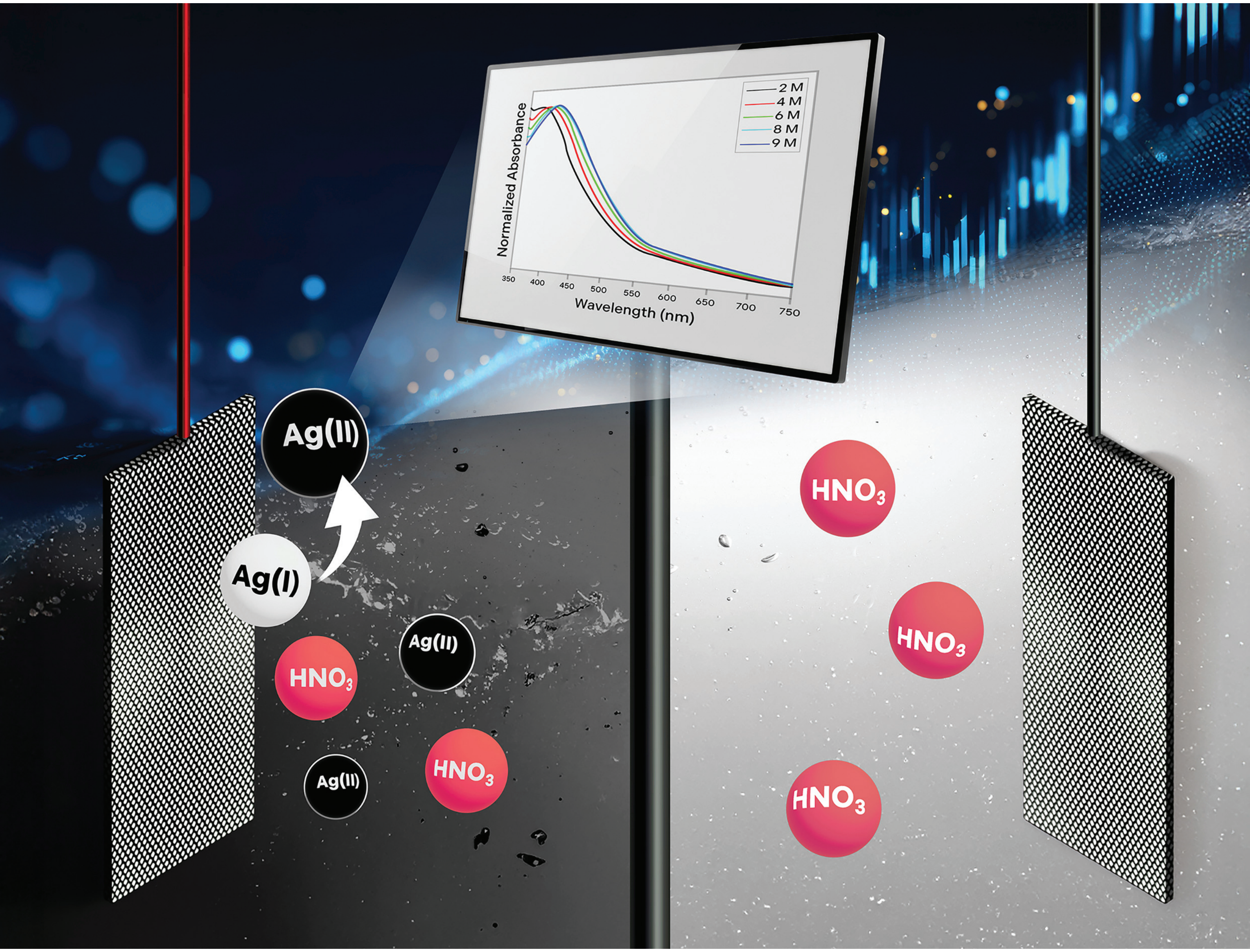
Volume 55
Number 2
13 January 2026
Pages 525-994

Dalton Transactions

An international journal of inorganic chemistry

rsc.li/dalton



ISSN 1477-9226

ROYAL SOCIETY
OF **CHEMISTRY**

PAPER
Briana R. Schrage *et al.*
Optimization and quantification of silver(II) for mediated electrochemical oxidation applications

Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Dalton Trans.*, 2026, **55**, 586

Received 13th November 2025,
Accepted 8th December 2025

DOI: 10.1039/d5dt02733k

rsc.li/dalton

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

Briana R. Schrage, *[a] Joshua E. Leach,[b] Ethan Villarreal,[c] Jisue Braatz[a] and Kristian G. Myhre[a]

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_3 solution. The optimization of Ag(II) electrooxidation was also determined by altering parameters such as HNO_3 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_2. 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,[1–3] wastewater streams,[4–6] and hazardous mixed waste.[7–9]

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,[8,10–15] Ce,[12,13,16–20] Co,[21–23] Fe,[1] Mn,[24] and Ru couples.[25] 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.[3,8,18]

The most notable demonstration of this technology for organic waste destruction is the cerium oxidation CEROX™ process developed and piloted by Nelson *et al.*[18,26] 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 ($E°$ = 1.98 V), surpassing that of Co(III) ($E°$ = 1.84 V), and Ce(IV) ($E°$ = 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

---

[a] *Radioisotope Science and Technology Division, Oak Ridge National Laboratory, 1 Bethel Valley Rd., Oak Ridge, Tennessee 37830, USA*
[b] *Department of Chemistry, Tennessee Technological University, Cookeville, Tennessee 38505, USA*
[c] *Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, Virginia 23284, USA*

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

A key challenge in working with the Ag(II)/Ag(I) system is the difficulty in monitoring Ag(II) concentrations in real time during the oxidation process. The Ag(I) precursor exhibits negligible absorbance in the ultraviolet–visible (UV–vis) region, and the oxidized Ag(II) form in HNO_3 is darkly colored with a characteristic UV–vis absorption. However, because of the strong oxidizing nature and instability of Ag(II), reliable determination of its molar extinction coefficient in solution is difficult. The quantification of Ag(II) in solution requires reliant and precise titration methods working in tandem with UV–vis measurements. Although some prior studies have reported extinction coefficients under varying HNO_3 concentrations, the extinction coefficient values only covered segmented 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 Ag(II) in HNO_3. The molar extinction coefficients of Ag(II) were determined in a wide range of 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 Ag(II) generation as a function of temperature, Ag(I) concentration, and HNO_3 concentration. The optimized conditions reported here provide the quantitative framework required for implementing 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 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 Ag(II) in 2–9 M HNO_3, measured with higher precision than previous reports; (ii) it presents a rigorous comparison of two Ag(II) quantification methods establishing a reliable analytical basis for real time Ag(II) monitoring; and (iii) it offers a systematic evaluation of the parameters controlling Ag(II) electrochemical generation, which is crucial for process optimization in future MEO applications.

Results and discussion

Electrooxidation of Ag(I) and quantification

Stock solutions of $AgNO_3$ were electrochemically oxidized in a glass H-cell to generate Ag(II) ions. The oxidized Ag(II) ion exhibits a characteristic dark brown to black color and is moderately stable in 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 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 Ag(II) remains a critical step in evaluating its stability and reactivity. Direct titration of Ag(II) is the most described method in the literature.[27,28] Direct titrations of Ag(II) in 2 M HNO_3 rely on the disappearance of the brown/black color as Ag(II) is reduced to Ag(I) in the presence of direct reducing agents ($H_2C_2O_4$, H_2O_2, and VO_2^+).[27] In previous literature studies,[28] the visual end point for direct titrations is challenging, so two back-titration methods were employed to quantify Ag(II).

To combat the challenges of direct titrations, two back-titration methods were studied and compared in this work. The $FeSO_4$ titrations for the quantification of Ag(II) were first performed by Noyes *et al.*[29] Samples of Ag(II) were quenched with an excess of $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ and titrated with $KMnO_4$. 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 Fe(II) ion occurred during the titration.

The second back-titration method employed in this study was a Ce potentiometric titration. Samples of Ag(II) were reacted with Ce(III), and the resultant Ce(IV) was potentiometrically titrated with standard Fe(II). Comparisons of $FeSO_4$ and Ce back-titrations are shown in Fig. 1. The two titration

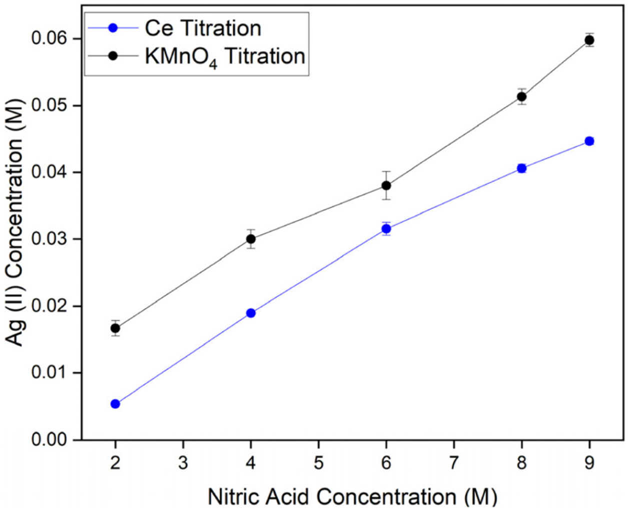


Fig. 1 Acid-dependent Ag(II) concentrations titrated with (blue) Ce redox titrations compared with (black) $KMnO_4$ back-titrations. Conditions: initial $AgNO_3$ stock = 0.1 M $AgNO_3$ in variable-molarity HNO_3, catholyte solution = 8 M HNO_3. The system was electrochemically oxidized for 40 min before aliquots were taken.

methods were performed on electrochemically generated samples of Ag(II), and aliquots were analyzed simultaneously through both methods in triplicate. The $KMnO_4$ back-titrations consistently resulted in a higher concentration of Ag(II) compared with the Ce titrations across the HNO_3 concentration range. Typically, $KMnO_4$ redox titrations are performed in solutions containing H_2SO_4, and the HNO_3 medium causes competing redox reactions with $KMnO_4$. HNO_3 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_3 is shown in Fig. 2. $AgNO_3$ 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.[30,31] Additionally, a bathochromic shift in the wavelength was observed because of increasing HNO_3 concentration caused by increasing complexation with nitrate ions [*e.g.*, $Ag(NO_3)_4{}^{2-}$].[15] The increase in molar absorptivity with HNO_3, 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_3, the enhanced ε 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.[32,33]

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_3 medium using spectroscopy measurements taken simultaneously with Ce titrations.[28,30,32,34] The same methodology was applied here, and the data have been extended up to 9 M HNO_3 as attempts to calculate extinction coefficients at 10 M HNO_3 resulted in inconsistent titration results due to competing nitric acid oxidation (Fig. 2).

Previous literature reports extinction coefficient values in HNO_3 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.[30,32,34] In this work, the trend of increasing extinction coefficient with increasing HNO_3 concentration is confirmed. The data follows a linear trend up to 9 M HNO_3 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_3 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 $Ag_6O_8{}^+$ 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.

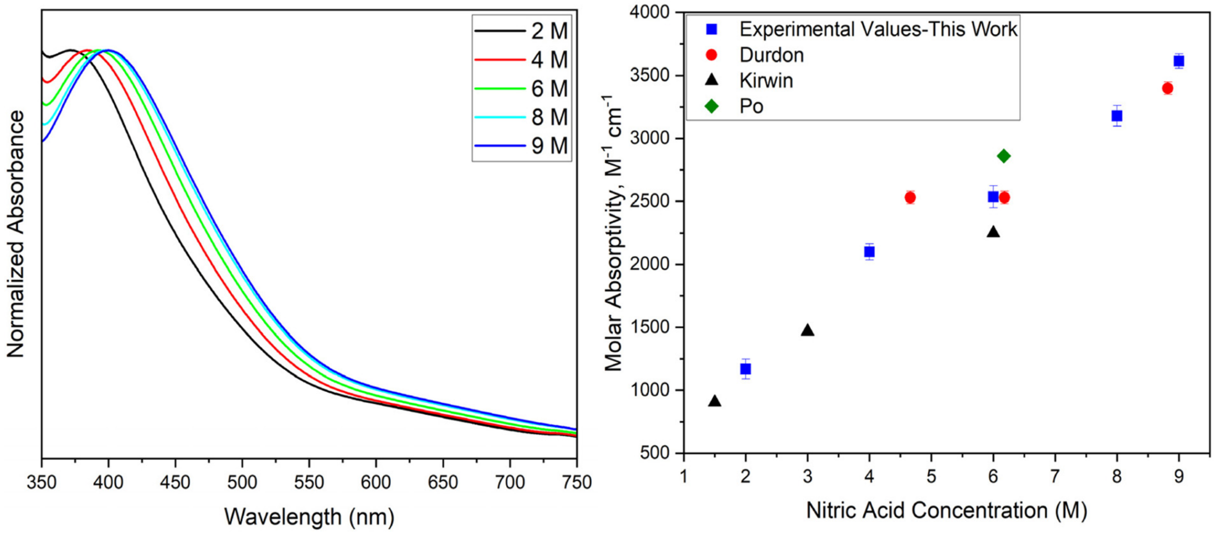


Fig. 2 (Left) The normalized absorption spectrum of Ag(II) in varying HNO_3 medium. (Right) A comparison of molar absorptivity values between this work and literature values.

Table 1 Comparison of wavelengths (nm) and extinction coefficients (M^{-1} cm^{-1}) for Ag(II) in HNO_3 medium

Wavelength (nm)	Extinction coefficient (M^{-1} cm^{-1})	Conditions	Ag(II) source	Ref.
390	2860 ± 50	6.17 M HNO_3	Dissolution of AgO	Po (1967)[32]
394	2530 ± 50	4.66 and 6.18 M HNO_3	Ozonolysis of $AgNO_3$	Dundon (1966)[34]
394	3400	8.82 M HNO_3	Ozonolysis of $AgNO_3$	Dundon (1966)[34]
NA	~900	1.5 M HNO_3	Ozonolysis of $AgNO_3$	Kirwin (1963)[30]
NA	~1450	3 M HNO_3	Ozonolysis of $AgNO_3$	Kirwin (1963)[30]
NA	~2250	6 M HNO_3	Ozonolysis of $AgNO_3$	Kirwin (1963)[30]
372	1171 ± 79	2 M HNO_3	Electrochemical oxidation of $AgNO_3$	This work
384	2100 ± 64	4 M HNO_3	Electrochemical oxidation of $AgNO_3$	This work
392	2537 ± 87	6 M HNO_3	Electrochemical oxidation of $AgNO_3$	This work
398	3191 ± 82	8 M HNO_3	Electrochemical oxidation of $AgNO_3$	This work
400	3614 ± 57	9 M HNO_3	Electrochemical oxidation of $AgNO_3$	This work

Effect of HNO_3 concentration

Oxidation of 0.5 M $AgNO_3$ was carried out for up to 2 h at 25 °C, and the effect of 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 HNO_3 were 4, 6, 8, and 9 M. As shown in Fig. 3, the stability of Ag(II) in 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 HNO_3 with a steady increase for approximately 70 min. The conversion rate at 9 M 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 HNO_3, with a maximum Ag(II) concentration of approximately 0.11 M after 60 min.[15] Overall, the Ag(II) ion is highly stabilized in higher concentrations of HNO_3, forming a stable nitrate complex.

Effect of Ag(I) concentration

The electrochemical oxidation of $AgNO_3$ at variable concentrations was carried out for up to 2 h in 8 M 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 $AgNO_3$ in 8 M 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 $AgNO_3$ 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-

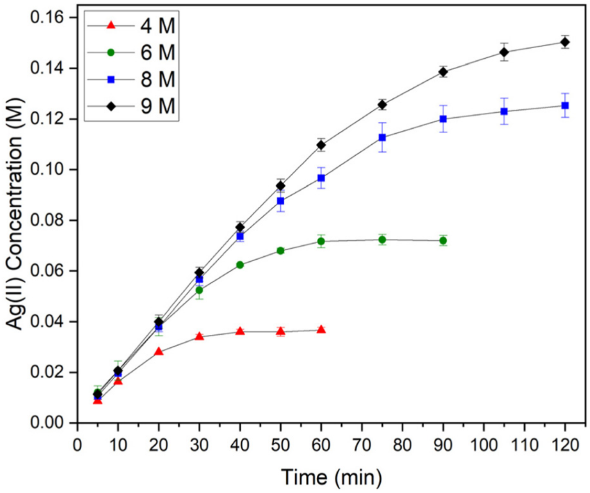


Fig. 3 Ag(II) formation as a function of HNO_3 concentration over time. Conditions: initial $AgNO_3$ stock = 0.5 M $AgNO_3$ in variable HNO_3 concentration, catholyte solution = 8 M HNO_3, temperature = 25 °C.

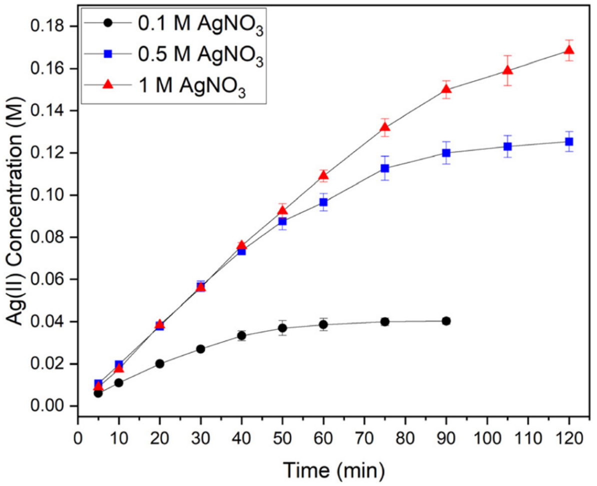


Fig. 4 Ag(II) formation as a function of $AgNO_3$ concentration over time. Conditions: initial $AgNO_3$ stock = variable $AgNO_3$ concentration in 8 M HNO_3, catholyte solution = 8 M HNO_3, temperature = 25 °C.

dation (*i.e.*, NO_x formation), which become more competitive at higher mediator concentration.

Effect of temperature

The oxidation of 0.5 M $AgNO_3$ was carried out for up to 2 h in 8 M HNO_3, 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_3 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.[15] The experimental data show that temperature has a strong deleterious effect on the stability of Ag(II) in HNO_3. 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.[35]

The speculation that higher temperature might lead to the formation of hydroxyl radicals ($^{\bullet}OH$) arises because Ag(II) is a powerful oxidant, and analogous systems in other acid systems [*e.g.*, Ag(II) in H_2SO_4] are known to oxidize anions or solvent components in a radical-type reaction.[36] However, we have thus far found no direct literature evidence that Ag(II) in HNO_3 under mild to moderate temperatures forms $^{\bullet}OH$ 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 $^{\bullet}OH$ generation is absent, corroborating radical probe evidence. Although $^{\bullet}OH$ 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 (≈2.0–2.3 V depending on medium) and in strongly oxidizing nitrate environments it can also oxidize NO_3^- to yield $NO_3^{\bullet}$, which can further participate in subsequent reactions forming $NO_2^{\bullet}$, $NO^{\bullet}$ 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.[37]

Therefore, the decay of Ag(II) at elevated temperatures likely involves not only hydration or $^{\bullet}OH$-generating pathways but also nitrate-radical-driven channels, which can accelerate Ag(II) loss and contribute to NO_x formation in the system.

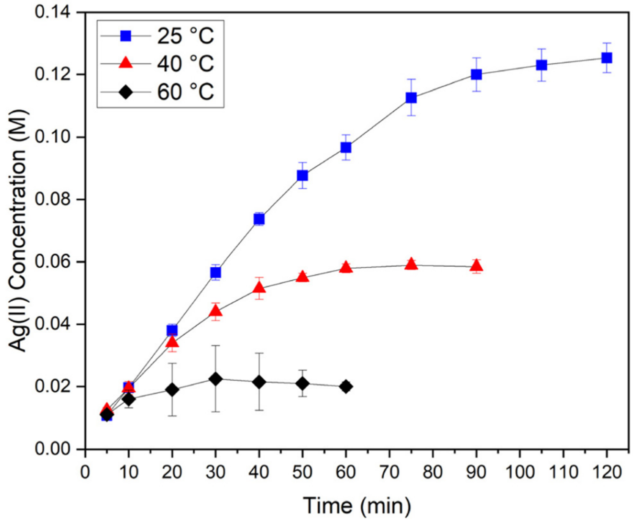


Fig. 5 Ag(II) formation as a function of temperature over time. Conditions: initial $AgNO_3$ stock = 0.5 M $AgNO_3$ in 8 M HNO_3, catholyte solution = 8 M HNO_3, variable temperature.

Conclusions

HNO_3 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 $KMnO_4$ back-titrations resulted in a similar concentrations of Ag(II) from 2–9 M HNO_3. The calculated concentrations of Ag(II) were found to be consistently higher with $KMnO_4$ back-titrations because of competing HNO_3 oxidation. Ce redox titrations were used to calculate the concentration of Ag(II) and determine the molar extinction coefficients from 2–9 M HNO_3 media. The resultant extinction coefficients track well with previous data, and we have expanded the data out to 9 M HNO_3.

The results collectively show that the electrochemical formation and stability of Ag(II) are strongly governed by HNO_3 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_3—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_3 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 optimization and using the data to continue MEO studies for the mineralization of organic substrates.

General information

Materials

$AgNO_3$ (99.9%, Thermo Scientific Chemicals) was used to prepare the Ag(II) stock solutions used in this work. $Ce(NO_3)_3$ (99.5%, Thermo Scientific Chemicals), HNO_3 (trace metal grade, Fisher Chemical), $KMnO_4$ (0.1 N standardized solution, Thermo Scientific Chemicals), and $(NH_4)_2Fe(SO_4)_2·6H_2O$ (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_2 to HNO_3.

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 $Ce(NO_3)_3$ in 2 M HNO_3 in a glass titration beaker. The resultant Ce(IV) was titrated using a standard ferrous ammonium sulfate solution. Back titrations with $(NH_4)_2Fe(SO_4)_2·6H_2O$ were conducted with a standard burette. Aliquots of Ag(II) from experiments were immediately reacted with an excess of standard $(NH_4)_2Fe(SO_4)_2·6H_2O$ to quench the Ag(II). The samples were diluted with water, and the excess Fe(II) was titrated with a standard $KMnO_4$ solution within 2 min of pulling samples. In titration experiments comparing Ce titrations with $KMnO_4$ back-titrations, a stock solution of 0.1 M $AgNO_3$ in HNO_3 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 $AgNO_3$ in HNO_3 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_3 concentration, temperature, and $AgNO_3$ concentration was determined by electrochemically oxidizing a $AgNO_3$ 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

This manuscript has been authored by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (https://www.energy.gov/doe-public-access-plan).

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.

Acknowledgements

Funding for this program was provided by the National Aeronautics and Space Administration's Science Mission Directorate and administered by the US Department of Energy Office of Nuclear Energy under contract DEAC05-00OR22725. Adam Parkison: Program manager, Funding acquisition.

References

1 R. G. Hickman, J. C. Farmer and F. T. Wang, Mediated Electrochemical Process for Hazardous Waste Destruction, in *Emerging Technologies in Hazardous Waste Management III*, American Chemical Society, 1993, vol. 518, pp. 430–438. DOI: 10.1021/bk-1993-0518.ch021.

2 J. Bringmann, K. Ebert, U. Galla and H. Schmieder, Electrochemical Mediators for Total Oxidation of Chlorinated Hydrocarbons: Formation Kinetics of Ag(II), Co (III), and Ce(IV), *J. Appl. Electrochem.*, 1995, **25**(9), 846–851, DOI: 10.1007/BF00772203.

3 D. Steele, Electrochemical Destruction of Toxic Organic Industrial Waste, *Platinum Met. Rev.*, 1990, **34**(1), 10–14.

4 C. Zhang, Z. Yu and X. Wang, A Review of Electrochemical Oxidation Technology for Advanced Treatment of Medical Wastewater, *Front. Chem.*, 2022, **10**, 1002038.

5 M. S. Najafinejad, S. Chianese, A. Fenti, P. Iovino and D. Musmarra, Application of Electrochemical Oxidation for Water and Wastewater Treatment: An Overview, *Molecules*, 2023, **28**(10), 4208.

6 National Research Council, Division on Engineering, Physical Sciences, Commission on Engineering, Technical Systems, Panel on Review, Evaluation of Alternative Chemical Disposal Technologies, *Review and Evaluation of Alternative Chemical Disposal Technologies*, National Academies Press, 1996.

7 J. Surma, *Electrochemical Oxidation of Chemical Weapons*, Pacific Northwest National Lab.(PNNL), Richland, WA (United States), 1994.

8 A. D. Turner, Organics Destruction Using the SILVER II Process, *Membr. Technol.*, 2002, **2002**(2), 6–12, DOI: 10.1016/S0958-2118(02)80092-1.

9 G. Pillay, S. R. Billingsley and J. J. Balkey, Electrochemical Treatment and Minimization of Defense-Related Wastes, *Fed. Facil. Environ. J.*, 2000, **11**(2), 115–127, DOI: 10.1002/ffej.3330110212.

10 M. Umeda and S. Sugikawa, *Waste Treatment in NUCEF Facility with Silver Mediated Electrochemical Oxidation Technique*, 2000.

11 A. C. Almon and B. R. Buchanan, Electrolytic Destruction of Spent Tributylphosphate Extractant Using Silver Catalyzed Electrochemical Oxidation, in *Report Number: WSRC-MS-90-123; CONF-,900977-7*, Research Org., Westinghouse Savannah River Co., Aiken, SC (USA), 1990.

12 M. Matheswaran, S. Balaji, S. J. Chung and I. S. Moon, Silver Ion Catalyzed Cerium(IV) Mediated Electrochemical Oxidation of Phenol in Nitric Acid Medium, *Electrochim. Acta*, 2007, **53**(4), 1897–1901, DOI: 10.1016/j.electacta.2007.08.042.

13 W. Smith, G. Purdy and S. McKee, *Comparison of Silver(II), Cobalt(III), and Cerium(IV) as Electron Transfer Mediators in the MEO Mixed Waste Treatment Process*, Los Alamos National Lab. (LANL), Los Alamos, NM (United States), 1997.

14 J. C. Farmer, F. T. Wang, R. A. Hawley-Fedder, P. R. Lewis, L. J. Summers and L. Foiles, Electrochemical Treatment of Mixed and Hazardous Wastes: Oxidation of Ethylene Glycol and Benzene by Silver(II), *J. Electrochem. Soc.*, 1992, **139**(3), 654–654, DOI: 10.1149/1.2069280.

15 M. Matheswaran, S. Balaji, S. J. Chung and I. S. Moon, Mediated Electrochemical Oxidation of Phenol in Continuous Feeding Mode Using Ag(II) and Ce(IV) Mediator Ions in Nitric Acid: A Comparative Study, *Chem. Eng. J.*, 2008, **144**(1), 28–34, DOI: 10.1016/j.cej.2008.01.005.

16 S. Balaji, S. J. Chung, R. Thiruvenkatachari and I. S. Moon, Mediated Electrochemical Oxidation Process: Electro-Oxidation of Cerium(III) to Cerium(IV) in Nitric Acid Medium and a Study on Phenol Degradation by Cerium(IV) Oxidant, *Chem. Eng. J.*, 2007, **126**(1), 51–57, DOI: 10.1016/j.cej.2006.05.021.

17 K. Dixit and R. Varma, Kinetics of Oxidation of Quinol by Cerium(IV), *J. Indian Chem. Soc.*, 1991, **68**(3), 161–162.

18 N. Nelson, Electrochemical Destruction of Organic Hazardous Wastes: The Cerium Oxidation Cerox$^{\text{TM}}$ Process Electrochemical Cell, *Platinum Met. Rev.*, 2002, **46**(1), 18–23.

19 R. M. Spotnitz, R. P. Kreh, J. T. Lundquist and P. J. Press, Mediated Electrosynthesis with Cerium(IV) in Methanesulphonic Acid, *J. Appl. Electrochem.*, 1990, **20**(2), 209–215, DOI: 10.1007/BF01033596.

20 N. Palanisami, S. J. Chung and I. S. Moon, Cerium(IV)-Mediated Electrochemical Oxidation Process for Removal of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans, *J. Ind. Eng. Chem.*, 2015, **28**, 28–31, DOI: 10.1016/j.jiec.2014.10.047.

21 J. C. Farmer, F. T. Wang, P. R. Lewis and L. J. Summers, Destruction of Chlorinated Organics by Cobalt(III)-Mediated Electrochemical Oxidation, *J. Electrochem. Soc.*, 1992, **139**(11), 3025–3025, DOI: 10.1149/1.2069027.

22 Y. Shen, Z. Yan and K. Wang, Cobalt(II) Mediated Electro-Oxidation of Toluene and Its Derivatives, *Chem. Eng. J.*, 2024, **488**, 150857.

23 R. A. Lubis, H. H. Bahti, I. Hastiawan and D. Mulcahy, Optimization in Mediated Electrochemical Oxidation Using Cobalt Sulfate as a Mediator, *Procedia Chem.*, 2015, **17**, 153–156.

24 H. Zhang and S.-M. Park, Kinetic Studies on the Oxidation of Cellulose and Its Model Compounds by Mn(III), *Carbohydr. Res.*, 1995, **266**(1), 129–142, DOI: 10.1016/0008-6215(94)00259-I.

25 L. Davidson, Y. Quinn and D. F. Steele, Ruthenium-Mediated Electrochemical Destruction of Organic Wastes, *Platinum Met. Rev.*, 1998, **42**(3), 90–98.

26 J. A. Varela, S. G. Oberg, T. M. Neustedter and N. Nelson, Non-Thermal Organic Waste Destruction: Characterization of the CerOx System 4, *Environ. Prog.*, 2001, **20**(4), 261–271, DOI: 10.1002/ep.670200415.

27 A. A. Noyes, C. D. Coryell, F. Stitt and A. Kossiakoff, Argentic Salts in Acid Solution. IV. The Kinetics of the Reduction by Water and the Formation by Ozone of Argentic Silver in Nitric Acid Solution1, *J. Am. Chem. Soc.*, 1937, **59**(7), 1316–1325.

28 V. Van Alsenoy, *Progress Report on the Analytical Determination of Ag, 2+*, Centre de l'Etude de l'Energie Nucleaire, 1997.

29 A. A. Noyes and A. Kossiakoff, Argentic Salts in Acid Solution. III. Oxidation Potential of Argentous—Argentic Salts in Nitric Acid Solution, *J. Am. Chem. Soc.*, 1935, **57**(7), 1238–1242.

30 J. Kirwin, F. Peat, P. Proll and L. Sutcliffe, A Kinetic and Spectrophotometric Examination of Silver(II) in Perchlorate Media, *J. Phys. Chem.*, 1963, **67**(8), 1617–1621.

31 J. Spessard, Spectra of Ions with 9d Electrons—I: Spectra of Copper(II) and Silver(II) in Perchloric, Nitric, Sulfuric, and Phosphoric Acid Media, *Spectrochim. Acta, Part A*, 1969, **25**(4), 731–748.

32 H. N. Po, J. H. Swinehart and T. L. Allen, Kinetics and Mechanism of the Oxidation of Water by Silver(II) in Concentrated Nitric Acid Solution, *Inorg. Chem.*, 1968, **7**(2), 244–249.

33 W. Grochala and Z. Mazej, Chemistry of Silver(II): A Cornucopia of Peculiarities, *Philos. Trans. R. Soc., A*, 2015, **373**(2037), 20140179.

34 R. W. Dundon and J. W. Gryder, The Kinetics of the Silver (II)-Thallium(I) Reaction in Nitric Acid, *Inorg. Chem.*, 1966, **5**(6), 986–989.

35 P. Rance, G. Nikitina, V. Korolev, M. Y. Kirshin, A. Listopadov and V. Egorova, Features of Electrolysis of Nitric Acid Solutions of Silver: I. Behavior of Ag(II) in HNO_3 Solutions, *Radiochemistry*, 2003, **45**(4), 346–352.

36 P. Połczyński, R. Jurczakowski and W. Grochala, Strong and Long-Lived Free-Radical Oxidizer Based on Silver(II). Mechanism of Ag(I) Electrooxidation in Concentrated H_2SO_4, *J. Phys. Chem. C*, 2013, **117**(40), 20689–20696, DOI: 10.1021/jp406442j.

37 P. Połczyński, R. Jurczakowski and W. Grochala, Stabilization and Strong Oxidizing Properties of Ag(II) in a Fluorine-Free Solvent, *Chem. Commun.*, 2013, **49**(68), 7480–7482, DOI: 10.1039/C3CC43072C.