Research Article

Ag(II)-mediated electrochemical oxidation technique for organic radioactive waste treatment and analytical applications

Gitika Saheb Singh[1] · D Banerjee[2] · C Srinivas[1]

Abstract

Present paper reports development of Ag(II)-mediated electrochemical oxidation technique for the management of radioactive organic wastes namely cation, anion & mixed ion exchange resins, tributyl phosphate in n-dodecane and its vacuum distillation residue, generated in nuclear facilities. Best conditions are found out for highly efficient mineralization of these wastes at normal temperatures using this technique. Additionally, the non-selective oxidizing power of Ag(II) is utilized to develop analytical methods for environmentally important parameters, viz., total organic carbon, chemical oxygen demand in waters, sulfur content of products like paper. These results are also presented.

Keywords Mediated electrochemical oxidation · Organic radioactive waste · Purex solvent · Total organic carbon and Chemical oxygen demand

1 Introduction

Oxygen is a non-selective oxidant at high temperatures (800–1000 °C) and this property is used in incineration process to manage different organic solid and liquid wastes with high volume reduction. However, incineration is losing its importance rapidly, in the recent decades, because of the emission of toxic furan, dioxin and other air pollutants in improperly controlled incineration process. Presence of radioactive materials and corrosive gases such as SO_2, NO_x, P_2O_5 in the off gas makes the incineration process more complex for the management of organic radioactive wastes such as ion exchange resins and tributyl phosphate solvent [1]. Eco-friendly alternative options to incineration are in various stages of development. Metal ion mediated electrochemical oxidation (MEO) is one such promising benign option, especially for treatment of organic radioactive wastes. MEO is a low-temperature mineralization reaction in aqueous medium at atmospheric pressure. Ag(II),Co(III) and Ce(IV)-mediated MEO methods have been studied for mineralization of different organic wastes arising from nuclear and defense facilities [2–7]. In the present study, MEO of cation, anion, mixed ion exchange resins, 30% TBP in n-dodecane solvent (hereinafter, TBP solvent) and its vacuum distillation residue (hereinafter, pot residue) using Ag(II) as mediator catalyst was carried out to arrive at the best conditions. Literature information, to the best of authors' knowledge, is not available for the listed organic materials in detail. Our MEO studies led to development of novel analytical methods for environmentally important parameters. These results are also presented.
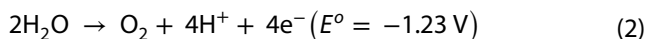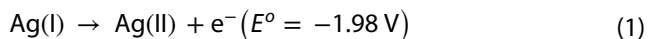
2 Theory

Electrolytic and chemical reactions in the MEO with Ag(II) as mediator catalyst are described below: All the standard electrode potentials shown in this paper are with respect to standard hydrogen electrode.

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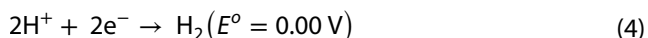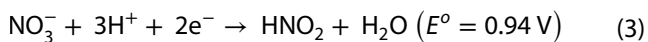
2.1 Electrolytic reactions in MEO [8]
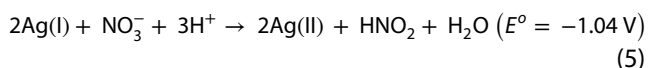
Reactions at anode

$$Ag(I) \rightarrow Ag(II) + e^- \left(E^o = -1.98\,V\right) \tag{1}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \left(E^o = -1.23\,V\right) \tag{2}$$

Reactions at cathode

$$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O \left(E^o = 0.94\,V\right) \tag{3}$$

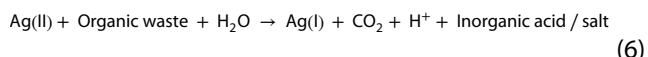$$2H^+ + 2e^- \rightarrow H_2 \left(E^o = 0.00\,V\right) \tag{4}$$

2 and 4 are undesirable side reactions. Pourbaix diagrams of Ag in water and water-chloride media at 25 °C were reported [9]. Under highly acidic conditions and electrode potentials exceeding 2.1 V, predominance of Ag(II) was shown. Anodic oxygen evolution, though thermodynamically favorable, is kinetically slow [10] because of the involvement of four electrons in the reaction. It was reported, in a related MEO study, that hydrogen gas did not form at the cathode when the nitric acid concentration was above 2 M [11]. In the light of these factors, experimental conditions in the present study, discussed below, are favorable for the predominance of Ag(II) and HNO_2 in the electrode reactions.
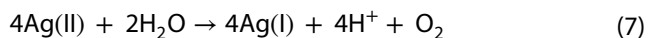
Net cell reaction from 1 and 3 is:

$$2Ag(I) + NO_3^- + 3H^+ \rightarrow 2Ag(II) + HNO_2 + H_2O \left(E^o = -1.04\,V\right) \tag{5}$$

Mineralization reaction in MEO

$$Ag(II) + Organic\ waste + H_2O \rightarrow Ag(I) + CO_2 + H^+ + Inorganic\ acid\,/\,salt \tag{6}$$

Anodically produced Ag(II) oxidizes not only organic waste but also water (reactions 6 and 7) and returns to Ag(I) state.

$$4Ag(II) + 2H_2O \rightarrow 4Ag(I) + 4H^+ + O_2 \tag{7}$$

The redox cycle repeats during electrolysis process. Therefore, Ag salt serves as a catalyst and not as a stoichiometric reagent. It follows from the algebraic sum of equations, 5 and 6, that the reaction which is catalyzed by Ag salt is the following:

$$Organic\ waste + HNO_3 + H_2O \rightarrow HNO_2 + CO_2 + inorganic\ acid\,/\,salt \tag{8}$$
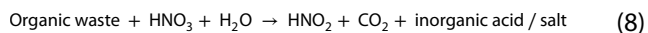
Without the intervention of catalyst, the reaction rate of resins and other organics in this study with nitric acid was insignificant. The mediator catalyst, Ag(II), was generated electrolytically in divided H-shaped electrochemical cell to avoid its wasteful reduction reaction with HNO_2.

Nitrous acid produced at cathode (Eq. 3) decomposes producing NO and NO_2 as shown below:

$$2HNO_2 \rightarrow H_2O + NO_2 + NO \tag{9}$$
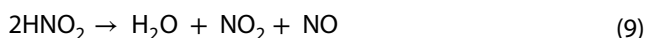
3 Materials and methods

Non-radioactive materials were used in the experimental study. Ion exchange resins made of poly(styrene-divinyl benzene) backbone with strongly acidic sulfonic acid (Indion 223H) and strongly basic quaternary ammonium group in chloride form (Indion GS 300) with 8% cross-linking and effective particle size of 0.45–0.55 mm were obtained from Ion Exchange (India) Private Limited, Mumbai. Chloride form of anion exchange resin (AER) was converted to nitrate form for MEO experiments by repeated contact with $NaNO_3$ solution until the solution was free from chloride. It was air-dried before use. Cation exchange resin (CER) in H^+ form was washed and air dried before use in experiments. Mixed ion exchange resins (MER) were prepared by mixing 30% by weight of CER with 70% of AER to maintain 1:1 capacity equivalency. TBP solvent and its pot residue were taken from Bhabha Atomic Research Centre, Mumbai and used as received. Other chemicals such as nitric acid, silver nitrate, barium hydroxide, sulfanilamide and potassium hydrogen phthalate of analytical grade were procured from Merck (India) Limited and used as received. Distilled water was employed for preparation of different reagent solutions.

3.1 Electrochemical cell

Divided electrochemical cells in the form of H-cell with sintered glass disc separator of moderate size (G4) as shown in Fig. 1 were used for electrolysis experiments. Each arm of the H cell accommodated about 100–300 mL of electrolyte. 0.3 M $AgNO_3$ in 8 M HNO_3 and 8 M HNO_3 of equal volume were used as anolyte and catholyte respectively unless otherwise stated.

Platinum coated on titanium and stainless steel in rectangular plate form were used as anode and cathode, respectively. The dimensions of the electrodes were, mostly, 3 mm thick, 20 mm wide and 180 mm long. In some experiments, similar electrodes with smaller dimensions were also used. These electrodes were procured from Komal Chemiequip Private Limited, Navi Mumbai, India. The cell was energized with DC power supply (0–30 A/0–30 V) procured from M/s Sairush Electronic Systems, Thane, India. Experiments were conducted under constant current conditions. H cell was placed in
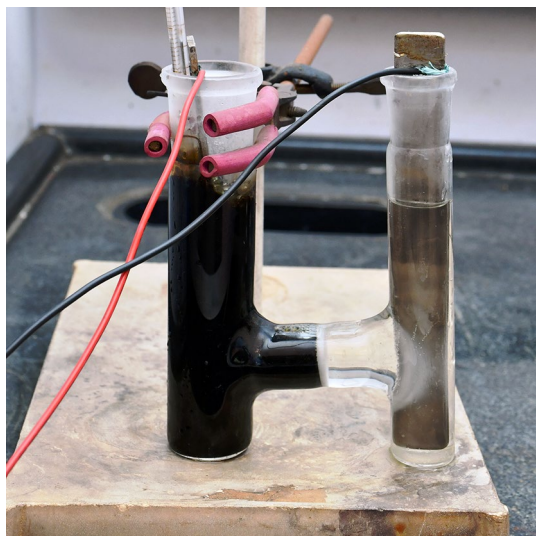
Fig. 1 H Cell for Electrolysis Experiments

temperature-controlled water bath in experiments conducted with temperature control.

3.2 Ag(II) formation study

Electrolytic Ag(II) formation reaction was studied by analyzing anolyte for Ag(II) concentration at regular intervals. The anolyte sample was mixed, without time delay, with known excess of standard ferrous sulfate reagent to form Fe(III) and Ag(I). The unreacted ferrous sulfate was back titrated with standard potassium dichromate solution using ferroin as indicator [3]. The reaction was repeated in the presence of CER.

### 3.3 Mineralization reaction study

The electrolytic reaction was coupled with mineralization reaction in H cell and studied in the following way:

Resin (0.5–1.0 g) was placed in the anolyte solution and contents were constantly mixed by air bubbling during electrolysis. Cell potential was adjusted until the desired constant current was obtained. The cell power was switched off after the completion of theoretical electrolysis time (Table 1). The anolyte becomes black because of the formation of nitrato complex of electro-generated Ag(II) with nitrate ion, $[Ag(NO_3)]^+$ [12]. In this study, this complex was referred to as Ag(II).The black anolyte solution, after sample collection for chemical oxygen demand (COD) analysis, was decolorized at room temperature by dropwise addition of 30% hydrogen peroxide solution to see whether resin particles were present. The redox reaction involved in this decolorization step is shown below:

Table 1 Coulombic charge, electrolysis time and COD for MEO of the moisture-free organic substrates

Organic substrate	Electrolysis time (h/A*)	Coulombic charge (C)	COD (g of O_2/g^{**})
CER/g	6.0	21,227	1.8
AER/g	7.6	27,360	2.3
30%TBP/n-dodecane/g	10.0	36,257	2.9
Pot residue/g	8.6	31,358	2.6

*Hours per ampere; **COD per gram of organic substrate

$$2Ag(II) + H_2O_2 \rightarrow 2Ag(I) + 2H^+ + O_2 \qquad (10)$$
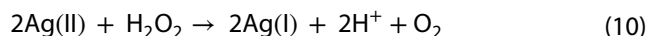
If the residual resin quantity in the anolyte was significant, the electrolytic reaction was continued in the same manner until the resin particles practically disappeared. COD analysis of the anolyte was done to determine the per cent oxidation of the MEO using the following formula:

$$\% \text{ Oxidation} = 100 - \frac{\left\{ \text{COD of anolyte} \left(\frac{mg}{mL} \right) \times \text{volume of anolyte (mL)} \times 100 \right\}}{\left\{ \text{COD of resin} \left(\frac{mg}{g} \right) \times \text{weight of resin in the experiment (g)} \right\}}$$

$$(11)$$

The same procedure was followed for study of the mineralization reactions of TBP solvent and pot residue. In few experiments, residual weight of resin or volume of solvent layer and COD of the anolyte were determined at desired electrolysis times by interrupting the reaction by switching off the power supply of the cell and air bubbler pump. Resin particles were separated from anolyte by decantation followed by washing with water and drying before weighing. Organic solvent layer was separated from anolyte using micropipette for volume measurement.

COD of anolyte, after suitable sample dilution, was determined by closed reflux digestion with acidic dichromate in the presence of silver sulfate catalyst and mercuric sulfate [13] in Thermoreactor (Spectroquant® TR 320) at 150 °C for two hours. The digested sample, after cooling, was analyzed for COD up to 25 ppm using Spectroquant® 600 instrument.

3.4 Current efficiency (CE)

CE was defined in the following way

$$CE = \frac{\text{Experimental coulombic charge for mineralization}}{\text{Theoretical coulombic charge for mineralization}}$$
$$= \frac{\text{Experimental electrolysis time for mineralization}}{\text{Theoretical electrolysis time for mineralization}}$$

$$(12)$$

It follows from the definition of CE that higher the numerical value of CE than one, lower the current efficiency of the MEO reaction as it implies use of more coulombic charge than required for the reaction.

Hypothetical mineralization equation, exemplified by CER and oxygen reduction equation below, were used to calculate the theoretical coulombic charge requirement for CER, AER and TBP solvent. CER with divinyl benzene cross linking of 8% can be represented by the formula shown in the reaction 13 shown below:

CER Mineralization Reaction

$$C_{8.16}H_{8.16}S_{0.92}O_{2.76} + 10.2\,O_2 \rightarrow 8.16\,CO_2 + 3.16\,H_2O + 0.92\,H_2SO_4 \tag{13}$$
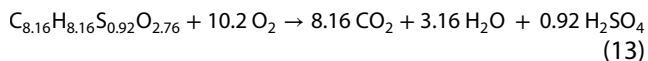
Oxygen Reduction Reaction

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{14}$$

COD of resins and TBP solvent were also determined from the hypothetical equations such as 13. Experimentally determined COD value was used for calculation of charge requirement for pot residue since its molecular formula was not known. Theoretical electrolysis time for different organic substrates was calculated from the following relation:

$$\text{Charge in coulombs} = \text{Current in Amperes} \times \text{Electrolysis Time in seconds} \tag{15}$$

Current efficiency in different electrolysis reactions was calculated in this manner.

4 Results and discussion

Table 1 shows the estimated values of coulombic charge, electrolysis time and COD for the MEO reaction of the organic substrates under study: Electrolysis time in Table 1 provided the benchmark for identifying best reaction conditions for the MEO. COD provided a convenient global parameter to evaluate the degree of oxidation in experiments.

It was observed that Ag(II) anodic generation was instantaneous as shown by the formation of black $[Ag(NO_3)]^+$ in the anolyte. Preliminary experiments with resins showed that important parameters that affect CE of MEO were mixing, temperature of anolyte, nitric acid concentration and ratio of millimoles of $AgNO_3$ to current in amperes (hereinafter, $ratio_{mmol,amp}$). Current density up to 100 mA/cm^2 was used in the present experiments without major impact. Literature information suggested that current density as high as 500 mA/cm^2 can be used in MEO reactions of this type [3].

4.1 Effect of anolyte mixing

Effect of anolyte mixing was evaluated by conducting MEO experiments on CER in 0.3 M $AgNO_3$ in 8 M HNO_3 with and without air bubbling of the anolyte under similar conditions. Air bubbling in the anolyte was adjusted so that the resin particles remained in suspended condition during electrolysis. Results showed that mixing of anolyte during the reaction decreased electrolysis time by three times compared to that in the absence of mixing. Electrochemical processes are heterogeneous at the electrode surface. Existence of Nernst diffusion layer and the substrate concentration gradient near the electrode leads to mass transport problems which can be overcome by mixing [14]. Moreover, organic substrates under study are insoluble in the anolyte. These factors explain the need and results of mixing. Therefore, mixing of anolyte by air bubbling was maintained in the same manner in all the electrolysis experiments.

4.2 COD$_{anolyte}$ and weight loss study

Table 2 shows the COD$_{anolyte}$ and weight loss of CER (one gram) at different electrolysis times at two amperes current and current density of 37 mA/cm^2. COD$_{anolyte}$ was calculated by multiplying anolyte COD value in mg/L with volume of anolyte in the experiment.

Low COD results of anolyte in Table 2 relative to the COD value of 1.8 g/g of CER (Table 1) show that accumulation of organic reaction products in dissolved form at any moment during the reaction is insignificant which can be attributed to the high reaction rates of Ag(II) with dissolved organic substances. Rate constants for aqueous Ag(II) reactions with selected aromatic compounds were reported to be in the range of 10^7 to 10^8 M^{-1} s^{-1} at room temperature indicating diffusion control [15]. The results in Table 2 also show that absence of resin particles in the anolyte is a practical indication of the completion of the MEO reaction. This is a simple way to follow the MEO reaction and used in this study. Similar results were obtained in experiments with AER. In some of the MEO studies

Table 2 Variation of weight loss and COD$_{anolyte}$ of CER with time

Electrolysis time (min)	COD$_{anolyte}$ (mg)	Weight loss (%)
0	0	0
30	180	48
60	66	85
90	27	100
105	< 3	100

reported, reaction product, CO_2 evolution was followed to quantify the reaction [6].

4.3 Ag(II) concentration study

Figure 2 shows the concentration of Ag(II) as a function of electrolysis time in the presence and absence of CER (one gram) at room temperature, current density of 24 mA/cm^2 and one ampere current. Figure 2 shows that Ag(II) concentration in the presence of CER is at least 100 times lower than that in the absence of CER at any instant during the electrolysis. It implies that Ag(II) reacts more rapidly with resin than with water under the experimental conditions. Ag(II) is an unusual oxidation state of silver. The second oxidation state of silver is uncommon as it implies the destruction of the closed shell d^{10} electronic configuration of the Ag(I) cation; the resulting highly electron-deficient Ag(II) cation claims its electron back in its reactions [16]. In the plateau regions of the curves of Fig. 2, electrolytic Ag(II) generation rate, presumably, equals its rate of consumption by reaction with resin and water. Figure 2 results also show the desirability of coupling the MEO reaction with electrolytic reaction.

4.4 Effect of nitric acid concentration

Results of MEO experiments on resins, CER and AER at 30 °C and 52 °C respectively with 0.3 M AgNO$_3$ in nitric acid at current density of 52 mA/cm^2 are shown in Table 3.

The results in Table 3 show that CE in the MEO of resins was much better in 8 M than in 4 M acid. In a kinetic and mechanistic study of the Ag(II) reaction with water [12], it was reported that Ag(II) oxidizes water (reaction 7) at rate which increases with decrease in acid and Ag(I) concentrations. The rate was also found to increase with increase in Ag(II) concentration and temperature. The second order rate constant of this reaction at 25 °C was estimated to
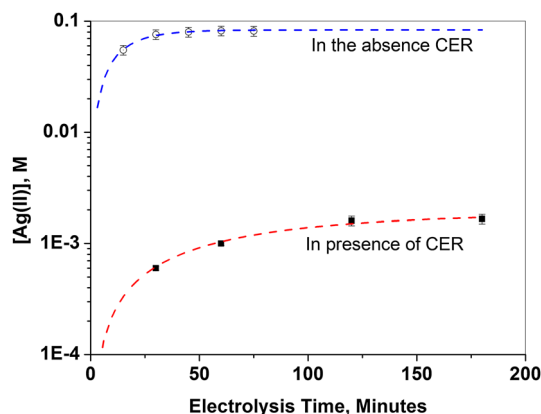
Table 3 Effect of nitric acid concentration on MEO of CER and AER

Resin	CE	Acid [M]
CER	1.1	8
CER	1.8	4
AER	3.2	4
AER	1.2	8

be of the order of 2 M^{-1} s^{-1} in 6 M HNO$_3$. This reaction was proposed to be important for providing active oxygen intermediates such as OH radicals for the initiation/progress of the oxidation of organic compounds with Ag(II) [3]. If Ag(II) reaction with water was useful for the MEO reaction, the trend in Table 2 should have been opposite. But it was not the case.

It is known that perchloric acid is a non-complexing acid in which the metal ions exist as aquo complexes. MEO reaction of CER was performed under similar conditions as above except that nitric acid was replaced by 3 M perchloric acid. Resin decomposition was not observed to occur even after three hours. If Ag(II) reaction with water was conducive to MEO, CER should have decomposed since Ag(II) standard oxidizing potential is higher (~ 2.0 V) in perchloric acid than in 6 M nitric acid(~ 1.8 V) facilitating water oxidation [17]. These observations indicate the need for reconsideration of the role of Ag(II) reaction with water in MEO. Based on results in Table 3, MEO experiments were, therefore, conducted with anolyte acid concentration of 8 M HNO$_3$.

4.5 Effect of temperature

Effect of temperature on the MEO reaction on CER at current density of 91 mA/cm^2 is shown in Table 4.

These results in Table 4 show that CER can be decomposed at normal temperatures (30–40 °C) with high current efficiency. CE at 59 °C was comparatively poor. At higher temperatures, the reaction of Ag(II) with water becomes important given that its activation energy is 23 kcal/mol [12]. Adverse effect of higher temperature on the MEO reaction was also reported [17]. Results of MEO of AER at different temperatures and current density of 7–50 mA/cm^2 are shown in Table 5.

Results in Table 5 show that AER can also, like CER, be decomposed at normal temperatures with Ag(II). In the

Fig. 2 Ag(II) concentration as a function of electrolysis time

Table 4 MEO experiments on CER at different temperatures

Anolyte temperature (°C)	CE
30	1.1*
40	1.15
59	1.4

*Current density = 52 mA/cm^2

Table 5 MEO experiments on AER at different temperatures

Anolyte temperature (°C)	CE
35	1.2
41	1.2
54	1.1
57	1.3
70	2.0

Table 6 MEO experiments on MER at different temperatures

Anolyte temperature (°C)	Current density (mA/cm^2)	CE
35	35	1.3
50	18.6	1.2
55	18.6	1.3
79	18.6	2.8

Table 7 MEO experiments on CER at different AgNO$_3$ concentration

Resin	(AgNO$_3$) (M)	Current (A)	Current density (mA/cm^2)	CE
CER	0.01	1	20	5
CER	0.05	0.4–1.0	6–16	1.1
CER	0.1	1	20	1.1
CER	0.3	2	6–91	1.1
AER	0.05	0.4	6	1.0
MER	0.05	0.4	11	1.4

Fig. 3 Effect of ratio$_{mmol,amp}$ on current efficiency of MEO of CER

temperature range of 35–54 °C, CE was good beyond which it deteriorated, presumably due to the increased reaction rate of Ag(II) with water at higher temperatures.

MEO results at different temperatures for mixed ion exchange resins (MER) at current density of 91 mA/cm^{2}are shown in Table 6. Results in Table 6 show that CE did not vary much in the temperature range of 35–55 °C. However, at temperature of 79 °C, CE was very poor confirming the adverse effect of Ag(II) reaction with water.

All the MEO experiments on different types of resins with Ag(II) showed that MEO could be efficiently conducted by maintaining temperature in the range of 35–50 °C during the cell reaction. Anolyte temperature far exceeding 50 °C should be avoided by providing cooling if necessary.

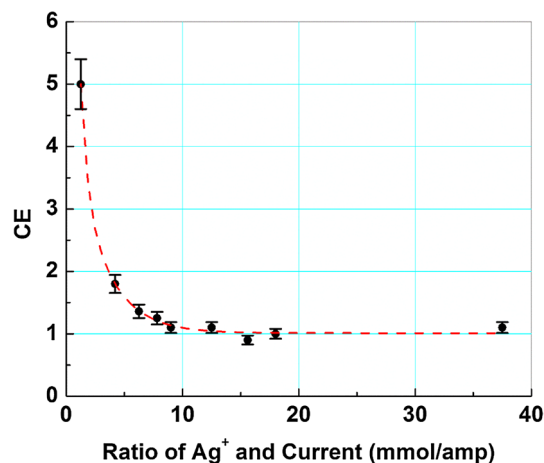## 4.6 Effect of AgNO$_3$ concentration

Ag(I) oxidizes at anode to produce Ag(II) which gains back its electron chemically from organic compound or water present in the anode compartment. Ag(II) should be, obviously, generated at high CE. Equally important is that the physical conditions, especially temperature, mixing and chemical composition of the anolyte such as Ag(I), Ag(II) concentration and acidity should ensure that Ag(II) reacts with organics and not water. Table 7 shows the effect of AgNO$_3$ concentration at 36 °C on the CE of the MEO.

The above results could be interpreted by invoking the ratio$_{mmol,amp}$. This ratio was observed to be one of the important variables in the resin reactions for obtaining high CE in the MEO reaction.

Higher the ratio$_{mmol,amp}$, better was CE. The rate at which Ag(I) converts to Ag(II) depends on the applied current; higher the current, faster the conversion. For example, as

in Table 7, if AgNO$_3$ is 0.01 M in anolyte (100 mL), total mmol of Ag(I) are one. If one ampere current is maintained, in short span of 100 s of electrolysis, entire one mmol of Ag(I) is consumed theoretically. On the other hand, if 0.3 M is used instead of 0.01 M under otherwise similar conditions, 50 min are available since in both cases, the rate of generation of Ag(II) is same, viz., 0.01 mmol/s. Effect of the ratio$_{mmol,amp}$ on MEO of CER at 36 °C is shown in Fig. 3.

Figure 3 shows that ratio$_{mmol,amp}$ ≥ 9 has given CE of nearly 100% and, therefore, a minimum ratio$_{mmol,amp}$ of 9.0 is recommended for high CE in the MEO of CER.

Figure 4 shows the effect of ratio$_{mmol,amp}$ on CE of MEO reaction with AER at 34–55 °C.

Figure 4 shows that the AER reaction was efficient *at ratio$_{mmol,amp}$ of ≥ 15*. Mixed resins also gave similar results as AER. This difference in ratio$_{mmol,amp}$ for CER and AER could be attributed to the difference in reactivities of resins with Ag(II).

In the MEO experiments under best conditions on resins, COD values of anolyte after reaction were in the range of 100–300 ppm indicating near quantitative oxidation.
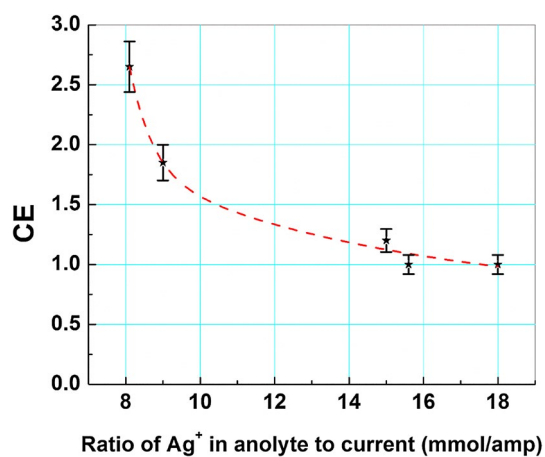
Fig. 4 Effect of $ratio_{mmol,amp}$ on current efficiency of MEO of AER

4.7 MEO experiments on TBP solvent

MEO experiments on TBP solvent at 30–50 °C and $ratio_{mmol,amp}$ of 18 were conducted based on the results obtained in resin experiments. Results are presented in Table 8.

Results in Table 8 show that TBP solvent, like resins, could be quantitatively decomposed with ~ 100% current efficiency over a wide range of current densities at normal temperatures. $Ratio_{mmol,amp} \geq 9$ was effective in the experiments. MEO reaction studies reported on radioactive TBP solvent [4] indicated that presence of uranium and temperatures up to 60 °C accelerated the reaction. In a mechanistic study of the MEO of dodecane [6] involving identification of numerous reaction intermediates using HPLC, nitrate radical was proposed as key initiator of the oxidation reaction.

Concentrated nitric acid participation in MEO reaction of TBP solvent as a supplementary oxidant of organic intermediates in the reaction could be one of the reasons for CE being < 1.0. In a study comparing the performance of Ag(II), Co(III) and Ce (IV) in the MEO of CER, role of nitric acid as a supplementary oxidant was proposed [17]. Nitric

acid-catalyzed hydrolysis of TBP portion in the solvent cannot be ruled out in this system. This results in formation of more hydrophilic reaction products such as di- and mono butyl phosphoric acids and butanol. This could be an added advantage for using higher concentration of nitric acid. Besides, cell resistance also decreases with increasing nitric acid concentration.

Spent TBP solvent contaminated with radioactive materials is normally subjected to vacuum distillation for purification and recycles in nuclear reprocessing plants. In this process, pot residue concentrated in radioactivity results and this should be managed safely. MEO of pot residue was also conducted. The results are presented in Table 9.

These results in Table 9 show that the pot residue can be quantitatively oxidized by MEO with Ag(II) at normal temperatures safely at $ratio_{mmol,amp}$ of ≥ 8

4.8 Recycle of anolyte, silver nitrate and nitric acid

It was established in our experimental studies on resins and solvents that the anolyte could be recycled repeatedly for at least 10 cycles efficiently. Accumulation of resin and TBP solvent mineralization acid products, viz., sulfuric acid from CER and phosphoric acid respectively did not affect the performance of MEO during recycle of anolyte. Higher concentration of nitric acid in the anolyte compared to that of sulfuric and phosphoric acids, presumably, favors the continued predominance of nitrato complex of Ag(II). Catholyte nitric acid concentration decreases due to its reduction to nitrous acid as shown in Eq. 3. Therefore, it should be replenished regularly or desirably, in situ nitrous acid oxidation to nitric acid step should be incorporated in the scheme for recycle [5]. Similarly, silver nitrate can and should be recovered and recycled [18]. These steps will enhance the process viability.

Electrolyte, after MEO reaction of radioactive resins and solvents, will be contaminated with radioactive elements. Resin waste from nuclear reactors, predominantly contains cesium, strontium and cobalt radioisotopes. TBP solvent waste from nuclear reprocessing plant contains alpha and beta activity. These radioisotopes should be separated by selective ion exchange or suitable methods so that the

Table 8 MEO experiments on TBP solvent

Current density (mA/cm^2)	CE	COD of anolyte (ppm)
53.0	1.0	< 25
41.7	0.9	< 25
18.6	1.0	104
18.6	1.0	239
91.0	< 1.0	71*

*$Ratio_{mmol,amp} = 9.0$; temperature: 30–60 °C

Table 9 MEO experiments on pot residue with Ag(II)

$Ratio_{mmol,amp}$	Current density (mA/cm^2)	CE	COD (ppm)	Anolyte temperature (°C)
8.6	90.0	1.0	116	40–45
37.5	20.4	0.8	653	35–36
43	17.0	0.7	1345	35–37

resultant low level radioactive aqueous waste can be disposed by standard methods.

5 Novel analytical applications of MEO

It became apparent in our detailed MEO studies that Ag(II) mineralizes variety of organics readily at room temperature. This formed the basis for the development of novel analytical methods for determination of environmentally important total organic carbon (TOC), chemical oxygen demand (COD) of waters and sulfur content of products such as paper. It is interesting to note that all these determinations are routinely done using different mineralization methods such as high temperature combustion methods (TOC), closed or open reflux digestion with potassium dichromate-concentrated sulfuric acid at 150 °C for two hours (COD) or Schrödinger flask combustion method (chlorine, sulfur etc.). It is also interesting to note that Ag(II) is used as catalyst in the traditional COD method to oxidize refractory organics such as alkanes in the water sample.

5.1 TOC analysis

In the proposed method, Ag(II) was generated as described in the previous MEO experiments. Its mineralization reaction with organic compound in the aqueous test sample was conducted for 3–5 min at room temperature in the set up shown in Fig. 5 using nitrogen as carrier gas. CO_2 was absorbed in standard barium hydroxide scrubber solution. TOC was estimated by determining the decrease in $Ba(OH)_2$ concentration by titrimetric procedure.

5.2 COD analysis

In the proposed method, COD was analyzed by addition of known excess of Ag(II) to aliquot of sample and its back titration with standard ferrous sulfate solution using ferroin as indicator. Alternatively, known volume of standard Ag(II) solution was titrated with test sample solution until colorless. COD was calculated from the Ag(II) consumption for given volume of sample.

5.3 Sulfur content determination

The method is based on the mineralization of the substrate using MEO followed by sulfate estimation. The method was validated by conducting MEO of sulfanilamide standard using anodically generated Ag(II) in H cell as described in the preceding experiments. Subsequently, paper samples were subjected to MEO in a similar manner. MEO leads to mineralization of these organic compounds. Sulfur present in the organic compound is mineralized to sulfuric acid during MEO reaction. Sulfate was estimated as barium sulfate by standard turbidimetric method. All the analytical methods were at least triplicated. Results of TOC, COD and sulfur estimation for different samples are shown in Table 10.

Results in Table 10 show the promise of the novel proposed analytical methods and that there is agreement between experimental and theoretical values by at least 90% in all analyses of standards. The proposed methods are less expensive and could, possibly, be within the reach of many academic laboratories with limited resources. Ag(II) can be electrolytically generated repeatedly on demand from the same anolyte. Detailed investigations on this method are in progress. It is of interest to investigate the possibility of using Ag(III) for these analytical applications in view of its much higher reactivity compared to Ag(II). Use of electrolytically generated $[Ag(OH)_4]^-$ for oxidation of recalcitrant organic dyes such as rhodamine in alkaline media was reported [19, 20].

6 Conclusions

Based on the results of present study, it can be concluded that MEO with Ag(II) is a very efficient method for mineralization of ion exchange resins, TBP solvent and its vacuum distillation residue at 30–50 °C. Best reaction conditions for efficient oxidation of these refractory organic wastes generated in nuclear industries have been identified which included ratio of the moles of Ag(I) to cell current, temperature, mixing and nitric acid concentration to achieve current efficiency > 80%. It is conclusively proved that no
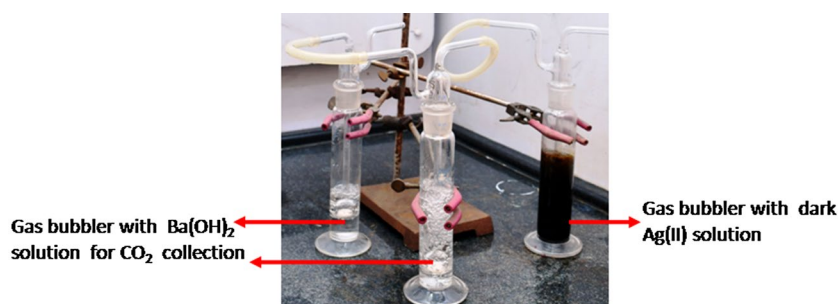
Fig. 5 TOC test set up

Gas bubbler with Ba(OH)$_2$ solution for CO$_2$ collection

Gas bubbler with dark Ag(II) solution

Table 10 Analytical results of different parameters using MEO

Sample	Analytical parameter	Expected value	Experimental mean value	% Error ($\approx$)	Sample size
Phenol	TOC (ppm)	3825	3567	7	0.2–0.3 mL
Potassium hydrogen phthalate (PHT)	TOC (ppm)	2350	2585	10	1.0 mL
Phenol	COD (ppm)	11,898	10,800	9	0.2–0.4 mL
PHT	COD (ppm)	480	450	6	2.0 mL
Sulfanilamide	Suflur (%)	18.6	17.5	6	0.2 g
Paper samples	Total Sulfur (%)	NA	0.06–0.1	NA	2.0 g

NA: not available

heating of anolyte is required for mineralization. However, it should be ensured that temperature due to ohmic heating and other factors does not raise much beyond 50 °C to maintain high current efficiency. It is also established that Ag(II) mediated oxidation can be used as a novel analytical method for estimation of environmentally important parameters such as TOC, COD and sulfur content. This method is simple, rapid, accurate and less expensive.

Author contributions GSS Senior Research Fellow in the research project, contributed to the planning and execution of experiments; DB guided and supervised the experimental work of Ms. Gitika Saheb Singh at Bhabha Atomic Research Centre, Mumbai. He also contributed to the ideas that emerged about the impact of mediated electrochemical oxidation electrolyte composition on the subsequent radioactive secondary waste treatment; CS contributed to the conception, planning, design and execution of experiments as well as interpretation of results and manuscript preparation.

Data availability It is available and transparent.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethics approval Not Applicable.

Consent for publication The authors agree for the publication of the work.

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