

Mediated Electrochemical Degradation of Polystyrene by Silver (II): Optimization and Kinetic Studies

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Abstract: The electro-generation kinetic of Ag (II) in nitric acid media was initially investigated experimentally, assessed with a theoretical model which showed a good agreement. The reaction was found to be kinetic-controlled on the DSA-O₂ anode surface. The Arrhenius model was employed and activation energy was estimated to be 44±2 kJ.mol⁻¹. Optimization studies at constant potential showed Ag (I) and HNO₃ concentrations promote the generation rate of Ag (II) while temperature and anolyte flow rate have inverse effects. The optimum conditions were found to be: Anolyte: T = 29 °C, Flow rate: 100 ml/min, 0.5M initial Ag (I) in 6M nitric acid as supporting electrolyte, Catholyte: 8M nitric acid.

The degradation kinetic of polystyrene (PS) by silver (II) process was then demonstrated and found to be fast and first order respect to Ag(II). Model validation was carried out successfully. FTIR results confirmed the degradation of PS.

Keywords: Mediated electrochemical degradation, silver (II), oxidation kinetics, polystyrene degradation.

Nomenclature	
V	Anolyte volume (liter)
S	Area of the anode (cm ²)
D	Diffusion coefficient of Ag (I) in concentrated aqueous solution (cm ² .sec ⁻¹)
	Diffusion layer thickness (μ)
[Ag (I)] ₍₀₎	Initial concentration of the Ag (I) ions at t =0 (mol.liter ⁻¹)
[Ag (I)] _s	Concentration of the Ag (I) ions on anode surface (mol.liter ⁻¹)
[Ag (I)] _(t)	Bulk Concentration of the Ag (I) ions at t time (mol.liter ⁻¹)
E ^p	Potential applied at the anode (V)
k	Rate constant for Ag(I) oxidation (S ⁻¹)
k _a	Apparent rate constant (mol ⁻¹ .lit.S ⁻¹)
p	The cell parameter (s ⁻¹)
T	Temperature (K)
R	Gas constant (J. mol ⁻¹ .K ⁻¹)
E _a	Activation energy (kJ.mol ⁻¹)
K ₁	Rate constant for Ag (II) reduction or PS degradation (S ⁻¹)
m	Reaction order of Ag (II) reduction

1. Introduction

The huge amount of plastic waste that resulted from mega polymer production units give rise to serious environmental concerns, as plastic does not degrade and remains in the municipal for decades. Incineration of waste polymers and thermal pyrolysis of polymers to liquid fuels (PTL) take place at high temperature above 600 °C. Catalytic cracking of polymers also calls for a relatively high temperature between 400 to 500°C and a catalyst.¹ Toxic or carcinogenic emissions including dioxins, furans, polyaromatic hydrocarbons are generally formed during these processes which are threats to the environment. Furthermore, high cost, catalyst deactivation and serious challenges involved in its regeneration are the main drawbacks for catalytic cracking of polymers.²

On the other hand, mediated electrochemical oxidation (MEO) as a clean technique has been introduced successfully for destruction of organic wastes. In this process, the hazardous, radioactive or mixed organic waste streams can be destructed electrochemically at low temperature (<100 °C) due to the high redox potential of the Ag (II)/Ag (I) couple, low cell voltage and pressure. Commonly employed mediator redox pairs in MEO processes are Ag (II)/Ag (I), Ce(IV)/Ce(III), Co(III)/Co(II) and Mn(III)/Mn(II). Silver (II) due to its high redox potential is the most powerful oxidizing agent in acidic media among these systems. Silver (II) ions may immediately react with the organics to destroy them or may first react with water to produce hydroxyl radicals resulting in oxidizing the organic compounds. The mechanism is yet to be fully understood.³⁻¹⁴

Unfortunately, the number of studies on degradation of polymer materials by MEO is scarce and mainly focused on the degradation chemistry. Polyolefins such as PP and PE are oxidized by aqueous solutions of metal ions as mediators mostly for pretreatment to improve their cohesive properties.^{9, 15-19}

According to Wiberg¹⁸, the degradation of a number of hydrocarbons based on polymers initially occurs by their hydrolysis which in turn leads to further oxidization.

Paire et al.¹⁹ showed in the absence of polarized anode silver (II) nitrate solution is not capable of oxidizing the aliphatic hydrocarbons. Studies on low molecular weight material depicted that simple aliphatic compounds compared to the parent structures react much more easily with silver (II) nitrate solution.¹⁵ They further clarified that as soon as the polymer becomes functionalized, further oxidation occurs rapidly by additional reaction of these groups leading to complete mineralization of the organic species.

Brewis and Dahm¹⁵ supposed that Ag (II) ions directly attack the carbon hydrogen bonds of polymer chain in the case of PP and HDPE. This causes organo-silver and carbon ions to be formed respectively. The carbonium ions hydrate quickly resulting in yielding alcohol as a result of oxidation.

Brewis et al.¹⁶ studied the behavior of some polymers such as PS during the MEO process in another project. Regarding PS, they concluded that polymer backbone oxidation with partial elimination of the pendant groups such as phenyl takes place. This elimination happens during either the oxidation or the secondary ion formation process. But the former is less probable.

Chain scission causes alkyl aryl ketone to be produced at the phenyl substituted position. However, an attack on the phenyl ring itself has been confirmed.

Earlier studies on kinetic of polyolefin destruction by the electrochemical mediators using precious metal anodes have shown a slow rate which hinder bulk plastic destruction.^{15-17, 20-21} The main aim of this study is to shed more lights on this issue by investigating the kinetic of PS degradation, as a case study, using silver-MEO technique. For this purpose, Ag (II) ions were initially generated in a recirculating batch-type electrochemical reactor. The effects of various operating parameters including temperature, mediator and supporting electrolyte concentrations were studied potentiostatically to optimize the process. Since kinetic and mass transfer characteristics of an electrochemical system are strongly depend on the type of electrode material and cell design used, initial studies were necessary to evaluate these characteristics for the Ag (I) oxidation for the flow cell type reactor employed in this study. Although some researchers such as Lehmani and co-workers²²⁻²⁸ have already studied the kinetics of the Ag (I) oxidation in nitric acid their research were restricted to a three electrode system using platinum as working electrode followed by organics destruction rather than polymeric material degradation.

1.1 Silver (II) Process Chemistry

Silver (II) ions which are produced electrochemically in a nitric acid media possess an extremely oxidizing nature and a result can play a major role in the oxidizing. Ag (II) ions are produced from electrolyzed silver nitrate solution in nitric acid media. The standard electrode potentials (E°) of the half-cell reaction under standard conditions at 25°C have been shown in Eq. (1, 2):



Thus, the overall reaction of the silver nitrate solution electrolysis would be:



The Nernst equation can be applied for Ag (II)/Ag (I) system at other

$$\text{concentrations: } E = E_0 + \frac{RT}{Fn} \ln(Q) \quad (4)$$

Which, R is the universal gas constant, T is the absolute temperature in Kelvin, F is the Faraday constant (coulombs mole⁻¹), n is the number of electrons transferred in the half reaction and Q represents the standard phrase as follows:

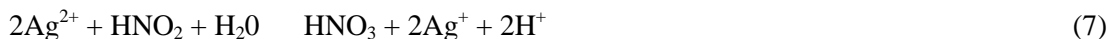
$$Q = \frac{[\text{Ag}^{2+}]^2 [\text{HNO}_2]}{[\text{Ag}^+]^2 [\text{NO}_3^-] [\text{H}^+]^3} \quad (5)$$

The reduction of Ag (II) by water is demonstrated in the following equation:



In order to prevent the undesirable reactions, both high concentrations of nitric acid and silver nitrate solution are needed.

According to Eq. (7) the reduction of Ag (II) ions in the anodic section is due to the migration of nitrous acid (HNO₂) produced at the catholyte to the anolyte and its reaction there.



This reaction reduces the chemical efficiency for silver (II) electrogeneration. Thus, a separator between the two compartments of cell is essential so as to "stop" the undesired species.

The Ag (II) ions generation mainly depends on the applied current to the cell, and as soon as the power is turned off this generation stops quickly. However, Ag (II) and concentrated nitric acid are corrosive agents; they react with some material such as steel or silicon. Therefore all parts of MEO system has to be glass-lined or Teflon-lined.

After electro-oxidation, the present Ag (II) ions appear to be a dark-brown solution (AgNO₃⁺).^{5,24}

According to Eq. (8), the silver electro-deposition can happen as the most common side reaction in the cathode compartment, created owing to silver ions migration from anolyte to catholyte through the membrane.



This reaction arises at low concentrations of nitric acid while it is suppressed by the higher concentration of this acid 6 M or above.⁸⁻¹¹

2. Materials and Methods

2.1 Chemicals

All the chemicals were purchased from Merck. Deionized water was employed for all washing applications or preparations. In this study Nafion[®] 115 membrane as a separator was obtained from E.I. du Pont de Company. A 2mm-thick titanium plate was used as the cathode and the dimensionally stable anode (DSA) was applied as the anode which was a titanium plate with thickness of 2 mm coated with a mixed oxide of IrO₂/Ta₂O₅ (70/30 mol%) of 10–12 μm thickness.

2.2 Apparatus

Fig. 1 shows the electro-oxidation of silver (I) in a membrane-divided electrochemical reactor assembled in our own laboratory. The membrane flow cell depicted in Fig. 2 is the most crucial part of this set-up. This cell contains a Ti cathode (1) and IrO₂/Ti DSA anode (3.3 × 3 cm² surface areas) (2). A Nafion[®] 115 membrane (3) divides the anode compartments from the cathode. 2-mm thick teflon spacers separate the electrodes from the membrane (4). The cell gaskets (5) are with openings cut out for the anode and cathode inlets and outlets. Teflon frames (6) lie at the end of the cell. Finally, the electrodes are directly connected to DC current.

A 350-ml solution of Ag (I) in nitric acid (0.5 M in 6 M) and a 350-ml nitric acid (8 M) were placed in the anolyte and catholyte reservoirs, respectively. The electrolyte solution was continuously circulated through the anolyte and catholyte compartments at a fixed flow rate. A constant potential 1.9 V was applied to the cell during the oxidation reaction in both the anolyte and catholyte vessels.

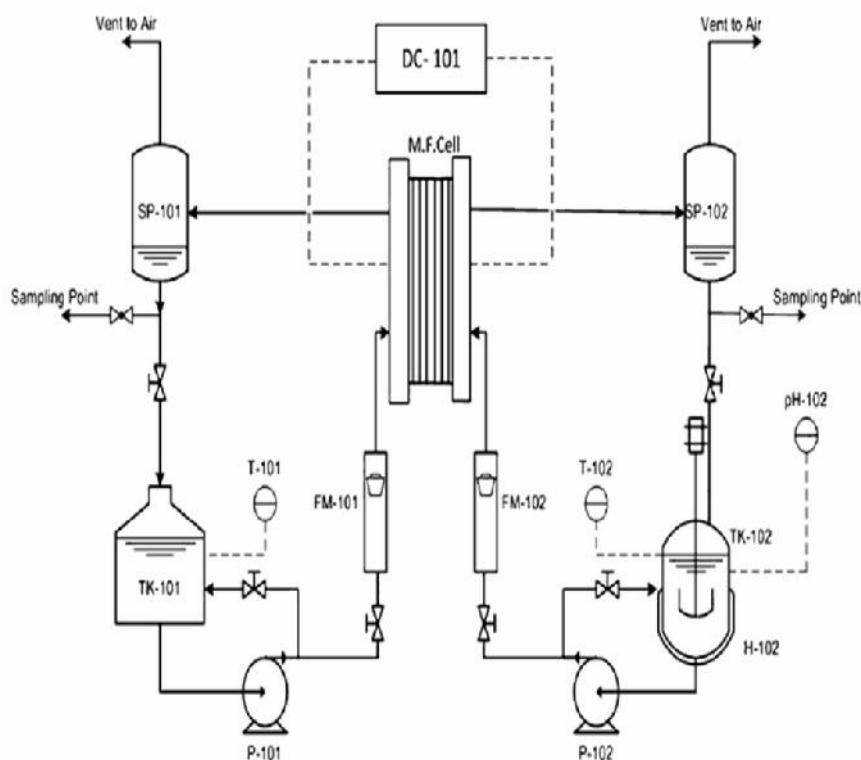


Fig. 1. Process flow diagram of MEO set-up utilized: membrane flow cell, anolyte circulation tank (TK-101), catholyte circulation tank (TK-102), magnetic pumps (P-101, P-102), flow meters (FM-101, FM-102), temperature indicators (T-101, 102), DC power supply (DC-101).

During the experiment, Ag (I) was oxidized to Ag (II) at the anode and nitric acid was reduced into nitrous acid at the cathode. Since silver (II) ions are sensitive to light and undergo reduction, precautions were taken by covering the set-up components with aluminum foil. In the catholyte reservoir, NO produced during the reduction of nitric acid was re-oxidized with continuous passage of oxygen into NO₂, and dissolved in water to reform nitric acid.

The concentration of Ag (II) in solution was determined rapidly and conveniently using back titration method.⁴

PS powder was obtained from PS granule using a ball mill, pre-treated by concentrated HNO₃ to have a homogeneous solution, diluted with DM water then AgNO₃ solution was added. Under the optimum conditions of the cell achieved for Ag (II) ion generation, this solution was subjected to electrolysis as anolyte in the set-up at 60-70 °C for 5-120 min. The samples were then taken and analysed by FTIR.

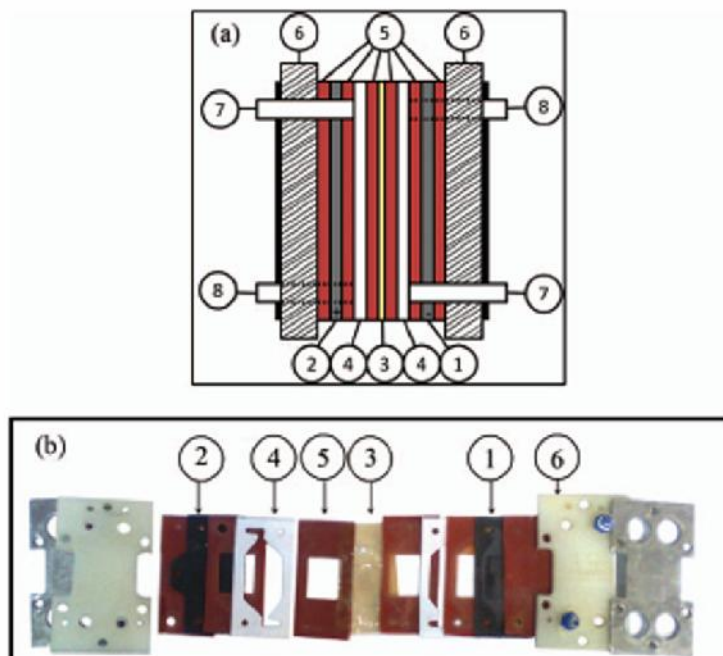


Fig. 2. Side view (a) and expanded view (b) of the membrane cell used in this study. 1-Ti cathode, 2-DSA-O₂ anode, 3-nafion 117, 4-spacer (Teflon), 5-gaskets, 6-cell body (Teflon), 7-electrolyte inlet, 8-electrolyte outlet.

Graphical Abstract

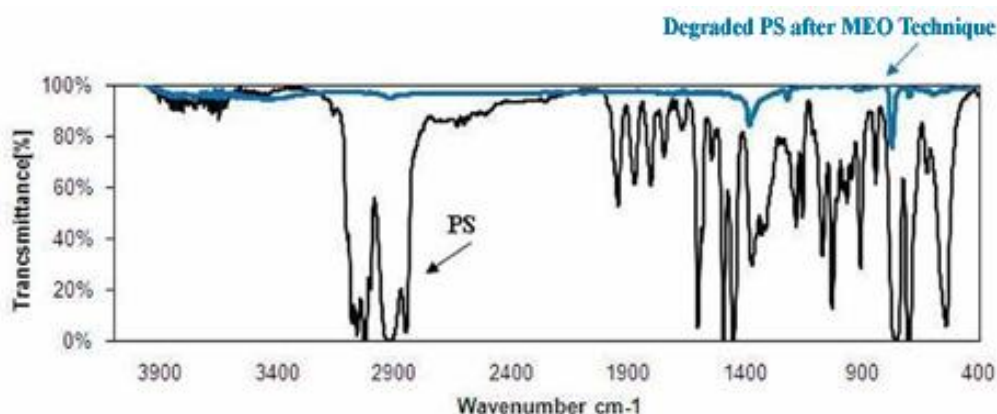


Table 1. Effect of nitric acid concentration on Ag (II) generation. (At 0.5 M AgNO₃, 29°C, 1.9 V, 100 ml/min).

HNO ₃ Concentration(N)	Max Ag(II) Concentration(M)	
Catholyte	4	0.018
	6	0.022
	8	0.029
Anolyte	4	0.017
	6	0.029

3. Results and Discussion

3.1. Effect of concentration of supporting electrolyte on Silver (II) generation

The supporting electrolyte employed for the silver (II) electro-generation can generally be sulphuric, nitric or perchloric acids. However, sulphuric acid low solubility toward metal ions, explosive perchloric acid, and instability of hydrochloric acid due to the oxidation of Cl⁻ to Cl₂ make nitric acid the best choice as it is highly soluble, stable, and low viscous.⁵⁻¹⁴ For these reasons, at this study the electro-oxidation of Ag (I) was studied under different nitric acid concentrations at a constant concentration of Ag (I) (0.5 M) at 29°C. Table 1 shows the maximum concentration of Ag (II) produced after a specified reaction time at different nitric acid concentrations in anolyte and catholyte. It is observed that the formation of Ag (II) is promoted upon increasing the nitric acid concentration, due to the higher stability of the [Ag (NO₃)]⁺ complex at higher acid concentration. The highest conversion was obtained at 8 and 6 M nitric acid concentrations in catholyte and anolyte, respectively. This is in consistent with the results previously reported by other workers.^{3,6}

3.2. Effect of Temperature on Silver (II) generation

The effect of temperature on the electrochemical oxidation of Ag (I) was investigated as a function of electrolysis time in the temperature range between 29-90 °C at fixed Ag (I) and nitric acid concentrations.

Fig. 3 shows the Ag (II) concentration generated with respect to the reaction time at different temperatures while Fig. 4 represents the steady-state concentration of the Ag (II) obtained after 50 min as a function of cell temperature. As seen, the Ag (II) concentration increases with electrolysis time within the anolyte in the recirculating batch reactor system then it levels off. The effect is more distinct at lower temperatures. These results clearly show that temperature has an inverse effect on the production rate and concentration of the produced Ag (II). A similar trend was also reported by other workers using three electrode system.^{3,11}

This is mainly due to the enhanced reactivity of Ag (II) with water lowering its stability at higher temperature and consequent reduction of the ions by water according to Eq. (6). Moreover, upon increasing the temperature, the nitrous acid production may also take place in the anolyte. As a result, the acid concentration decreases, lowering the stability of the silver (II) complex and its consequent reduction by nitrous acid according to Eq. (7).

3.3. Effect of initial concentration of the mediator on Silver (II) generation

Figure 5 shows the effect of initial concentration of Ag (I) on the production rate of Ag (II) for two different Ag (I) concentrations at a fixed nitric acid concentration. As evident, the Ag (II) concentration increases with electrolysis time at both concentrations of Ag (I) examined. However, a higher Ag (II) concentration was obtained with a higher initial Ag (I) concentration. The effect is more pronounced at steady-state which was taken after 50 min. This may be because the coulombic efficiency of the overall process could be improved by increasing the initial metal ion concentration. This effect is also predominant in efficiency of PS degradation which will be discussed later in this paper. The results are in good agreement with the previous studies.^{3,6,11}

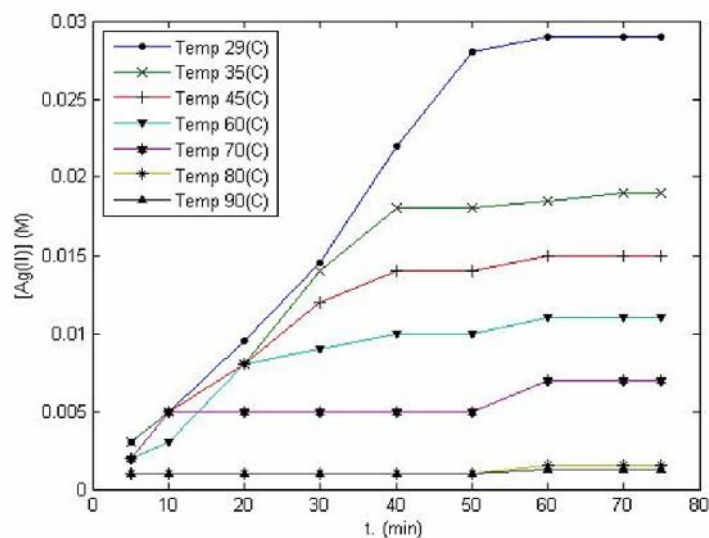


Fig. 3. Effect of temperature on Ag (II) generation as a function of time.(At 0.5 M AgNO₃, 6 M HNO₃, 1.9 V, 100 ml/min).

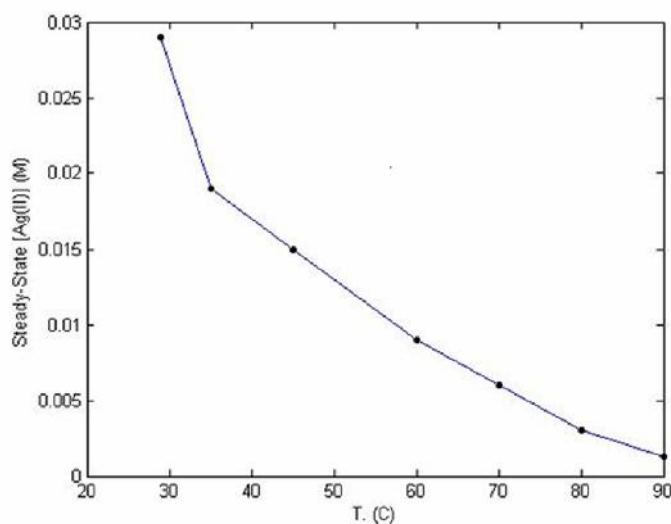


Fig. 4. Effect of temperature on the formation of steady-state Ag (II) concentration.(At 0.5 M AgNO₃, 6 M HNO₃, 1.9 V, 100 ml/min).

3.4. Effect of flow rate on Silver (II) generation

The effect of anolyte flow rate on the generation of Ag (II) was also studied and the results are depicted in Fig. 6. According to these results, the concentration of Ag (II) in the anolyte rises up by electrolysis time then it levels off after steady-state which is more distinguished at lower flow rates. The results verify that flow rate has also an inverse effect on the production rate of Ag (II). This is probably due to the low residence time of the anolyte in the anodic compartment of the cell at high flow rates. Similar trend has been reported by other researchers.¹⁴

According to the results obtained so far, the optimum conditions for electrochemical generation of silver (II) were found to be: Anolyte: 0.5M initial Ag (I) in 6M nitric acid as supporting electrolyte, T = 29 C, Flow rate: 100 ml/min, Catholyte: 8M nitric acid.

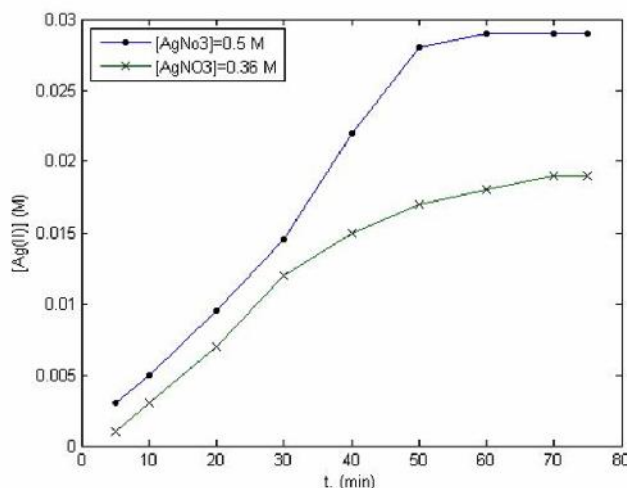


Fig. 5. Effect of initial concentration of the mediator on the formation of Ag (II). (At 6 M HNO₃, 29°C, 1.9 V, 100 ml/min).

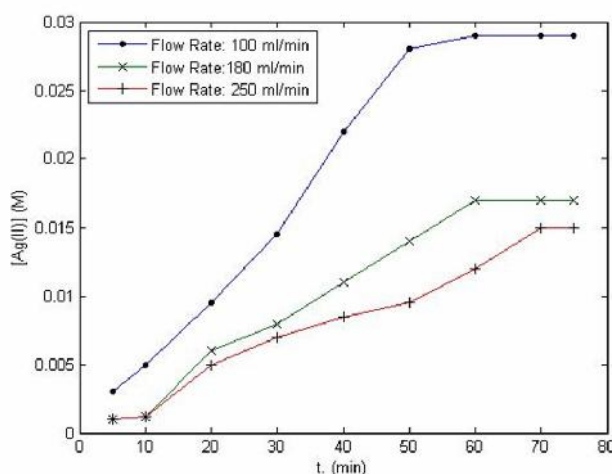


Fig. 6. Effect of Flow rate on the formation of Ag (II). (At 0.5 M AgNO₃, 6 M HNO₃, 29°C, 1.9 V).

3.5. Kinetic model of Ag (II) generation

The silver (II) generation kinetics at process conditions can be determined by using the Nernst's law as described in Eq. (4).²⁴ Then the electro-generation of silver (II) can be modeled. During the oxidation of silver (I) in concentrated acidic media, the silver (I) flux to the anode surface is defined by solving Fick's law. Assuming that the profile of concentration in the diffusion layer is formed rapidly, the solution of the following equation shows a linear profile. The differential balance controlling the system is thus:

$$\frac{d[Ag(II)]}{dt} = \frac{SD}{VU} ([Ag(I)]_{(t)} - [Ag(I)]_s) - k \frac{[Ag(II)]^2}{[Ag(I)]_{(t)}} \quad (9)$$

Where, S is the anode area, D is the diffusion coefficient of Ag (I) in concentrated aqueous solution, V is the anolyte volume, U is the diffusion layer thickness, k (S^{-1}) is the rate constant for oxidation of Ag (I), $[Ag(I)]_s$ is the Ag (I) concentration on anode surface, and $[Ag(I)]_{(t)}$ is the bulk concentration of the Ag (I) ions at t time. According to the Eq. (9) the first term on the right-hand side is the Ag (I) ions flux through the diffusion layer while the second term is related to the oxidation kinetics by silver (I).

Moreover the initial conditions are:

At $t = 0$ $[Ag(I)]_{(0)} = C_0$, $[Ag(II)]_{(0)} = 0$ and conservation of matter forces

$$[Ag(I)]_{(t)} + [Ag(II)]_{(t)} = C_0 \quad (10)$$

The concentrations at the anode surface also follow Nernst's law:

$$E^p - E^0 = \frac{RT}{F} \ln \frac{[Ag(II)]_s}{[Ag(I)]_s} \quad (11)$$

Where, E^p represents the potential applied at the anode which was measured directly vs. the saturated calomel electrode (SCE) in flow type cell and E^0 describes the apparent potential of the Ag (II)/Ag (I) couple, and was measured by Nernst's law (Eq. (4))

In addition the following equation can be written because the diffusion coefficients of Ag (II) and Ag (I) are similar:²⁵

$$[Ag(I)]_s + [Ag(II)]_s = C_0$$

Thus

$$[Ag(I)]_s = \frac{C_0}{1 + \exp\left[\frac{F(E^p - E^0)}{RT}\right]} \quad (12)$$

For the oxidation kinetics, Morin²⁵ obtains the following differential equation

$$\frac{dy(t)}{dt} + py(t) + k_a y^2(t) - p(C_0 - [Ag(I)]_{el}) = 0 \quad (13)$$

Which $y(t) = [Ag(II)]_{(t)}$, $k_a = k/C_0$ is the apparent rate constant in $mol^{-1}.lit.S^{-1}$ and $p = SD/V$ is the cell parameter in s^{-1} find out by Lingane.²⁶

Then Eq. (13) was solved by Matlab software and the least squares method was used for the curve fitting. A theoretical model related to the response data was employed for the fitting process in order to predict the data with one or more coefficients. This method estimates the coefficients by minimizing the summed square of residuals.

Therefore the experimental curve $[Ag(II)] = f(t)$ fitted the theoretical model obtained from Eq. (13) (Fig. 7). By the adjustment of the parameters, the rate constant (k) was determined in Eq. (9). The p parameter was calculated from the slope of the experimental curve at $t = 0$ because at short times, Eq. (9) can be converted to the following:

$$Ag(II)_{(t)} = [p(C_0 - Ag(I)_{el})] \times t \quad (14)$$

The p parameter was found to be $2.33 \times 10^{-5} (S^{-1})$ according to the experimental curve (Fig. 7). Supposing that the silver nitrate solution diffusion coefficient (D) in concentrated media at 29 °C and concentration of 0.5 $mol.lit^{-1}$ is approximately $1.554 \times 10^{-5} (cm^2.sec^{-1})$,²⁹ the diffusion layer thickness will be equal to 222 micron.

The model constants k_a and k obtained in this study equal to $4.5 \times 10^{-3} (mol^{-1}.lit.S^{-1})$ and $2.25 \times 10^{-3} (S^{-1})$, respectively, which is one order of magnitude higher than those reported by other authors.²³⁻²⁷ The rate constants obtained for Ag (II) generation by others are tabulated in Table 2 for comparison purposes. The difference can be attributed to different type of cell and anode employed in these studies (flow cell vs. stationary cell and DSA-O₂ anode vs. Au / Pt anodes). According to the model, at optimum conditions the contribution of mass transfer is 4.75 times faster than its kinetic showing a somewhat kinetic-controlled reaction for Ag(II) generation on DSA-O₂ anode in the flow type cell employed in this study (1.907×10^{-5} vs. $4.01 \times 10^{-6} (mol.(lit.S)^{-1})$ for mass flux and electron transfer rate, respectively).

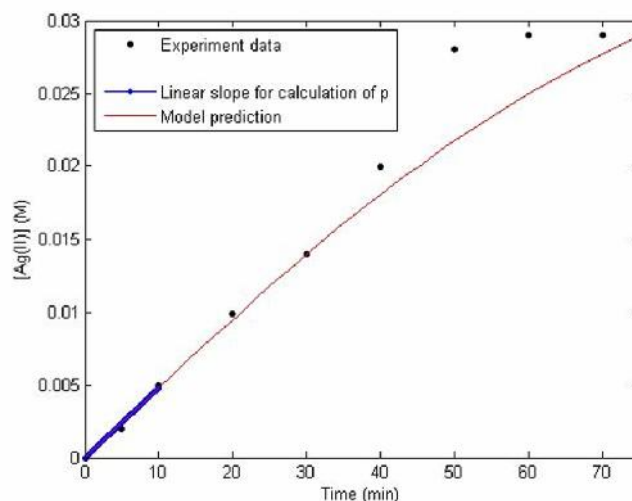


Fig. 7. Generation kinetic of silver (II). (At 0.5 M AgNO₃, 6 M HNO₃, 29°C).

3.5.1. Temperature dependence of rate constant

The influence of temperature on the kinetics of silver (I) was also investigated. For determination of the activation energy the Arrhenius form of the parameters was employed:

$$k_a = A \exp\left[\frac{-E_a}{RT}\right] \quad (15)$$

Therefore, activation energy is defined from the slope of the linear plot of $\ln k_a$ against the reciprocal of absolute temperature, which is represented in Fig. 8. The regression factor is close to one and it thus confirms the good agreement between experimental data with the linear plot. The activation energy, E_a was estimated to be 44 ± 2 kJ mol⁻¹ which is less than half of than those reported by Lehmani²⁴ and Noyes²⁷ who found this value to be 100 ± 4 and 129 ± 2 kJ mol⁻¹, respectively. This discrepancy is likely attributed to the nature of the anode material and its surface used in these studies. Noyes used platinum while Lehmani employed gold as anode material for Ag (I) oxidation. Both workers might employ these anodes because of their stability in Ag (II) / HNO₃ media. However, the anode used in this study is a commercially available dimensional stable anode for oxygen evolution (DSA_O₂) which is composed of a titanium plate coated with IrO₂ as electro catalyst. Of course, one generally expects application of an electrocatalyst decreases the activation energy of the Ag (I) oxidation reaction. The activation energies for silver (I) oxidation obtained by different workers are listed in Table 2 for comparison.

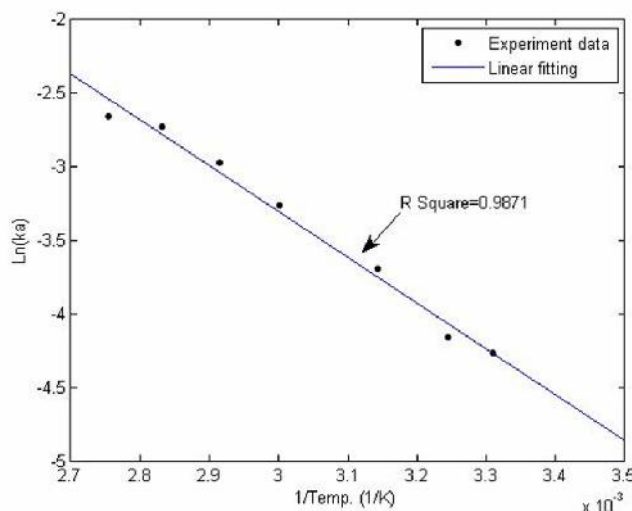


Fig. 8. Temperature dependence on the oxidation kinetic. (At 0.5 M AgNO₃, 6 M HNO₃).

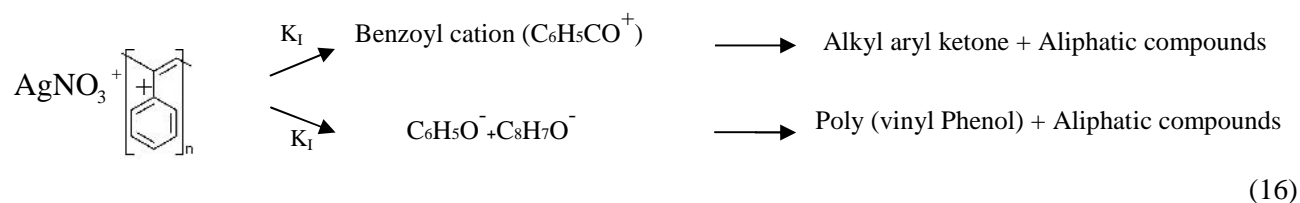
Table 2. Activation energies obtained for electrochemical oxidation of Ag (I) by various authors.

Ref.	Method of Oxidation	Anode material	Initial conditions	k for Ag(I) oxidation (S ⁻¹)	E _a (kJ mol ⁻¹)
Po. et al. ²³	UV spec.		[AgNO ₃] ₀ =0.01M [HNO ₃] ₀ =6M	(2.38 ± 0.3) × 10 ⁻⁴	96 ± 2
Lehmani et al. ²⁴	Potentiometry (Three electrode)	Au	[AgNO ₃] ₀ =0.1M [HNO ₃]=6M	(7.4 ± 0.3) × 10 ⁻⁴	100 ± 4
Morin et al. ²⁵	Coulometry		[AgNO ₃] ₀ =0.1M [HNO ₃]=6M	(9.4 ± 0.5) × 10 ⁻⁴	NA
Noyes et al. ²⁷	Chemical	Pt	[AgNO ₃] ₀ =0.05M [HNO ₃]=1-4 M	(7.7 ± 0.9) × 10 ⁻⁴	129 ± 2
This work	Potentiostatically Flow-type cell	DSA_O ₂	[AgNO ₃] ₀ =0.5M [HNO ₃]=6M	(2.25 ± 0.2) × 10 ⁻³	44 ± 2

3.6. Electrochemical degradation of PS by Ag (II)

The silver (II) ion has strong oxidizing properties and can possibly be used as mediator for oxidation /or degradation of polymeric compounds. Therefore, in this work the PS degradation and its kinetic have been studied in a flow-type cell and the corresponding rate law was investigated.

The oxidative degradation of PS produces a number of degraded products such as benzoyl cation (C₆H₅CO⁺), negative ions: C₆H₅O⁻, C₈H₇O⁻ and positive ions: C₇H₇O⁺, C₈H₉O⁺, C₇H₅O₂⁺, alkyl aryl ketone, poly (vinyl phenol)¹⁶ and some aliphatic compounds³⁰ according to Eq. (16).



A full detection and characterization of these products calls for rigorous analytical methods which are presently out of the scope of this study. However, in order to investigate the possibility of electrochemical degradation of PS by silver(II) ions under the optimum conditions found for Ag (II) generation in this study, FTIR study was initially carried out to examine this ability qualitatively. Because of the need to penetrate silver (II) ions into PS granules, some precautions were initially taken including PS size reduction to powder size and pretreatment with concentrated HNO₃, facilitating the mediated electrochemical oxidation.

The FTIR analysis of the PS powder along with that of the pretreated PS after MEO electrolysis by Ag (II) are obtained and represented in Fig. 9. According to these results, most characteristic peaks corresponding to PS were successfully eliminated after MEO electrolysis by Ag (II). However, the weak peaks in the region of 1350–1500 cm⁻¹ which confirms fairly presence of aliphatic groups, the peaks in 675–900 cm⁻¹ and between 3000 and 3050 cm⁻¹ which show a slight residual of aromatic compounds can also be observed confirming oxidation of the PS by Ag (II) ions. Attacks on the aromatic ring and pendant groups are confirmed by fragment ions related to phenol and benzoquinone groups. However PS attacks on both the backbone forming the same groups and the ring forming of phenolic or quinone type groups have been observed as reported earlier.^{16-17, 20}

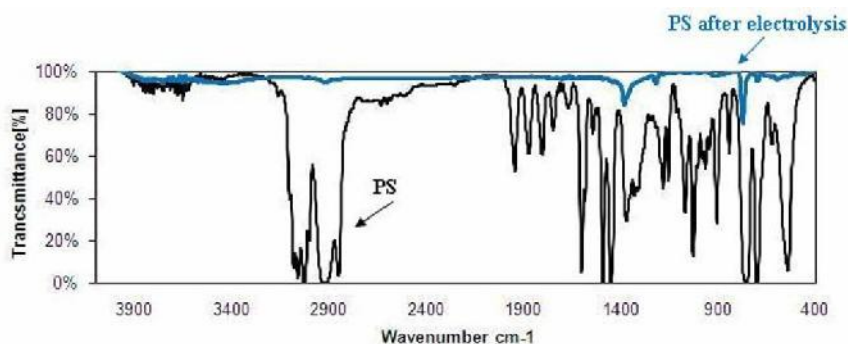


Fig. 9. FTIR spectrum for PS powder and after MEO electrolysis by Ag (II).

3.6.1. Kinetics of PS degradation

Following the model employed by other workers for MEO of organics by Ag (II), the succeeding rate law is considered to predict the rate constant and the reaction order for degradation of PS by Ag (II):

$$-\frac{dAg(II)}{dt} = K_1 [Ag(II)]^m [PS]^n \quad (17)$$

The study of degradation kinetic of PS is simply performed by taking a great excess of PS powder.²⁴ The reaction order in respect to PS thus equals one ($n=1$). Eq. (17) can thus be simplified as:

$$-\frac{dAg(II)}{dt} = K_1' [Ag(II)]^m \quad (18)$$

With $K_1' = K_1 [PS]$

The experimental results obtained for consumption of Ag (II), or in other words degradation of PS, are plotted against time in Fig. 10. As seen, the concentration of Ag (II) is reduced rapidly within the first few minutes, then no significant changes in the Ag (II) concentration is observed with excess time despite continuous generation of the Ag (II) in the flow cell. The initial results clearly show that the degradation rate of PS by Ag (II) should be fast. However, since the excess amount of PS with high molecular weight (200,000) is used compared with Ag (II) (The ratio of Ag (II)/ PS was 1:10 by weight) on one hand, and a high rate of the Ag (II) consumption compared with its generation on the other hand, the continuous generation of Ag (II) in the small-scale laboratory cell (10 cm²area) was not sufficient to distinguish the Ag (II) consumption after 10 minutes.

In order to evaluate the kinetic parameters, the results for Ag (II) reduction rate are calculated and plotted against its concentration based on Eq. (18) and shown in Fig. 11 along with a curve fitting. According to these results, a linear relationship ($R^2 = 0.9939$) which shows a first order ($m=1$) in respect to silver (II) concentration, is predominant.

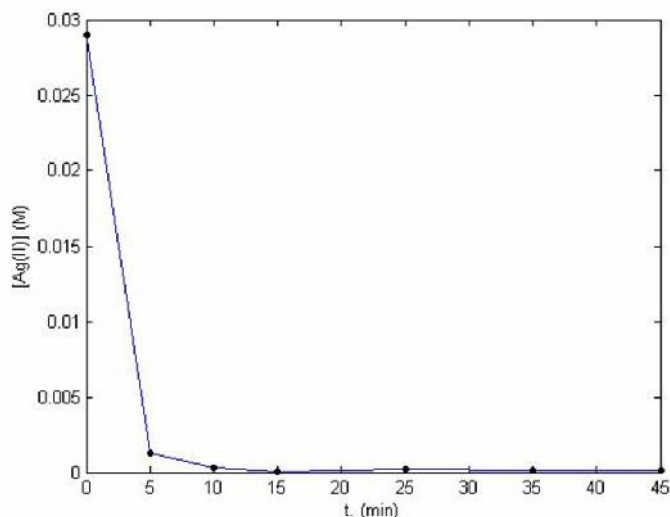


Fig. 10. Plot of Ag (II) concentration vs. time after PS addition to the analyte (At 0.5 M AgNO₃, 6 M HNO₃, 70°C).

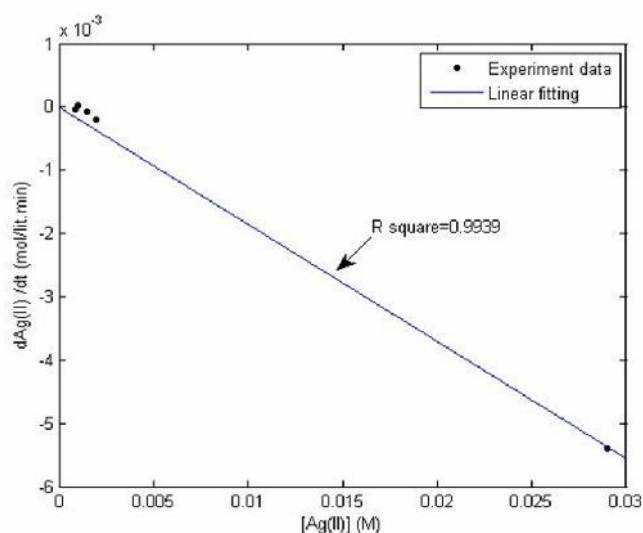


Fig. 11. Plot of dAg (II)/dt vs. Ag (II) concentration after PS addition to the analyte (At 0.5 M AgNO₃, 6 M HNO₃, 70°C).

3.6.2. Model validation

To validate the predominance of first order reduction of Ag (II) in respect to its concentration, Lehmani²⁴ derived the following simple equations for organics oxidation using Nernst's law assuming that the concentration of silver (I) remains constant in the electrolyte:

$$\frac{dE}{dt} = -\frac{RT}{F} K_1' \quad (19)$$

Then,

$$E(t) = E(t=0) - \frac{RT}{F} K_1' t \quad (20)$$

Accordingly, the potential E [(Ag (II) / (Ag (I)))] of the DSA_O₂ anode was measured experimentally against SCE vs. time during the PS degradation and the results are represented in Fig. 12. An admirable linear variation is obviously verified confirming the first order results obtained from Fig. 11.

The value for the rate constant of Ag (II) reduction or PS degradation at 70°C at 100 ml/min based on Eq. (18) was found from Fig. 10 to be $K'_1 = 0.0182 \text{ (S}^{-1}\text{)}$. For comparison purposes, the kinetic parameters for mediated electrochemical oxidation of some other organic compounds by Ag (II) process are also listed in Table 3. As seen, the rate constant, K'_1 obtained in this study is somewhat lower than those reported previously for oxidation of organics such as formic acid or acetic acid.^{24,28} This may be due to the fact that, undeniably the carbon chain is much longer in PS than those organics, and this avoids chain scission easily.¹⁶⁻¹⁷ As a result, the kinetics for PS degradation should be reduced.

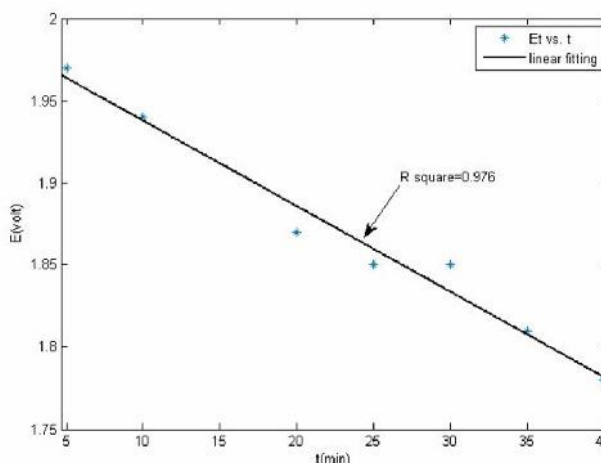


Fig. 12. Plot of E [(Ag (II) / (Ag (I)))] vs. time during the PS degradation with silver (II). (At 0.5 M AgNO₃, 6 M HNO₃, 70°C).

Table 3. Rate constants for organic oxidation obtained by various authors.

Ref.	Initial conditions	Organics to be oxidized	K'_1 For Ag (II) reduction or organic oxidation (S^{-1})	Reaction order, m
Lehmani ²⁴	[AgNO ₃] ₀ =0.1M [HNO ₃]=6M	Acetic acid [CH ₃ COOH] ₀ = 0.017 M	1.55±0.05	1
		Formic acid [HCOOH] ₀ =0.057 M	2.46±0.13	1
Miller & Morrow ²⁸	[AgNO ₃] ₀ =0.01M [HNO ₃]=6M [HCOOH] ₀ = 0.12 M	Formic acid	0.371±0.005	1
This work	[AgNO ₃] ₀ =0.5M [HNO ₃]=6M	PS	0.018±0.0002	1

4. Conclusions

The kinetic of electrochemical generation of Ag (II) was experimentally studied with respect to various parameters, including temperature, flow rate, concentrations of supporting electrolyte and the mediator in a flow type electrochemical reactor. The Ag (II) generation rate was promoted with HNO₃ concentration but decreased by temperature then it levels off. The effect is more distinct at low temperatures due to instability of the silver (II) complex. A higher Ag (II) concentration was obtained with a higher initial Ag (I) concentration due to improved overall coulombic efficiency. However, anolyte flow rate has an inverse effect on the generation rate of Ag (II) probably due to low residence time. The optimum conditions were found to be: Anolyte: 0.5M initial Ag (I) in 6M nitric acid as supporting electrolyte, T = 29 °C, Flow rate: 100 ml/min, Catholyte: 8M nitric acid.

By using a theoretical model, the rate constant for the generation of silver (II) was assessed by Matlab software. The proposed kinetics was evaluated by comparing the calculated and experimental data. According to the model at optimum conditions, a diffusion layer thickness of 222 micron was estimated on the DSA- O₂ anode. The contribution of mass transfer is 4.75 times faster than the kinetic parameter showing a kinetic-controlled reaction. Nevertheless, the rate constant obtained in this study for Ag (II) generation is one order of magnitude higher than those reported earlier. The Arrhenius model was employed to evaluate temperature dependence of the rate constant which was found to be linear. The activation energy was estimated to be 44±2 kJ mol⁻¹ for DSA-O₂ anode which is less than half of those previously reported for precious metals due to the nature of the anodes and their surfaces.

The electrochemical degradation of polystyrene by the silver (II) process was successfully demonstrated. FTIR study was carried out to examine the possibility of degradation. Most characteristic peaks corresponding to PS were eliminated after MEO electrolysis by Ag (II). The PS degradation kinetic has also been studied and a first order reaction in respect to silver (II) concentration was found and validated. The PS degradation rate was found to be fast with the rate constant 0.018 (S⁻¹).

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