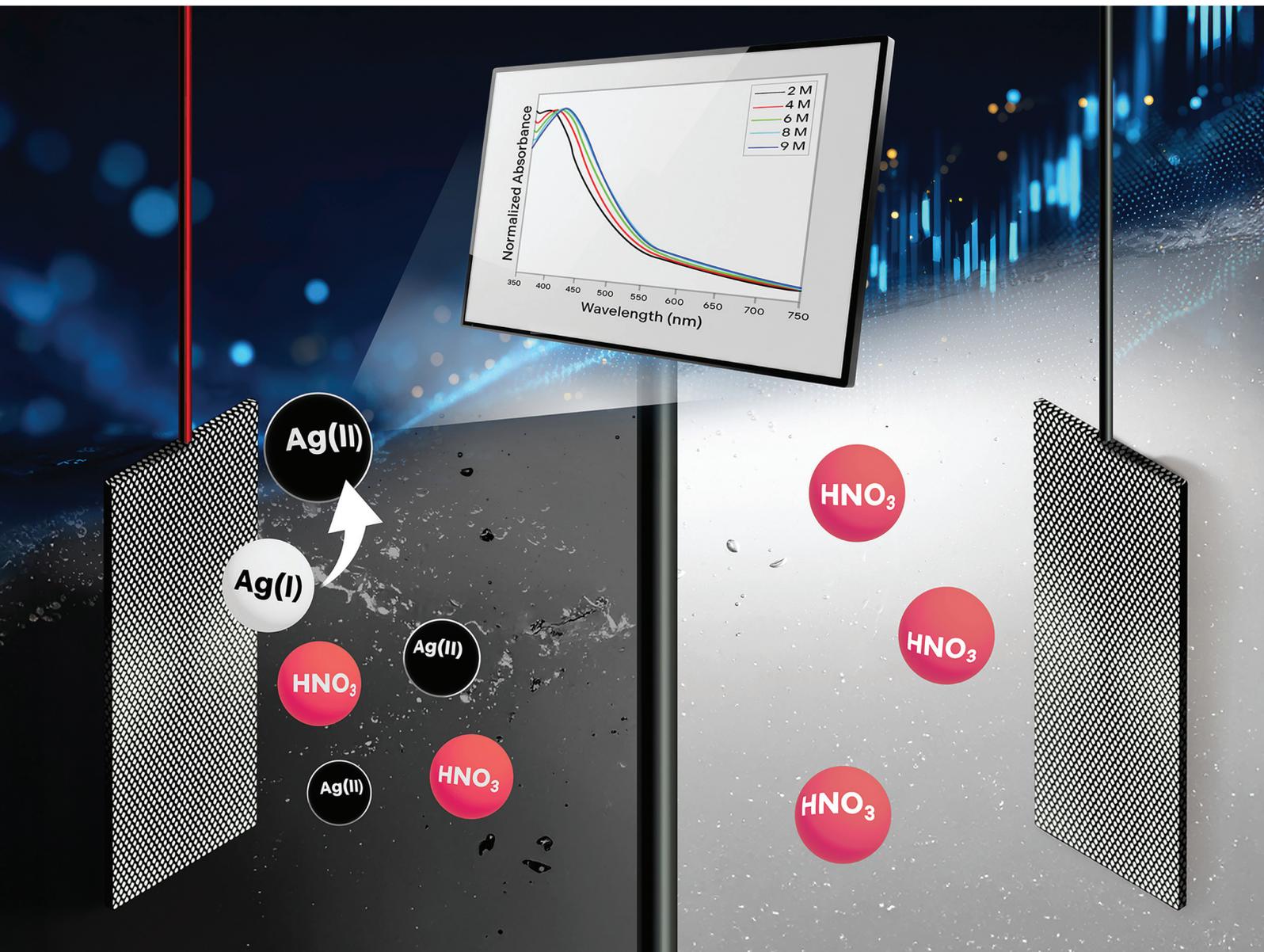


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PAPER

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## Optimization and quantification of silver(II) for mediated electrochemical oxidation applications

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Mediated electrochemical oxidation (MEO) is a low-temperature, low-pressure, aqueous mineralization process used to treat organic waste. A powerful metal oxidant is used as a mediator in an acidic solution. Although Ce and Co are thoroughly studied mediators, Ag is a preferred choice because of the higher efficiency rates of mineralization observed with this system. Importantly, the quantification methodology and spectroscopic characteristics of the Ag(II) ion must be obtained. In this study, we determined molar extinction coefficients of the primary absorption band associated with the Ag(II) ion in 2–9 M HNO<sub>3</sub> solution. The optimization of Ag(II) electrooxidation was also determined by altering parameters such as HNO<sub>3</sub> concentration, mediator concentration, and temperature. The optimization studies and extinction coefficient data provide parameters for implementation of Ag as a suitable mediator for MEO processing of organic waste.

### Introduction

Mediated electrochemical oxidation (MEO) is a powerful technology suitable for the destruction and breakdown of organic waste molecules into their simplest constituents. This aqueous mineralization process can take place at ambient temperature and pressure conditions, making it an attractive alternative to incineration. MEO avoids emitting any toxic and corrosive by-products such as furan and dioxins that are typically generated during incineration of organics. During the process, organic substrates are degraded by an oxidized metal mediator ion through a series of reactive intermediates to form water, inorganic salts, and CO<sub>2</sub>. After the organic substrate reacts with the metal ion, the mediator is reoxidized in a closed cycle to continue the process. Over the last few decades, MEO has been used to mineralize industrial and chemical waste streams,<sup>1–3</sup> wastewater streams,<sup>4–6</sup> and hazardous mixed waste.<sup>7–9</sup>

The MEO process relies on using a redox-active metal ion that is electrochemically oxidized at the anode to generate a powerful oxidizing species capable of decomposing organic compounds. In this process, this mediator continuously cycles between its oxidized and reduced forms, allowing for indirect oxidation of organic contaminants without direct electrode

contact. Various transition metal couples have been evaluated as mediators, including Ag,<sup>8,10–15</sup> Ce,<sup>12,13,16–20</sup> Co,<sup>21–23</sup> Fe,<sup>1</sup> Mn,<sup>24</sup> and Ru couples.<sup>25</sup> Among these, Ce, Co, and Ag have shown particular promise for large-scale application because of their stability, redox reversibility, and effectiveness across a range of organic matrices.<sup>3,8,18</sup>

The most notable demonstration of this technology for organic waste destruction is the cerium oxidation CEROX<sup>TM</sup> process developed and piloted by Nelson *et al.*<sup>18,26</sup> This process employs a Ce-based MEO system to achieve complete oxidation of refractory organic materials at relatively low temperatures, thereby minimizing secondary waste generation and avoiding the use of aggressive reagents. Through controlled electrochemical regeneration of the mediator, MEO offers a highly adaptable and environmentally benign pathway for treating complex organic waste streams.

In this study, the Ag(II)/(I) redox couple was investigated as a mediator for MEO. Chemically, Ag(II) is the most attractive choice because of its exceptionally high redox potential ( $E^\circ = 1.98$  V), surpassing that of Co(III) ( $E^\circ = 1.84$  V), and Ce(IV) ( $E^\circ = 1.74$  V). Although Ag is an incredibly powerful mediator for MEO, it faces challenges in applications involving chlorinated substrates. Unlike Ce and Co, which can tolerate chlorinated compounds, Ag forms insoluble AgCl, halting the process and necessitating additional treatment steps. However, in the absence of chlorinated species, Ag(II) is the optimal choice because of its demonstrated high destruction efficiency at relatively low operating temperatures (<100 °C). The objective of this study is not to evaluate the full electrochemical oxidation performance of Ag(II) in MEO operations, but rather to establish the quantitative

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foundation necessary for MEO application. Accurate extinction coefficient, reliable  $\text{Ag(II)}$  quantification methods, and a clear understanding of how acid strength, mediator loading and temperature affect  $\text{Ag(II)}$  generation are critical prerequisites for any reactor-scale MEO investigation. Therefore, the present work focuses on fundamental characterization and optimization of  $\text{Ag(II)}$  production, providing essential parameters required for future electrochemical oxidation and mineralization studies.

A key challenge in working with the  $\text{Ag(II)}/\text{Ag(I)}$  system is the difficulty in monitoring  $\text{Ag(II)}$  concentrations in real time during the oxidation process. The  $\text{Ag(I)}$  precursor exhibits negligible absorbance in the ultraviolet–visible (UV–vis) region, and the oxidized  $\text{Ag(II)}$  form in  $\text{HNO}_3$  is darkly colored with a characteristic UV–vis absorption. However, because of the strong oxidizing nature and instability of  $\text{Ag(II)}$ , reliable determination of its molar extinction coefficient in solution is difficult. The quantification of  $\text{Ag(II)}$  in solution requires reliable and precise titration methods working in tandem with UV–vis measurements. Although some prior studies have reported extinction coefficients under varying  $\text{HNO}_3$  concentrations, the extinction coefficient values only covered segmented  $\text{HNO}_3$  concentration ranges, prompting a need for more robust data.

In this work, two titration methodologies were compared and used to determine the concentration of  $\text{Ag(II)}$  in  $\text{HNO}_3$ . The molar extinction coefficients of  $\text{Ag(II)}$  were determined in a wide range of  $\text{HNO}_3$  concentrations (2–9 M). This work provides complementary data that highlight previous literature trends as well as provide an increased level of precision and accuracy in measurements. Titration quantification methods were then used to optimize  $\text{Ag(II)}$  generation as a function of temperature,  $\text{Ag(I)}$  concentration, and  $\text{HNO}_3$  concentration. The optimized conditions reported here provide the quantitative framework required for implementing  $\text{Ag(II)}$  in future MEO oxidation experiments. Collectively, these results establish the analytical and operational basis needed for future studies evaluating the electrochemical oxidation performance of  $\text{Ag(II)}$  in practical MEO systems. This study advances the field in three key ways: (i) it provides the most extensive continuous set of molar extinction coefficient for  $\text{Ag(II)}$  in 2–9 M  $\text{HNO}_3$ , measured with higher precision than previous reports; (ii) it presents a rigorous comparison of two  $\text{Ag(II)}$  quantification methods establishing a reliable analytical basis for real time  $\text{Ag(II)}$  monitoring; and (iii) it offers a systematic evaluation of the parameters controlling  $\text{Ag(II)}$  electrochemical generation, which is crucial for process optimization in future MEO applications.

## Results and discussion

### Electrooxidation of $\text{Ag(I)}$ and quantification

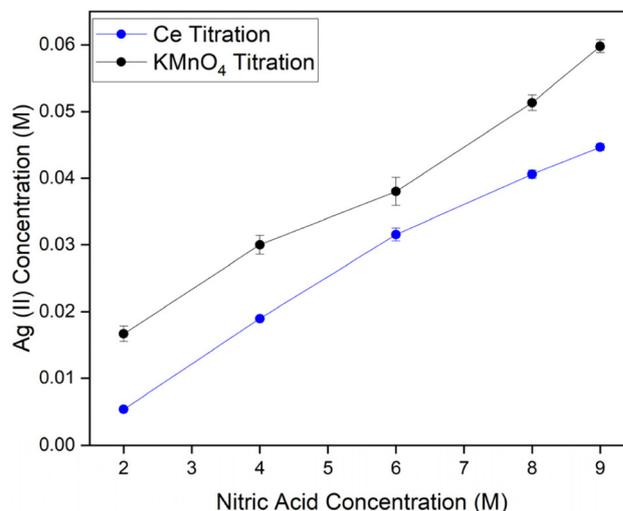
Stock solutions of  $\text{AgNO}_3$  were electrochemically oxidized in a glass H-cell to generate  $\text{Ag(II)}$  ions. The oxidized  $\text{Ag(II)}$  ion exhibits a characteristic dark brown to black color and is moder-

ately stable in  $\text{HNO}_3$  but slowly decomposes upon reaction with trace water or organics. Therefore, all titration and spectroscopic measurements were conducted promptly after electrolysis to minimize decomposition.

The concentration of electrochemically formed  $\text{Ag(II)}$  is influenced by several factors, including the acidity of the anolyte, the concentration of the metal mediator, and the temperature of the cell. Although these dependencies have been described in the literature, accurate quantification of  $\text{Ag(II)}$  remains a critical step in evaluating its stability and reactivity. Direct titration of  $\text{Ag(II)}$  is the most described method in the literature.<sup>27,28</sup> Direct titrations of  $\text{Ag(II)}$  in 2 M  $\text{HNO}_3$  rely on the disappearance of the brown/black color as  $\text{Ag(II)}$  is reduced to  $\text{Ag(I)}$  in the presence of direct reducing agents ( $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{O}_2$ , and  $\text{VO}_2^+$ ).<sup>27</sup> In previous literature studies,<sup>28</sup> the visual end point for direct titrations is challenging, so two back-titration methods were employed to quantify  $\text{Ag(II)}$ .

To combat the challenges of direct titrations, two back-titration methods were studied and compared in this work. The  $\text{FeSO}_4$  titrations for the quantification of  $\text{Ag(II)}$  were first performed by Noyes *et al.*<sup>29</sup> Samples of  $\text{Ag(II)}$  were quenched with an excess of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and titrated with  $\text{KMnO}_4$ . Similar to previous work, samples over 6 M were diluted in water, and end points were meticulously determined to ensure no reduction of nitrate by the  $\text{Fe(II)}$  ion occurred during the titration.

The second back-titration method employed in this study was a Ce potentiometric titration. Samples of  $\text{Ag(II)}$  were reacted with  $\text{Ce(III)}$ , and the resultant  $\text{Ce(IV)}$  was potentiometrically titrated with standard  $\text{Fe(II)}$ . Comparisons of  $\text{FeSO}_4$  and Ce back-titrations are shown in Fig. 1. The two titration



**Fig. 1** Acid-dependent  $\text{Ag(II)}$  concentrations titrated with (blue) Ce redox titrations compared with (black)  $\text{KMnO}_4$  back-titrations. Conditions: initial  $\text{AgNO}_3$  stock = 0.1 M  $\text{AgNO}_3$  in variable-molarity  $\text{HNO}_3$ , catholyte solution = 8 M  $\text{HNO}_3$ . The system was electrochemically oxidized for 40 min before aliquots were taken.



methods were performed on electrochemically generated samples of Ag(II), and aliquots were analyzed simultaneously through both methods in triplicate. The KMnO<sub>4</sub> back-titrations consistently resulted in a higher concentration of Ag(II) compared with the Ce titrations across the HNO<sub>3</sub> concentration range. Typically, KMnO<sub>4</sub> redox titrations are performed in solutions containing H<sub>2</sub>SO<sub>4</sub>, and the HNO<sub>3</sub> medium causes competing redox reactions with KMnO<sub>4</sub>. HNO<sub>3</sub> is a strong oxidizer, and the resultant concentrations of Ag(II) are shown to be consistently higher than in the Ce titrations. As a result, all Ag(II) quantification experiments were performed with Ce potentiometric titrations. This allowed the results of this work to be compared with previous literature data because previous reports also relied on Ce titration methods for Ag(II) quantification.

### UV-vis spectrophotometry

The absorption spectrum of Ag(II) in variable concentrations of HNO<sub>3</sub> is shown in Fig. 2. AgNO<sub>3</sub> does not absorb in the UV-vis range, but Ag(II) displays a single absorption peak at 372–400 nm, attributed to the Ag(II) d–d transition.<sup>30,31</sup> Additionally, a bathochromic shift in the wavelength was observed because of increasing HNO<sub>3</sub> concentration caused by increasing complexation with nitrate ions [e.g., Ag(NO<sub>3</sub>)<sub>4</sub><sup>2-</sup>].<sup>15</sup> The increase in molar absorptivity with HNO<sub>3</sub>, along with subtle broadening of the absorption band near 420 nm, suggests changes in the coordination environment and stability of Ag(II). At concentrations above 7–8 M HNO<sub>3</sub>, the enhanced  $\epsilon$  values, similarly seen in the literature may indicate partial disproportionation of Ag(II) to Ag(I)/Ag(III) species, which is consistent with the known instability of Ag(II) in highly oxidizing media.<sup>32,33</sup>

The experimental extinction coefficient of Ag(II) can be calculated if the concentration can be accurately determined by

titrations. Previously, researchers have attempted to determine the molar extinction coefficient of Ag(II) in HNO<sub>3</sub> medium using spectroscopy measurements taken simultaneously with Ce titrations.<sup>28,30,32,34</sup> The same methodology was applied here, and the data have been extended up to 9 M HNO<sub>3</sub> as attempts to calculate extinction coefficients at 10 M HNO<sub>3</sub> resulted in inconsistent titration results due to competing nitric acid oxidation (Fig. 2).

Previous literature reports extinction coefficient values in HNO<sub>3</sub> concentrations ranging from 1.5 to 8.8 M, which are summarized in Table 1. Dundon *et al.* report slightly higher extinction coefficients than the previous work conducted by Kirwin *et al.*, and Po reports a single value that falls within the range of values.<sup>30,32,34</sup> In this work, the trend of increasing extinction coefficient with increasing HNO<sub>3</sub> concentration is confirmed. The data follows a linear trend up to 9 M HNO<sub>3</sub> with an  $R^2$  value of 0.990. As mentioned previously, Ag(II) reacts rapidly with solvent and reduces back to Ag(I), adding to the challenge of obtaining accurate and reproducible values. Additionally, the extinction coefficients are the same at high and low concentrations of Ag(II) and follow the Beer–Lambert law, as previously noted. The extinction coefficient obtained in this work follows the same increasing trend with HNO<sub>3</sub> concentration reported by Po, Dundon, and Kirwin, however, the absolute values differ slightly. These discrepancies likely arise because many earlier studies used ozonolysis, which is now known to produce mixed-valent species such as Ag<sub>6</sub>O<sub>8</sub><sup>+</sup> that alter the observed absorbance. In contrast, the present study relies solely on the electrochemical generation of Ag(II), producing a more homogeneous nitrate-bound Ag(II) species. This difference in synthetic pathway, combined with synchronized titration-UV-Vis measurements, provides improved consistency and precision relative to historical data.

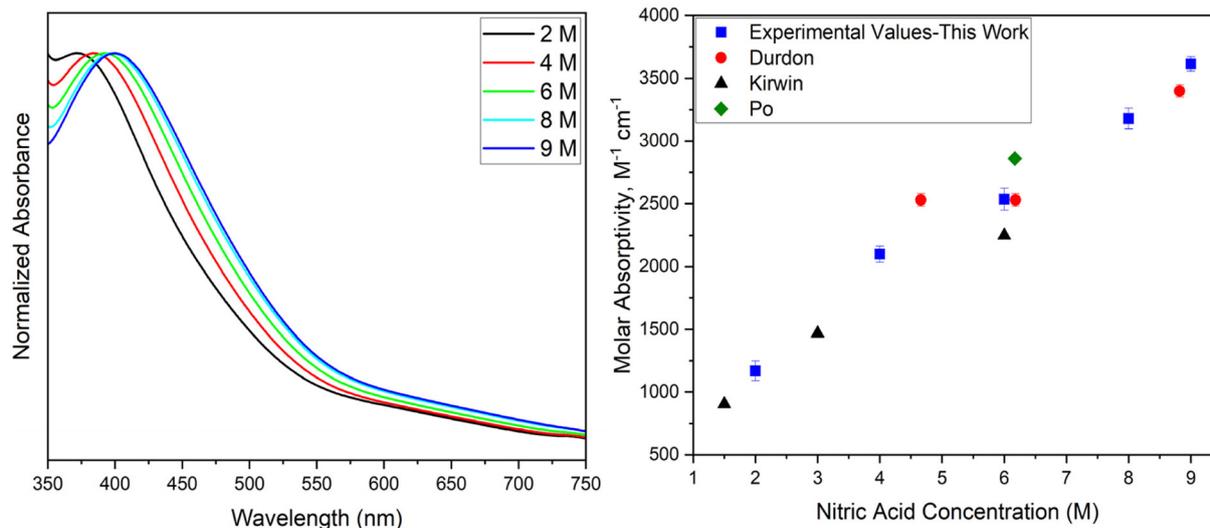


Fig. 2 (Left) The normalized absorption spectrum of Ag(II) in varying HNO<sub>3</sub> medium. (Right) A comparison of molar absorptivity values between this work and literature values.



**Table 1** Comparison of wavelengths (nm) and extinction coefficients ( $M^{-1} \text{ cm}^{-1}$ ) for Ag(II) in  $\text{HNO}_3$  medium

Wavelength (nm)	Extinction coefficient ( $M^{-1} \text{ cm}^{-1}$ )	Conditions	Ag(II) source	Ref.
390	$2860 \pm 50$	6.17 M $\text{HNO}_3$	Dissolution of AgO	Po (1967) <sup>32</sup>
394	$2530 \pm 50$	4.66 and 6.18 M $\text{HNO}_3$	Ozonolysis of $\text{AgNO}_3$	Dundon (1966) <sup>34</sup>
394	3400	8.82 M $\text{HNO}_3$	Ozonolysis of $\text{AgNO}_3$	Dundon (1966) <sup>34</sup>
NA	~900	1.5 M $\text{HNO}_3$	Ozonolysis of $\text{AgNO}_3$	Kirwin (1963) <sup>30</sup>
NA	~1450	3 M $\text{HNO}_3$	Ozonolysis of $\text{AgNO}_3$	Kirwin (1963) <sup>30</sup>
NA	~2250	6 M $\text{HNO}_3$	Ozonolysis of $\text{AgNO}_3$	Kirwin (1963) <sup>30</sup>
372	$1171 \pm 79$	2 M $\text{HNO}_3$	Electrochemical oxidation of $\text{AgNO}_3$	This work
384	$2100 \pm 64$	4 M $\text{HNO}_3$	Electrochemical oxidation of $\text{AgNO}_3$	This work
392	$2537 \pm 87$	6 M $\text{HNO}_3$	Electrochemical oxidation of $\text{AgNO}_3$	This work
398	$3191 \pm 82$	8 M $\text{HNO}_3$	Electrochemical oxidation of $\text{AgNO}_3$	This work
400	$3614 \pm 57$	9 M $\text{HNO}_3$	Electrochemical oxidation of $\text{AgNO}_3$	This work

### Effect of $\text{HNO}_3$ concentration

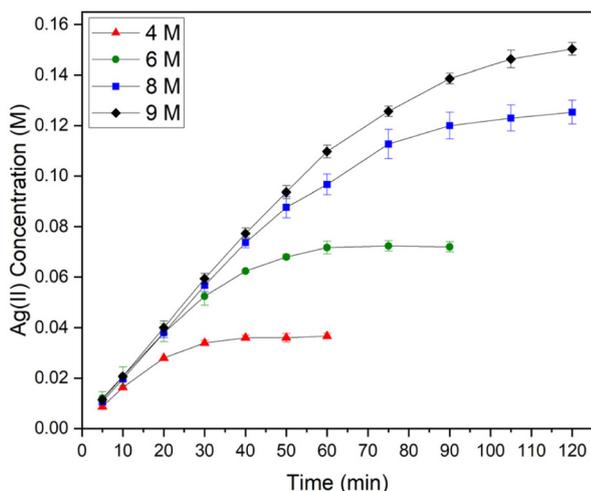
Oxidation of 0.5 M  $\text{AgNO}_3$  was carried out for up to 2 h at 25 °C, and the effect of  $\text{HNO}_3$  concentration on Ag(II) generation was studied. The H-cell was maintained at 2.5 V over this time, and the concentrations of  $\text{HNO}_3$  were 4, 6, 8, and 9 M. As shown in Fig. 3, the stability of Ag(II) in  $\text{HNO}_3$  increases with increasing acid concentration. The conversion of Ag(I) to Ag(II) increases at a steady state for 30 and 40 min at 4 and 6 M, respectively. It then reaches a maximum of 0.035 and 0.070 M Ag(II). The low conversion rates can be attributed to parasitic water oxidation, which is often seen at low acid concentrations. The conversion from Ag(I) to Ag(II) is much higher at 8 and 9 M  $\text{HNO}_3$  with a steady increase for approximately 70 min. The conversion rate at 9 M  $\text{HNO}_3$  reached an overall maximum, resulting in a concentration of 0.15 M Ag(II) at 120 min. This trend is similarly seen in the literature, where Matheswaran *et al.* reported the best conversion rate in 10 M  $\text{HNO}_3$ , with a maximum Ag(II) concentration of approximately 0.11 M after 60 min.<sup>15</sup> Overall, the Ag(II) ion is highly stabilized in higher concentrations of  $\text{HNO}_3$ , forming a stable nitrate complex.

### Effect of Ag(I) concentration

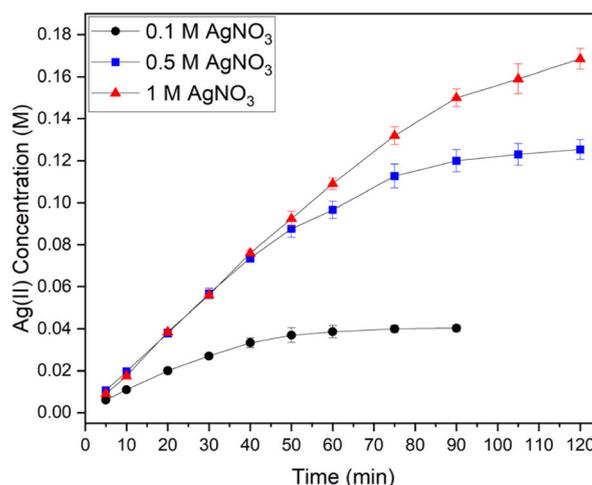
The electrochemical oxidation of  $\text{AgNO}_3$  at variable concentrations was carried out for up to 2 h in 8 M  $\text{HNO}_3$ . The H-cell was maintained at 2.5 V over this time at a constant temperature of 25 °C. The concentrations of Ag(I) were 0.1, 0.5, and 1 M, although the solubility of  $\text{AgNO}_3$  in 8 M  $\text{HNO}_3$  is limited above 1 M.

As shown in Fig. 4, the rate of Ag(II) formation increases with increasing Ag(I) concentration. The 0.1 M  $\text{AgNO}_3$  solution plateaus and yields a maximum Ag(II) concentration of only approximately 0.04 M after 90 min, whereas 0.5 and 1 M reach 0.12 and 0.17 M Ag(II) after 120 min, respectively. The oxidation rate for 0.5 and 1.0 M solutions is nearly identical during the first hours, suggesting that the process is initially mass-transport-limited. Beyond 60 min, the 1 M solution exhibits a slightly higher conversion, likely due to a larger reservoir of Ag(I) available for oxidation.

At longer reaction times, the apparent plateau in Ag(II) concentration may indicate a steady-state balance between the electrochemical generation and the concurrent chemical secondary reactions, such as disproportionation or solvent oxi-



**Fig. 3** Ag(II) formation as a function of  $\text{HNO}_3$  concentration over time. Conditions: initial  $\text{AgNO}_3$  stock = 0.5 M  $\text{AgNO}_3$  in variable  $\text{HNO}_3$  concentration, catholyte solution = 8 M  $\text{HNO}_3$ , temperature = 25 °C.



**Fig. 4** Ag(II) formation as a function of  $\text{AgNO}_3$  concentration over time. Conditions: initial  $\text{AgNO}_3$  stock = variable  $\text{AgNO}_3$  concentration in 8 M  $\text{HNO}_3$ , catholyte solution = 8 M  $\text{HNO}_3$ , temperature = 25 °C.



dation (*i.e.*, NO<sub>x</sub> formation), which become more competitive at higher mediator concentration.

### Effect of temperature

The oxidation of 0.5 M AgNO<sub>3</sub> was carried out for up to 2 h in 8 M HNO<sub>3</sub>, and the effect of temperature on Ag(II) generation was studied. The H-cell was maintained at 2.5 V over this time, and the temperatures studied were 25, 40, and 60 °C. As shown in Fig. 5, the stability of Ag(II) in HNO<sub>3</sub> substantially decreases with increasing temperature, and solutions heated to 60 °C rapidly show decoloration of the black Ag(II) species in solution.

At higher temperatures, the concentration of Ag(II) reduces from 0.12 to 0.02 M when increasing the anolyte temperature from 25 to 60 °C. This trend has been similarly observed in the literature and is attributed to the side reaction of water with Ag(II) at increased temperatures.<sup>15</sup> The experimental data show that temperature has a strong deleterious effect on the stability of Ag(II) in HNO<sub>3</sub>. In other words, the concentration decays more rapidly at elevated temperature, and the plateau in Ag(II) concentration is reached sooner. Rance *et al.* report that the reaction order with respect to Ag(II) decreases at higher temperature, which is consistent with an increased rate of chemical decay, possibly from disproportionation or water/solvent oxidation acceleration.<sup>35</sup>

The speculation that higher temperature might lead to the formation of hydroxyl radicals (<sup>•</sup>OH) arises because Ag(II) is a powerful oxidant, and analogous systems in other acid systems [*e.g.*, Ag(II) in H<sub>2</sub>SO<sub>4</sub>] are known to oxidize anions or solvent components in a radical-type reaction.<sup>36</sup> However, we have thus far found no direct literature evidence that Ag(II) in HNO<sub>3</sub> under mild to moderate temperatures forms <sup>•</sup>OH radicals in measurable yields. Therefore, the statement that radical formation increases the mineralization efficiency must be treated

carefully. It may be true, if organic substrates are present, that radicals generated by side reactions help destroy organics. However, in purely Ag(II) stability experiments, one should not assume <sup>•</sup>OH generation is absent, corroborating radical probe evidence. Although <sup>•</sup>OH formation has been discussed as a possible decomposition pathway for Ag(II), it is not the only radical process relevant in concentrated nitric acid. Ag(II) possesses a very high oxidation potential ( $\approx 2.0$ – $2.3$  V depending on medium) and in strongly oxidizing nitrate environments it can also oxidize NO<sub>3</sub><sup>−</sup> to yield NO<sub>3</sub><sup>•</sup>, which can further participate in subsequent reactions forming NO<sub>2</sub><sup>•</sup>, NO<sup>•</sup> and other nitrogen–oxide radicals. These species have been observed in related high-potential Ag(II) systems and are consistent with the elevated redox potentials reported for Ag(II) in strongly oxidizing media up to 2.9 V.<sup>37</sup>

Therefore, the decay of Ag(II) at elevated temperatures likely involves not only hydration or <sup>•</sup>OH-generating pathways but also nitrate-radical-driven channels, which can accelerate Ag(II) loss and contribute to NO<sub>x</sub> formation in the system.

## Conclusions

HNO<sub>3</sub> solutions of Ag(I) were electrochemically oxidized to Ag(II) using an H-cell separated by a Nafion membrane. The quantification of Ag(II) was successfully determined by titration methods. Comparisons of Ce titrations with KMnO<sub>4</sub> back-titrations resulted in a similar concentrations of Ag(II) from 2–9 M HNO<sub>3</sub>. The calculated concentrations of Ag(II) were found to be consistently higher with KMnO<sub>4</sub> back-titrations because of competing HNO<sub>3</sub> oxidation. Ce redox titrations were used to calculate the concentration of Ag(II) and determine the molar extinction coefficients from 2–9 M HNO<sub>3</sub> media. The resultant extinction coefficients track well with previous data, and we have expanded the data out to 9 M HNO<sub>3</sub>.

The results collectively show that the electrochemical formation and stability of Ag(II) are strongly governed by HNO<sub>3</sub> concentration, Ag(I) loading, and temperature. Increasing acid concentration enhances Ag(II) yield and persistence through nitrate complexation, which suppresses disproportionation and solvent oxidation. In contrast, higher temperature accelerates both decomposition pathways—Ag(II) disproportionation to Ag(I)/Ag(III) and oxidation of water or HNO<sub>3</sub>—resulting in rapid loss of the oxidized species. Ag(I) concentration affects the attainable Ag(II) level but becomes limited once the system reaches a steady state between generation and decay.

The determination of a suitable titration quantification method of Ag(II) allowed for gathering extinction coefficients in HNO<sub>3</sub> solutions up to 9 M. These data can be used to eventually monitor the electrooxidation of Ag(II) in MEO processes that use Ag as a mediator. Overall, the interplay of electrochemical generation and chemical decay determines the observable Ag(II) concentration, and the results emphasize that maintaining high acid strength and moderate temperature is critical for maximizing mediator efficiency in MEO systems. We are continuing our investigations into Ag(II) parameter

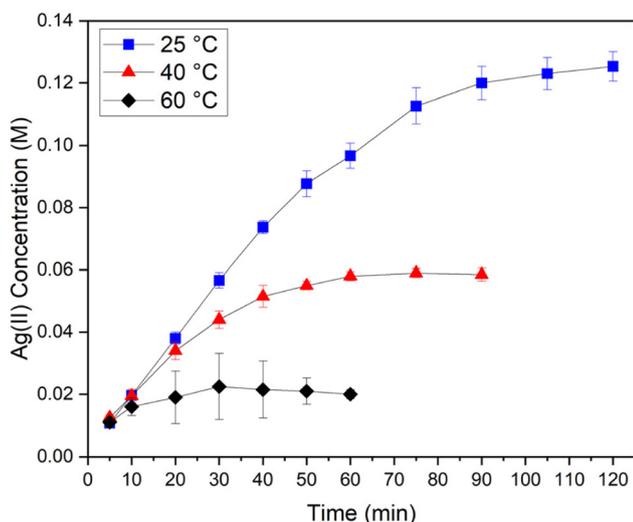


Fig. 5 Ag(II) formation as a function of temperature over time. Conditions: initial AgNO<sub>3</sub> stock = 0.5 M AgNO<sub>3</sub> in 8 M HNO<sub>3</sub>, catholyte solution = 8 M HNO<sub>3</sub>, variable temperature.



optimization and using the data to continue MEO studies for the mineralization of organic substrates.

## General information

### Materials

AgNO<sub>3</sub> (99.9%, Thermo Scientific Chemicals) was used to prepare the Ag(II) stock solutions used in this work. Ce(NO<sub>3</sub>)<sub>3</sub> (99.5%, Thermo Scientific Chemicals), HNO<sub>3</sub> (trace metal grade, Fisher Chemical), KMnO<sub>4</sub> (0.1 N standardized solution, Thermo Scientific Chemicals), and (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (certified, 0.100 N ± 0.006 N [0.1 M], LabChem) were used without further purification.

### Electrochemical setup

The electrochemical oxidation of Ag was carried out in a custom-built H-cell. The compartments accommodate 250 mL in both the anolyte and catholyte chambers and were kept separate by a proton exchange membrane (Nafion 117). Pt-coated Ti mesh and a Pt-coated Ti rod were used as the anode and cathode, respectively. All experiments were conducted with the H-cell under constant voltage (2.5 V) using a Multicomp Pro DC power supply (0–30 V/0–30 A). The anolyte solution was continuously stirred on a stir/hot plate using a magnetic stir bar, and the temperature of the anolyte solution was monitored with a thermometer. The catholyte solution was equipped with an air bubbler to regenerate HNO<sub>2</sub> to HNO<sub>3</sub>.

### Ag(II) quantification titrations

The concentration of Ag(II) was determined through two redox titration methods. A Mettler Toledo Titrator Excellence T5 equipped with a Pt-Ring Sensor DMi140-SC electrode was used for all Ce redox titrations. Aliquots of Ag(II) from experiments were immediately reacted with a 0.1 M stock solution of Ce(NO<sub>3</sub>)<sub>3</sub> in 2 M HNO<sub>3</sub> in a glass titration beaker. The resultant Ce(IV) was titrated using a standard ferrous ammonium sulfate solution. Back titrations with (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O were conducted with a standard burette. Aliquots of Ag(II) from experiments were immediately reacted with an excess of standard (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O to quench the Ag(II). The samples were diluted with water, and the excess Fe(II) was titrated with a standard KMnO<sub>4</sub> solution within 2 min of pulling samples. In titration experiments comparing Ce titrations with KMnO<sub>4</sub> back-titrations, a stock solution of 0.1 M AgNO<sub>3</sub> in HNO<sub>3</sub> was oxidized at 2.5 V for 40 min. After this time, aliquots of Ag(II) were sampled and simultaneously titrated using both methods to conduct a comparative analysis. All experiments were performed in triplicate. Standard deviations are reported in SI. Strict control over glassware dryness, sample transfer times (<2 min), and rapid titration minimized Ag(II) decomposition, resulting in high reproducible datasets. The level of repeatability demonstrates the feasibility and robustness of the combined electrochemical-analytical workflow presented here.

### Extinction coefficient measurements

All UV–vis measurements were taken using a Cary 6000 spectrophotometer. A stock solution of 0.1 M AgNO<sub>3</sub> in HNO<sub>3</sub> was electrochemically oxidized using the H-cell to form Ag(II). Great care was taken to dry all cuvettes and glassware before measurements. Aliquots of Ag(II) were pipetted from the H-cell and minimally diluted to reduce reaction with the solvent. Samples were transferred with dry glass pipettes, and the absorbance measurement was collected. UV–vis measurements were done in conjunction with Ce redox titrations within 2 min to determine the concentration of Ag(II). All measurements were performed in triplicate.

### Ag(II) formation studies

The formation of Ag(II) as a function of HNO<sub>3</sub> concentration, temperature, and AgNO<sub>3</sub> concentration was determined by electrochemically oxidizing a AgNO<sub>3</sub> solution and taking aliquots of the sample at various time points. The aliquots were immediately titrated using the Ce redox titration method.

## Author contributions

Briana Schrage: Conceptualization, methodology, data curation, supervision, visualization, writing – original draft preparation. Joshua Leach: Data curation, investigation. Ethan Villarreal: Data curation, investigation. Jisue Braatz: Formal analysis, writing – review and editing. Kristian Myhre: Writing – review and editing, funding acquisition, supervision.

## Conflicts of interest

There are no conflicts to declare.

## Note

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## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5dt02733k>.



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