Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21274

91 (2017) 138–145
October

Advanced oxidation of industrial effluents under microwave irradiation: state of the art

Vayos Karayannis[a], Konstantinos Moustakas[b,*], Argyris Vatalis[a], Pavlos Sapalidis[a], Asimina Domopoulou[a]

[a]*Department of Environmental Engineering, Western Macedonia University of Applied Sciences, 50100 Kozani, Greece, Tel. +30 24610 68022-3; emails: vkarayan@teiwm.gr (V. Karayannis), vatalis@teiwm.gr (A. Vatalis), psapalidis@yahoo.gr (P. Sapalidis), adomopo@teiwm.gr (A. Domopoulou)*
[b]*School of Chemical Engineering, National Technical University of Athens, Zografou Campus, 15773 Athens, Greece, Tel. +30 210 7723108; email: konmoust@central.ntua.gr*

Received 30 January 2017; Accepted 29 July 2017

ABSTRACT

In the present study, recent progress in using microwave energy to enhance advanced oxidation of industrial effluents of poor biodegradability is reviewed and evaluated. The aim is to assess the potential of microwave-assisted advanced oxidation as an effective and viable remediation method, alternative to conventional treatment procedures. The use of microwave technology to overcome intrinsic drawbacks and improve environment-friendly processing of various wastes represents a challenging scientific area. Particularly, the oxidation/degradation efficiency under microwave irradiation of industrial wastewaters appears to be influenced by key operating factors including microwave frequency (915 or 2,450 MHz) and power level (200–800 W), oxidizing agent (usually H_2O_2), catalyst type and loading (up to 1 g·L^{-1}), pH (frequently 2–5 or even 7 and 9) and initial pollutant concentration. Due to a synergistic effect mainly attributed to increased generation of oxidative hydroxyl radicals (·OH) induced by the microwave energy, the oxidation process of various pollutants (pesticides/herbicides, pharmaceuticals, dyes, etc.) is enhanced. Thus, almost complete pollutant degradation, reaction acceleration (reaction usually occurs in only 1–15 min), decreased consumption of chemicals and microorganisms destruction are achieved at low temperatures.

Keywords: Advanced oxidation; Industrial effluents; Microwave irradiation; Environment-friendly processing

1. Introduction

In the present work, recent advances in employing the microwave technology to enhance oxidation/degradation of pollutants, especially in industrial wastewater, are reviewed and summarized in order to assess their potential as viable and efficient remedial alternatives to conventional procedures.

Microwave radiation is emerging as a novel technology that has gained widespread acceptance as an effective thermal method. Microwave energy offers many advantages, including rapid heat transfer and volumetric and selective heating, for energy-efficient, thus eco-friendly, industrial processing over conventional techniques [1,2]. Hence, microwave processes can be an effective and economical approach to reduce the treatment time considerably, thereby leading to substantial energy and cost savings [3,4]. These characteristics provide sufficient motivation to promote the use of microwaves in "greener" processing. So far, microwave technology has already been employed in various environmental applications, including environmental and green chemistry, sintering for transformation of lignite ashes into ceramics,

* Corresponding author.

Presented at the 13th IWA Specialized Conference on Small Water and Wastewater Systems & 5th IWA Specialized Conference on Resources-Oriented Sanitation, 14–16 September, 2016, Athens, Greece.

determination and/or oxidation/remediation of soil pollutants, solid waste treatment, anaerobic digestion feedstock pretreatment, disinfection of medical wastes, synthesis of shuttle-like zinc oxide nanoparticles, preparation of activated carbon from biomass waste (coconut leaves) by NaOH activation, and also pyrolysis of biomass for energy recovery and conversion into valuable energy products [5–13].

The degradation of various pollutants of poor biodegradability by their transformation into non-toxic substances has received much attention in the last years: pharmaceutical wastewater, aqueous phenanthrene, insecticides (e.g., imidacloprid), 17α-ethynylestradiol in secondary-treated wastewater, dispersive textile dyes, especially reactive azo dyes, brilliant blue, methylene blue and even cyanotoxins are included [14–17]. For that purpose, several advanced oxidation processes (AOPs) have been increasingly applied as potentially efficient treatment methods: photo-Fenton/Fenton-like degradation, heterogeneous UV or simulated solar photocatalytic processes, photochemical treatment with H_2O_2/UV, photo-electro-catalytic oxidation and high-frequency ultrasound degradation are reported and also new photocatalysts, such as Fe(III)/TiO_2–montmorillonite, TiO_2/Ti electrodes and even lignite ashes coated with TiO_2 have been tested [18–20]. Actually, the end effect of the aforementioned processes is the production of hydroxyl radicals (·OH) that have a very strong oxidation potential, thus being powerful oxidizing agents for industrial pollutant degradation. For assessing the effluent quality achieved prior to discharge, a well-known parameter, chemical oxygen demand (COD) that estimates the amount of oxidizable organic matter in effluents is usually monitored [21]. However, the energy consumption and operational cost of these oxidation methods can vary from pollutant to pollutant and also depends on their loading rates, especially in full-scale operation of industrial interest. Moreover, some of these methods require chemical reagents that may cause secondary pollution. Besides, traditional chemical oxidation processes, such as ozonation and chlorination often used in wastewater reclamation may result in by-products potentially altering the toxic and mutagenic properties of effluents [22,23]. Therefore, the use of microwave irradiation to improve degradation processes for many types of wastes and overcome the aforementioned drawbacks emerges to be a challenging scientific area [24,25].

2. Microwave-assisted advanced oxidation of industrial effluents

The most commonly used microwave frequency of 2,450 MHz corresponds to significant penetration depth within most of the materials, and therefore, it is suitable for most reaction conditions. Nevertheless, many industrial-scale microwave systems are in the range of 915 MHz. At this frequency microwave has three times higher penetrating capacity and greater energy efficiency (>80%) than that at 2,450 MHz [26]. Microwave energy can contribute to accelerating pollutant purification reactions, enhancing the oxidation process and diminishing hazardous products formation, while also decreasing the consumption of chemicals [27]. It is demonstrated in the following reported literature that the assistance of microwave irradiation does not mainly consist of a beneficial thermal effect alone. In fact, the same result cannot be achieved by conventional caloric methods. It should rather be attributed to an increased formation of hydroxyl radicals, which is likely due to some sort of surface restructuring induced by the microwave energy. Such non-thermal effects of microwave are able to enhance various chemical reactions, treat wastewater systems and destroy microorganisms at low temperatures [28–30].

2.1. Microwave-assisted photocatalytic oxidation

Particularly in TiO_2 photocatalytic oxidation of various pollutants, the influence of microwaves can provide significant enhancement of photodegradation kinetics, as assessed by several recent studies.

A microwave non-thermal effect involving lattice distortion and oxygen vacancies in a P25 TiO_2 photocatalyst appropriately heat treated in the temperature range 645°C–800°C, which caused the initial anatase-to-rutile ratio of 81/19 to decrease to 1/99 at the highest temperature, beneficially affects the catalyst photoactivity. Consequently, reaction kinetics were accelerated during microwave-assisted (2,450 MHz) photodegradation of 4-chlorophenol. Changes in the defect sites (e.g., oxygen vacancies) inherently present in pristine titania were attributed to the heat treatment applied [31]. The UV/H_2O_2/microwave (MW) combined process appeared to be eight times faster than other process variations (MW, H_2O_2, H_2O_2/MW and UV/MW) for the decolorization of an azo-dye (tartrazine) solution. Actually, color removal of approximately 92% was attained within 24 min of irradiation. H_2O_2 initial concentration = 2.0 mmol·L^{-1} and pH = 2.6 were the estimated to be the optimal conditions [32]. In another research, the combined A-TiO_2/activated carbon (AC)/MW process (nanosized anatase or rutile TiO_2-supportedAC), which was developed for the MW-induced degradation of parathion, displayed many advantages in comparison with the MW/AC degradation, and the supported A-TiO_2/AC showed higher MW catalytic activity than R-TiO_2/AC. Specifically, 81.55% extent of degradation was attained using the supported A-TiO_2/AC/MW within 1.0 min MW irradiation of 50 mg·L^{-1} parathion solution, whereas complete degradation was achieved by prolonging the irradiation time to 2.5 min, under the conditions of 0.8 g·L^{-1} catalyst dose, pH = 5, and MW radiation of 750 W power and 2,450 MHz frequency. These results represent a promising approach for the removal of parathion in wastewater treatment applications [33]. A synergy effect upon application of microwave energy (200–600 W MW irradiated continuously through a wave-guide on 1 L of 0.5 mM 2,4-D aqueous solution) together with UV irradiation (200 W), ozone, and a photocatalyst (TiO_2 film deposited on alumina balls) seems to play an important role in the O_3-assisted photocatalysis for the degradation of 2,4-dichlorophenoxyacetic acid, resulting in the highest rate constant, being 4.5 times that obtained with MW/UV/photocatalyst combination and more than six times that obtained by injection only of ozone [34].

Besides, a novel microwave-enhanced photocatalytic membrane distillation process was proposed for the treatment of organic wastewater containing inorganic ions (humic acid solution containing Ca^{2+}) [35]. Actually, coupling microwave energy with UV irradiation effectively decreased the deposit on membrane surface by destabilizing complex

compounds. Hence, the membrane fouling was prevented. Moreover, the beneficial effect of microwaves on the membrane distillation process, when applied to coal gasification wastewater treatment, was proved to be sufficient for a COD removal rate higher than 96% after 120 h operation. The advanced treatment of biologically pretreated Lurgi coal gasification wastewater was also investigated by a novel system, integrating microwave catalytic oxidation (using a sewage sludge-based AC catalyst loaded with Mn oxides) and moving bed biofilm reactor (MBBR) process, with high efficiencies in eliminating biorefractory compounds [36]. Furthermore, microwave-assisted coal desulfurization by photocatalytic oxidation treatment (H_2O_2/nano-ZnO/UV) is also possible, depending on coal particle size, irradiation time, catalyst and H_2O_2 concentrations [37].

In other study, microwave (500 W maximum) discharge electrodeless lamps (light intensity of 254–300 nm being 9–10 $mW{\cdot}cm^{-2}$) were investigated as light sources in the presence of H_2O_2 (40 $mmol{\cdot}L^{-1}$) for the photooxidation of guaiacol (100 $mg{\cdot}L^{-1}$) to value-added carboxylic acids. It should be noted here that the production of chemicals from lignin sources (such as guaiacol) by green and economically feasible technologies is examined as a promising alternative route for the substitution of fossil fuels. The combined microwave-assisted heating and photooxidation with special UV lamps in the presence of H_2O_2 led to a more effective degradation of guaiacol than with conventional photocatalysis. This synergistic effect is attributed to an increased hydroxyl radicals production, playing a crucial role in the aromatic-ring opening reaction of guaiacol and production of carboxylic acids [38].

2.2. Microwave-assisted photo-Fenton/Fenton-like oxidation

Also, Fenton (Fe^{2+}/H_2O_2) and/or Fenton-like (Fe^{3+}/H_2O_2) process assisted by microwave energy, appears to be an innovative and less expensive solution, with advantages of highly effective and fast processing for the treatment of wastewater containing organic contaminants. This combination also permits to optimize the operational parameters, especially to reduce the necessary iron catalyst concentrations, thus satisfying environmental demands.

In fact, by the assistance of microwave irradiation (P = 162 W, $[H_2O_2]_0$ = 2.35 mg L^{-1} and $[Fe^{2+}]_0$ = 95 $\mu g{\cdot}L^{-1}$), the oxidative degradation of amoxicillin was significantly improved over classical Fenton's reaction, and amoxicillin was no longer detected in the reaction system in less than 5 min [39]. In other research regarding pharmaceutical wastewater, riboflavin sodium phosphate was treated using microwave-enhanced Fenton-like process with satisfactory oxidation efficiency, specifically total organic carbon (TOC) removal rate of 57.5% in only 6 min under the optimal conditions (ferric sulfate 1.5 $mg{\cdot}L^{-1}$ and hydrogen peroxide 10 $mL{\cdot}L^{-1}$), while coloration was completely removed. Although low ferric sulfate dose was used, a flocculation/precipitation (second step) equally important as the first oxidation/decomposition step also occurred [40].

Moreover, the application of microwave-enhanced Fenton oxidation noticeably accelerated the conversion of dyes such as methylene blue, due to the fast and selective heating of water and hydrogen peroxide molecules. In fact, a 93.0% dye conversion rate after only 1 min irradiation time was achieved, even higher than that of methylene blue treated by conventional Fenton process for 65 min. The dye decomposition increases with the H_2O_2 and Fe^{2+} initial concentrations and slightly with pH values lower than 7, with optimum pH value of about 3 [41]. Also, a certain synergy between microwaves and Fenton oxidation system can shorten the reaction time, greatly improve the COD removal rate wastewater and even reduce the dosage of Fenton reagent for dye wastewater containing the weak acid brilliant red B and the anionic surfactant sodium dodecyl sulfate: 99.1% color and 89.9% COD removal rates were obtained in 10 min reaction time (microwave power = 539 W, pH = 2.5, H_2O_2 dosage = 4 $mL{\cdot}L^{-1}$ and $FeSO_4$ dosage = 100 $mg{\cdot}L^{-1}$) [42]. Such synergistic effect resulting in significant promotion of dye degradation in wastewater was also investigated systematically in the application of microwave irradiation/Fenton oxidation coupling coagulation process [43]. In this study, microwave radiation is considered to provide a non-thermal efficiency accelerating the production of hydroxyl radicals and promoting the molecular polarization of organic substances. Destabilization and coagulation mechanisms should also count [44]. Furthermore, the microwave-enhanced Fenton reaction followed by hydroxide precipitation was investigated in the oxidation of ethylenediaminetetraacetic acid (EDTA) that can form very stable complexes with heavy metal ions, greatly inhibiting conventional metal-removal technologies. The COD reduction order achieved, from high to low, was found to be Cu(II)–Ni(II)–EDTA ≈ Cu(II)–EDTA > Ni(II)–EDTA [45].

Non-thermal effects based in advanced oxidation pathways through holes and ·OH radicals generation along with thermal effects was the mechanism proposed for the removal of pyridine (a toxic and volatile N-containing organic pollutant, occurring in effluents from herbicides and pesticides manufacturing industries) by microwave irradiation (750 W), this appearing to be an effective alternative degradation technique. The largest pyridine removal (from 20 to 0.5 $mg{\cdot}L^{-1}$) was obtained in 5 min, at pH = 9 [46]. For the microwave-induced degradation of another herbicide, atrazine, the role of surface chemistry in mineral micropores of a solvent–sorbate–sorbent system was also investigated. Actually, surface chemistry affects the interactions of sorbate and solvent molecules with the pore wall surfaces of microporous Y zeolites with different densities (0.16–2.62 site nm^{-2}) and types (Mg^{2+}, Ca^{2+}, H^+, Na^+ and NH^{4+}), thus influencing the transmission and absorption of microwave energy (2,450 MHz). The presence of surface cations at around 0.23 site nm^{-2} on the pore wall surface was found to be optimal for atrazine degradation [47]. The aforementioned substantial performance improvements in the oxidation of several organic pollutants, in terms of high degradation yields and short reaction times, by coupling microwave energy to AOPs would easily justify additional capital and electricity costs, although the degradation mechanism and variation in the formation of intermediate species remains relatively obscure [48].

In order to extend the narrow acidic pH range, a limitation of traditional Fenton process, to a nearly neutral condition, and thus broaden the application of this method in wastewater treatment, the introduction of Cu^{2+} as assistant catalyst into microwave-assisted Fenton/Fenton-like system was investigated for the removal of *p*-nitrophenol (PNP),

an environmentally harmful and difficultly biodegradable substance. By the proposed process, clearly improved PNP degradation efficiency was achieved in a short time, and over 20% of Fe^{2+}/H_2O_2 consumption was saved. This would be attributed to strengthened generation of ·OH radicals by the cooperation of Cu^{2+} and Fe^{2+} due to a certain concealed mechanism. Indeed, the optimal pH range in Fenton reaction was extended from 2.0–3.5 to 2.0–5.5. Other critical operating parameters appear to be the H_2O_2 and CuO dosage, as well as the microwave power and irradiation time [49,50]. A new heterogeneous catalyst, delafossite-type $CuFeO_2$, was also examined in microwave-enhanced Fenton-like process for rapid decolorization of azo-dye effluent (orange G). In fact, 99.9% decolorization efficiency was achieved within 15 min at pH = 5 by the synergistic effect of MW irradiation, with bimetallic oxide catalyst showing much higher ability for activating peroxide than single-metal oxides [51]. Moreover, a simple Cu^{2+}/H_2O_2 Fenton-like system was reported for the microwave degradation of recalcitrant compounds such as polyphenols (optimal experimental conditions of 680 W microwave power and 12 mol·L^{-1} relatively concentrated H_2O_2). This method can be an efficient solution for the treatment of olive mill wastewater an effluent with high organic matter content and high COD and biochemical oxygen demand values. Specifically, wastewater decolorization reached 98.0% and phenolic compounds decreased to 81.8% of their initial concentration after 12 min [52]. Furthermore, Mn^{2+} ion was introduced into a microwave-enhanced Fenton system for removing bisphenol A (BPA) in wastewater. Under the optimal operating parameters (microwave power = 300 W, pH = 4, Mn^{2+} = 2.7 g·L^{-1}, Fe^{2+} = 2.1 mg·L^{-1}, [H_2O_2] = 34.0 mg·L^{-1}, t = 6.0 min and initial BPA concentration = 100.0 mg·L^{-1}), the BPA degradation efficiency and TOC removal reached 99.7% and 53.1%, respectively [53].

Besides, the impact of microwave irradiation during Fenton oxidation is significant both on the efficient improvement of sludge dewaterability and the reduction of reaction time, as it was confirmed studying the morphological characteristics of sludge under optimized conditions (microwave power = 648 W, pH = 3, Fe^{2+} = 0.4 g·L^{-1}, [H_2O_2] = 6.0 g·L^{-1} and t = 2.0 min) [54]. The advantages offered by the application of microwave irradiation techniques over conventional methods for effective biological waste sludge treatment and generation of environmentally clean and value-added end products are also outlined in other relevant studies [3,4,55–57].

2.3. Microwave-assisted chemical oxidation

Another promising approach for the treatment of sludge, in order to degrade adsorbed micropollutants that can be problematic for the safe reuse or disposal of biosolids, seems to be the combination of microwave irradiation with chemical oxidation, MW/H_2O_2 and MW/$S_2O_8^{2-}$ (>97% antibiotic degradation in 15 min, at 160°C, 1.2 g H_2O_2 and 0.87 g $S_2O_8^{2-}$ per gram of total solids, respectively). Comparatively, MW/$S_2O_8^{2-}$ is reported to provide 48% more overall metal solubilization and twofold higher improvement in dewaterability [58].

Moreover, for the rapid activation of persulfate, and thus of production of $SO_4^{-\bullet}$, which is a powerful oxidant, the combination of microwave energy with catalytic ion Ag^+ was showed to be an efficient method. In fact, when applied to the oxidation of dimethyl phthalate (DMP), a pollutant of environmental concern in aqua media, 80% of DMP and 70% of COD were degraded in 140 s under the optimal conditions (800 W microwave power, 0.083 mmol·L^{-1} $Na_2S_2O_8$ concentration and 0.042 mmol·L^{-1} Ag^+ concentration) [59]. Also, from the contribution of both microwave irradiation and persulfate oxidation in treating landfill leachate, specific effects occur, usually additive and even synergistic. Exceptionally, it was found that the combination was antagonistic only at the highest temperature tested (85°C), where microwave irradiation may cause generation of oxidizing radicals at adverse rates [60]. In further study regarding the treatment of landfill leachate, the previous researchers compared formation and degradation behavior of organic acids under microwave oxidation process and under conventional heating oxidation. In both oxidation methods tested, TOC could not be degraded without persulfate addition [61].

AC has also been extensively used in microwave catalysis technology for environmental pollution abatement. Particularly for the pretreatment of persistent old-age landfill leachate, microwave-assisted catalytic oxidation in the presence of AC displayed superior treatment effectiveness compared with each separate process [62]. In petroleum industry, a significant synergetic effect was observed between microwave irradiation and Fe^0/granular activated carbon (GAC) microelectrolysis system for the pretreatment of refinery wastewater. Actually, the biodegradability of the wastewater was improved by approximately 60% (in terms of COD removal efficiency) by the microwave-enhanced microelectrolysis treatment under the optimal conditions (500 W microwave power, 15 min reaction time, 30 g·L^{-1} iron filings dosage, 5.75 g·L^{-1} GAC dosage and initial pH = 3), thus rendering the pretreatment process favorable for the subsequent biological process [63]. Also, milder reaction conditions can be applied and higher rates be achieved for petroleum oxidative desulfurization under microwave treatment compared with conventional heating technologies (a best sulfur removal rate of 96% was achieved for diesel compared with 64% if only applied oxidizing reagent) [64].

Moreover, MnO_2, a relatively mild reagent, under microwave-irradiation, is reported to act as an efficient oxidizer for the high-yield oxidation of arylmethylene compounds to the corresponding aldehydes and ketones as well as benzylic ethers to esters (mixing of reactants with 25 wt% of MnO_2 and heating at 105°C for 150–240 s, with a solvent-free procedure and oxidant recyclability) [65] or in sulfuric acid solution for the rapid (45 min) removal of polychlorinated biphenyls from soil contaminated by capacitor oil (800 W MW power with the assistance of 0.1 g δ-MnO_2 and 0.2 mL water in 1.0 g) [66]. The type of MnO_2 tested in each study affected the pollutant removal: in the first, nano-MnO_2 showed reactivity superior to synthetic (Attenburrow) MnO_2 and commercial MnO_2, while in the second, the removal efficiency followed an order of δ-MnO_2 > α-MnO_2 > β-MnO_2. ε-MnO_2 (akhtenskite) was also proved to be a kind of excellent microwave catalyst for the degradation of tetracycline in water by microwave-induced oxidation (degradation efficiency of 96.96% in 30 min, under 400 W MW irradiation and pH = 1) [67].

Recently, a new microwave catalytic oxidation process was reported, based on two kinds of catalysts, the

commercially available AC and Mn_2O_3 nanoparticle modified activated carbon (Mn_2O_3/AC), without adding any oxidant, for the degradation of 4-nitrophenol (4-NP). This is one of the most important derivatives of phenol, intermediate of pesticide, pharmaceuticals, dyes, oil refineries and organic chemical manufacturing, which can be largely harmful for humans even at low concentration. The Mn_2O_3/AC catalyst showed much higher catalytic activity than pure AC

Table 1
Advanced oxidation/degradation of industrial effluents under microwave irradiation

Methods	Effluents	Results	References
MW/TiO_2 photocatalytic oxidation	4-Chlorophenol	Enhancement of photodegradation kinetics	[13,31]
UV/H_2O_2/MW	Azo-dye (tartrazine)	Rapid degradation	[32]
A-TiO_2/AC/MW irradiation–Fenton oxidation coupling coagulation process	Dye wastewater/parathion degradation	Removal of parathion in wastewater treatment applications	[33]
MW/UV/O_3/photocatalysis	Chlorophenoxyacetic herbicide	Important role in the O_3-assisted photocatalysis	[34]
MW-enhanced photocatalytic membrane distillation process	Organic wastewater containing inorganic ions	COD removal rate >96%	[35]
Lurgi coal gasification wastewater	Sewage sludge	Eliminating biorefractory compounds	[36,37]
MW discharge electrodeless lamps/H_2O_2	Photooxidation of guaiacol to value-added carboxylic acids	More effective degradation	[38]
Fenton (Fe^{2+}/H_2O_2)/MW and/or Fenton-like (Fe^{3+}/H_2O_2)/MW	Organic contaminants, dye degradation, oxidation of EDTA, pharmaceutical wastewater	Effective and fast processing reduction of the necessary Fe catalyst concentrations/COD removal/TOC removal	[39–45]
Surface chemistry/MW irradiation	Organic pollutants from herbicides and pesticides manufacturing industries	Degradation technique	[46,47]
MW to AOPs	Several organic pollutants	Enhancements between 30% and 1,300%	[48]
MW catalytic oxidation/MW "irradiation-standing" process/MW-assisted Fenton-like	*p*-Nitrophenol (PNP)/orange G/olive mill wastewater/bisphenol A	PNP and high organic matter content and recalcitrant compounds degradation	[49–53]
MW irradiation with chemical oxidation (MW/H_2O_2, MW/Fenton and MW/$S_2O_8^{2-}$)	Biological waste sludge/dewaterability of sludge	Degradation of adsorbed micropollutants/reduce reaction time	[54–58]
MW irradiation with catalytic Ag^+ ion	Dimethyl phthalate, treating landfill leachate	Degradation of dimethyl phthalate, degradation behaviors of organic acids	[59–61]
Activated carbon/MW catalysis	Pretreatment of persistent old-age landfill leachate	Environmental pollution abatement/biodegradability of the wastewater	[62–64]
MW-irradiation/MnO_2	Arylmethylene compounds/benzylic ethers/polychlorinated biphenyls/tetracycline	Oxidation to aldehydes and ketones/esters/removal from soil/degradation	[65–67]
Activated carbon (AC)/Mn_2O_3 nanoparticle (Mn_2O_3/AC)/MW "photoelectric effect"	4-Nitrophenol	Effective degradation	[68]
Catalyst of pristine Bi_2O_3/MW and Pt/resin catalyst/MW	*p*-Nitrophenol/methyl orange dye wastewater	Highly efficient treatment of polluted water/degradation of methyl orange	[69,70]
One-pot catalytic system	Aromatic, cyclic hydrocarbons	Highly efficient oxidation	[71–73]
Sequential microwave/aeration process	Synthetic solutions	Ammonia removal from aqueous systems	[74]

and Mn_2O_3 particles. Indeed, 4-NP degradation efficiency reached 99.6% in 5 min, corresponding to 93.5% TOC removal, under optimal conditions (400 W MW power, 2 g Mn_2O_3/AC dosage and 100 mg·L^{-1} initial concentration), which was attributed to the generation of ·OH radicals due to the microwave "photoelectric effect" [68]. Furthermore, microwave catalyst of pristine Bi_2O_3 was developed for the highly efficient treatment of PNP polluted water (99.74% degradation and 94.20% TOC removal) by microwave catalytic oxidation. The process involves excitation of Bi_2O_3 and electron–hole pair generation by MW irradiation, adsorbance of H_2O onto the catalyst surface and its transformation into ·OH radicals [69] In addition, Pt/resin catalyst was prepared and its performance was investigated in the microwave-assisted oxidation of methyl orange, showing high catalytic efficiency for dye degradation under the optimal treatment conditions (700 W MW power, 7 min irradiation, 6 g·L^{-1} catalyst dosage and 150 mg·L^{-1} H_2O_2 concentration, for 50 mg·L^{-1} initial dye concentration). Introduction of H_2O_2 into the system can further improve the methyl orange degradation ability to some extent [70].

An one-pot catalytic system is also reported, employing in situ generated sodium ferrate for highly efficient oxidation of aromatic and cyclic hydrocarbons in the presence of Au(III) and Pd(II) metal ion catalysts under eco-friendly microwave-assisted method [71]. Moreover, microwave-enhanced catalytic wet peroxide procedure, with supported Cu catalyst and Cu/Ni bimetallic catalyst, were used for quinoline oxidation attaining the highest TOC abatement = 81.12% (under MW power = 500 W, [H_2O_2] = 22.75 mmol·L^{-1} and [Cu/Ni] = 4 g·L^{-1}, at pH = 7). After the Ni incorporation, the catalytic activity of Cu catalyst was improved by about 20% along with its stability enhancement [72–73].

Besides, the effectiveness of using microwave-enhanced advanced oxidation (MW/H_2O_2) for treating dairy manure for resource recovery was demonstrated in a continuous-flow microwave (915 MHz) wastewater treatment system: about 84% of total phosphorus and 45% of total COD were solubilized with the highest H_2O_2 dosage (0.4% H_2O_2 per %TS) [26]. Moreover, the application of sequential microwave/aeration process was considered as an effective approach for ammonia removal from aqueous systems (81.7% maximum ammonia removal, with 650 W microwave power over 120 s irradiation followed by 10 min aeration, for 100 mL synthetic solution) [74].

In Table 1, a comprehensive overview of microwave-assisted advanced oxidation methods for industrial effluents degradation is provided. Several microwave-enhanced heterogeneous photocatalytic, photo-Fenton/Fenton-like and chemical oxidation processes, using standard or newly developed catalysts, and focusing on a highly efficient and fast processing for the degradation of various pollutants of low biodegradability including pesticides/herbicides, pharmaceuticals, dyes, etc., are summarized.

3. Conclusions

The advanced oxidation of organic pollutants in industrial effluents can efficiently be enhanced (up to practically complete pollutant degradation) under microwave irradiation, thus accelerating purification reactions, decreasing the consumption of chemicals and destroying microorganisms at low temperatures.

The synergistic effect observed is mainly attributed to an increased formation of oxidative hydroxyl radicals (·OH) due to a sort of surface restructuring induced by the microwave energy, than to a beneficial microwave thermal effect alone.

Microwave frequency (915 or 2,450 MHz) and power level (200–800 W), irradiation time (1–15 min in most of cases) and temperature (<160°C), oxidizing agent (usually H_2O_2), catalyst loading (up to 1 g·L^{-1}), aeration, pH (frequently 2–5 and rarely 7 or 9) and initial pollutant concentration (rather dilute solutions) are key operating factors influencing the oxidation efficiency.

In conclusion, microwave-assisted AOPs appear to be promising alternatives for the treatment of pollutants of poor biodegradability. It should be noticed, however, that, generally, full-scale application for real industrial wastewater still remains underway.

Acknowledgments

This study has been financed through the Research Program "Innovative recycling-valorization of industrial solid byproducts in the development of new materials for the treatment and advanced oxidation of industrial liquid effluents" (Scientific Coordinator: Professor Vayos G. Karayannis) funded by the Specific-Account Research Committee (ELKE) of Western Macedonia University of Applied Sciences, Greece (Grant number: 80144).

References

[1] A.-M. Galan, I. Calinescu, A. Trifan, C. Winkworth-Smith, M. Calvo-Carrascal, C. Dodds, E. Binner, New insights into the role of selective and volumetric heating during microwave extraction: investigation of the extraction of polyphenolic compounds from sea buckthorn leaves using microwave-assisted extraction and conventional solvent extraction, Chem. Eng. Process., 116 (2017) 29–39.

[2] J. Li, J. Dai, G. Liu, H. Zhang, Z. Gao, J. Fu, Y. He, Y. Huang, Biochar from microwave pyrolysis of biomass: a review, Biomass Bioenergy, 94 (2016) 228–244.

[3] Y. Avsar, U. Kurt, Thermotechnical comparison of conventional heating and microwave radiation method for dewatering of sewage sludge, Desal. Wat. Treat., 72 (2017) 274–280.

[4] P.M. Mawioo, H.A. Garcia, C.M. Hooijmans, K. Velkushanova, M. Simonič, I. Mijatović, D. Brdjanovic, A pilot-scale microwave technology for sludge sanitization and drying, Sci. Total Environ., 601–602 (2017) 1437–1448.

[5] A.H. Jawad, M.A.M. Ishak, A.M. Farhan, K. Ismail, Response surface methodology approach for optimization of color removal and COD reduction of methylene blue using microwave-induced NaOH activated carbon from biomass waste, Desal. Wat. Treat., 62 (2017) 208–220.

[6] H. Carrere, G. Antonopoulou, R. Affes, F. Passos, A. Battimelli, G. Lyberatos, I. Ferrer, Review of feedstock pretreatment strategies for improved anaerobic digestion: from lab-scale research to full-scale application, Bioresour. Technol., 199 (2016) 386–397.

[7] L. Peng, D. Deng, F. Ye, Efficient oxidation of high levels of soil-sorbed phenanthrene by microwave-activated persulfate: implication for in situ subsurface remediation engineering, J. Soils Sediments, 16 (2015) 28–37.

[8] F. Mushtaq, T.A.T. Abdullah, R. Mat, F.N. Ani, Optimization and characterization of bio-oil produced by microwave assisted pyrolysis of oil palm shell waste biomass with microwave absorber, Bioresour. Technol., 190 (2015) 442–450.

[9] J.-K. Koo, S.-I. Jeong, Sustainability and shared smart and mutual – green growth (SSaM-GG) in Korean medical waste management, Waste Manage. Res., 33 (2015) 410–418.
[10] H. Djahaniani, L. Aghadadashi-Abhari, B. Mohtat, N-Methylimidazole-mediated synthesis of aryl alkyl ethers under microwave irradiation and solvent free conditions, J. Serb. Chem. Soc., 80 (2015) 459–464.
[11] A. Tsukui, C.M. Rezende, Microwave assisted extraction and green chemistry, Rev. Virtual Quim., 6 (2014) 1713–1725.
[12] V.G. Karayannis, A.K. Moutsatsou, E.L. Katsika, Synthesis of microwave-sintered ceramics from lignite fly and bottom ashes, J. Ceram. Process. Res., 14 (2013) 45–50.
[13] S. Horikoshi, Microwave technology in environmental chemistry, J. Inst. Electr. Eng. Jpn., 132 (2012) 23–25.
[14] K. Loganathan, Ozone-based advanced oxidation processes for the removal of harmful algal bloom (HAB) toxins: a review, Desal. Wat. Treat., 59 (2017) 65–71.
[15] J.R. Alvarez-Corena, J.A. Bergendahl, F.L. Hart, Advanced oxidation of five contaminants in water by UV/TiO_2: reaction kinetics and byproducts identification, J. Environ. Manage., 181 (2016) 544–551.
[16] Z. Frontistis, M. Kouramanos, S. Moraitis, E. Chatzisymeon, E. Hapeshi, D. Fatta-Kassinos, N.P. Xekoukoulotakis, D. Mantzavinos, UV and simulated solar photodegradation of 17α-ethynylestradiol in secondary-treated wastewater by hydrogen peroxide or iron addition, Catal. Today, 252 (2015) 84–92.
[17] K. Soutsas, V. Karayannis, I. Poulios, A. Riga, K. Ntampegliotis, X. Spiliotis, G. Papapolymerou, Decolorization and degradation of reactive azo dyes via heterogeneous photocatalytic processes, Desalination, 250 (2010) 345–350.
[18] I. Fatimah, I. Sumarlan, T. Alawiyah, Fe(III)/TiO_2-montmorillonite photocatalyst in photo-Fenton-like degradation of methylene blue, Int. J. Chem. Eng., 2015 (2015) 1–9.
[19] N. Philippidis, S. Sotiropoulos, A. Efstathiou, I. Poulios, Photoelectrocatalytic degradation of the insecticide imidacloprid using TiO_2/Ti electrodes, J. Photochem. Photobiol., A, 204 (2009) 129–136.
[20] E. Katsika, A. Moutsatsou, V. Karayannis, A. Ntziouni, Preparation and characterization of lignite ashes coated with TiO_2 for environmental application, J. Chem. Technol. Metall., 52 (2017) 940–949.
[21] K. Moustakas, S. Malamis, Water Is Necessary For Life – WIN4Life, Conference 19–21 September 2013, Tinos Island, Greece, Desal. Wat. Treat., 53 (2015) 3149–3150.
[22] I.K. Kalavrouziotis, E. Kostakioti, P.H. Koukoulakis, A.H. Papadopoulos, M. Leotsinidis, E. Sakazli, The impact of Cl × Cd interrelationship on planning wastewater reuse in cabbage, Water Air Soil Pollut., 214 (2011) 565–573.
[23] N.-C. Shang, Y.-H. Yu, H.-W. Ma, C.-H. Chang, M.-L. Liou, Toxicity measurements in aqueous solution during ozonation of mono-chlorophenols, J. Environ. Manage., 78 (2006) 216–222.
[24] N. Wang, P. Wang, Study and application status of microwave in organic wastewater treatment – a review, Chem. Eng. J., 283 (2016) 193–214.
[25] S. Horikoshi, N. Serpone, Coupled microwave/photoassisted methods for environmental remediation, Molecules, 19 (2014) 18102–18128.
[26] A. Srinivasan, P.H. Liao, K.V. Lo, Microwave treatment of dairy manure for resource recovery: reaction kinetics and energy analysis, J. Environ. Sci. Health, Part B, 51 (2016) 840–846.
[27] P.P. Mehta, P. Mane, Microwave chemistry: a review, Int. J. Pharm. Technol., 7 (2015) 3210–3226.
[28] J. Liu, G. Jia, Non-thermal effects of microwave in sodium chloride aqueous solution: insights from molecular dynamics simulations, J. Mol. Liq., 227 (2017) 31–36.
[29] S. Duhan, A. Kar, L. Nain, A.S. Patel, S.K. Dash, Development of continuous flow microwave and hot water bath system for destruction of spoilage microorganisms in food, Indian J. Agric. Sci., 87 (2017) 210–214.
[30] S. Horikoshi, N. Serpone, On the influence of the microwaves' thermal and non-thermal effects in titania photoassisted reactions, Catal. Today, 224 (2014) 225–235.
[31] S. Horikoshi, Y. Minatodani, H. Tsutsumi, H. Uchida, M. Abe, N. Serpone, Influence of lattice distortion and oxygen vacancies on the UV-driven/microwave-assisted TiO_2 photocatalysis, J. Photochem. Photobiol., A, 265 (2013) 20–28.
[32] F. Parolin, U.M. Nascimento, E.B. Azevedo, Microwave-enhanced UV/H_2O_2 degradation of an azo dye (tartrazine): optimization, colour removal, mineralization and ecotoxicity, Environ. Technol., 34 (2013) 1247–1253.
[33] Z. Zhang, J. Jiatieli, D. Liu, F. Yu, S. Xue, W. Gao, Y. Li, D.D. Dionysiou, Microwave induced degradation of parathion in the presence of supported anatase- and rutile-TiO_2/AC and comparison of their catalytic activity, Chem. Eng. J., 231 (2013) 84–93.
[34] H. Lee, S.H. Park, Y.-K. Park, S.-J. Kim, S.-G. Seo, S.J. Ki, S.-C. Jing, Photocatalytic reactions of 2,4-dichlorophenoxyacetic acid using a microwave-assisted photocatalysis system, Chem. Eng. J., 278 (2015) 259–264.
[35] J. Wang, X. Sun, Y. Yuan, H. Chen, H. Wang, D. Hou, A novel microwave assisted photo-catalytic membrane distillation process for treating the organic wastewater containing inorganic ions, J. Water Process Eng., 9 (2016) 1–8.
[36] P. Xu, W. Ma, B. Hou, Z. Shi, A novel integration of microwave catalytic oxidation and MBBR process and its application in advanced treatment of biologically pretreated Lurgi coal gasification wastewater, Sep. Purif. Technol., 177 (2017) 233–238.
[37] N. Amjed, I.A. Bhatti, A. Nazir, M. Iqbal, Microwave-assisted desulfurization of coal by photo-catalytic oxidation treatment, Energy Sources Part A, 39 (2017) 1043–1049.
[38] D. Zhang, B. Sun, L. Duan, Y. Tao, A. Xu, X. Li, Photooxidation of guaiacol to organic acids with hydrogen peroxide by microwave discharge electrodeless lamps, Chem. Eng. Technol., 39 (2016) 97–101.
[39] V. Homem, A. Alves, L. Santos, Microwave-assisted Fenton's oxidation of amoxicillin, Chem. Eng. J., 220 (2013) 35–44.
[40] X. Qi, Z. Li, Efficiency optimization of a microwave-assisted Fenton-like process for the pretreatment of chemical synthetic pharmaceutical wastewater, Desal. Wat. Treat., 57 (2016) 11756–11764.
[41] S.-T. Liu, J. Huang, Y. Ye, A.-B. Zhang, L. Pan, X.-G. Chen, Microwave enhanced Fenton process for the removal of methylene blue from aqueous solution, Chem. Eng. J., 215–216 (2013) 586–590.
[42] K.-F. You, J.-H. Fang, Q.-L. Qian, Treatment of the weak acid brilliant red B dyeing wastewater by microwave enhanced Fenton oxidation, Wool Textile J., 41 (2013) 53–56.
[43] G. Zhang, B. Yang, X. Xu, Y. Cui, Research on synergistic effect of microwave irradiation-Fenton oxidation coupling coagulation process to treat dye wastewater, Adv. Mater. Res., 610–613 (2013) 2028–2032.
[44] A. Domopoulou, K. Moustakas, A. Baklavaridis, N. Koukouzas, V. Karayannis, Wastewater treatment for reuse employing industrial by-products as alternative coagulants, Desal. Wat. Treat., (2017). doi:10.5004/dwt.2017.20698.
[45] Q. Lin, H. Pan, K. Yao, Y. Pan, W. Long, Competitive removal of Cu-EDTA and Ni-EDTA via microwave-enhanced Fenton oxidation with hydroxide precipitation, Water Sci. Technol., 72 (2016) 1184–1190.
[46] O.A. Zalat, M.A. Elsayed, A study on microwave removal of pyridine from wastewater, J. Environ. Chem. Eng., 1 (2013) 137–143.
[47] E. Hu, H. Cheng, Impact of surface chemistry on microwave-induced degradation of atrazine in mineral micropores, Environ. Sci. Technol., 47 (2013) 533–541.
[48] U.M. Nascimento, E.B. Azevedo, Microwaves and their coupling to advanced oxidation processes: enhanced performance in pollutants degradation, J. Environ. Sci. Health, Part A, 48 (2013) 1056–1072.
[49] X. Miao, N. Wang, S. Zhao, W. Pan, and P. Wang, Treatment of PNP wastewater by microwave assisted Cu(II)-Fenton catalytic oxidation process, Chin. J. Environ. Eng., 8 (2014) 2299–2305.
[50] W.-Q. Pan, G.-S. Zhang, T. Zheng, J. Zhang, P. Wang, Treatment of p-nitrophenol in water by Fenton-like reaction with microwave coupling, Zhongguo Huanjing Kexue/China Environ. Sci., 34 (2014) 3112–3118.

[51] M.-Q. Cai, Y.-Z. Zhu, Z.-S. Wei, J.-Q. Hu, S.-D. Pan, R.-Y. Xiao, C.-Y. Dong, M.-C. Jin, Rapid decolorization of dye Orange G by microwave enhanced Fenton-like reaction with delafossite-type $CuFeO_2$, Sci. Total Environ., 580 (2017) 966–973.
[52] H. Iboukhoulef, A. Amrane, H. Kadi, Microwave-enhanced Fenton-like system, Cu(II)/H_2O_2, for olive mill wastewater treatment, Environ. Technol., 34 (2013) 853–860.
[53] S. Li, G. Zhang, P. Wang, H. Zheng, Y. Zheng, Microwave-enhanced Mn-Fenton process for the removal of BPA in water, Chem. Eng. J., 294 (2016) 371–379.
[54] J. Zhang, K. Yang, H. Wang, L. Zheng, F. Ma, B. Lv, Impact of microwave treatment on dewaterability of sludge during Fenton oxidation, Desal. Wat. Treat., 57 (2016) 14424–14432.
[55] J.-H. Jang, J.-H. Ahn, Evaluation of a microwave-heating anaerobic digester treating municipal secondary sludge, Environ. Technol., 34 (2013) 885–889.
[56] S.N. Mehdizadeh, C. Eskicioglu, J. Bobowski, T. Johnson, Conductive heating and microwave hydrolysis under identical heating profiles for advanced anaerobic digestion of municipal sludge, Water Res., 47 (2013) 5040–5051.
[57] V.K. Tyagi, S.-L. Lo, Microwave irradiation: a sustainable way for sludge treatment and resource recovery, Renew. Sustain. Energy Rev., 18 (2013) 288–305.
[58] N. Bilgin Oncu, I. Akmehmet Balcioglu, Microwave-assisted chemical oxidation of biological waste sludge: simultaneous micropollutant degradation and sludge solubilisation, Bioresour. Technol., 146 (2013) 126–134.
[59] D. Sun, X. Yan, W. Xue, Oxidative degradation of dimethyl phthalate (DMP) by persulfate catalyzed by Ag+ combined with microwave irradiation, Adv. Mater. Res., 610–613 (2013) 1209–1212.
[60] Y.-C. Chou, S.-L. Lo, J. Kuo, C.-J. Yeh, A study on microwave oxidation of landfill leachate—contributions of microwave-specific effects, J. Hazard. Mater., 246–247 (2013) 79–86.
[61] Y.-C. Chou, S.-L. Lo, J. Kuo, C.-J. Yeh, Derivative mechanisms of organic acids in microwave oxidation of landfill leachate, J. Hazard. Mater., 254–255 (2013) 293–300.
[62] C.J. Li, Y. Li, H. Zhang, L.Y. Tian, J. Lv, Activated carbon in environment pollution abatement based on microwave catalysis technology, Appl. Mech. Mater., 329 (2013) 13–17.
[63] G. Qin, D. Gong, Pretreatment of petroleum refinery wastewater by microwave-enhanced Fe^0/GAC micro-electrolysis, Desal. Wat. Treat., 52 (2014) 2512–2518.
[64] H. Shang, H. Zhang, W. Du, Z. Liu, Development of microwave assisted oxidative desulfurization of petroleum oils: a review, J. Ind. Eng. Chem., 19 (2013) 1426–1432.
[65] B. Nammalwar, C. Fortenberry, R.A. Bunce, S.K., Lageshetty, K.D. Ausman, Efficient oxidation of arylmethylene compounds using nano-MnO_2, Tetrahedron Lett., 54 (2013) 2010–2013.
[66] Z.-R. Lin, L. Zhao, Y.-H. Dong, Application of microwave-irradiated manganese dioxide in the removal of polychlorinated biphenyls from soil contaminated by capacitor oil, Environ. Technol., 34 (2013) 637–644.
[67] Y.-Y. Peng, J. Tao, J.-W. Feng, X.-Y. Wang, L.-B. Liao, G.-C. Lv, Degradation of tetracycline in water by microwave induced catalytic oxidation of akhtenskite, Rengong Jingti Xuebao/J. Synth. Cryst., 43 (2014) 1651–1656.
[68] C. Yin, J. Cai, L. Gao, J. Yin, J. Zhou, Highly efficient degradation of 4-nitrophenol over the catalyst of Mn_2O_3/AC by microwave catalytic oxidation degradation method, J. Hazard. Mater., 305 (2016) 15–20.
[69] Y. Qiu, J. Zhou, J. Cai, W. Xu, Z. You, C. Yin, Highly efficient microwave catalytic oxidation degradation of p-nitrophenol over microwave catalyst of pristine α-Bi_2O_3, Chem. Eng. J., 306 (2016) 667–675.
[70] D.-Y. Xu, Q.-Z. Lu, P. Dai, and M.-L. Li, Microwave assisted catalytic oxidation of methyl orange in aqueous solution by using Pt/resin catalyst, J. Chem. Eng. Chin. Univ., 28 (2014) 195–200.
[71] M. Srivastava, A. Srivastava, A. Goyal, A. Mishra, P. Tomer, J. Dwivedi, D. Kishore, One-pot oxidation of aromatic and cyclic hydrocarbons using the Au (III) and Pd (II) catalyst under microwave irradiation, J. Phys. Org. Chem., 30 (2017) e3602.
[72] B. Zhang, H. You, F. Wang, Z. Yang, Influence of nickel incorporation on the structure and catalytic behavior of Cu-catalyst for heterogeneous catalytic wet peroxide oxidation of quinoline under microwave irradiation, Catal. Commun., 88 (2017) 56–59.
[73] B. Zhang, H. You, F. Wang, Microwave-enhanced catalytic wet peroxide oxidation of quinoline: the influence of pH and H_2O_2 dosage and identification of reactive oxygen species, RSC Adv., 7 (2017) 14769–14775.
[74] S. Dong, M. Sartaj, Statistical analysis of thermal and nonthermal effects of sequential microwave/aeration process for the removal of ammonia from aqueous solution, Desal. Wat. Treat., 57 (2016) 20005–20015.