

Influence of iron and cobalt on oxalic acid degradation during underwater non-thermal plasma treatment of simulated chemical decontamination effluents

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Abstract

Underwater nonthermal plasma treatment was compared across four simulated decontamination effluents containing oxalic acid and different iron and cobalt additions, using one batch per composition. Ion chromatography (IC) and ultraviolet-visible spectroscopy tracked oxalate and optical responses. The Fe-only batch retained 42.2 mg L⁻¹ IC-detectable oxalate after 60 min (79.5% of its measured initial value), with persistent near-ultraviolet absorption; the other three compositions reached below 1 mg L⁻¹ at 20 or 30 min. Ferrozine-treated aliquots showed qualitative assay colour responses. These comparisons support considering solution composition and residual optical response alongside IC results when assessing treatment.

Introduction

Chemical decontamination removes oxide films and associated radionuclides from nuclear-system components [1, 2]. Oxalic acid is used to dissolve corrosion products in processes such as chemical oxidation reduction decontamination, but residual oxalate and dissolved metals complicate subsequent waste treatment [3, 4]. Oxalate destruction therefore needs to be evaluated in the presence of the metals released during decontamination. Stable Fe and Co provide chemical surrogates for examining these solution-phase interactions under non-radioactive conditions.

Advanced oxidation treatments offer several routes for organic-acid destruction [5, 6]. Electrical discharges in water or gas bubbles can generate reactive species and radiation that participate in aqueous oxidation [7–10]. We previously investigated oxalic acid mineralisation in a multihole dielectric-barrier-discharge (MH-DBD) reactor using IC and total organic carbon (TOC) measurements together with ¹³C tracing [11]. Carbon conversion in metal-containing solutions requires separate assessment because complexation, precipitation and oxidant reactions may alter both treatment and analytical response.

Iron-oxalate chemistry is particularly relevant because Fe(III) forms oxalato complexes [12] that undergo photochemical reactions involving iron reduction and ligand oxidation [13–15]. Iron also participates in oxidant activation and consumption. These competing processes motivate joint examination of oxalate concentration and optical response during plasma treatment. Cobalt addition changes both metal composition and chloride concentration, making the overall solution composition an important basis for comparing the treatment profiles.

Four 1-L batches with the same oxalic acid addition and different Fe(III) and Co(II) additions were compared using ion chromatography (IC) and ultraviolet-visible (UV-Vis) spectroscopy. Ferrozine-treated aliquots [16] were used to qualitatively explore possible Fe(III)/Fe(II) interconversion associated with plasma-generated species. IC-detectable oxalate profiles and optical responses were compared across metal-free, Co-only, mixed Fe-Co and Fe-only solutions, with one batch per formulation.

Table 1
Composition of the four solutions calculated from reagent additions; every solution received 100 mg L⁻¹ (1.11 mmol L⁻¹) oxalic acid. Ox denotes the molar amount of oxalic acid added

Solution	Metal salts (mg L⁻¹)	Fe / Co (mmol L⁻¹)	Fe:Ox / Co:Ox (mol mol⁻¹)	Cl⁻ (mmol L⁻¹)
OA	None	0 / 0	- / -	0
OA + Co	CoCl ₂ 260	0 / 2.002	- / 1.80:1	4.005
OA + Fe+Co	FeCl ₃ 30 CoCl ₂ 130	0.185 / 1.001	1:6.01 / 0.90:1	2.557
OA + Fe	FeCl ₃ 60	0.370 / 0	1:3.00 / -	1.110

Experimental

Reagents and solution composition

Each solution contained 0.10 g of anhydrous oxalic acid in 1 L of deionised water (ReagentPlus, ≥ 99%, Sigma-Aldrich 241172), corresponding to an acid addition of 100 mg L⁻¹ or 1.11 mmol L⁻¹. FeCl₃ (anhydrous, 97%, Sigma-Aldrich 157740) and CoCl₂ (anhydrous, 97%, Sigma-Aldrich 232696) were added as listed in Table 1. The metal-free, Co-only, mixed-metal and Fe-only formulations are labelled OA, OA + Co, OA + Fe+Co and OA + Fe, respectively. Concentrations and molar ratios in the table were calculated from weighed reagent masses and anhydrous formula masses without purity correction. Ferrozine (Sigma-Aldrich 82950, 97%; C₂₀H₁₃N₄NaO₆S₂, 492.46 g mol⁻¹, CAS 69898-45-9) was used for the colour reaction with Fe(II).

Plasma treatment and sampling

The MH-DBD electrode assembly and discharge arrangement have been described previously [11]. The assembly comprised a stainless-steel tube electrode (2.5-mm outer diameter), an alumina dielectric tube (5-mm outer diameter, 1-mm wall) and a quartz tube (14-mm outer diameter, 2-mm wall) with 0.2-mm microholes. Oxygen supplied between the alumina and quartz tubes entered the liquid through the microholes, where the discharge developed (Fig. 1a). The working liquid volume was 1 L. An alternating-current high-voltage generator (DBD-60, NT Electronics, Korea) supplied the discharge, with oxygen flowing at 20 L min⁻¹. Recorded power was 85–95 W. No external cooling was used; initial bulk temperatures were approximately 16–19°C and final temperatures approximately 38–40°C.

Samples were collected before ignition and at 10-min treatment intervals, through 50 min for OA and 60 min for the metal-containing solutions. Aliquots for IC and UV-Vis originated from the corresponding treatment batch. One batch was treated for each composition, and the external laboratory supplied one

concentration value per IC sample. The resulting series describe changes within individual batches. The implications of this design and the available sample-handling records are considered in the discussion.

Ion chromatography and data treatment

Oxalate was analysed by ion chromatography at the Korea Polymer Testing & Research Institute (Koptri) using in-house method Koptri-W-DL10. A 930 Compact IC Flex system (Metrohm) equipped with a conductivity detector and a Metrosep A Supp 5 column (150 × 4.0 mm; Metrohm) was used. The eluent comprised 3.2 mmol L⁻¹ Na₂CO₃ and 1.0 mmol L⁻¹ NaHCO₃ in deionised water, delivered at 0.7 mL min⁻¹. The injection volume was 20 µL. Oxalate concentrations were reported in mg L⁻¹. For samples reported as not detected (ND), the instrument detection limit of 0.1 mg L⁻¹ and tenfold dilution gave a sample-basis detection limit of 1 mg L⁻¹. ND results were retained as upper-bound information. The analytical basis and reported concentrations are provided in Section S1 and Table S1.

“IC-detectable oxalate” denotes the concentration reported under the analytical procedure used here. Concentrations are presented directly and as C/C_0 , where C_0 is the measured initial value for each batch. This normalisation expresses change relative to the corresponding measured baseline. Matrix-specific recovery, complex dissociation during analysis and recovery of particulate oxalate were not independently evaluated in this study; concentrations are interpreted within the scope of the reported analytical procedure. Descriptive log-linear fits use quantified points (Table S2; Fig. S1), and ND observations provide upper bounds for assessing extrapolation.

UV-Vis measurements and ferrozine treatment

Spectra were collected at 1-nm intervals on an OPTIZEN POP spectrophotometer (K LAB, Korea) in a 1-cm cell. The retained exports span 200–800 nm for OA + Fe and OA + Fe+Co aliquots without ferrozine, 200–500 nm for OA, 200–400 nm for OA + Co and 200–700 nm for ferrozine-treated OA + Fe aliquots. Pure water was used as the UV-Vis blank. Processing consisted of subtracting the recorded blank spectrum once at each wavelength while retaining the exported spectral shape, including clipped values. Absorbances at 275, 300 and 365 nm were used to compare optical changes across the sampling series.

Ferrozine stock solution was prepared at 0.05 g per 50 mL. Each 6-mL OA + Fe aliquot was mixed immediately after sampling with 4 mL of the stock solution. The mixtures were unbuffered. The ferrozine-to-total-iron molar ratio, calculated from the reagent amounts, was 3.66:1 (Table S3).

Ferrozine spectra were evaluated as qualitative responses of the assay mixtures. They contain high absorbances reaching 3.000 and an abrupt change between 560 and 561 nm. Matrix-matched calibration, dilution linearity and incubation-time dependence were not established for these aliquots. Fe(III) can also interfere with Fe(II) determination through time-dependent colour development [17]. These conditions define the scope of the assay comparison and preclude conversion to reactor Fe(II) concentrations or fractions.

Results and discussion

The sampled solutions were largely colourless to faintly tinted in the retained aliquot photographs (Fig. 2). The photographs provide a qualitative record of sample appearance alongside the concentration and spectral measurements.

Persistence of IC-detectable oxalate in the Fe-only batch

The four batches had different initial IC results despite receiving the same oxalic acid addition: 87.0 mg L⁻¹ for OA, 65.7 mg L⁻¹ for OA + Co, 94.3 mg L⁻¹ for OA + Fe+Co and 53.1 mg L⁻¹ for OA + Fe. These differences may reflect sample preparation, solution chemistry and analytical recovery. Each measured initial concentration therefore serves as the reference for its subsequent profile. The oxalic acid addition is expressed on an oxalic-acid mass basis, while IC results are reported on an oxalate mass basis.

The IC concentration profiles differed among the four compositions (Fig. 3; Table S1). In OA + Fe, IC-detectable oxalate changed from 53.1 to 42.2 mg L⁻¹ over 60 min, a decrease of 20.5%; 79.5% of the measured initial value remained. Intermediate values fluctuated between 45.2 and 49.8 mg L⁻¹. OA reached ND at the 20-min sampling point and remained ND through 50 min. OA + Co and OA + Fe+Co reached ND at 30 min and remained ND through 60 min. At the 10-min sampling resolution, the first transition to ND occurred after 10 min and by 20 min for OA, and after 20 min and by 30 min for the two Co-containing batches.

Persistence in the Fe-only batch contrasts with the decline in the mixed-metal batch, which contained half the Fe dose together with added Co. The present profiles describe the combined formulations, with Fe dose and Co addition changing together. The Co-only and metal-free batches also differed in their first ND sampling times.

Chloride concentrations calculated from reagent additions were 1.110 mmol L⁻¹ in OA + Fe, 4.005 mmol L⁻¹ in OA + Co and 2.557 mmol L⁻¹ in OA + Fe+Co (Table 1). The higher-chloride Co-only batch showed a rapid decline, whereas the lower-chloride Fe-only batch retained oxalate. This ordering motivates examination of metal chemistry together with chloride, pH and conductivity when comparing these matrices.

Descriptive fits of the oxalate concentration profiles

Descriptive fits of $\ln(C) = b - kt$ give k values of 0.104, 0.123, 0.129 and 0.00309 min⁻¹ for OA, OA + Co, OA + Fe+Co and OA + Fe, respectively (Table S2). The first three estimates use two or three quantified observations over 10 or 20 min, whereas the Fe-only estimate uses seven observations over 60 min. The fitted slopes summarise the concentration changes within these respective observation windows and are treated as descriptive parameters.

The ND observations provide a check on extrapolation of the early quantified-point fits. At the first ND sampling time, the fitted curves predict 10.90 mg L⁻¹ for OA, 1.97 mg L⁻¹ for OA + Co and 2.27 mg L⁻¹ for

OA + Fe+Co, all above the reported limit of 1 mg L⁻¹ (Fig. S1). The fits are therefore used within their stated intervals, while the measured concentrations and ND bounds define the overall treatment profiles.

Near-UV absorption in the iron-containing solutions

OA + Fe retained a broad near-UV response with a shoulder around 270–280 nm and a tail towards the visible region (Fig. 4a). Blank-corrected absorbance at 300 nm changed from 0.867 initially to 0.816 at 60 min, while A_{275} changed from 1.342 to 1.221 and A_{365} from 0.218 to 0.207 (Table S4). Ferrioxalate exhibits ligand-to-metal charge-transfer absorption in the UV-visible region [18]. Together, persistent near-UV absorption and IC-detectable oxalate are consistent with iron-oxalate species contributing to the optical response.

Figure 4c directly compares the two A_{300} time courses. In OA + Fe+Co, A_{300} decreased from 0.247 to 0.102 by 30 min and was 0.119 at 60 min; A_{365} decreased from 0.078 to 0.012 and 0.009 at those times (Fig. 4b). The near-UV response remained measurable when IC reported ND, showing that the two measurements capture distinct aspects of the treated solution. Possible contributors include optical background, metal complexes and other absorbing components. These paired measurements suggest that tracking residual optical response alongside IC-detectable oxalate can help characterise treatment progress in metal-containing solutions. Full exported spectral ranges are shown in Fig. S2.

Selected reactor photographs of OA + Fe+Co show a more apparent greenish tint in Fig. 1c and a weaker tint in Fig. 1d. Later photographs in the full acquisition record, outside these panels, again show a greenish tint. Changes in metal-oxalate populations are one possible contributor to the appearance, alongside illumination, bubbles and camera settings. The selected sequence provides qualitative process context.

Ferrozine spectra and interpretation

The retained aliquot photograph shows a purple colour after ferrozine addition (Fig. 5d). Ferrozine-treated OA + Fe aliquots produced a strong visible response, including the pre-ignition sample (Fig. 5a). A_{562} decreased from 2.440 initially to 2.328 at 10 min, then fluctuated to 2.554 at 60 min (Fig. 5b; Table S4). The exported spectra show a decrease of 0.263–0.472 absorbance units between 560 and 561 nm (Fig. 5c), and some readings reached 3.000. The enlarged spectral region makes these recorded features explicit and supports the qualitative treatment of the assay data.

The purple colour and visible absorption are consistent with formation of the Fe(II)-ferrozine complex in the assay mixture [16]. With iron supplied as Fe(III), this response is consistent with reduction occurring during preparation, treatment or the post-sampling assay. Combined with residual oxalate and persistent near-UV absorption, it supports considering coupled complexation and redox processes. Photochemistry and time-dependent reactions after sampling can also affect the response [14, 15, 17]. The aliquot series therefore provides qualitative context for possible iron redox changes during treatment, with the spectra representing post-sampling assay mixtures.

Chemical interpretation and relevance to decontamination effluents

The Fe-only batch combines residual IC-detectable oxalate with sustained near-UV absorption, whereas the mixed-metal batch shows a decline in both signals. This contrast supports examining solution composition when interpreting the different concentration and optical responses. Complexation could affect both reactivity and analytical recovery. In a separate study of heated solutions (up to 120°C), temperature, iron species and dissolved oxygen affected oxalate degradation [19]. Figure 6 summarises literature reactions relevant to interpreting the present observations.

Ferrioxalate photochemistry couples iron reduction to ligand oxidation [13–15, 18]. Fe(II)-oxalate can react with hydrogen peroxide or dioxygen through pathways that regenerate Fe(III), with hydroxyl-radical formation demonstrated for the peroxide reaction [20]. Fe(II) can also consume hydroxyl radicals [6], potentially competing with oxalate oxidation. This competition may have contributed to the oxalate persistence observed in the Fe-only batch. The net effect of iron redox chemistry would depend on the balance between radical generation, competitive consumption and iron-oxalate photochemistry.

Plasma-generated hydrogen peroxide is a possible participant in aqueous oxidation [7–10]. The ferrozine response, residual oxalate and persistent near-UV absorption together support considering iron coordination and possible Fe(III)/Fe(II) interconversion when interpreting net oxalate removal. Figure 6 links candidate reduction and reoxidation pathways using formal reactions and a representative tris(oxalato) complex; photoreduction illustrates one possible reduction route. Ferrozine binding [16, 21] is shown separately as a post-sampling assay reaction.

Ozone is another candidate oxidant in oxygen-fed discharges [7–10]. Dissolved Co(II) accelerated oxalate ozonation near neutral pH in a separate study [22]. This literature result provides a possible chemical context for examining the Co-containing formulations.

These comparisons identify formulation-level behaviour in one batch per composition, with metal and chloride contents changing together. Matrix-specific IC recovery was not independently assessed in this study. Post-sampling storage conditions and measurement delays were incompletely documented. Hydrogen peroxide, ozone, radical yields, dissolved-oxygen profiles and reactor iron-speciation time courses were not measured, so the pathway discussion, including possible sustained redox cycling, is based on the literature. Similar power input alone does not establish equal oxidant delivery. Within this scope, the persistent Fe-only profile suggests that iron-containing formulations merit particular attention when assessing residual oxalate during treatment.

Our earlier mineralisation results apply to separate, metal-free batches [11]. Further controlled, replicated composition comparisons with independent IC recovery and iron-speciation measurements would help distinguish individual chemical and analytical contributions.

Conclusions

Under the tested underwater plasma conditions, the Fe-only batch retained 42.2 mg L⁻¹ IC-detectable oxalate after 60 min, corresponding to 79.5% of its measured initial value, together with a persistent near-UV signal. The other three compositions reached below 1 mg L⁻¹ at the 20- or 30-min sampling point. IC concentration profiles and UV-Vis optical responses provide complementary descriptions of these formulations, while ferrozine-treated aliquots provide qualitative assay observations. These single-batch comparisons suggest that treatment assessment can benefit from considering both solution composition and residual optical response, particularly for formulations showing persistent IC-detectable oxalate.

Declarations

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

Data availability The IC concentration data, selected absorbances, fit results and supporting figures are included in this article and its Supplementary Information. The underlying UV-Vis instrument exports, processed spectral data, calculation files and analysis code are available from the corresponding authors upon reasonable request.

Author contributions Ki-baek Shin led and designed the study, performed the experiments, analysed the data, and drafted, reviewed and revised the manuscript. Kilyoung Ko, Sunjin Kim, Jong-bum Kim and Jin Kim performed experiments and reviewed the manuscript. Jin-joo Kim, Jintae Hong and Yong Cheol Hong interpreted the data and reviewed the manuscript. Kangil Kim reviewed and revised the manuscript.

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Supplementary information The Supplementary Information contains full-range spectral plots, fit diagnostics, IC concentration results, stoichiometric calculations, selected absorbances and

descriptions of sample mapping and data processing.

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