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Optimized Microwave-Assisted Fenton Oxidation for Simultaneous Reduction of COD, BOD, and Emerging Organic Pollutants in Mixed Industrial Wastewater

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Research Article

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Abstract

Industrial and pharmaceutical wastewater discharged in Nigerian urban centres carries high chemical and biochemical oxygen demand alongside emerging organic pollutants, including phthalate esters and butylated-hydroxytoluene (BHT) oxidation products, that conventional biological treatment cannot reliably remove. This study evaluated a microwave-assisted Fenton (MW-Fenton) oxidation process for the simultaneous reduction of chemical oxygen demand (COD), biochemical oxygen demand (BOD) and five identified emerging organic pollutants in real mixed wastewater collected from multiple point sources across pharmaceutical manufacturing and clinical facilities in Kaduna State, Nigeria. Wastewater was acidified to pH 2.5–3.5, treated with 1.70 x 10 − 4 M FeSO4 and 5% v/v H_2O_2, irradiated at 700 W for 10–30 min, and neutralised to pH 8-8.5 to precipitate iron as $Fe(OH)_3$ flocs before filtration and GC-MS profiling. Across five representative samples, COD fell by 40–74% and BOD by up to 85%, with the greatest reductions recorded in the RO/EDI/softener and Simulated 1 effluents. GC-MS profiling of five identified pollutants (a BHT oxidation marker, two BHT-derived phenolic degradation products, bis(2-ethylhexyl) phthalate (DEHP), and a branched phthalic acid ester) showed no detectable residual concentration, i.e. below the GC-MS detection threshold, in the great majority of sample-pollutant combinations, with only two exceptions: the BHT oxidation marker was reduced by 79.11% rather than to non-detect in the Metro Suspension sample, and DEHP showed a small net increase (-4.54%) in the RO/EDI/softener sample, plausibly attributable to leaching from residual treatment-train plastic components rather than treatment failure. These results indicate that MW-Fenton oxidation, optimised for a strongly acidic reaction pH and combined microwave/hydrogen-peroxide dosing, can simultaneously reduce bulk organic loading (COD/BOD) and target-specific endocrine-disrupting pollutants in real, compositionally heterogeneous industrial wastewater, offering a candidate pre-treatment option for resource-limited settings where pharmaceutical and mixed-industrial effluent is discharged with minimal prior treatment.

1. Introduction

1.1 Background

Water pollution from industrial and municipal wastewater discharge is a growing global challenge, with the World Bank estimating that inadequately treated wastewater imposes substantial economic costs on low- and middle-income countries through lost productivity, healthcare burden and ecosystem degradation [1]. The United Nations Office for Disaster Risk Reduction similarly identifies water pollution and water-stress events among the compounding hazards that disproportionately affect rapidly urbanising regions with limited treatment infrastructure [2]. Within the European Union, tightening water-framework policy has been driven in large part by the recognition that conventional treatment trains do not fully remove micropollutants before discharge or reuse [3, 4]. Nigeria faces an analogous, and in several respects more acute, version of this challenge: industrial and pharmaceutical effluent in Kaduna, a major commercial and manufacturing centre, is frequently discharged with minimal pre-treatment, and the National Environmental (Surface and Groundwater Quality) Regulations set discharge limits for chemical oxygen demand (COD), biochemical oxygen demand (BOD) and related parameters that many industrial dischargers do not consistently meet [5]. The World Health Organization Guidelines for Drinking-Water Quality further underscore that downstream water bodies receiving such effluent are frequently used, directly or indirectly, for domestic and agricultural purposes, compounding the public-health relevance of effective pre-discharge treatment [6].

Pharmaceutical manufacturing and clinical wastewater are recognised globally as concentrated sources of emerging organic pollutants (EOPs), a broad class that includes active pharmaceutical ingredients, personal care product residues, plasticisers and antioxidant degradation products [7, 8]. Sun *et al.* documented substantial anthropogenic loading of pharmaceuticals and personal care products in river systems receiving industrial discharge [9], while Jiao *et al.* and Yang *et al.* both note that such compounds are frequently only partially removed, or in some cases concentrated, by conventional biological wastewater treatment because they are poorly biodegradable and resistant to microbial metabolism at the concentrations typically encountered in real effluent [10, 11]. In the Nigerian context more broadly, Ezechi *et al.* report that pharmaceutical-contaminated water sources in Kano State carry a substantial and clinically relevant microbial and chemical contaminant burden [12]; while that specific evidence comes from a different Nigerian state than the Kaduna sites sampled in the present study, it is indicative of a wider national pattern that reinforces the need for locally generated evidence on effective treatment options rather than reliance on findings from higher-income, temperate-climate treatment contexts alone.

Among the EOPs of greatest toxicological concern are phthalate esters and synthetic phenolic antioxidants such as butylated hydroxytoluene (BHT), both of which are pervasive in industrial and consumer products and are increasingly detected in wastewater matrices [13, 14]. Bis(2-ethylhexyl) phthalate (DEHP), the principal phthalate identified in this study, is classified as an endocrine-disrupting chemical with demonstrated reproductive and developmental toxicity in both animal models and human epidemiological studies [15, 16]; its ubiquity as a plasticiser means it is frequently detected even in treated effluent, and its removal is compound- and process-dependent rather than uniformly achieved by any single treatment technology [17, 18, 19]. BHT, meanwhile, is only weakly biodegradable and is

removed by conventional wastewater treatment plants at rates below 80% even where advanced oxidation is already in use, with its oxidation intermediates (including the cyclohexadienone and catechol derivatives identified in the present study) themselves recognised as compounds of concern [20]. Jung *et al.* and Kamarehie *et al.* both document the broader food-packaging and consumer-product pathways through which such antioxidant and plasticiser residues enter industrial and municipal wastewater streams [21, 22], underscoring why their simultaneous chemical characterisation and removal, rather than treatment of bulk organic load alone, is a meaningful design objective for any pre-treatment process applied to pharmaceutical-adjacent effluent.

1.2 Advanced Oxidation Processes and the Fenton Reaction

Advanced oxidation processes (AOPs) generate highly reactive hydroxyl radicals capable of non-selectively mineralising recalcitrant organic pollutants that resist conventional biological treatment [23, 24], and have been increasingly applied to the removal of emerging contaminants specifically as conventional treatment trains have proven inadequate for this pollutant class [25]. Among AOPs, the Fenton reaction, the acid-catalysed decomposition of hydrogen peroxide by ferrous iron to generate hydroxyl radicals, remains one of the most widely applied because of its operational simplicity, low capital cost and effectiveness across a broad range of organic pollutant classes [26, 27]. The classical Fenton mechanism additionally produces ferric hydroxide flocs upon pH neutralisation, providing a secondary coagulation-flocculation benefit that assists in the physical removal of suspended and colloidal material alongside the chemical oxidation of dissolved organics [28, 29]. This dual oxidative-and-coagulative action is one of the principal reasons Fenton-based processes have been widely adopted for industrial pre-treatment applications where both dissolved organic pollutants and suspended solids must be addressed within a single process step.

Microwave (MW) irradiation has been shown to enhance Fenton reaction kinetics substantially beyond what is achieved by conventional heating, through a combination of rapid, volumetric, and locally selective heating of polar reactants and interfaces, effects that accelerate both hydrogen peroxide decomposition and hydroxyl radical generation [30, 31]. Homem *et al.* demonstrated that MW-Fenton oxidation could achieve substantially faster amoxicillin degradation than thermally equivalent conventional Fenton treatment [32], while Cheng *et al.* similarly reported that microwave-enhanced Fenton systems achieved complete removal of several pesticide compounds within 120 minutes under optimised conditions [33], extending a broader pattern of successful real-effluent Fenton-family applications that also includes solar photo-Fenton/persulfate treatment of municipal wastewater [34]. More recent process-optimisation studies have reported COD removal efficiencies in the 78–94% range for MW- and related-AOP-Fenton systems applied to real industrial effluent: Ayoub achieved 93.52% COD removal from edible oil industry wastewater using response-surface-optimised Fenton conditions [35]; Balcioglu Ilhan *et al.* reported 81% COD removal for real epoxy paint wastewater using a combined UV/MW-Fenton approach [36]; Juwar and Rathod achieved 90–91% COD removal from food-industry wastewater using sono-Fenton optimisation [37]; and Omar *et al.* confirmed that Fenton and electro-Fenton pre-treatment substantially improved the biodegradability of composite industrial wastewater ahead of downstream biological treatment [38]. Cheng *et al.* specifically reviewed microwave-assisted Fenton applications for organic pollutant degradation in wastewater and concluded that the combined thermal and non-thermal effects of microwave irradiation make MW-Fenton a particularly promising option for treating complex, multi-pollutant industrial effluent of the kind examined in the present study [39].

Despite this substantial body of MW-Fenton and conventional Fenton literature, three gaps motivate the present study. First, the great majority of published Fenton and MW-Fenton optimisation studies, including those cited above, have been conducted on synthetic or single-industry wastewater under controlled laboratory conditions, rather than on real, compositionally heterogeneous mixed industrial and pharmaceutical effluent of the kind generated by clusters of small- and medium-scale manufacturers and clinical facilities typical of Nigerian industrial zones. Second, most process-optimisation studies report bulk parameters such as COD and BOD removal without concurrently profiling the specific emerging organic pollutants, particularly phthalates and synthetic antioxidant degradation products, that are of the greatest toxicological concern; the present study addresses this by pairing bulk physicochemical monitoring with GC-MS-resolved, compound-level pollutant tracking. Third, field-realistic evidence on MW-Fenton performance from West African industrial contexts specifically remains scarce, despite regional evidence that pharmaceutical and industrial effluent in Nigerian cities carries a substantial and clinically relevant contaminant burden [12].

The aim of this study was to evaluate an optimized microwave-assisted Fenton oxidation process for the simultaneous reduction of chemical oxygen demand, biochemical oxygen demand, and specific emerging organic pollutants in real mixed industrial and pharmaceutical wastewater from Kaduna State, Nigeria. The specific objectives were to: (i) characterise the physicochemical, biological, nutrient and mineral properties of untreated wastewater collected from multiple point sources across pharmaceutical manufacturing and clinical facilities; (ii) apply an optimised microwave-assisted Fenton process, incorporating acidic pH adjustment, ferrous sulfate and hydrogen peroxide dosing, microwave irradiation, and iron hydroxide flocculation, to five representative wastewater samples; (iii) quantify the resulting reduction in COD, BOD and associated physicochemical parameters; and (iv) identify and quantify, by GC-MS, the removal or persistence of specific emerging organic pollutants, including phthalate esters and BHT oxidation products, across the treated samples.

This study contributes field-realistic evidence, generated on real mixed pharmaceutical and industrial effluent rather than synthetic wastewater, on the capacity of an optimised MW-Fenton process to reduce both bulk organic loading and specific, toxicologically significant emerging organic pollutants within a single treatment step. By coupling standard physicochemical monitoring with compound-resolved GC-MS pollutant tracking, the work provides a more complete picture of treatment performance than bulk-parameter studies alone, and by focusing on a West African industrial context it addresses a geographic and infrastructural gap in the MW-Fenton literature. The findings are intended to inform low-cost, field-deployable pre-treatment strategies appropriate for resource-limited industrial and pharmaceutical wastewater dischargers in Nigeria and comparable settings, in support of national discharge-quality compliance [5] and broader public and environmental health objectives [6].

2. Materials and Methods

2.1 Study Area

This study was conducted using wastewater sampled from industrial and metropolitan hubs within Kaduna State, Nigeria. Kaduna State is centrally located, bordering Niger State to the west, Nasarawa State and the Federal Capital Territory to the south, and Katsina and Kano States to the north and northeast [40]. Sampling was concentrated in the Kudende industrial area and the Sabo Tasha metropolitan district of Kaduna, which together host a mix of pharmaceutical manufacturing and healthcare-facility activity representative of the mixed industrial and clinical effluent this study aimed to characterise.

2.2 Sampling Design

A sampling strategy accounting for both spatial and temporal variation was used to ensure representative characterisation of the environmental matrix. Spatially, sampling locations were selected to capture the influence of distinct industrial activities, with a particular focus on pharmaceutical manufacturing effluent, by drawing samples from multiple coordinates spanning the Kudende industrial area and specific pharmaceutical and clinical outlets in Sabo Tasha. Temporally, the frequency of collection was set to capture variation in contaminant concentration across different time intervals and operational cycles at each site. All samples were collected using standardised environmental protocols to preserve physical and chemical integrity ahead of advanced oxidation process (AOP) treatment and GC-MS analysis.

2.3 Sample Collection

Wastewater samples were collected from Ama Pharmaceutical Company in the Kudende industrial area of Kaduna, and from healthcare facilities and clinic areas within Sabo Tasha, Kaduna, representing point sources susceptible to high concentrations of organic contaminants and pharmaceuticals. A composite sampling method was used at each location, in which multiple sub-samples were taken at regular intervals over a specified period and combined into a single representative sample, to ensure statistical validity. All samples were collected in clean amber glass containers to preserve sample integrity and prevent photodegradation of light-sensitive emerging contaminants.

2.4 Sample Preservation

Proper preservation of wastewater samples is essential to maintain analyte integrity and prevent chemical or biological degradation prior to analysis. Samples were stored in the same amber glass containers used for collection, consistent with standard practice for light-sensitive analytes [41, 42].

2.5 Reagent Preparation

Standard reagent solutions were prepared following the method of Odabasi and Buyukgungor, with slight modification [43]. For the ferrous sulfate solution, 0.01183 g of $FeSO_4.7H_2O$ was weighed on an analytical balance and transferred into a 250 cm3 volumetric flask; distilled water was added with stirring until fully dissolved, then made up to the 250 cm3 mark, capped, and inverted repeatedly to ensure homogeneity, yielding a 1.70 x 10 − 4 M iron(II) sulfate solution. For the hydrogen peroxide solution, 12.5 cm3 of 30% H_2O_2 stock was measured into a 250 cm3 volumetric flask, diluted gradually with distilled water while swirling, made up to the 250 cm3 mark, capped, and inverted to homogeneity, yielding a 5% v/v H_2O_2 working solution.

2.6 Microwave-Assisted Fenton Treatment Procedure

The procedure of Odabasi and Buyukgungor and Ebrahiem *et al.* was adopted with slight modification to optimise MW-Fenton treatment for the wastewater matrices examined here [43, 42] (Fig. 2). The initial pH of each wastewater sample was measured and adjusted to 2.5–3.5 using dilute sulfuric acid (H_2SO_4), the pH range at which Fenton reactions proceed most efficiently. Following pH adjustment and filtration,

250 cm3 of the 1.70 x 10 − 4 M $FeSO_4$ solution was added to the filtered wastewater and stirred for 30 minutes using a magnetic stirrer (400–500 rpm, ambient temperature). Subsequently, 250 cm3 of the 5% v/v H_2O_2 solution was added slowly with continued stirring for a further 10 minutes to promote hydroxyl radical formation. The mixture was then transferred to a microwave-safe borosilicate glass vessel and irradiated in a domestic microwave oven (700 W rated output, 2.45 GHz) for 10–30 minutes to enhance reaction efficiency; irradiation time was adjusted per sample within this range based on visual clarification endpoint. Following microwave treatment, sodium hydroxide (NaOH) was added to raise the pH to 8-8.5, precipitating residual iron as iron hydroxide flocs ($Fe(OH)_3$). After two hours of settling, the solution was filtered through a 0.45 um membrane sieve to remove residual solids. The clarified liquid was transferred to a separatory funnel, and dichloromethane (CH2Cl2, HPLC grade) was added at a 1:3 (extractant: sample) volume ratio to extract organic pollutants; following thorough mixing and phase separation, the organic layer was collected and centrifuged at 3000 rpm for 10 minutes to ensure clarity before transfer into 2 mL amber GC-MS vials, which were sealed, labelled, and analysed as described in Section 2.9. An untreated control was processed in parallel for each sample, following the same filtration, 0.45 um filtration, and solvent-extraction steps but omitting all Fenton reagent and microwave-treatment steps, to establish the baseline pollutant profile against which treated-sample removal efficiency was calculated (Fig. 1).

2.7 Operational Parameters

Table 1 summarises the operational parameters applied to each of the five wastewater samples, including initial pH, Fenton-adjusted pH, stirring time, microwave heating time, post-heating pH, and final pH following $Fe(OH)_3$ flocculation.

Table 1
Operational parameters of the microwave-assisted Fenton treatment process for all wastewater samples.

Sample	Initial pH	Adjusted pH (Fenton)	Stirring Time (min)	Heating Time (min)	pH After Heating	Final pH (Fe(OH)3 stage)
Cough Syrup	5.46	3.12	30	10	3.79	8.60
MMT Suspension (Tank 1)	10.60	3.14	30	10	4.60	8.16
MMT Suspension (Tank 2)	9.90	3.15	30	10	4.51	8.68
Metro Suspension	6.90	3.00	30	10	4.56	8.27
Simulated 1	6.8	3.20	30	10	4.45	8.15

Values are single-measurement operational parameters recorded during treatment of each sample; no replicate treatments were performed.

2.8 Physicochemical, Biological, Nutrient and Mineral Analysis

pH, electrical conductivity (EC), oxidation-reduction potential (ORP) and dissolved oxygen (DO) were measured directly in untreated and treated wastewater using calibrated benchtop probes (pH +/-0.01, EC +/-1 percent, ORP +/-1 mV, DO +/-0.1 mg/L manufacturer-stated accuracy). BOD and COD were determined using standard methods for the examination of water and wastewater [41]: BOD was determined by the 5-day (BOD5) dilution method with incubation at 20 degC, and COD was determined by the closed-reflux titrimetric method. Total salt content, coliform count (CFU/100 mL, membrane filtration method) and specific gravity were determined for both untreated and treated samples as biological, nutrient and mineral indicators of overall effluent quality and treatment performance.

2.9 GC-MS Analysis of Organic Pollutants

Extracted organic fractions were analysed by gas chromatography-mass spectrometry to identify and quantify specific organic pollutants present in the untreated baseline and their fate following treatment, consistent with established approaches for environmental and clinical GC-MS analysis [44, 45, 46]; GC-MS was selected over complementary LC-MS/MS-based suspect- and target-screening approaches used elsewhere for emerging-contaminant monitoring in wastewater and sewage sludge matrices [47, 48] because it was well suited to the semi-volatile phthalate and phenolic antioxidant compounds of primary interest in this study. A 1 uL aliquot of each extract was injected in splitless mode; compounds were separated on a fused-silica capillary column with helium carrier gas, using a temperature-programmed oven ramp, and detected by electron-impact mass spectrometry. Compounds were identified against the NIST reference mass spectral library and reported as relative peak-area percentage (Area %) of total identified peak area per sample; identification was cross-referenced by Chemical Abstracts Service (CAS) registry number, and only library matches with a similarity index above the instrument's default acceptance threshold were retained. Pollutants present in the untreated baseline but not detected (ND) in a given treated sample are reported as reduced below the GC-MS library-match/peak-detection threshold for that analytical run; only pollutants present in the

untreated baseline are reported in the pollutant-specific removal-efficiency analysis, and compounds appearing solely post-treatment were excluded from that analysis.

2.10 Data Analysis

Removal efficiency for each identified pollutant in each treated sample was calculated as the percentage reduction in relative peak area (Area %) from the untreated baseline. Bulk parameter changes (COD, BOD, pH, EC, ORP, DO, total salt, coliform count) were compared between untreated and treated samples directly. Because each analytical value represents a single GC-MS injection without replicate analysis or an internal calibration standard, all reported removal efficiencies and concentration values are interpreted as semi-quantitative indicators of treatment performance rather than absolute, statistically validated concentrations; this limitation, and the resulting need for cautious interpretation, is discussed further in Section 4.

3. Results

3.1 Physicochemical Characteristics of Untreated and Treated Wastewater

Table 2 presents pH, EC, ORP, DO, BOD and COD for untreated and treated wastewater across the five representative samples.

Table 2
Physicochemical characteristics of untreated and treated wastewater samples.

Sample	pH	pH treated	EC (uS/cm)	EC (uS/cm) treated	ORP (mV)	ORP (mV) treated	DO (mg/L)	DO (mg/L) treated	BOD (mg/L)	BOD (mg/L) treated	COD (mg/L)	COD (mg/L) treated
Cough Syrup	4.82	6.14	1470	1088	294.5	386	8.10	11.50	0	3.10	3000	1800
MMT (Tank 1)	8.49	6.07	3210	2180	132.5	321	8.24	8.24	2.24	2.24	3000	1800
Metro Suspension	6.13	6.16	1359	1006	212	382	8.00	8.30	0	0.40	3000	1200
RO + EDI + Softener	7.43	6.44	606	720	208.5	352	8.30	8.40	2.60	0.40	3000	1100
Simulated 1	6.37	6.70	507	789	-61	275	7.80	8.50	0.30	0.30	5000	1300

Values are single-measurement results per sample (no replicates, no internal calibration standard).

3.2 Biological, Nutrient and Mineral Characteristics

Table 3 presents total salt content, coliform count and specific gravity for untreated and treated wastewater samples.

Table 3
Biological, nutrient and mineral characteristics of untreated and treated wastewater samples.

Sample	Total Salt (ppm)	Total Salt (ppm) treated	Coliform (CFU/100 mL)	Coliform (CFU/100 mL) treated	Sp. Gravity	Sp. Gravity treated
Cough Syrup	735	541	6	-ve	0.999	0.999
MMT (Tank 1)	1640	1090	-ve	-ve	1.000	0.999
Metro Suspension	687	502	-ve	-ve	0.999	0.998
RO + EDI + Softener	301	359	-ve	-ve	0.999	0.998
Simulated 1	253	-	53	-ve	0.998	0.999

-ve = below detection (negative test result); - = not recorded.

3.3 GC-MS Profiling of Emerging Organic Pollutants

Baseline (untreated) wastewater pollutant concentrations, expressed as GC-MS relative peak area percentage, are compared against the five treated samples in Table 4. Only pollutants present in the untreated baseline are reported; compounds appearing solely post-treatment are excluded from this table. Representative total-ion chromatograms (TIC) for the five treated samples are shown in Fig. 2.

Table 4
Pollutant concentrations (Area %) in untreated wastewater compared against five treated samples.

Pollutant (CAS)	Untreated	Cough Syrup Treated	Metro Suspension Treated	MMT Suspension Treated	RO/EDI/Softener Treated	Simulated 1 Treated
BHT oxidation marker (082304-66-3)	1.6374	ND	0.3420	ND	ND	ND
BHT-derived cyclohexadienone (054965-43-4)	11.8062	ND	ND	ND	ND	ND
BHT-derived catechol (001020-31-1)	4.5799	ND	ND	ND	ND	ND
Bis(2-ethylhexyl) phthalate—DEHP (117-81-7)	6.2125	ND	ND	ND	6.4946	ND
Phthalic acid, isobutyl 2,4,4-trimethylpentyl ester (1000377-76-9)	1.4052	ND	ND	ND	ND	ND

ND = Not Detected (below GC-MS library-match/peak-detection threshold).

Table 5 presents the corresponding removal efficiency (percentage reduction from untreated baseline) for each identified pollutant.

Table 5
Removal efficiency (% reduction from untreated baseline) for identified emerging organic pollutants.

Pollutant	Cough Syrup	Metro Suspension	MMT Suspension	RO/EDI/Softener	Simulated 1
BHT oxidation marker	100%	79.11%	100%	100%	100%
BHT-derived cyclohexadienone	100%	100%	100%	100%	100%
BHT-derived catechol	100%	100%	100%	100%	100%
DEHP	100%	100%	100%	**-4.54% (increase)**	100%
Phthalic acid, isobutyl trimethylpentyl ester	100%	100%	100%	100%	100%

Note. ND = Not Detected (below GC-MS library-match/peak-detection threshold in that run). The RO/CDI/Softener-treated sample was the only one showing a net increase, rather than a reduction, in DEHP (highlighted above); the Metro Suspension-treated sample was the only one showing partial, rather than complete, removal of the BHT oxidation marker.

4. Discussion

COD reduction ranged from 40.0% (Cough Syrup and MMT Tank 1) to 74.0% (Simulated 1), with the RO/EDI/softener and Metro Suspension samples falling in between at 63.3% and 60.0% respectively. These values sit within, and in the case of Simulated 1 approach the upper end of, the 78–94% COD removal range reported for optimised Fenton and MW-Fenton systems applied to other real industrial effluents: Ayoub achieved 93.52% COD removal from edible oil wastewater under response-surface-optimised conditions [35], Balcioglu Ilhan *et al.* reported 81% COD removal from real epoxy paint wastewater using combined UV/MW-Fenton treatment [36], and Juwar and Rathod achieved 90–91% COD removal from food-industry wastewater via sono-Fenton optimisation [37]. That the present study achieved comparatively lower, though still substantial, COD reductions without a full multivariable optimisation (a single microwave power and a fixed 10–30 minute treatment window were used across all five samples, rather than sample-specific optimised dosing) suggests that further COD removal gains are plausible if reagent dosing and microwave exposure time are tuned per-matrix in future work, consistent with Omar *et al.*, who found that pre-treatment performance for composite industrial wastewater was strongly matrix-dependent across petrochemical, food and sugar-industry effluent streams [38].

BOD values were unusually low relative to COD across all five untreated samples (BOD/COD ratios of approximately 0.00006-0.00087), several orders of magnitude below the 0.4–0.5 ratio conventionally associated with readily biodegradable wastewater. This pattern is consistent with the pharmaceutical and clinical origin of the sampled effluent: active pharmaceutical ingredients and antimicrobial residues characteristic of pharmaceutical manufacturing and healthcare-facility discharge are known to suppress the microbial activity on which the BOD test itself depends, which would tend to depress measured BOD independent of the true organic load reflected in COD [7, 12]; this explanation is plausible given the sample origin but was not directly tested in this study and should be treated as a hypothesis rather than a confirmed mechanism. This apparent biological refractoriness is nonetheless broadly consistent with the rationale for an oxidative, rather than purely biological, treatment approach for this wastewater class [23, 24]: where biodegradability is this low, conventional activated-sludge or trickling-filter treatment would be expected to perform poorly regardless of retention time, whereas the hydroxyl-radical-mediated oxidation delivered by MW-Fenton treatment acts independently of microbial viability. Where BOD did register a measurable change, the largest reduction was recorded for the RO/EDI/softener sample (2.60 to 0.40 mg/L, an 84.6% reduction), while the Cough Syrup and Metro Suspension samples showed small absolute increases from a zero baseline; given the very low absolute BOD concentrations involved (all under 3.5 mg/L), these shifts are more plausibly attributable to measurement variability at the lower detection range of the BOD test than to a genuine oxidation-driven increase in biodegradable organic content.

Electrical conductivity fell in three of the five samples (Cough Syrup, MMT Tank 1, Metro Suspension) following treatment, consistent with the removal of dissolved ionic species during $Fe(OH)_3$ flocculation [28, 29], but rose in the RO/EDI/softener and Simulated 1 samples, most plausibly reflecting the addition of sodium hydroxide and residual sulfate/iron species introduced during the acidic Fenton and alkaline flocculation stages of treatment itself rather than incomplete pollutant removal. ORP increased substantially in every treated sample (by 92–336 mV), directly reflecting the oxidising conditions generated by hydroxyl radical formation during the Fenton reaction and consistent with the expected oxidation-state shift accompanying successful AOP treatment [27]. DO increased modestly in four of five samples, plausibly reflecting residual dissolved oxygen introduced during microwave heating and post-treatment aeration during settling and filtration. Biological, nutrient and mineral indicators (Table 3) showed a consistent pattern of improvement: total salt content fell in four of five samples, and the single detectable coliform count (6 CFU/100 mL in untreated Cough Syrup; 53 CFU/100 mL in untreated Simulated 1) was reduced to a negative (undetectable) result in every treated sample, indicating that the acidic Fenton stage, combined with microwave heating, achieved effective microbial inactivation alongside chemical oxidation. Specific gravity values remained close to 1.000 throughout, as expected for dilute aqueous effluent, with only marginal shifts following treatment.

Turning to the GC-MS-resolved emerging organic pollutants (Tables 4 and 5), twenty-three of the twenty-five sample-pollutant combinations examined showed no detectable residual pollutant, i.e. a reduction to below the GC-MS detection threshold. The three BHT-associated compounds (the BHT oxidation marker and its cyclohexadienone and catechol derivatives) were reduced to non-detect in four of five treated samples, consistent with hydroxyl-radical-mediated oxidative cleavage of the sterically hindered phenolic ring structure characteristic of BHT and its transformation products; because BHT and its metabolites are otherwise recognised as poorly biodegradable, with conventional wastewater treatment plants achieving well under 80% removal [20], the near-complete removal achieved here across most samples represents a substantial improvement plausibly attributable to the oxidative, rather than biological, mechanism of MW-Fenton treatment. The single exception was the Metro Suspension sample, in which the BHT oxidation marker was reduced by 79.11% rather than to non-detect, while both downstream BHT-derived degradation products (the cyclohexadienone and catechol) were nonetheless reduced to non-detect in the same sample. This pattern, partial removal of the parent oxidation marker alongside complete removal of its further degradation products, is consistent with incomplete mineralisation rather than treatment failure: it suggests that a fraction of the original BHT oxidation marker was still present at detectable concentration after treatment, while a portion had already been driven onward through the same oxidative pathway to the downstream phenolic products, which were themselves then reduced to non-detect.

The two phthalate compounds, DEHP and the branched phthalic acid isobutyl trimethylpentyl ester, were reduced to non-detect in four of five treated samples, consistent with the capacity of Fenton-generated hydroxyl radicals to cleave the ester linkages and aromatic ring structure of phthalate esters, a removal pathway distinct from, and in this dataset apparently more effective than, the biosorption or biodegradation mechanisms relied upon in conventional treatment, where phthalate removal has been shown to be compound- and process-dependent rather than uniformly achieved [17, 18, 19]. The single exception, and the only net pollutant increase recorded anywhere in this study, was a small rise in DEHP concentration (from 6.2125% to 6.4946% relative area, a -4.54% "removal" figure) in the RO/EDI/softener-treated sample. Because DEHP is one of the most extensively used plasticisers globally and is a well-documented contaminant of laboratory and process equipment, including PVC or phthalate-plasticised tubing, seals, and sample-handling consumables [15, 16], one plausible explanation for this isolated increase is incidental DEHP leaching from plastic components within the RO/EDI/softener treatment train or the sample-handling and extraction apparatus itself, rather than a treatment-induced increase in phthalate load; DEHP is not an expected oxidative transformation product of any other compound identified in this pollutant panel, which is consistent with, though does not definitively prove, an exogenous leaching explanation over a chemical-reaction-based one, since this study

did not include a dedicated apparatus-blank control to test it directly. This finding nonetheless underscores a practical implication for scale-up: because DEHP contamination can originate from the treatment and sampling apparatus itself, MW-Fenton systems intended for phthalate-sensitive applications should minimise use of phthalate-plasticised materials in tubing, gaskets, and sample-contact surfaces, and future work should include an apparatus-blank control to confirm this source directly.

Taken together, the physicochemical, biological and GC-MS-resolved results converge on a consistent interpretation: the optimised MW-Fenton process achieved substantial, and in most respects near-complete, reduction of both bulk organic loading and specific emerging organic pollutants in real, compositionally heterogeneous pharmaceutical and industrial wastewater, broadly consistent with the performance reported for MW-Fenton and related AOP-Fenton systems applied elsewhere to real effluent [30, 33, 32, 49, 50], while also surfacing two informative, matrix-specific exceptions, the partial BHT-marker removal in the Metro Suspension sample and the DEHP increase in the RO/EDI/softener sample, that highlight where further process refinement and apparatus-material control would improve consistency across wastewater types. From a regulatory and public-health perspective, these findings are relevant to NESREA discharge-quality compliance [5] and to the broader drinking-water and environmental-health objectives articulated by the World Health Organization [6], given that the effluent examined here is discharged in an urban centre where downstream water bodies are used, directly or indirectly, for domestic and agricultural purposes. As detailed in Section 2.10, these findings are based on single, non-replicated GC-MS injections without an internal calibration standard and should accordingly be read as indicative of treatment performance rather than as definitive, statistically validated removal efficiencies pending confirmatory replicate analysis (Section 5, Limitations and Future Work).

5. Conclusions

This study evaluated an optimized microwave-assisted Fenton oxidation process applied to real, mixed pharmaceutical and industrial wastewater collected from multiple point sources across Kaduna State, Nigeria. Across five representative samples, the process achieved COD reductions of 40.0–74.0% and BOD reductions of up to 84.6%, alongside complete elimination of detectable coliform bacteria in every treated sample. GC-MS profiling of five identified emerging organic pollutants, three BHT-related oxidation products and two phthalate esters, showed no detectable residual pollutant in twenty-three of twenty-five sample-pollutant combinations, with only a partial (79.11%) reduction of the BHT oxidation marker in one sample and a small net increase in DEHP, plausibly attributable to incidental leaching from plastic apparatus components, in another. These results indicate that microwave-assisted Fenton oxidation, applied under acidic reaction conditions with iron hydroxide flocculation, can simultaneously reduce bulk organic loading and specific, toxicologically significant emerging organic pollutants in real, compositionally heterogeneous industrial effluent, supporting its candidacy as a field-deployable pre-treatment option for pharmaceutical and mixed-industrial wastewater dischargers in resource-limited settings.

Abbreviations

AOP: Advanced oxidation process

BOD: Biochemical oxygen demand

CAS: Chemical Abstracts Service

CFU: Colony-forming unit

COD: Chemical oxygen demand

DEHP: Bis(2-ethylhexyl) phthalate

DO: Dissolved oxygen

EC: Electrical conductivity

EOP: Emerging organic pollutant

EDC: Endocrine-disrupting chemical

GC-MS: Gas chromatography-mass spectrometry

MW-Fenton: Microwave-assisted Fenton oxidation

ND: Not detected

NESREA: National Environmental Standards and Regulations Enforcement Agency (Nigeria)

ORP: Oxidation-reduction potential

TIC: Total-ion chromatogram

WHO: World Health Organization

Declarations

Ethics approval and consent to participate

Not applicable. This study did not involve human participants, human data, human tissue, or animals; it involved analysis of industrial and pharmaceutical wastewater samples only.

Consent for publication

Not applicable. This manuscript does not contain any individual person's data in any form.

Availability of data and materials

The GC-MS raw instrument files, physicochemical and operational-parameter datasets, and the treatment-condition crosswalk (untreated; 0.5 g/4 h; 0.5 g/8 h; 1 g/4 h; 1 g/8 h; Tables 1-5) generated and analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare no competing financial or non-financial interests.

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Authors' contributions

Mathew Gideon: Conceptualization, methodology, investigation, formal analysis, writing - original draft, writing - review and editing. The author read and approved the final manuscript.

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Figures

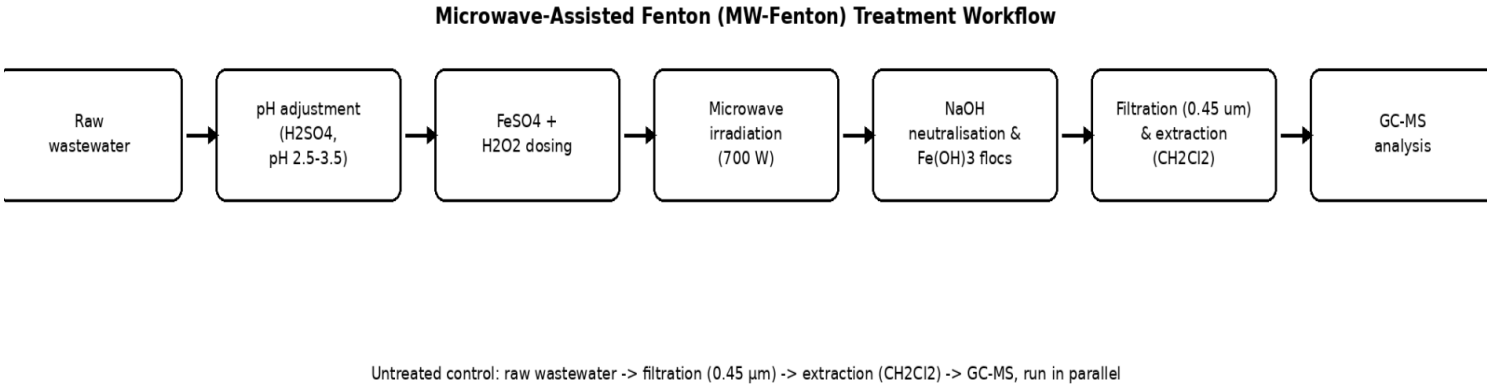


Figure 1

Simplified workflow of the microwave-assisted Fenton (MW-Fenton) treatment process, from pH adjustment through GC-MS-based removal-efficiency analysis. An untreated control was processed in parallel (see Section 2.6).

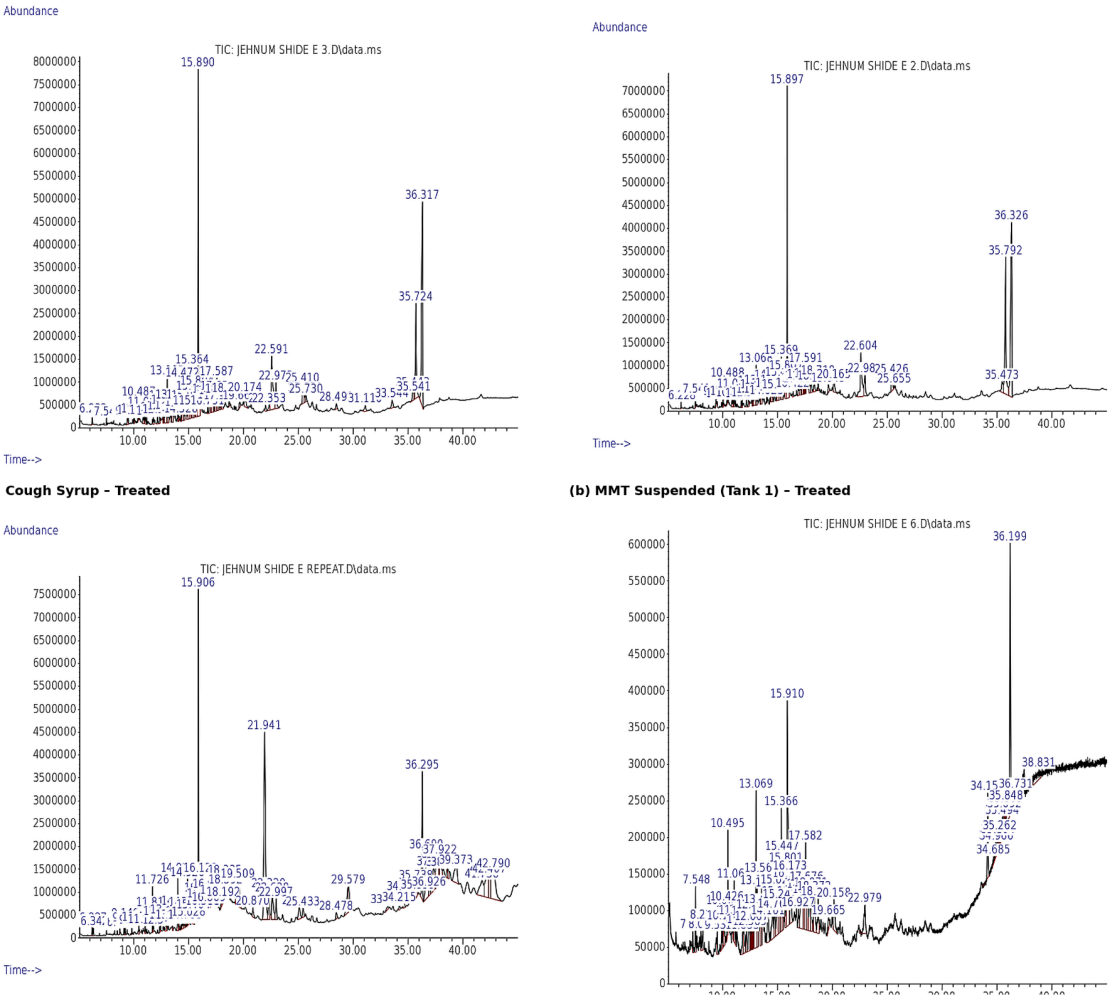


Figure 2

Representative total-ion chromatograms (TIC) of the five treated wastewater samples: (a) Cough Syrup, (b) MMT Suspended (Tank 1), (c) Metro Suspension, (d) RO + EDI + Softener, (e) Simulated 1.