\[
\ln\left(\frac{[TKN]_t}{[TKN]_0}\right) = -\frac{A k_m(TKN)}{v} t \tag{7.18}
\]
Fig. 7.22 Linearised form of kinetic models for electrochemical oxidation of nRAS solution based on COD and TKN removal (a & c) by graphite/graphite electrode system (b & d) SS 304/graphite electrode system (Conditions: pH, 8.0, temperature, 25°C; COD$_0$, 2480 mg/L and TKN$_0$, 310 mg/L).
The values of $k_m$ at different current densities were calculated from the plot (Fig. 7.22) and presented in Table 7.5 for graphite/graphite and SS 304/graphite electrode systems. The linear plot of Eqn (7.17) & (7.18) showed that the removal of COD and TKN followed pseudo first order kinetic model. Hence, the mass transport may be regarded as the rate controlling step for the electro chemical oxidation of nRAS solution. The calculated mass transfer coefficient [$k_{m(COD)}$] for COD was found to vary in the range from $0.15 \times 10^{-5}$ to $0.37 \times 10^{-5}$ ms$^{-1}$ for graphite/graphite system and $0.12 \times 10^{-5}$ ms$^{-1}$ to $0.26 \times 10^{-5}$ ms$^{-1}$ for the SS 304/graphite systems. In the case of TKN removal, the $K_{m(TKN)}$ was varied from $0.22 \times 10^{-5}$ ms$^{-1}$ to $0.28 \times 10^{-5}$ ms$^{-1}$ for graphite/graphite system and for $0.12 \times 10^{-5}$ to $0.18 \times 10^{-5}$ ms$^{-1}$ for SS 304/graphite system (Table 7.5). The results illustrate that mass transfer coefficient for graphite/graphite system was higher than SS304/graphite system because COD and TKN removal rate was higher for graphite/graphite system than for SS304/graphite. Further, the removal of ammonia is favoured when indirect oxidation is dominant by rule of competition, whereas the removal of COD takes place under the dominance of direct and indirect oxidations [124]. Ammonia oxidation takes place by indirect oxidation with electro-generated hypochlorous acid, according to a mechanism analogous to the breakpoint chlorination reactions [125-126].
Table 7.5 Evaluation of mass transfer coefficients for electrochemical oxidation of nRAS solution using graphite/graphite and SS 304/graphite electrode systems (Conditions: pH, 8.0; temperature, 25°C; COD$_0$, 2480 mg/L and TKN$_0$, 310 mg/L).

<table>
<thead>
<tr>
<th>j (mA/cm$^2$)</th>
<th>$k_m$ (x10$^{-5}$ ms$^{-1}$)</th>
<th>Graphite/graphite</th>
<th>SS304/graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Based on COD removal</td>
<td>Based on TKN removal</td>
</tr>
<tr>
<td>25</td>
<td>0.156</td>
<td>0.219</td>
<td>0.12</td>
</tr>
<tr>
<td>50</td>
<td>0.251</td>
<td>0.250</td>
<td>0.219</td>
</tr>
<tr>
<td>75</td>
<td>0.376</td>
<td>0.282</td>
<td>0.265</td>
</tr>
</tbody>
</table>

7.6.8. Thermodynamic parameters for electrochemical oxidation of nRAS solution

The thermodynamic parameters such as change in Gibbs-free energy ($\Delta G$), change in enthalpy ($\Delta H$), and change in entropy ($\Delta S$) were calculated for the electrochemical oxidation of RAS solution using graphite/graphite electrode system.

$$\Delta G = -RT \ln K_e$$  \hspace{1cm} (7.19)

$$\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$  \hspace{1cm} (7.20)
Fig. 7.23 Determination of change in enthalpy of electrochemical oxidation of nRAS solution (Conditions: \( j, 50 \text{ mA/cm}^2 \); \( t_{\text{eco}}, 120 \text{ min} \); applied potential, 4.5 V, temperature, 25°C; COD\(_0\), 2480 mg/L and TKN\(_0\), 310 mg/L).

Where, \( K_e = \frac{[\text{COD}]_{\text{opt}}}{[\text{COD}]_0} \), ([COD]\(_{\text{opt}}\) and [COD]\(_0\) are the concentrations of COD at optimum electrochemical oxidation time (120 min) and at initial condition (\( t = 0 \)). The various parameters were estimated using classical Van’t Hoff equation and the values are presented in Table 7.6. The \( \Delta H \) and \( \Delta S \) values were obtained from the slope and intercept of the plot drawn between \( \ln K_e \) and \( 1/T \) as shown in Fig. 7.23.

The results reveal that the increase in temperature from 283 K to 323 K increased the rate constant for organic removal. The increase in applied thermal energy might increase the mass transport coefficient of the oxidants, generated at the electrode surface, to diffuse into bulk solution for oxidation of organic compounds. The negative
change in enthalpy suggested that electrochemical oxidation of nRAS solution by graphite/graphite electrode system was exothermic in nature. The negative $\Delta S$ value illustrates that the decreased randomness of the organic content at the electrode surface; i.e. the generation of secondary oxidants was most responsible for the oxidation of organic content oxidation in the bulk solution. The positive $\Delta G$ value indicates the requirement of additional energy to sustain the electrochemical oxidation process to take place in nRAS solution.

Table 7.6 Thermodynamic parameters for the electrochemical oxidation of nRAS solution (Conditions: $j$, 50 mA/cm$^2$; $t_{\text{ec}}$, 120 min; temperature, 25°C; COD$_0$, 2480 mg/L and TKN$_0$, 310 mg/l)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Equilibrium constant $(K_e)$</th>
<th>$\Delta G$ (J/mol)</th>
<th>$\Delta H$ (KJ/mol)</th>
<th>$\Delta S$ (J/ mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>0.841</td>
<td>407.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>0.877</td>
<td>319.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>0.904</td>
<td>254.24</td>
<td>-5.32</td>
<td>-1.89</td>
</tr>
<tr>
<td>313</td>
<td>0.916</td>
<td>228.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>0.932</td>
<td>189.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.7. Thermal evaporation of electro chemical oxidized EnRAS solution

Electro chemical oxidized nRAS (EnRAS) solution was thermally evaporated to dryness to recover the residual calcium chloride salt and water. Various heating modes of thermal evaporation were carried out to get the residual salt.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Mode of Evaporation</th>
<th>Mass of recovered salt (g/L)</th>
<th>Period of evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solar evaporation</td>
<td>260</td>
<td>5 days under sunlight</td>
</tr>
<tr>
<td>2</td>
<td>Hot air evaporation</td>
<td>260</td>
<td>5 hr</td>
</tr>
<tr>
<td>3</td>
<td>Thermal Evaporator</td>
<td>260</td>
<td>4 hr</td>
</tr>
</tbody>
</table>

7.7.1. Batch study on thermal crystallization of EnRAS solution

A known volume of EnRAS solution was collected in a cylindrical vessel of different diameters to vary the diameter to height (D/H) ratio for the evaporation of EnRAS solution to crystallize the salt from electro chemical oxidized RAS solution. Diameter to height ratio was varied from 0.38 to 2.33 for the equal volume of EnRAS solution and dried in hot air oven operating at 110°C. At different time interval, specific weight of the solution was measured as shown in table. 5.11. The table shows that the increase in D/H ratio decreased the time required for crystallization of EnRAS solution.
This may be explained as the increase in surface area of the solution increased the magnitude of evaporation, thereby the time of evaporation was increased with increase in D/H ratio.

Table 7.8 Batch study on evaporative crystallization of EnRAS solution

<table>
<thead>
<tr>
<th>Period of evaporation time, h</th>
<th>Specific gravity of the EnRAS solution at D/H ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.375</td>
</tr>
<tr>
<td>0</td>
<td>1.248</td>
</tr>
<tr>
<td>0.5</td>
<td>1.265</td>
</tr>
<tr>
<td>1</td>
<td>1.29</td>
</tr>
<tr>
<td>1.5</td>
<td>1.32</td>
</tr>
<tr>
<td>2</td>
<td>1.35</td>
</tr>
<tr>
<td>2.5</td>
<td>1.39</td>
</tr>
<tr>
<td>3</td>
<td>1.42</td>
</tr>
<tr>
<td>3.5</td>
<td>1.45</td>
</tr>
</tbody>
</table>
7.7.2. Design of induced solar dryer for evaporation and recovery of water and salt from EnRAS solution

In order to recover water from EnRAS solution, a reactor was fabricated for the evaporative crystallization as shown in Fig. 7.24. Acrylic sheet was used to fabricate the reactor with dimensions Length, 20 cm; Breath, 20 cm and height, 5 cm. The reactor was provided with two compartments to hold the EnRAS solution on the top compartment and hot air was supplied to the bottom compartment to heat and evaporate the EnRAS solution. The heating compartment was baffled to increase the flow area of the hot air to increase the rate of heat transfer.

The reactor material was selected based on the chemical and thermal stability during evaporative crystallization of electro chemical oxidized RAS solution (Table. 7.9). Amongst the studied materials Teflon sheet (thickness, 3mm) was found to be stable and effective for the evaporative crystallization of EnRAS solution.
Fig. 7.24 Evaporative crystallization reactor for the thermal evaporation to recover water from EnRAS solution (a) Side view (b) Top View (all the values are expressed in mm)
Table 7.9 Selection of material for the fabrication of evaporative crystallization of EnRAS solution

<table>
<thead>
<tr>
<th>Material of construction</th>
<th>Results</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>Material was unstable</td>
<td>• Uniform hot air supply</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Need proper insulation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Angle of roof sheet</td>
</tr>
<tr>
<td>Teflon sheet</td>
<td>1) Material was stable</td>
<td>Effective angle of roof sheet vary from 45° to 30°.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Angle of roof sheet (70°, 60°, 50°, 45°, 30°)</td>
</tr>
<tr>
<td></td>
<td>2) Hot air outlet</td>
<td>The materials of construction became</td>
</tr>
<tr>
<td></td>
<td></td>
<td>unstable when the hot air outlet temperature reached above 40°C.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for heat transfer (30°C, 40°C, 50°C)</td>
</tr>
</tbody>
</table>

7.7.2.1. Effect of roof angle for water recovery from thermal evaporation of EnRAS solution

The roof angle for evaporative crystallization reactor was varied from 30° to 70° for the effective collection of condensate. The results revealed that effective collection
of condensate was observed for the roof angle 30° to 45°. The outlet hot air temperature was maintained at 40°C for the evaporation of water molecules from neutralized RAS solution. The crystallized salt in the compartment was characterized for the structural and composition using SEM-EDX analysis (Fig. 7.25). The result revealed that the recovered salt was chloride salt of calcium and sodium. The harvested crystallized salt at the original solution density of 1.8 yielded sodium chloride salt alone; and thus the critical point to separate out sodium chloride from calcium chloride in the EnRAS solution.

Fig. 7.25 Scanning electron microscopy and Energy dispersive X-ray analysis of the crystallized salt from thermal evaporator

7.8. Conclusions

The treatment of organic compounds in nRAS solution was studied by various advanced oxidation methods. Among the studied advanced oxidation processes electrochemical oxidation was found to be effective for the removal of organic compounds
from synthetic and real nRAS solution using graphite/graphite and SS 304/graphite electrode system. Graphite/graphite electrode system was found to be an ideal electrode system for the electro chemical oxidation of organics in nRAS solution. The thermodynamic study revealed that, electro oxidation of organic compounds in nRAS solution was exothermic and non-spontaneous in nature. Further, the generations of hazardous total trihalomethanes were removed by integrated electro chemical oxidation followed by activated carbon packed bed column. Also, the electro chemical oxidized solution was thermal evaporated to recover the water and salt.