Review

Current status of microwave application in wastewater treatment—A review

Neelancherry Remya, Jih-Gaw Lin*

Institute of Environmental Engineering, National Chiao Tung University, 1001, University Road, Hsinchu City 30010, Taiwan

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ABSTRACT

Microwave (MW) irradiation has gained a great deal of attention owing to the molecular level heating. However, the commercialization of MW technology for real-time wastewater (WW) treatment requires the understanding of basic mechanism of MW and MW coupled treatment methods. This review addresses the basic theory and mechanism of MW, current application of MW in WW treatment, MW reactors and economical aspects of MW in WW treatment. The different combinations of MW application in WW treatment, including MW alone, MW with oxidants, MW with catalyst and MW with advanced oxidation processes (AOPs) are discussed in detail. Moreover, the effect of MW heating and the factors affecting MW coupled treatment methods are discussed with respect to the treatment efficiency. Finally, the future research challenges in the application of MW for WW treatment are emphasized.

1. Introduction

Advanced oxidation processes (AOPs) are highly efficient and novel methods for the rapid oxidation/degradation of many organic and inorganic substances. In the recent years, AOPs have emerged as potentially powerful methods for transforming organic pollutants into non-toxic substances [1]. The most widely adopted AOPs include photodegradation, Fenton, photo-Fenton, ultrasonication and ozonation (O_3). AOPs rely on the generation of reactive free radicals, especially hydroxyl radicals ($^{\bullet}OH$). It is highly powerful oxidizing agent having an oxidation potential of 2.33 V, which can undergo rapid and non-selective reaction with most organic and many inorganic solutes. Unlike conventional physicochemical processes, AOPs provide faster reaction rate; at the same time, AOPs are effective in the removal of various bio-refractory organics present in water and wastewater (WW) [2,3]. The operational cost of many AOPs is relatively expensive. The AOPs such as O_3 and combination of O_3 and hydrogen peroxide (H_2O_2) could be useful for achieving 50% phenol degradation ($t_{1/2}$) at relatively lower energy requirements; whereas, the photodecomposition of phenol (UV alone) requires the highest energy consumption [4]. Fig. 1 shows the power consumption for phenol degradation under different combinations of AOPs. The energy consumption and operational cost of AOPs could vary from pollutant to pollutant and also based on their loading rates. However, the energy consumption of many AOPs shown in Fig. 1 will shoot-up when they are scaled-up for real-time applications [5]. In addition, several AOPs require chemicals like ferric or ferrous salts to initiate oxidation process, which may cause secondary pollution. These drawbacks have challenged the scientists to improve the AOPs and to explore new methods for WW treatment.

Microwave (MW) irradiation has acquired a great deal of attention in domestic, industrial and medical applications. MW has been used in various environmental applications including pyrolysis [6–8], phase separation and extraction processes [9–15], soil remediation [16–21], remediation of hazardous and radioactive wastes [22], coal desulphurization [23–25], sewage sludge treatment [26,27], chemical catalysis [28,29] and organic/inorganic syntheses [30–35]. The application of MW for environmental engineering projects is based on the property of the MW, i.e. rapid and selective heating. In pyrolysis, a partially vitrified material of relatively low porous texture is produced from carbonaceous waste owing to very high temperatures. The application of MW during

Fig. 1. Power consumption of different AOPs for $t_{1/2}$ degradation of phenol [4].

Fig. 2. The interaction of MW with different materials [95].

pyrolysis accelerates the development of the vitrified material due to the strong MW absorption (rapid heating by MW absorption) of the carbonaceous waste. Similarly, the rapid heating property of MW is used for soil remediation, remediation of hazardous and radioactive wastes, and chemical catalysis. On the other hand, the selective heating property of MW is used in coal desulphurization, separation and purification processes.

MW is also a useful technique for water and WW treatment. It can be applied alone, i.e. MW alone [36–38], pooled with oxidants and catalysts or coupled with AOPs like Fenton process, UV (photolysis) or photocatalysis (UV/titanium dioxide, TiO_2). In the past, MW was coupled with oxidants like H_2O_2 for enhanced pollutant degradation [39–44]. Subsequently, MW enhanced catalytic degradation has been an emerging field of research [3,45–68]. A variety of MW-absorbing materials with high surface area and a wide range of pore size distribution were developed for enhancing the degradation of organic pollutants under MW [58]. When a MW-absorbing material is used, for example activated carbon (AC), hot-spots are formed on the surface of the AC; thus, produces selective heating, spur in the molecular rotation and finally decreases the activation energy [60]. In addition, the efficiency of MW for pollution degradation was also amplified by coupling MW with photo-Fenton and Fenton like processes [69,70], photolysis [71,72], photolysis in the presence of H_2O_2 [1,73,74] and photocatalysis [5,75–91]. The integration of MW with electrodeless discharge lamps (EDLs), generating UV–vis light when irradiated with electromagnetic field, is also an emerging field of research in the recent years [87]. The above description reveals that MW has received much attention in the recent decades due to its greater potential in various applications and ease in the operation. The application and effect of MW heating in environmental engineering [92,93] and the photochemistry of MW with catalysts [94] have been reviewed. However, a basic understanding of MW theory, its application in pollution removal and the various combinations of MW applications, i.e. combining MW with other treatment techniques, are necessary to promote the application of MW for water and WW treatment. Thus, this review is focused to address the application of MW for the enhanced degradation of organic pollutants in aqueous solution.

2. Microwave (MW)

2.1. MW theory and mechanism

MW is a part of the electromagnetic spectrum occurring in the frequency range of 300 MHz to 300 GHz. It has been used for heating since 1937; however, the first commercial MW oven operating at 2.45 GHz was introduced in 1947 [95]. Thereafter, MW was developed considerably for various heating applications [92] but the use of M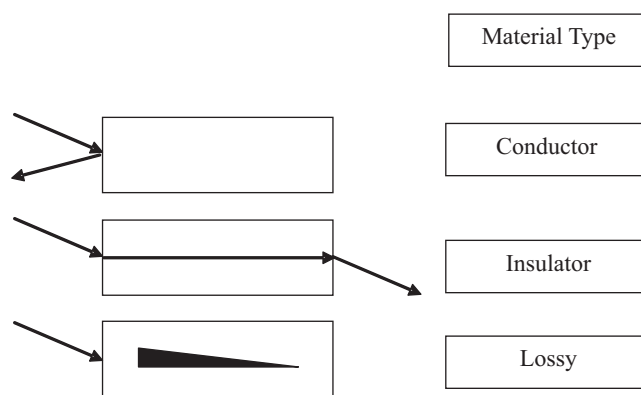W for chemical transformations improved tremendously after the application of MW oven in laboratory in 1975 [71]. In recent years, MW has been used widely in the field of environmental engineering. MW can provide rapid heating of materials depending on the dissipation factor of the material (loss tangent). Dissipation factor is the ratio of relative loss factor (ε'') to the dielectric constant (ε') of a material. Dielectric constant is a relative measure of the MW energy density in the material and the relative loss factor accounts for the internal loss mechanisms, i.e. the amount of MW energy that is lost in the material as heat. Therefore, a lossy material with a high ε'' is easily heated by MW energy. Fig. 2 illustrates the interaction of MW with different materials. The MW is reflected from the surface of electric conductors such as metals and insulators that are transparent to MW; however, a metal in powder form or of fine particle size can be heated by MW. In addition, insulator materials can be heated in MW by using heat facilitator such as magnetite, silicon carbide or carbon, where the MW first heats the facilitator and subsequently the insulator [96].

The principal heating mechanisms of MW are dipolar polarization, conduction mechanism and interfacial polarization. A dipolar polarization results from intermolecular inertia, which is responsible for majority of MW heating observed in the solvent systems. When the dipole is subjected to a high-frequency alternating electric field of the MW, rotation (reversing) of the dipole cannot adequately follow the rate of change of direction of the electric field. This leads to a time delay, causing a substantial quantity of energy to be spent that turns into heat [59]. The conduction mechanism happens when an electrical conductor is irradiated with MW. At that time, the charge carriers (electrons, ions, etc.) move through the material under the influence of the electric field resulting in a polarization. Subsequently, the induced currents cause heating of the sample due to electrical resistance. The combination of conduction and dipolar polarization produces interfacial polarization, which is important for systems comprised of conducting and non-conducting materials.

2.2. MW in chemical reactions

MW is highly effective for improving the efficiency of many chemical reactions compared to the traditional thermal heat source. Usually, MW effects cannot be achieved by conventional heating. The similarity and differences between the conventional and MW heating mechanisms in terms of yield and purity of products have been reviewed by Nuchter et al. [97]. The MW effects are mainly classified as thermal or nonthermal effects. The thermal effects result from MW heating, which may result in a different temperature regime, whereas nonthermal effects are specific effects resulting from nonthermal interaction between the substrate and MW [98]. However, the operation of nonthermal effects is still controversial. MW thermal effects are due to rapid heating, volumetric

heating, superheating, hotspots and selective heating. In contrast, non-thermal effects are associated with surface polarization. However, the formation of thermal gradient and the nonthermal effects of MW (i.e., nuclear spin rotation and spin alignment) are relevant only for solvent-free or dry media reactions and for very viscous or biphasic reaction systems without effective stirring [99].

The rapid heating and attainment of high temperatures in MW chemistry indicates that most reported rate enhancements could be attributed to simple thermal or kinetic effects [33]. In heterogeneous catalysis, the responsible factor for improved degradation efficiency is mainly due to the interfacial polarization mechanism. The rapid pollutant degradation in the MW system with adsorbent (i.e. AC) is mainly by the hot-spot formation on the surface of the AC, which is a unique mechanism of MW. This is useful to speed-up the reactions in many processes. Generally, the delocalized π-electrons in the surface of the AC are free to move. During the MW irradiation, the kinetic energy of electrons on the surface of the AC is increased, which enables the electrons to jump out of the material resulting in the formation of hot-spot by ionizing the surrounding atmosphere [93]. These hot-spots are actually plasmas, which are confined to a tiny region of space and last for fraction of a second. The temperature of hot-spot can ordinarily reach 1200 °C [92]. The hot-spots cause thermal or temperature effects resulting from the differences between the temperature at the reaction site and temperature in the medium or reactor system. This facilitates the destruction of complex chemical bonds by decreasing the activation energy and increasing the rate of reaction.

MW application for pollutant removal reduces the reaction time and at the same time increases the yield and purity of products in most of the cases [60,61]. In addition, the use of strong MW absorbers such as granular activated carbon (GAC) would result in the rapid increase in temperature and improvement in the speed of reaction [57,60]. Due to the unique property of MW, it provides selective heating of material with quick start up and stopping in which the heating starts from interior of the material body. However, some studies reveal that MW does not induce relevant selective heating effects under the applied reaction conditions. This may be due to the superposition of different factors like similar dielectric property of the target compound and the matrix, lower target compound concentration on the catalyst surface preventing sufficient MW heating and temporal discrepancies between activation time for the compound desorption and residence time [100–102]. On the other hand, the quantum energy of MW causes the vibration of molecules, which helps to decrease the activation energy. Finally, this reduces the equipment size and waste [103].

2.3. MW application in WW treatment

The WW treatment is a process of removing contaminants and organic material from WW using various techniques, systems and methods. Several physical, chemical and biological methods have been used for the treatment of WW. The quality of a good WW treatment system is the higher pollutant degradation/mineralization efficiency with cost-effectiveness and ease of operation. The rapid and effective heating properties of MW lead to its application in WW treatment. MW has been a powerful tool in the degradation of

various organic compounds including pesticides, ammonia nitrogen and organic dyes. The energy of one mole of photon from MW (E) at a frequency range of 1–100 GHz is equal to 0.4–40 J. However, the energy of MW is insufficient to disrupt the chemical bonds of many organic compounds [104]. Therefore, MW has been combined with adsorbents, catalysts and AOPs for increasing the treatment efficiency of various pollutants and also to shorten the reaction time. In the past, MW has been combined with wide variety of AOPs such as UV, Fenton, UV/Fenton, UV/H_2O_2, UV/TiO_2, UV/Bi_2WO_6 and O_3. This review is focused to address the following most commonly preferred MW-assisted systems for WW treatment: (1) MW alone, (2) MW with oxidants, (3) MW with catalysts, i.e. MW enhanced catalytic degradation (MECD), (4) MW with Fenton process, (5) MW with direct photolysis (MWDP) and (6) MW with photocatalysis (MWPC). In general perspective, domestic WW treatment also includes sludge management/treatment. However, some industrial/process WWs produce negligible amount of sludge and the major emphasize of MW is for WW treatment. Thus, the sludge treatment by MW is omitted in this review.

3. MW alone

MW produces homogeneous and quick thermal reactions due to the molecular-level heating. MW has been used in various environmental remediation processes, especially in WW treatment [36–38]. MW alone is found to be more useful treatment process for ammonia removal. Under optimum conditions, complete removal of ammonia nitrogen was achieved in a lab-scale reactor, which demonstrates that the heating and molecular movement produced by MW alone has a great potential for ammonia removal [36]. On the other hand, nearly 80% ammonia evaporation was obtained by introducing MW alone in a pilot-scale treatment system [37]. The decrease in the ammonia removal efficiency in the pilot-scale system is due to the higher target pollutant concentration, higher working volume and probable occurrence of other contaminants. The experimental conditions of the above mentioned lab-scale and pilot-scale treatment systems are listed in Table 1.

The installation and operational costs of MW system are expensive; therefore, optimization of maximum power utilization and recovering part of the process heat through heat exchangers is advisable to minimize the overall cost. However, MW can reduce the treatment time required and can also produce high treatment efficiency for selective compounds, for instance, ammonia. On the other hand, a complete treatment of more complex WWs with multiple pollutants or the removal/degradation of highly bio-refractory pollutant like pentachlorophenol (PCP) is highly difficult with MW alone. Therefore, many researchers combined MW with oxidants, catalysts or AOPs.

4. MW with oxidants

The main advantage of combining MW with oxidants is the stimulation of free radical generation from the oxidants and rapid polarization of the pollutant molecule [42]. When combining MW and oxidants, higher reaction temperature could be reached within a shorter time frame compared to the traditional thermal or cat-

Table 1
Optimum conditions of operation and degradation efficiencies of ammonia by MW.

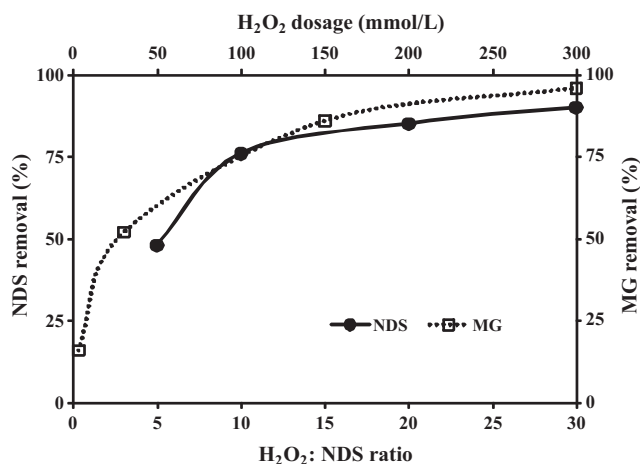| S. No. [Ref. No.]	Type	Initial concentration (mg/L)	Volume of waste water	pH	MW power	Treatment time (min)	Removal efficiency (%)	Remarks
1 [36]	Lab-scale reactor	500	100 mL	11	750 W	3	100	Thermal effects due to dipolar polarization of polar compounds (H_2O and NH_3) caused enhancement in treatment efficiency
2 [37]	Pilot-scale reactor	2400–11,000	28 L	12	4.8 kW	60	80	

Fig. 3. Effect of H_2O_2 dosage on MW-assisted degradation of 1,5-naphthalenedisulfonic acid (NDS) and malachite green (MG) [40,41].

alytic oxidation method. This assists in the faster degradation of pollutants. The two most common oxidants used along with MW are hydrogen peroxide (H_2O_2) and persulfate ($S_2O_8^{2-}$). Table 2 shows the list of studies combined MW with oxidants.

The dipolar polarization mechanism is responsible for enhancing the degradation of various pollutants in the systems combining MW and oxidants. This mechanism creates elevated temperature within a shorter span as compared to conventional heating methods, which provokes the increased decomposition of H_2O_2 into $^•OH$ as shown in Eq. (1) [105]. Subsequently, the $^•OH$ generated in the system undergoes adduction reaction with the target pollutants and the resulting intermediates. As a result, rapid and improved degradation rates are observed [41]. On the other hand, H_2O_2 can act as $^•OH$ quencher at high concentrations as shown in Eqs. (2)–(4), consequently lowering the $^•OH$ concentration which decreases the degradation rates. The effect of H_2O_2 dosage on MW-assisted degradation of 1,5-naphthalenedisulfonic acid (NDS) and malachite green (MG) is shown in Fig. 3. It can be noticed in Fig. 3 that the higher H_2O_2 dosages have not amplified the degradation efficiency of the target compounds, i.e. NDS and MG. The MG degradation rates of 0.115 and 0.063 mg/mmol/min were observed at the H_2O_2 dosages of 150 and 300 mmol/L respectively. The decrease in degradation rate at the highest H_2O_2 dosage could be due to the scavenging effect of H_2O_2. Therefore, the optimum dosage of H_2O_2 must be determined to maintain a higher degradation rate as well as to minimize the cost of overall treatment.
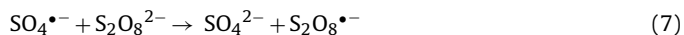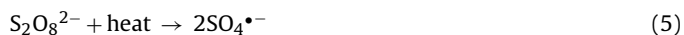
$$H_2O_2 \rightarrow 2HO^• \tag{1}$$

$$HO^• + H_2O_2 \rightarrow HO_2^• + H_2O \tag{2}$$

$$2HO_2^• \rightarrow H_2O_2 + O_2 \tag{3}$$

$$HO^• + HO_2^• \rightarrow H_2O + O_2 \tag{4}$$

Potassium persulfate ($K_2S_2O_8$) is also capable of absorbing MW for the generation of active free radicals and heat point as shown in Eq. (5). Several researchers reported that MW with persulfate oxidation has produced better degradation efficiency of dimethoate and azo dyes as compared with direct photodegradation [42,44]. Temperature plays a major role in MW-assisted degradation process with persulfate because at extremely high temperature the radical itself could act as a scavenger (Eqs. (6) and (7)). For example, perfluorooctanoic acid (PFOA) degradation (250 μM) of 91, 84 and 48% was observed after 1 h of MW-assisted reaction with persulfate at 130, 90 and 60 °C, respectively [43]. The continuation of the reaction for 4 h showed a PFOA degradation of 99% at 90 °C; whereas, only 93% degradation was observed at 130 °C in the similar reaction

Table 2
List of studies coupled MW with oxidants.

S. No. [Ref. No.]	Contaminant and its type	Oxidant	Reaction condition/chemical oxidation scheme	Degradation efficiency, % (time, min)	Mineralization efficiency, % (time, min)	Remarks
1 [40]	Malachite green (MG) (cationic triphenylmethane dye)	H_2O_2	Initial concentration – 100 mg/L, volume – 30 mL, H_2O_2 – 30–300 mmol/L, MW output power – 900 W (continuous mode), temperature – 100 °C.	96 (5)	–	1. No degradation was achieved when MW alone is applied for MG degradation. 2. Decrease in H_2O_2 dosage to 150 mmol/L decreased the MG degradation efficiency to 85%. 3. The increase in degradation was hypothesized to be the increased formation of OH·
2 [41]	1,5 naphthalene disulphonic acid (NDS) (sulphonated aromatic compound)	H_2O_2	Initial concentration – 1 mM, volume – 10 mL, H_2O_2; NDS ratio – 5–30, MW output power – 300 W (continuous mode), temperature – 80 °C.	90 (20)	~50 (30)	1. Increase in H_2O_2 concentration increased degradation efficiency. 2. Combination of MW/H_2O_2 was essential for the degradation of NDS.
3 [42]	Dimethoate (organophosphorous compound)	$K_2S_2O_8$	Initial concentration – 1×10^{-4} mol/L, $K_2S_2O_8$ – 0.05%, pH – 6.8, MW output power – 750 W, temperature – 100 °C.	100 (4)	–	1. MW/$K_2S_2O_8$ seems to be most effective compared to UV/nano-TiO$_2$ and UV/nano-TiO$_2$/$K_2S_2O_8$ systems for dimethoate degradation.
4 [43]	Perflurooctanoic acid (PFOA) (perflurocarboxylic acid)	$Na_2S_2O_8$	Initial concentration – 253.8 μM, volume – 50 mL, PFOA ≅ 50 mM, MW output power – 800 W, temperature – 60–130 °C.	99.3 (240)	74.3 (240)	1. Increase in temperature beyond 90 °C decreased the degradation efficiency of PFOA. 2. The increased efficiency is due to the activation of persulfate thermally to form SO_4^-
5 [44]	Acid orange 7 (AO7) (azo dye)	$Na_2S_2O_8$	Initial concentration – 20–1000 mg/L, volume – 250 mL, sodium persulfate (SPS)/AO7 ratio – 10/1 to 50/1, MW output power – 800 W, temperature – 20 °C.	100 (5)	90–95 (11)	1. The reaction rate was enhanced when the ratio increased from 10:1 to 50:1 and remained constant thereafter. 2. MW/$Na_2S_2O_8$ method is highly efficient compared to UV method for the decolorization of dyes at higher concentrations i.e. 1000 mg/L.

condition. Therefore, identifying the optimum MW temperature is an important step in MW-assisted systems with persulfate.

$$S_2O_8^{2-} + heat \rightarrow 2SO_4^{\bullet-} \quad (5)$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad (6)$$

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \quad (7)$$

It can be seen in Table 2 that MG, NDS, dimethoate, PFOA and azo dyes could be degraded by combining MW with oxidants. In all these studies, the MW power was kept between 300 and 900 W, which demonstrates that complete degradation of malachite green, NDS, dimethoate, PFOA and azo dyes could be achieved under MW with oxidant system. Moreover, the ratio of oxidant and pollutant concentration plays a major role in the efficiency of MW with oxidant systems. Since H_2O_2 is more effective under acidic pH levels, combining MW with persulfate could be a wise option for water treatment around neutral pH.

5. MW with catalyst

In chemical catalysis, catalyst is used to speed-up or speed-down a chemical reaction without the consumption of the catalyst. The liquid-phase oxidation using a solid catalyst is a potential method for the removal of dissolved toxic pollutants from WW. On the other hand, catalytic wet air oxidation (CWAO) is a promising technology to degrade non-biodegradable organic substances in industrial effluents even to the degree of mineralization. However, CWAO possess the limitations such as severe operation conditions, i.e. high temperature (180–315 °C), high pressure (2–25 MPa) and demand of noble metallic catalyst [52]. On the other hand, the combination of MW with catalysts of strong MW absorbing property is well recognized as the technological advancement in the application of MW for various processes. In the process of MW with catalyst, the principle of chemical catalysis is combined with MW (i.e. catalyst surface absorbs MW and speed-up the degradation process) for rapid and effective/complete removal of organic pollutants from water/WW.

This catalyst may be absorber, semiconductor, ferromagnetic metal or transition metal oxides. Several researchers have conducted catalytic oxidation process using Fe^0, $CoFe_2O_4$, CuO_n–La_2O_3/γ-Al_2O_3 with ClO_2, delaminated Fe exchanged Ti-pillared interlayered montmorillonite (Fe-Ti-PILC), and different forms of AC, carbon supported metal catalyst and high valence nickel oxides (Table 3). For MECD experiments, the catalysts could be freely suspended in the reactor or used as a fixed bed based on the mode of reactor operation, i.e. batch or continuous fixed-bed operation. In batch mode operations, the required amount of catalyst is added to the reaction mixture under constant stirring. Unlike other catalysts, AC based catalysts were presorbed by the pollutant prior to MW assisted degradation to eliminate the adsorption effect of AC on pollutant degradation.

Table 3 shows that the application of Fe^0 and $CoFe_2O_4$ as MW absorbents has produced tremendous increase in the degradation efficiency of various pollutants including PCP and brilliant green. Moreover, a complete removal of these compounds was observed under optimal conditions (Table 3) [45,46]. MECD using CuO_n–La_2O_3/γ-Al_2O_3 with ClO_2 could overcome the limitations of the traditional ClO_2 catalytic oxidation process such as limited range of pH and longer reaction time [47,48]. For example, 94% of ramazol golden yellow dye was degraded by MECD using CuO_n–La_2O_3/γ-Al_2O_3 with ClO_2 in 1.5 min [47]. Likewise, MW with catalytic wet H_2O_2 oxidation in the presence of heterogeneous catalyst, i.e. Fe-Ti-PILC, has the capability of enhancing the degradation rate of various pollutants. This could be noticed by comparing the phenol degradation studies shown in Table 3 [49].

The combination of MW with MW-absorbing materials like AC is useful to achieve higher degradation efficiency in a shorter period of time owing to the hot-spot formation [50–59]. It is also reported that the regeneration capacity of GAC has increased when treated with MW [53]. Moreover, adsorbent/ferrite composite namely, rice hull/$MnFe_2O_4$ were also successfully applied for MW assisted COD removal from organic WW [60]. The combination of MW with MW-absorbing materials acts sequentially and simultaneously in two ways for pollutant removal, i.e. (i) as adsorbent and (ii) as MW-absorbent. As adsorbent, AC can remove many organic and inorganic pollutants from solution and assist in prolonged oxidation time for target compound. Several MW studies demonstrated that the rate of temperature increase in the presence of AC was 10 times more than the conventional aqueous systems under same MW power and frequency [52]. The application of MW heating with GAC and its advantages has been reviewed in detail [93]. The induction of higher temperature could be attributed to the phenomena of hot-spot formation in the MW field. However, the hot-spot formation could be inhibited when it is coated with ionic compound like sodium carbonate [56]. So far, the combination of MW with AC or GAC has been applied successfully for the degradation of phenols, PNP, dyes and other chlorinated compounds (Table 3).

Recently, carbon supported metal catalyst is used to decrease the activation energy and to act as the oxidation centre for the oxidation of pollutants [57–59]. Carbon supported base metal (such as Cu) catalysts and carbon supported noble metal (such as Pt) catalysts were used along with MW. Although metals such as copper and platinum reflect MW as a shielding material, MW can penetrate metallic particle when its size is lower than the depth of penetration or skin depth calculated as per Eq. (8) [57].

$$\delta = \left(\frac{2}{\omega \mu_0 \sigma} \right)^{0.5} \quad (8)$$

where δ is the skin depth, ω is the angular frequency, μ_0 is the permeability of free space ($\mu_0 = 4\pi \times 10^{-7}$ H/m) and σ is the electric conductivity (metal specific). When the average size of metal particle on GAC is less than the depth of penetration (Eq. (8)), MW penetrates through the metal particle. The loss of penetration through metal and strong adsorption as well as MW absorption capacity of GAC would result in the rise in temperature by a carbon supported metal catalyst. The carbon supported metal catalysts have been effective in the degradation of p-nitrophenol (PNP) and PCP compared to GAC alone [57,58]. Fig. 4 shows the degradation efficiencies of different compounds under MECD with MW-absorbing catalyst and carbon supported metal catalyst. GAC is the mostly widely used MW-absorbing material, and it could able to produce around 85–100% removal efficiency for wide range of pollutants. MW with GAC is effective in the removal of higher pol-
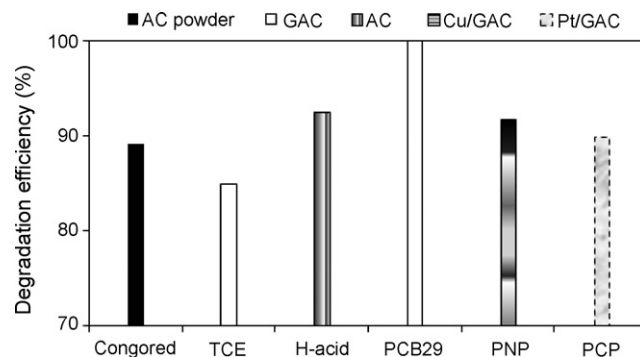

Fig. 4. Performance of MECD with MW-absorbing catalyst and carbon supported metal catalyst in the degradation of different compounds (operating conditions are different for each compound).

Table 3
List of studies coupled MW with catalysts/adsorbents.

S. No. [Ref. No.]	Contaminant and its type	Catalyst (absorbent)	Reaction condition/chemical oxidation scheme	Degradation efficiency, % (time, min)	Mineralization efficiency, % (time, min)	Remarks
1 [45]	Pentachlorophenol (PCP) (organochlorine compound)	Fe^0	Initial concentration – 1000 mg/L, catalyst concentration – 0.1–0.5 g, MW output power – 700 W (continuous mode), temperature – 540 °C.	99.9 (0.5)	–	At similar conditions, without MW, the degradation efficiency was only 3%.
2 [46]	Brilliant green (BG) (triarylmethane dye)	$CoFe_2O_4$	Initial concentration – 20 mg/L, $CoFe_2O_4$ – 0.02–0.1% (w/w), MW output power – 100–900 W, temperature – 700 °C, pH – 4–10.	100 (2)	–	The degradation was highly dependent on pH and the optimal degradation occurred at a pH of 6.56.
3 [47]	Remazol golden yellow dye	CuO_n–La_2O_3/γ-Al_2O_3 (with ClO_2)	Initial concentration – 200 mg/L, volume – 100 mL, ClO_2 concentration – 80 mg/L, MW power – 400 W, temperature – 77 °C, pH – 7	94 (1.5)	68 (1.5)	The fluorescence technology verified that there was $OH^\bullet$ produced in microwave enhanced ClO_2 catalytic oxidation system and the formation quantity of $OH^\bullet$ increased with irradiation time.
4 [48]	Phenol	CuO_n–La_2O_3/γ-Al_2O_3 (with ClO_2)	Initial concentration – 100 mg/L, volume – 100 mL, CuO_n–La_2O_3/γ-Al_2O_3 – 50 g/L, ClO_2 – 80 mg/L, MW output power – 50 W, temperature – 47 °C.	91.66 (5)	50.35 (5)	Introduction of catalyst reduced the treatment time and oxidant dosage requirement due to thermal effect of MW
5 [49]	Phenol	Delaminated Fe exchanged Ti-pillared interlayered montmorillonite (Fe-Ti-PILC)	Initial concentration – 2×10^{-3} mol/L, volume – 100 mL, catalyst – 1.5 g/L, temperature – 70 °C, pH – 9–10.	100 (8)	50.3 (8)	It is hypothesized that the curtailment of reaction time from 90 to 8 min by the application of MW irradiation for complete degradation of phenol is due to the acceleration in the conversion rate of H_2O_2 to free radicals.
6 [50]	Congo red (secondary diazo dye)	Activated carbon powder	Initial concentration – 50 mg/L, volume – 25 mL, activated carbon powder – 0–3.6 mg/L, MW output power – 800 W, temperature – 850 °C, pH – 8.	87.79 (1.5)	–	The increase in amount of catalyst dosage or irradiation time further increased the degradation efficiency (>89%). Hot spot formation on activated carbon powder was mainly responsible for congo red degradation.
7 [51]	Trichloroethylene (TCE) (Chlorinated hydrocarbon)	Granulated activated charcoal	Fluidized bed reactor with a loading of 1 g GAC per 0.5 ml of pure TCE, Argon flow rate – 0.1 ft^3/min, temperature – 230 °C.	100 (2.5)	100 (2.5)	The most effective decomposition was achieved when GAC bed was fluidized with gas that contained water and TCE vapors.
8 [52]	H-acid (1-amino-8-naphthol-3,6 disulfonic acid) (An important intermediate product for the preparation of dyestuffs)	Activated carbon (AC)	Initial concentration – 3000 mg/L, volume – 20 mL, AC – 10 g, air flow – 0.5 L/min, MW output power – 800 W, temperature – 103 °C.	92.6 (20)	84.2 (60)	Simultaneous effect of AC and air flow was critical for the removal of H-acid.
9 [53]	2,4,5-trichlorobiphenyl (PCB29) (Polychlorinated biphenyl)	GAC	Initial concentration – 2 mg/L, flow rate – 3 mL/min, GAC loading – 10 g, MW output power – 700 W, temperature – 1000 °C.	~100 (3)	–	It was deduced that the degradation of PCB29 might occur through pyrolysis, fixation and volatilization.
10 [54]	Petroleum refinery waste water	GAC	Initial COD – 5500 mg/L, volume – 150 mL, GAC – 5 wt.%, MW power – 660 W, temperature – 150 °C, pressure – 0.8 MPa	–	90 (30)	BOD_5/COD ratio was increased from 0.04 to 0.47 within 30 min.

11 [55]	p-Nitriphenol (PNP) (phenolic compound with nitro group)	GAC fixed bed	Initial concentration – 1330 mg/L, solution flow rate – 6.4 mL/min, GAC loading – 45 g, air flow rate – 120 mL/min, MW output power – 500 W, temperature – 220–300 °C.	90 (180)	–	BOD$_5$/COD ratio was increased from 0.302 to 0.613 after 780 min.
12 [56]	Pentachlorophenol (PCP) (organochlorine compound)	GAC	PCP – 198 mg, GAC loading – 10 g, MW output power – 850 W, temperature – 1000 °C, pH – 10.	~100 (10)	98 (10)	MW treated GAC exhibited larger specific surface area, micropore area and total pore volume compared to virgin GAC
13 [57]	p-Nitriphenol (PNP) (phenolic compound with nitro group)	Carbon supported copper (Cu/GAC)	Initial concentration – about 1700 mg/L, solution flow rate – 6.4 mL/min, catalyst loading – 52.5 g, air flow – 120 mL/min, MW output power – 400 W	91.8 (300)	88 (300)	Cu/GAC catalyst showed higher PNP degradation and TOC removal than virgin GAC under MW. At low concentration of PNP (6–20 mg/L) the removal efficiency was higher than 98%.
14 [58]	p-Nitriphenol (PNP) (phenolic compound with nitro group), pentachlorophenol (PCP) (organochlorine)	Carbon supported platinum (Pt/GAC)	Initial concentration – about 1500 mg/L, solution flow rate – 6.4 mL/min, catalyst loading – 52.5 g, air flow – 120 mL/min, MW output power – 400 W, temperature – 1000 °C.	PNP – 86 (300) PCP – 90 (240)	PNP – 85 (300) PCP – 71 (240)	Pt/GAC showed higher PNP and PCP degradations compared to GAC alone. It is hypothesized that the existence of Pt particles could decrease activation energy of reaction and act as "reaction centre" in the oxidation of PNP.
15 [59]	Polychlorobenzene (chlorobenzene (CB) 1,2 dichlorobenzene (o DCB), 1,3 dichlorobenzene (m-DCB), 1,4-dichlorobenzene (p-DCB) and pentachlorobenzene (PeCB) (aromatic organic compounds)	Hypophosphite (NaH$_2$PO$_2$) and Pd-loaded activated carbon (pd content 10 wt.%)	Initial concentration – 1 mM, catalyst dosage – 2.5 or 5 mg, MW output power – 300 W, final temperature – 90 °C for all polychlorobenzene except PeCB and 180 °C for PeCB, pH – 4–10.	m-DCB – 95 (7) o DCB – 94 (7) CB – 91 (7) p-DCB – 86 (7) PeCB – 75 (40)	–	The optimal condition for the dechlorination of PeCB necessitated the presence of 10 mM NaH$_2$PO$_2$, 5 mg Pd/C and 5.0 mM NaOH solution.
16 [60]	Organic waste water (photoresist developer wastewater from printed circuit board industry)	Rice hull/MnFe$_2$O$_4$ composite (RHM)	Initial COD concentration – 2088 mg/L, initial acid concentration – 0.52 mol/L, volume – 100 mL, RHM – 2 g, MW output power – 700 W, temperature – 1000 °C.	–	73.5 (6)	The COD removal efficiency increased up to 20% by RHM compared to rice hull ash.
17 [61]	Lindane (chlorinated pesticide)	NaOH treated sepiolite (SNa400), NiOx impregnated sepiolite (SNi400)	Initial concentration – 8.6 × 10^{-4} M, sepiolite – 0.5 g/4 cm^3 of 8.6 × 10^{-4} M lindane, MW power – 15–300 W, final temperature – 120 °C.	97 (5)	–	SNa400 showed rapid decomposition of lindane compared to SNi400 (80% efficiency in 5 min).
18 [63]	Phenol	Nickel oxides	Initial concentration – 200 mg/L, volume – 20 mL, catalyst loading – 2 mg/mL of phenol solution, MW output power – 100 W, temperature – 40 °C, pH – 7.	100 (2)	100 (8)	Phenol degradation was strongly dependent on the oxidation state of nickel, surface area and surface acidity of nickel oxides
19 [64]	4-Chlorophenol (4-CP) (phenolic compound)	Nickel oxides	Initial concentration – 100 mg/L, volume – 60 mL, catalyst loading – 0.12 g, MW output power – 300 W, temperature – 40 °C, pH – 7.	100 (1)	100 (30)	High valence nickel oxide improved 4-CP degradation.
20 [3]	4-Chlorophenol (4-CP) (phenolic compound)	Fabricated nickel oxide	Initial concentration – 200 mg/L, volume – 60 mL, catalyst loading – 0.12 g, MW output power – 300 W, temperature – 70 °C, pH – 7.	100 (0.5)	100 (5)	4-CP degradation was strongly dependent on the oxidation state of nickel and surface area of nickel oxide.
21 [65]	4-Chlorophenol (4-CP) (phenolic compound)	Fabricated nickel oxide	Initial concentration – 200 mg/L, volume – 60 mL, catalyst loading – 0.12 g, MW output power – 300 W, temperature – 40 °C, pH – 7.	100 (1)	100 (20)	Increase in temperature from 40 to 70 °C decreased the time required for complete degradation of 4-CP

Table 3 (Continued).

S. No. [Ref. No.]	Contaminant and its type	Catalyst (absorbent)	Reaction condition/chemical oxidation scheme	Degradation efficiency, % (time, min)	Mineralization efficiency, % (time, min)	Remarks
22 [66]	Crystal violet (CV) (triphenyl methane dye)	Nano-nickel oxide	Initial concentration – 100 mg/L, volume – 50 mL, catalyst dosage – 0.040 g, MW output power – 750 W, pH – 9.	97 (5)	81 (5)	Higher oxidation state of nickel in the prepared catalyst along with the large surface area improved the degradation of CV.
23 [67]	2,4-Dichlorophenoxy acetic acid (2,4-D) (chlorophenoxyacetic herbicide)	Boron doped diamond electrode	Initial concentration – 100 mg/L, flow rate – 150 mL/min, Na_2SO_4 (supporting electrolyte) – 0.05 M, MW output power – 127.5 W, temperature – 18 °C.	91 (180)	89 (180)	The removal efficiencies of 2,4-D and COD were 1.49 and 1.53 times higher than the treatment carried out with electrolyte alone (without MW) due to the enhancement in diffusion coefficient and adsorption amount by microwave radiation.
24 [68]	Methyl orange (Azo dye)	Platinum electrode	Initial concentration – 200 mg/L, Na_2SO_4 (supporting electrolyte) – 0.05 M, current density – 10 mA/cm², MW output power – 127.5 W, temperature – 18 °C, pH – 5.7.	100 (210)	78 (90)	Decolorization efficiency reached nearly 71% in 30 min, 90% in 60 min and MO solution is almost completely decolored after 90 min.

Note: GAC catalysts were pre-adsorbed by the respective pollutants to abate the adsorption effect of GAC on degradation.

lutant concentration [52,55–57]. Moreover, MW with GAC systems can be operated in a wide range of pH (4–12) and the separation of GAC from the liquid (after treatment) can be done very easily. However, 100% mineralization (as TOC) was not observed in all the MW with GAC systems (Table 3, 6–16). This indicates that MW with GAC system can be used as a preliminary treatment for rapid degradation of pollutant. Subsequently, the remaining quantity of target pollutant and the metabolites accumulated in the system (if any) could be removed by other physicochemical or biological processes.

On the other hand, several MECD studies conducted using nickel oxide as catalyst is also shown in Table 3. The catalytic activity of nickel oxide is mainly influenced by the oxidation state of metal ion, content of active oxygen and morphology of the material. The active oxygen species on the nickel oxide surface can be enhanced by fabricating the nickel oxides through the precipitation–oxidation method [63]. The coupling effect between the MW and active oxygen species on high valence nickel oxide surface could donate electrophilic oxygen ions (O_2^-, O^- and O^{2-}). These ions will be useful in the degradation of pollutant and to improve the efficiency of the process [3]. Nearly, 100% phenol, 4-chlorophenol and crystal violet removals were reported in MW with nickel oxides systems in a short span of time, i.e. 5–20 min. Moreover, higher TOC removal was observed in these systems. The performance of MW coupled nickel oxide systems is higher when the temperature was controlled at 40 °C. However, the effect of different temperatures on the performance of MW coupled nickel oxide systems is yet to be explored.

6. MW with Fenton process

The reaction of H_2O_2 with Fe^{2+} or Fe^{3+} is referred as Fenton reaction or Fenton like reaction, respectively [70]. MW enhanced Fenton or Fenton like process has shown better efficiency for the treatment of aqueous as well as soil pollutants than sole Fenton reaction [69,70]. This could be due to the increased WW temperature by the superheating effect of MW. Moreover, MW enhanced Fenton or Fenton like process has the advantages such as compact floc formation, improved settling and elimination in the requirement of membrane separation for sludge removal [70]. On the other hand, photo-Fenton reaction, i.e. the Fenton reaction in UV light, increases the efficiency of Fenton's process by the decomposition of photoactive $Fe(OH)^{2+}$. This leads to the addition of large number of •OH in the system. The combination of MW with photo-Fenton, combining the polarization effect of MW and the chemical activation effect of UV, was more effective for the degradation/mineralization of WW compared to photo-Fenton alone. It is hypothesized that the improved degradation is owing to the decomposition of $Fe(OH)^{2+}$, but the detailed mechanism is not yet explored.

Table 4 shows the list of studies combined MW with Fenton and photo-Fenton processes. In addition, the detailed experimental conditions, outcomes of the studies and critical remarks are provided in the same table. It can be noticed in Table 4 that the coupling of MW with Fenton and photo-Fenton processes has improved the degradation rate of various pollutants by at least 50 times as compared to the Fenton and photo-Fenton processes without MW. For example, 95% degradation of both chlorfenvinphos and cypermethrin was reached in about 4 min under MW with photo-Fenton process whereas only 86% of degradation was observed after 5 h in photo-Fenton process without MW [69].

7. MW in photochemical reactions

Photochemical reaction proceeds with the absorption of light. In photolysis, the chemical breakdown is caused by the energy of incident photons. On the other hand, photo-induced electrons

Table 4
Studies coupled MW with other AOPs.

S. No. [Ref. No.]	Contaminant and its type	Type of AOP	Reaction condition/chemical oxidation scheme	Degradation efficiency, % (time, min)	Mineralization efficiency, % (time, min)	Remarks
1 [69]	Residual water with chlorfenvinphos and cypermethrin	MW-photo-Fenton process	Waste water composition – 400:1 (v/v) of water and pesticide (13.8% (m/v) chlorfenvinphos and 2.6% (m/v) cypermethrin), volume – 10 mL, Fe(II) solution – 2.1×10^{-3} mol/L and H_2O_2 – 1.1 mol/L, MW output power – 950 W, temperature – 140 °C.	–	95 (4)	Without MW, only 86% of degradation was observed after 5 h of photo-Fenton process.
2 [70]	Pharmaceutical waste water	MW-Fenton like process	Initial COD loading – 49912.5 mg/L, volume – 50 mL, H_2O_2 dosage – 1300 mg/L, $Fe_2(SO_4)_3$ dosage – 4900 mg/L, MW output power – 300 W, temperature – 28 °C, pH – 4.42.	–	57.53 (6)	1. MW-Fenton process improved the degradation efficiency and the settling quality of sludge. 2. In addition, it reduced the yield of sludge and improved the biodegradability of effluent.
3 [71]	Atrazine (organic compound with an s triazine-ring)	MW/UV (EDLs)	Initial concentration – 50 mg/L, volume – 50 mL, EDLs λ – 254, 297, 313, 365, 405, 436, 546, 577 and 579 nm, light intensity – 9–10 mW/cm^2, MW output power – 900 W.	100 (4)	–	Dechlorination–hydroxylation mechanism is one of the main degradation mechanisms of atrazine.
4 [72]	Bromophenol blue (BPB) (triphenyl methane dye)	MW/UV (EDLs)	Initial concentration – 100 mg/L, volume – 50 mL, EDLs λ – 400–760 nm, light intensity – 440 cd/m^2, MW output power – 900 W, temperature – 100 °C.	100 (10)		MW/UV could cause benzene ring open to generate aliphatic intermediates.
5 [73]	Acid orange 7 (AO7) (azo dye)	MW/UV (EDLs)/H_2O_2	Initial concentration – 100 mg/L, volume – 750 mL, air – 0.15 m^3/h, MW output power – 700 W (continuous mode), temperature – 38 ± 1 °C.	~95 (30)	30 (30)	MW/EDL/H_2O_2 process was 32% more effective than H_2O_2/TEL (traditional electrode lamp) process in the degradation of AO7.
6 [74]	Phenol	MW/UV/H_2O_2	Initial concentration - 200 mg/L, volume – 300 mL, MW output power – 1 kW, temperature – 50 °C, low pressure Hg lamp – 8 W.	90 (9)	95 (30)	MW irradiation increased both phenol conversion and TOC removal efficiency above 50%.
7 [1]	Phenol, chlorobenzene, nitrobenzene, 4-chlorophenol (4-CP), and pentachlorophenol (PCP)	MW/UV/H_2O_2	Initial concentration – 10^{-3} mol/L (except PCP with concentration – 6×10^{-6} mol/L), H_2O_2 concentration – 5×10^{-3} mol/L, MW output power – 900 W, conventional high-pressure Hg discharge lamp – 400 W, temperature – 20 °C.	–	–	1. Simultaneous MW/UV/H_2O_2 remediation was more efficient than MW/H_2O_2 and UV/H_2O_2 based treatments. 2. The degradation of phenol and chlorobenzene were increased respectively by a factor of 21 and 6 for MW/UV/H_2O_2 based treatment compared to the sum of degradation from MW/H_2O_2 and UV/H_2O_2 remediation. 3. Combined effect of MW and UV showed modest enhancement in the degradation rate of nitrobenzene, 4-CP and PCP.
8 [75]	2,4-Dichlorophenoxy acetic acid (2,4-D) (chlorophenoxyacetic herbicide)	MW/UV (EDLs)/TiO_2	Initial concentration – 0.04 mM, TiO_2 loading – 50 g/10 ml of 2,4-D solution, light irradiance – 2 mW/cm^2 with a wavelength of 314, 366, 405, 436, 546 and 577 nm, MW output power – 700 W, temperature – 200 °C, pH – 4.9.	100 (20)	–	The rate of degradation (2×10^{-3} mM/min) showed that the MW/UV/TiO_2 was 10 times more efficient than photocatalytic method.
9 [76]	Methylene blue (MB) (heterocyclic aromatic compound)	MW/UV (EDLs)/TiO_2	Initial concentration – 100 mg/L, volume – 50 mL, TiO_2 loading – 0.1 mg, EDLs λ – 250–760 nm, MW power – 900 W, temperature – 100 °C, pH – 7.	96 (15)	50 (15)	The decomposition of MB could be by the enhanced production of active radicals.
10 [77]	Bisphenol A (BPA) (endocrine disruptor)	MW/UV (EDLs)/TiO_2	Initial concentration – 0.1 mM, volume – 30 mL, TiO_2 loading – 60 mg, light irradiance – 0.9 mW/cm^2, MW output power – 1.5 kW, temperature – 150 °C, pressure – 1 MPa, pH – 6.7	–	100 (90)	MWPC two-fold faster mineralization compared to the photocatalysis method because of the accelerated generation of the highly oxidizing OH.

Table 4 (*Continued*)

S. No. [Ref. No.]	Contaminant and its type	Type of AOP	Reaction condition/chemical oxidation scheme	Degradation efficiency, % (time, min)	Mineralization efficiency, % (time, min)	Remarks
11 [78]	Reactive brilliant red X-3B (X-3B) (azo dye)	MW/UV (EDLs)/novel grain TiO$_2$ (GT01)	Initial concentration – 400 mg/L, volume – 1000 mL, catalyst dosage – 4 g/L, air flow rate – 0.25 m^3/h, MW output power – 700 W, temperature – 38 ± 1 °C.	100 (180)	65 (180)	The increase in mineralization in presence of MW was due to the production of more hydroxyl radicals, acceleration of surface reaction between dyes and hydroxyl radicals, avoiding catalyst absorbing excessive dye on surface, etc.
12 [79]	X-3B (azo dye)	MW/UV (EDLs)/novel grain TiO$_2$ (GT01) or TiO$_2$	Initial concentration – 400 mg/L, volume – 1000 mL, catalyst dosage – 4 g/L, air flow rate – 0.25 m^3/h, MW output power – 700 W, temperature – 38 ± 1 °C.	100 (180) by GT01 100 (120) by TiO$_2$	–	1. GT01 showed higher degradation efficiency of X-3B compared to Digussa P25 for the initial 40 min after which the latter showed enhanced degradation efficiency. 2. After 40 min, the pseudo first order degradation constant for GT01 and Digussa P25 was 0.0203/min and 0.0253/min.
13 [80]	Atrazine (organic compound with an s triazine-ring)	MW/UV (EDLs)/TiO$_2$ nanotubes	Initial concentration – 20 mg/L, volume – 50 mL, TiO$_2$ nanotubes – 0.05 g, EDLs λ – 254 nm, MW power – 900 W, pH – 8.1	100 (5)	98.5 (20)	MW enhanced degradation rates were faster than that of photolysis and photocatalysis.
14 [81]	Mono-chloroacetic acid (MCAA) (carboxylic acid)	MW/UV (EDLs)/nanoporous TiO$_2$	Initial concentration – 0.1 mol/L, volume – 150 mL, air flow rate – 0.03 m^3/h, EDL intensity – 5.56 μW/cm^2, MW output power – 900 W and 1000 W, temperature – 100 °C.	100 (490)	–	The intensity of UV light and initial pH of the solution influenced the reaction efficiency.
15 [5]	4-Chlorophenol (4-CP) (phenolic compound)	MW/UV (EDLs)/TiO$_2$/H$_2$O$_2$	Initial concentration – 30 mg/L, volume – 500 mL, catalyst loading – 1 g/L, H$_2$O$_2$ (0.1% v/v), EDLs – (100 W, 254 nm), MW output power – 750 W, temperature – 28–29 °C.	90 (120)	–	4-CP degradation rates doubled in the presence of MW irradiation with EDL than the degradation with UV alone which is attributed to the generation of OH$^\bullet$ from H$_2$O$_2$, induced by the localized superheating of MW.
16 [82]	4-Chlorophenol (4-CP) (phenolic compound)	MW/UV (EDLs)/TiO$_2$/H$_2$O$_2$	Initial concentration – 30 mg/L, MW output power – 750 W, solution flow rate – 2 L/min, EDL (peak emission 254 nm), temperature – 28–29 °C.	82.85 (120)	–	After 120 min, the degradation efficiency was 2.55 and 38.76% respectively with MW and UV/TiO$_2$.
17 [83]	Pentachlorophenol (organochlorine compound)	MW/UV (EDLs)/F-Si-comodified TiO$_2$	Initial concentration – 40 mg/L, volume – 50 mL, TiO$_2$ – 0.18 g, EDLs λ – 254, 297, 313, 365, 405, 436, 546, 577 and 579 nm, MW output power – 900 W.	99 (20)	71 (20)	The degradation efficiency with UV alone was 82% in 20 min under the same reaction conditions.
18 [84]	Rhodamine B (RhB) (cationic dye)	MW/UV (EDLs)/TiO$_2$ supported on AC	Initial concentration – 30 mg/L, volume – 50 mL, TiO$_2$–AC – 0.075 g, EDLs λ – 254, 297, 313, 365, 405, 436, 546, 577 and 579 nm, MW output power – 900 W, temperature – 1000 °C, pH – 7.45.	93.1 (10)	–	The increase in degradation efficiency was attributed to several factors such as surface hydrophobicity caused on the catalyst in presence of MW, strong interaction between TiO$_2$ and AC which was ascribed to an extended adsorption of RhB on AC followed by a transfer to titania where it was photocatalytically degraded, etc.
19 [85]	Rhodamine B (RhB) (cationic dye)	MW/UV (EDLs)/Bi$_2$WO$_6$	Initial concentration – 10 mg/L, volume – 50 mL, Bi$_2$WO$_6$ (catalyst) – 0.05 g, EDLs.	94 (60)	78 (60)	The surface hydrophobicity and additional defects on the catalyst surface in the presence of MW caused improvement in RhB degradation.
20 [86]	Phenol	MW/UV (EDLs)/TiO$_2$ supported on AC	Initial concentration – 10 mg/L, volume – 50 mL, catalyst – 0.1 g, MW output power – 900 W, temperature – 1000 °C.	87 (30)		The strong MW absorption and light absorption capacity of the catalyst resulted in improved degradation of phenol.

(e$^-$) and positive holes (h$^+$) are produced under UV-irradiation ($\lambda < 387$ nm) of photocatalyst, which accelerates the dissociation process in photocatalysis. These charged species can generate free $^\bullet$OH for the degradation of target pollutant. The performance of the photochemical degradation can be improved by increasing the temperature of the reaction. Therefore, several researchers utilized MW heating for increasing the photochemical reaction temperature and to enhance the process efficiency. The application of photochemistry in the MW field provides an opportunity to combine chemical activation by two distinctive electromagnetic radiations, i.e. (1) thermo-chemical activation by dielectric heating under low-energy MW ($E = 0.4$–40 J per mole of photon at $\upsilon = 1$–100 GHz) and (2) chemical activation by excited reactions under UV–vis radiation ($E = 600$–170 kJ per mole of photon at $\lambda = 200$–700 nm) [104]. In MW-assisted photochemical reaction, greater efficiency is obtained through non-thermal effect of MW which was attributed to changes in the pre-exponential factor A in the Arrhenius equation, $k = Ae^{-Ea/RT}$ [79,88]. Moreover, the coupling of UV-irradiation with MW increases the formation of $^\bullet$OH, which could be demonstrated by electron spin resonance (ESR) studies [91]. A combination of classic UV light (utilizing traditional mercury lamp) and MW integrating the effects of MW- and UV-irradiations in the treatment of aqueous pollutants have shown tremendous improvement in the degradation efficiency of various organic substrates. In addition, MW with UV is applied in organic synthesis [106]. Table 4 shows the list of MW coupled photochemical reaction studies, their reaction conditions and experimental outcomes. Although photocatalytic degradation has effectively accelerated by MW, traditional mercury lamp could not be laid in MW field owing to the destruction of metal electrodes under MW [73].

The discovery of EDL paved a way to overcome this problem. An EDL consists of a glass tube (quartz or Pyrex) filled under a reduced pressure with argon and an excitable substance (e.g. Hg, HgI$_2$, Cd, I$_2$, KI, P, Se, S) [107] and generates UV–vis light under MW [108]. The glass tube, referred as plasma chamber, has a number of free electrons. When the energy from MW source flows into the plasma chamber, the free electrons are accelerated by the energy of electromagnetic field. As a result, the electrons collide with the gas atoms and ionize them to release more electrons. Repetition of this process causes the formation of more and more electrons over short period of time. These energetic electrons collide with the heavy-atom particles (such as Hg) present in the plasma and excite them from ground state to higher energy levels. The excitation energy is then released as electromagnetic radiation of high energy with different spectral characteristics based on the composition of the envelope. The energy of these photons can be utilized for breaking strong chemical bonds. The application of EDL in photochemistry, EDL preparation, structure and modifications are reviewed in detail [106]. Moreover, thin nanoporous titania films can be prepared and applied on the EDLs for photocatalysis applications [109].

7.1. MW with direct photolysis (MWDP)

MWDP with and without oxidants has been applied in various WW treatment studies. MWDP using classic UV lamp has been applied for the oxidative decomposition of aqueous phenol. In MW/UV system, MW makes the pollutant to be at higher electronically excited state, which favors the formation of more $^\bullet$OH; subsequently, results in the rapid degradation. In MW integrated UV/H$_2$O$_2$ system, MW is responsible in the production of more $^\bullet$OH in addition to the electronic excitation of the pollutant. The simultaneous MW/UV/H$_2$O$_2$ remediation technique offers an attractive alternative solution for environmental remediation issues compared to conventional oxidation or photocatalytic degradation methods. Table 4 lists several MW with direct photolysis studies conducted in the past. This non-catalytic remediation method has

the advantage of thermal enhancement of the processes initiated by MW or followed by the absorption of light [1]. MWDP using EDL has also shown excellent improvement in the treatment efficiency of various pollutants such as atrazine, bromophenol blue (BPB), acid orange 7 (AO7), phenol and 2,4-dichlorophenoxy acetic acid (2,4 D). The improvement in the treatment efficiency with the use of EDL is due to the simultaneous effect of UV–vis and MW.

7.2. MW with photocatalysis (MWPC)

MW-assisted photocatalysis has been developed to overcome the drawbacks of UV/Fenton, UV/H$_2$O$_2$, i.e. formation of secondary pollutants with the use of ferrous or ferric salts and use of costly oxidants, respectively. The main catalysts used in MWPC are TiO$_2$ (in the forms of grain, nanoporous and nanotube), F-Si-comodified TiO$_2$, TiO$_2$ supported on AC and ferroelectric bismuth tungstate (Bi$_2$WO$_6$). The MW-assisted photocatalysis system can be successfully operated by facilitating the combination of the three variables: (i) the type and variation of semiconductor photocatalyst (slurry vs. thin film), (ii) external or internal lamp (classical UV lamp vs. EDL, and (iii) the frequency of MW (2.45 GHz) [81]. Recent studies have demonstrated an outstanding improvement of the degradative efficiency by the coupling of MW with EDL and catalysts (Table 4). This improvement could be attributed to the generation of more $^\bullet$OH and the polarization effect of highly defected TiO$_2$ [76]. Horikoshi et al. [91] proved that about 20% more radicals are generated in MW-assisted photocatalysis compared to photocatalysis alone. Under MW, the surface of TiO$_2$ becomes more hydrophobic, and thereby, increases the contact of pollutant and the catalyst surface. Subsequently, the additional defect site generated on the TiO$_2$ surface would increase the transition probability of e$^-$/h$^+$ pair and decrease their recombination on the TiO$_2$ surface [5]. A similar reason can be ascribed to the improved photocatalytic efficiency of MW-EDL systems with catalysts like Bi$_2$WO$_6$ [85]. In addition, dyes can be photodegraded concurrently by both catalytic process and self-photosensitization [90]. MWPC was successfully applied for the destruction of various pollutants such as dyes (AO7 and reactive brilliant red X-3B), herbicides (2,4-D) and endocrine disruptors (bisphenol-A). MWPC is suitable even under inferior photodecomposition conditions such as small quantities of TiO$_2$, low concentration of oxygen and low light irradiation (Table 4). As a whole, coupling MW with photocatalysis can resolve various problems encountered in photocatalytic process [90].

7.3. Comparison of MWDP and MWPC

Fig. 5 illustrates the degradation efficiencies of MW, MWDP and MWPC for various pollutants. It is clearly evident that the energy of MW was insufficient to disrupt the chemical bonds of
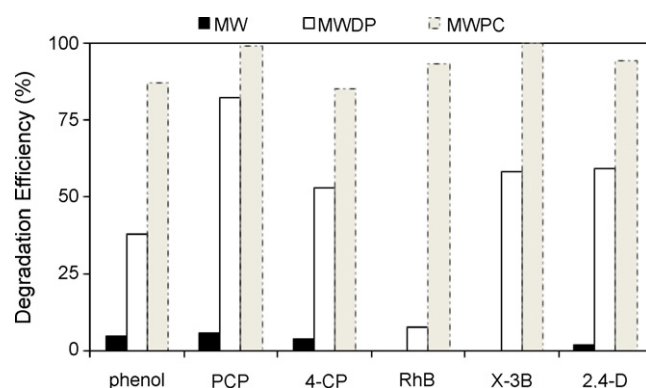

Fig. 5. Comparison of MW, MWDP and MWPC for different pollutants.

common organic molecules. The diminutive removal efficiency of phenolic compounds under MW could be attributed to the heating effect [86]. Whereas, the degradation of phenolic compounds under MWDP could be due to the combined result of thermal effect of MW and the energy of UV–vis light from EDLs. As seen in Fig. 5, the polarization effect of highly defected catalyst provided the highest degradation efficiency of various target compounds in MWPC [82–84]. The composite TiO$_2$/AC catalyst largely reserves the excellent adsorption capacity, which ensures an integrative process at the same time, i.e. pollutant adsorption, MW-absorption and photocatalytic reaction. In addition, the strong MW- and light-absorbing capacity of TiO$_2$/AC along with rapid activation of the catalyst by MW serves as the effective catalytic system for organic pollutant degradation [86].

8. Factors affecting MW reactions

Several factors can influence the pollutant degradation and mineralization efficiency of MW system including MW power, irradiation time and treatment temperature. Generally, the efficiency of MW system increases gradually with increase in MW power and irradiation time [42]. This could be attributed to the generation of additional heat, which favors the impetuous and rapid molecular motion. Numerous researchers have increased the irradiation time for enhancing the removal efficiencies of various pollutants such as ammonium, brilliant green, H-acid and *p*-nitrophenol [36,46,52,56]. On the other hand, the degradation rates of dimethoate and pentachlorophenol (PCP) were enhanced by increasing the MW power [42,45]. MW energy causes the polarization of molecules leading to electronic vibration, which results in the generation of heat. Therefore, the increase in the MW power input rises proportionately the reaction temperature [45,110]. The relationship between the power input and rate of increase in reaction temperature in a MW-assisted system with AC is shown in Fig. 6(a). Moreover, the effect of MW power on the mineralization efficiency of H-acid and petroleum refinery WW is shown in Fig. 6(b). These two figures demonstrate that increase in MW power increases proportionately the heating and reaction rate. Therefore, the treatment time required for removing a target compound could be shortened by increasing the MW power input. In some cases, the efficiency of MW system was found to decrease under very high temperatures; thus, it is mandatory to identify the optimum MW power and reaction temperature for the degradation of particular target pollutant.

8.1. MW with oxidants/catalysts

A rapid degradation of pollutants could be achieved in MW with oxidant/catalyst systems under a set of optimized condition. Apart from the dosage of oxidant/catalyst, the treatment efficiency of a MW system can be strongly influenced by the operating parameters such as MW power, pH and air supply (for CWAO). The increase in MW power proportionately enhances the reaction temperature [52]. Moreover, the MW power is regarded as the most important factor when GAC is used as MW-absorbing material [53]. On the other hand, determining the optimum pH of a MW system is equally important because the pH could affect the surface charge of adsorption, the degree of ionization and speciation of adsorbate during the reaction. However, contradictory observations could be seen in literature with regard to the effect of pH on the MW systems. Some researchers faced insignificant effect of pH in the decomposition of dimethoate in MW with persulfate system [42]. On the other hand, few researchers reported an increment in the PFOA decomposition efficiency under acidic pH. This could be attributed to the formation of sulfate radicals as a result of acid catalysis [43].
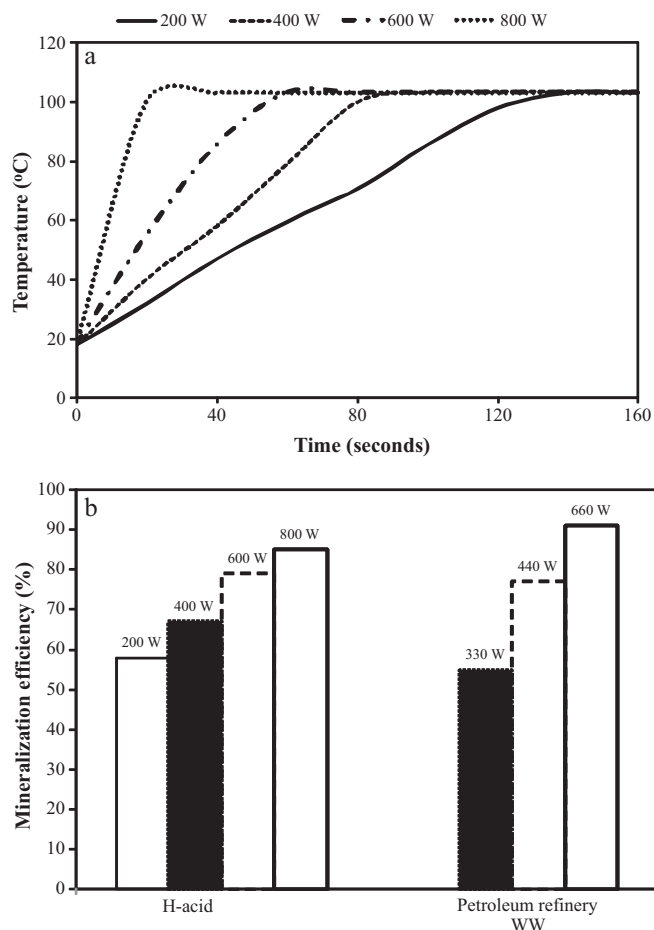

Fig. 6. (a) Effect of MW power on increase in reaction temperature in MW with AC system [110]. (b) Effect of MW power on the mineralization of H-acid (as TOC) and petroleum refinery WW (as COD).

In MW with adsorbent/catalyst system, the pollution degradation occurs in the catalyst surface owing to dipolar polarization whereas in MW with CWAO (gas–liquid–solid) systems it is due to the interfacial polarization [62]. In MW assisted CWAO systems, O$_2$ acts as an electron acceptor as like conventional CWAO systems. Therefore, the MW assisted CWAO system depends on oxygen supply. In many investigations, rapid pollutant degradation was observed under high airflow rates in the initial stage of the experiments [52,55]. Zhang et al. [52] observed H-acid mineralization efficiency of 12% (TOC) without air supply, whereas the TOC removal increased up to 81% with an air supply of 0.5 L/min. The rapid degradation with air supply could be due to the increase in oxygen partial pressure, which favors the oxidation reaction at a faster rate. As a result, the overall removal efficiency of the process is increased many folds.

8.2. MW-photochemical reactions

In either MWDP or MWPC, the reaction efficiency depends on several factors such as light intensity, TiO$_2$ dosage, pH and inorganic oxidizing species including H$_2$O$_2$, Na$_2$S$_2$O$_8$ and Fe(NO$_3$)$_3$. The influences of these factors on MWPC are listed in Table 5. Moreover, the formation of reactive oxidant species ($^\bullet$OH) is influenced by the quantity of oxygen in the solution [75]. The presence of oxygen as the electron acceptor is recommended to prevent the recombination between the generated positive holes and electrons [81]. However, in EDL/TiO$_2$ system the high transference rate decreases the need of dissolved oxygen concentration in the solution. Sev-

Table 5
Influence of various parameters on MWPC.

Parameter	Influence on MWPC
Light intensity	(1) In most of the experiments, the experimental range of light intensity was 0–9.4 mW/cm^2. (2) At higher light intensity, more active sites are formed on the catalytic surface that increases the reaction rate irrespective of the nature of pollutant [90]. (3) At lower light intensity, the reaction rate decreases because of the lower light energy which is not sufficient to initiate the activation of catalyst and the breakage of chemical bonds. (4) The influence of light intensity depends on the reaction conditions such as the reaction mixture amount and the dissolved pollutant amount.
TiO$_2$ dosage	(1) The increase in TiO$_2$ dosage increases the total surface area, i.e. the number of active sites. (2) Over dosing TiO$_2$ will reduce the intensity of light penetration and increase the scattering of light. This could counteract on the positive effect coming from the dosage increment; and finally, decrease the overall performance of the system [111]. (3) The experimental range of TiO$_2$ dosage adopted for the degradation of various pollutants was 0–10 mg/L.
pH	(1) pH has a complex effect on the rate of photocatalytic reaction. (2) It depends on the type of pollutant and catalyst. (3) In alkaline medium, the anionic state of compound favors the UV absorption and production of more hydroxyl radical from hydroxyl ion ($h^+_{vb} + OH^- \rightarrow OH^\bullet$), which cause the enhancement in degradation efficiency. The anions like chloride anion can react with hydroxyl radicals ($OH^{\bullet+} Cl^- \rightarrow OH^-$), and absorb the UV radiation [81]. (4) In acidic medium, the presence of more H$^+$ ions by which more conduction band electrons can transfer to the surface of catalyst to react with O$_2$ to produce more hydroxyl radical and improves the degradation efficiency. (5) pH has a significant effect on the electrostatic charge of TiO$_2$ surface, which determines the density of TiOH$_2^+$ groups [112]. (6) MW irradiation efficiently weakened the effect of initial pH.
Inorganic oxidizing species	(1) Inorganic oxidizing species enhance the rates of degradation of different organic pollutants effectively because they trap the photogenerated electron more effectively than oxygen [78]. $H_2O_2 + e^- \rightarrow OH^\cdot + OH^-$ (9) $S_2O_8^{2-} + e^- \rightarrow SO_4^- + SO_4^{2-}$ (10) $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (11) (2) With increase in H$_2$O$_2$ dosage the degradation efficiency increases abruptly at low dosage due to enhancement in formation of hydroxyl radical by H$_2$O$_2$ self decomposition by UV illumination as shown in Eq. (1). (3) At high concentration, H$_2$O$_2$ can act as quencher; consequently lowering the concentration of hydroxyl radical as shown in Eqs. (2)–(4).

eral studies have shown higher photodegradation rates under low oxygen concentration (nitrogen-purging) in the presence of MW. This could be ascribed to the specific interactions of MW with the UV-illuminated TiO$_2$ particle surface. In addition, the number of coating cycles/layers of a catalyst surface plays a significant role in the treatment efficiency [81]. Generally, the thinner layers are difficult to activate and the thicker layers lag in some important properties like transparency, good mechanical strength or excellent adhesion to various supports. Therefore, all the above mentioned factors need to be optimized for establishing a successful MWPC system for WW treatment.

9. Reactors for MW operations

A modified domestic microwave oven (2450 MHz) is generally used for the aqueous phase MW-assisted degradation experiments [45,55]. The MW reactors are usually made-up of glass/Pyrex as ves-

sel or column type reactor, which is operated either in batch [50] or continuous-flow mode [55]. The schematic representation of the above mentioned MW reactors are shown in Fig. 7. A batch mode reactor is equipped with infrared pyrometer, MW power and temperature controllers. The vessel reactor operating with batch mode consists of magnetic stirrer for mixing the reactor contents. On the other hand, a perforated quartz plate is provided with the glass column reactor operating in batch mode to sustain catalyst [56]. In the continuous flow mode reactors, the glass column reactor is connected to metering pump and pressure gauge at the inlet, and at the effluent end, the reactor is connected to a heat exchanger and pressure regulating valve [98]. The MW reactor is generally operated within the emission limits set for the MW ovens, i.e. less than 5 mW/cm^2, measured at a distance 5 cm away from the oven [95]. During MW-assisted studies, the required amount of oxidants/catalysts is added in to the reactor under constant stirring (in batch mode). On the other hand, several studies were conducted

Table 6
Power consumption under various MW-assisted treatment methods.

Process [Ref. No.]	Pollutant	Initial conc. (mg/L)	Mass removed (mg)	Time (min)	MW power (W)	Energy consumption (KWh/kg)	Catalyst loading (g)	E (kWh/kg pollutant/g catalyst)
MW alone [83]	PCP	40	0.1	20	900	2542.4	–	–
MW with catalyst [58]		1500	2004	240	400	0.8	52.5	42
MW with UV (EDL) [83]		40	1.6	20	900	182.9	–	–
MW with UV (EDL) and Fe-Si-TiO$_2$ [83]		40	2.0	20	900	151.5	0.2	30
MW alone [5]	4-CP	30	0.4	120	750	3921.6	–	–
MW with catalyst [64]		100	6.0	1	300	0.8	0.1	0.1
MW with UV (EDL) and TiO$_2$ [5]		30	13.5	120	750	111.1	0.5	56
MW with catalyst [63]	Phenol	200	4.0	2	100	0.8	0.4	0.3
MW with UV and H$_2$O$_2$ [74]		200	67.5	9	1000	2.2	–	–
MW alone [36]	Ammonia	500	5	3	750	7.5	–	–
MW with oxidant [40]	MG	100	2.9	5	900	26	–	–
MW with catalyst [52]	H-acid	3000	55.6	20	800	4.8	10	48
MW with UV (EDL) [71]	Atrazine	50	2.5	4	900	24	–	–

with fixed bed column reactors using catalysts such as zero valent iron, different forms of AC and carbon supported metal catalyst. While using AC, the catalyst is saturated by the pollutant prior to MW assisted degradation so as to eliminate the adsorption effect of AC on pollutant degradation. The CWAO in MW reactor is achieved by incorporating the mixing of WW and air before the inlet in a continuous mode reactor. MW photochemistry is done with a batch mode reactor, with EDL placed in the reaction vessel.

In MW experiments, the sample size to be treated and MW operating conditions are so important for selecting a suitable MW combination for real-time applications. Therefore, a thorough analysis of the energy consumption in each MW combinations can be useful for its cost-effective application in pollution degradation process. The economic analyses of various MW studies (limited to operational cost) are shown in Table 6. The total power consumed in each process and the total power consumed per unit mass of pollutant removal is worked out as per Eqs. (11) and (12), respectively.

$$\text{total power consumed (kWh)}$$
$$= \frac{\text{power used (W)} \times \text{reaction time (min)}}{1000 \times 60} \quad (12)$$

$$\text{power consumed per unit mass of pollutant removal (kWh/kg)}$$
$$= \frac{\text{total power consumed}}{(C_o - C_t)V} \quad (13)$$

where C_o and C_t are the initial and final pollutant concentrations, respectively. V is working volume of the reaction mixture. The total power consumed in MW alone was the highest compared to MW in combination with catalyst, UV and UV/TiO$_2$. However, MW alone is economical for the removal of polar compound such as ammonia. On the other hand, the MW with catalyst and MW with UV/TiO$_2$ are the two least energy consuming processes and also shown higher pollution degradation. Moreover, the power consumed in the above mentioned two processes for phenol degradation are much lower than the power consumed in other AOPs reported in Fig. 1. As a whole, these data demonstrate that MW with catalyst or photocatalysis is a powerful tool for WW treatment.

10. Future research challenges

As a whole, the coupling of MW with other AOPs is an innovative treatment technique for the degradation of highly bio-refractory and recalcitrant pollutants. Especially, the coupling of MW with EDLs is a pioneering methodology in the MW based pollution removal process. Recent studies have demonstrated an outstanding improvement in the degradation efficiency of various substrates by the coupling of MW with EDLs as shown in Table 4. On the other hand, EDL has some unique advantages such as good photochemical efficiency, long life, low cost and simple photocatalytic equipment. The influence of light intensity produced by an EDL on the degradability of various pollutants has been a major area of research in the recent years. The light intensity of EDL depends on the variations of MW power level and its irradiation wavelength (based on the ratio and nature of the gases in EDL). Therefore, operating a MWPC with EDL under optimized conditions of MW and maximum EDL efficiency could increase the photocatalytic efficiency and overall degradability of the target pollutant. Also, it will be useful to reduce the cost of treatment process. Moreover, optimization of MW system for maximum power utilization and energy efficiency, i.e. by recovering a part of process heat through heat-exchangers, could be a future research goal in commercializing the MW technology for real-time WW treatment. At the same time, most of the MW studies with EDL listed in Table 4 were applied for the degradation of synthetic WW with single or multiple pollutants. But the real-time WW is grey in color and contains suspended matter, which
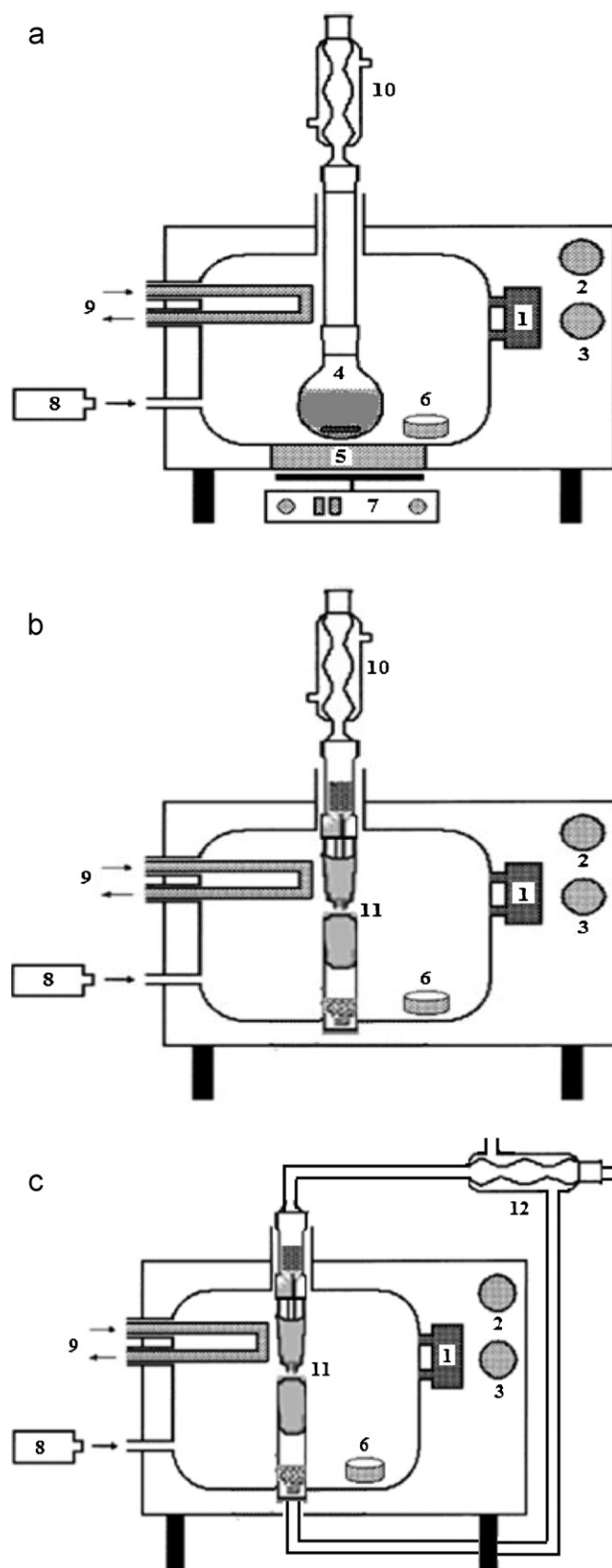

Fig. 7. Schematic diagram of the MW reactors for wastewater treatment (a) Pyrex vessel reactor operating in batch mode [113], (b) glass column reactor operating in batch mode [45], and (c) glass column reactor operating in continuous mode with heat exchange between inflow and outflow [55], {1} MW generator; {2} time adjuster; {3} power adjuster; {4} Pyrex vessel reactor with reaction mixture and a magnetic stir bar; {5} aluminium plate; {6} solid absorber inside the oven cavity; {7} magnetic stirrer; {8} infrared pyrometer; {9} circulating water in a glass tube; {10} condenser; {11} glass column reactor; {12} heat exchanger.

will interrupt the transmittance of UV light. As a result, there could be a possibility in the reduction of the overall performance of the MW process with EDLs. Therefore, the above mentioned drawbacks need to be investigated in the future to promote the MW technology for real-time WW treatment.

11. Conclusions

The current status of MW technology for WW treatment was reviewed in detail. The literature demonstrates that MW based pollutant degradation has many advantages: (1) reduces the reaction time, (2) increases the selectivity of reaction, (3) decreases the activation energy, (4) improves the speed of reaction, (5) reduces the equipment size and waste, (6) provides ease of control, and (7) increases the yield and purity of products. These advantages are mainly due to the thermal and non-thermal effects of MW, i.e. superheating, polarization, dielectric properties, hot spot formation, nuclear spin rotation and spin alignment. The combination of MW with oxidants, catalysts and AOPs is an emerging process for WW treatment. At the same time, several other operational parameters including pH, MW power, oxidant/catalyst dosage, irradiation time and air supply could influence the performance of MW systems. MW coupled UV system with an EDL (with or without catalyst) seems to be a simple, economic, efficient, prospective and environmentally friendly MW system for the detoxification of aqueous pollutants. Several studies have shown tremendous improvement in the degradation efficiency of various substrates under MW coupled EDL systems. However, optimizing the MW power, maximizing the light intensity of EDL and recovering the process heat of MW are the ways to commercialize the MW system for real-time WW treatment.

References

[1] P. Klán, M. Vavrik, Non-catalytic remediation of aqueous solutions by microwave-assisted photolysis in the presence of H_2O_2, J. Photochem. Photobiol. A 177 (2006) 24–33.

[2] Y. Shiying, W. Ping, Y. Xin, W. Guang, Z. Wenyi, S. Liang, A novel advanced oxidation method to degrade organic pollutants in wastewater: microwave-activated persulfate oxidation, J. Environ. Sci. 21 (2009) 1175–1180.

[3] T.L. Lai, C.C. Lee, G.L. Huang, Y.Y. Shu, C.B. Wang, Microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides, Appl. Catal. B: Environ. 78 (2008) 151–157.

[4] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[5] A. Zhihui, Y. Peng, L. Xiaohua, Degradation of 4-chlorophenol by microwave irradiation enhanced advanced oxidation processes, Chemosphere 60 (2005) 824–827.

[6] Y.F. Huang, W.H. Kuan, S.L. Lo, C.F. Lin, Total recovery of resources and energy from rice straw using microwave-induced pyrolysis, Bioresour. Technol. 99 (2008) 8252–8258.

[7] J.A. Menéndez, M. Inguanzo, J.J. Pis, Microwave-induced pyrolysis of sewage sludge, Water Res. 36 (2002) 3261–3264.

[8] J.A. Menéndez, A. Domínguez, M. Inguanzo, J.J. Pis, Microwave-induced drying, pyrolysis and gasification (MWDPG) of sewage sludge: vitrification of the solid residue, J. Anal. Appl. Pyrol. 74 (2005) 406–412.

[9] S.J. Haswell, N. Howarth, Perturbation of a solid phase separation process by a non-thermal microwave effect, Anal. Chim. Acta 387 (1999) 113–120.

[10] M.M. Punt, G.S.V. Raghavan, J.M.R. Belanger, J.R.J. Pare, Microwave-assisted process for the extraction of contaminants from soil, J. Soil Contamin. 8 (1999) 577–592.

[11] H.S. Tai, C.J.G. Jou, Application of granular activated carbon packed-bed reactor in microwave radiation field to treat phenol, Chemosphere 38 (1999) 2667–2680.

[12] M. Ericsson, A. Colmsjo, Dynamic microwave-assisted extraction coupled on-line with solid-phase extraction and large-volume injection gas chromatography: determination of organophosphate esters in air samples, Anal. Chem. 75 (2003) 1713–1719.

[13] B. Pérez-Cid, I. Lavilla, C. Bendicho, Application of microwave extraction for portioning of heavy metals in sewage sludge, Anal. Chim. Acta 378 (1999) 201–210.

[14] B. Pérez-Cid, A.F. Alborés, E.F. Gòmez, E.F. Lòpez, Use of microwave single extractions for metal fractionation in sewage sludge samples, Anal. Chim. Acta 431 (2001) 209–218.

[15] A.B. Prevot, M. Gulmini, V. Zelano, E. Pramauro, Microwave-assisted extraction of polycyclic aromatic hydrocarbons from marine sediments using nonionic surfactant solutions, Anal. Chem. 73 (2001) 3790–3795.

[16] Z. Kawala, T. Atamanczuk, Microwave-enhanced thermal decontamination of soil, Environ. Sci. Technol. 32 (1998) 2602–2607.

[17] R.A. Abramovitch, H. Bangzhou, D.A. Abramovitch, S. Jiangao, In situ decomposition of PAHs in soil and desorption of organic solvents using microwave energy, Chemosphere 39 (1999) 81–87.

[18] R.A. Abramovitch, L. ChangQing, E. Hicks, J. Sinard, In situ remediation of soils contaminated with toxic metal ions using microwave energy, Chemosphere 53 (2003) 1077–1085.

[19] S. Yuan, M. Tian, X. Lu, Microwave remediation of soil contaminated with hexachlorobenzene, J. Hazard. Mater. 137 (2006) 878–885.

[20] C.J. Jou, An efficient technology to treat heavy metal-lead-contaminated soil by microwave radiation, J. Environ. Manage. 78 (2006) 1–4.

[21] L. Lin, S. Yuan, J. Chen, L. Wang, J. Wan, X. Lu, Treatment of chlorophenicol-contaminated soil by microwave radiation, Chemosphere 78 (2010) 66–71.

[22] G.G. Wicks. R.L. Schulz, Microwave remediation of hazardous and radioactive wastes, WSRC-MS-99-00762 (1999), http://sti.srs.gov/fulltext/ms9900762/ms9900762.html.

[23] S.H. Weng, J. Wang, Exploration on the mechanism of coal desulphurization using microwave irradiation and acid washing method, Fuel Process. Technol. 31 (1992) 233–240.

[24] A.C. Ferrando, J.M. Andrés, L. Membrado, Coal desulphurization with hydro-iodic acid and microwaves, Coal Sci. Technol. 24 (1995) 1729–1732.

[25] J.I. Hayashi, The role of microwave irradiation in coal desulphurization with molten caustics, Fuel 69 (1990) 739–742.

[26] W.T. Wong, W.I. Chan, P.H. Liao, K.V. Lo, A hydrogen peroxide/microwave advanced oxidation process for sewage sludge treatment, J. Environ. Sci. Health A 41 (2006) 2623–2633.

[27] G.Q. Yin, P.H. Liao, K.V. Lo, An ozone/hydrogen peroxide/microwave enhanced advanced oxidation process for sewage sludge treatment, J. Environ. Sci. Health A 42 (2007) 1177–1181.

[28] G. Bond, R.B. Moyes, D.A. Whan, Recent applications of microwave heating in catalysis, Catal. Today 17 (1993) 427–437.

[29] H. Zhang, D.O. Hayward, D.M.P. Mingos, Effects of microwave dielectric heating on heterogeneous catalysis, Catal. Lett. 88 (2003) 33–38.

[30] D.S. Wu, C.Y. Han, S.Y. Wang, N.L. Wu, I.A. Rusakova, Microwave-assisted solution synthesis of SnO nanocrystallites, Mater. Lett. 55 (2002) 155–159.

[31] W.X. Chen, J. Zhao, J.Y. Lee, Z.L. Liu, Microwave heated polyol synthesis of carbon nanotubes supported Pt nanoparticles for methanol electrooxidation, Mater. Chem. Phys. 91 (2005) 124–129.

[32] Y.M. Zhang, P. Wang, N. Han, H.F. Lei, Microwave irradiation: a novel method for rapid synthesis of D,L-lactide, Macromol. Rapid Comm. 28 (2007) 417–421.

[33] C.O. Kappe, Controlled microwave heating in modern organic synthesis, Angew. Chem. Int. Edit. 43 (2004) 6250–6284.

[34] C.O. Kappe, Microwave dielectric heating in synthetic organic chemistry, Chem. Soc. Rev. 37 (2008) 1127–1139.

[35] S. Mallakpour, Z. Rafiee, Use of ionic liquid and microwave irradiation as a convenient, rapid and eco-friendly method for synthesis of novel optically active and thermally stable aromatic polyamides containing N-phthaloyl-L-alanine pendent group, Polym. Degrad. Stabil. 93 (2008) 753–759.

[36] L. Lin, S. Yuan, J. Chen, Z. Xu, X. Lu, Removal of ammonia nitrogen in wastewater by microwave radiation, J. Hazard. Mater. 161 (2009) 1063–1068.

[37] L. Lin, J. Chen, Z. Xu, S. Yuan, M. Cao, H. Liu, X. Lu, Removal of ammonia nitrogen in wastewater by microwave radiation: a pilot-scale study, J. Hazard. Mater. 168 (2009) 862–867.

[38] G. Cravotto, A. Binello, S. Di Carlo, L. Orio, Z.-L. Wu, B. Ondruschka, Oxidative degradation of chlorophenol derivatives promoted by microwaves or power ultrasound: a mechanism investigation, Environ. Sci. Pollut. Res. 17 (2010) 674–687.

[39] B.R. Prasannakumar, I. Regupathi, T. Murugesan, An optimization study on microwave irradiated, decomposition of phenol in the presence of H_2O_2, J. Chem. Technol. Biotechnol. 84 (2009) 83–91.

[40] Y.M. Ju, S.G. Yang, Y.C. Ding, C. Sun, C.A. Gu, Z. He, C. Qin, H. He, B. Xu, Microwave-enhanced H_2O_2-based process for treating aqueous malachite green solutions: intermediates and degradation mechanism, J. Hazard. Mater. 171 (2009) 123–132.

[41] M. Ravera, A. Buico, F. Gosetti, C. Cassino, D. Musso, D. Osella, Oxidative degradation of 1,5-naphthalenedisulfonic acid in aqueous solutions by microwave irradiation in the presence of H_2O_2, Chemosphere 74 (2009) 1309–1314.

[42] L. Zhang, X. Guo, F. Yan, M. Su, Y. Li, Study of the degradation behavior of dimethoate under microwave irradiation, J. Hazard. Mater. 149 (2007) 675–684.

[43] Y.C. Lee, S.L. Lo, P.T. Chiueh, D.G. Chang, Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate, Water Res. 43 (2009) 2811–2816.

[44] Y. Shiying, W. Ping, Y. Xin, W. Guang, Z. Wenyi, S. Liang, A novel advanced oxidation process to degrade organic pollutants in wastewater: microwave-activated persulfate oxidation, J. Environ. Sci. 21 (2009) 1175–1180.

[45] C.J. Jou, Degradation of pentachlorophenol with zero-valence iron coupled with microwave energy, J. Hazard. Mater. 152 (2008) 699–702.

[46] L. Zhang, M. Su, X. Guo, Studies on the treatment of brilliant green solution by combination microwave induced oxidation with $CoFe_2O_4$, Sep. Purif. Technol. 62 (2008) 458–463.

[47] X. Bi, P. Wang, C. Jiao, H. Cao, Degradation of remazol golden yellow dye wastewater in microwave enhanced ClO_2 catalytic oxidation process, J. Hazard. Mater. 168 (2009) 895–900.

[48] X. Bi, P. Wang, H. Jiang, Catalytic activity of $CuO_n–La_2O_3/\gamma-Al_2O_3$ for microwave assisted ClO_2 catalytic oxidation of phenol wastewater, J. Hazard. Mater. 154 (2008) 543–549.

[49] J.G. Mei, S.M. Yu, J. Cheng, Heterogeneous catalytic wet peroxide oxidation of phenol over delaminated Fe–Ti-PILC employing microwave irradiation, Catal. Commun. 5 (2004) 437–440.

[50] Z. Zhang, Y. Shan, J. Wang, H. Ling, S. Zang, W. Gao, A. Zhao, H. Zhang, Investigation on the rapid degradation of congo red catalyzed by activated carbon powder under microwave irradiation, J. Hazard. Mater. 147 (2007) 325–333.

[51] G.C.J. Jou, Application of activated carbon in a microwave radiation field to treat trichloroethylene, Carbon 36 (1998) 1643–1648.

[52] Y. Zhang, X. Quan, S. Chen, Y. Zhao, F. Yang, Microwave assisted catalytic wet air oxidation of H-acid in aqueous solution under the atmospheric pressure using activated carbon as catalyst, J. Hazard. Mater. 137 (2006) 534–540.

[53] X. Liu, G. Yu, W. Han, Granular activated carbon adsorption and microwave regeneration for the treatment of 2,4,5-trichlorobiphenyl in simulated soil-washing solution, J. Hazard. Mater. 147 (2007) 746–751.

[54] Y. Sun, Y. Zhang, X. Quan, Treatment of petroleum refinery wastewater by microwave-assisted catalytic wet air oxidation under low temperature and low pressure, Sep. Purif. Technol. 62 (2008) 565–570.

[55] L. Bo, X. Quan, S. Chen, H. Zhao, Y. Zhao, Degradation of p-nitrophenol in aqueous solution by microwave assisted oxidation process through a granular activated carbon fixed bed, Water Res. 40 (2006) 3061–3068.

[56] X. Liu, X. Quan, L. Bo, S. Chen, Y. Zhao, Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation, Carbon 42 (2004) 415–422.

[57] L.L. Bo, Y.B. Zhang, X. Quan, B. Zhao, Microwave assisted catalytic oxidation of p-nitrophenol in aqueous solution using carbon-supported copper catalyst, J. Hazard. Mater. 153 (2008) 1201–1206.

[58] L. Bo, X. Quan, X. Wang, S. Chen, Preparation and characteristics of carbon-supported platinum catalyst and its application in the removal of phenolic pollutants in aqueous solution by microwave-assisted catalytic oxidation, J. Hazard. Mater. 157 (2008) 179–186.

[59] H. Hidaka, A. Saitou, H. Honjou, K. Hosoda, M. Moriya, N. Serpone, Microwave-assisted dechlorination of polychlorobenzenes by hypophosphite anions in aqueous alkaline media in the presence of Pd-loaded active carbon, J. Hazard. Mater. 148 (2007) 22–28.

[60] S. Lv, X. Chen, Y. Ye, S. Yin, J. Cheng, M. Xia, Rice hull/$MnFe_2O_4$ composite: preparation, characterization and its rapid microwave-assisted COD removal for organic wastewater, J. Hazard. Mater. 171 (2009) 634–639.

[61] R. Salvador, B. Casal, M. Yates, M.A. Martín-Luengo, E. Ruiz-Hitzky, Microwave decomposition of a chlorinated pesticide (Lindane) supported on modified sepiolites, Appl. Clay Sci. 22 (2002) 103–113.

[62] I. Polaert, L. Estel, A. Ledoux, Microwave-assisted remediation of phenol wastewater on activated charcoal, Chem. Eng. Sci. 60 (2005) 6354–6359.

[63] T.L. Lai, C.C. Lee, K.S. Wu, Y.Y. Shu, C.B. Wang, Microwave-enhanced catalytic degradation of phenol over nickel oxide, Appl. Catal. B: Environ. 68 (2006) 147–153.

[64] T.L. Lai, W.F. Wang, Y.Y. Shu, Y.T. Liu, C.B. Wang, Evaluation of microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides, J. Mol. Catal. A: Chem. 273 (2007) 303–309.

[65] T.L. Lai, J.Y. Liu, K.F. Yong, Y.Y. Shu, C.B. Wang, Microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides under low temperature, J. Hazard. Mater. 157 (2008) 496–502.

[66] H. He, S. Yang, K. Yu, Y. Ju, C. Sun, L. Wang, Microwave induced catalytic degradation of crystal violet in nano-nickel dioxide suspensions, J. Hazard. Mater. 173 (2009) 393–400.

[67] J. Gao, G. Zhao, W. Shi, D. Li, Microwave activated electrochemical degradation of 2,4-dichlorophenoxyacetic acid at boron-doped diamond electrode, Chemosphere 75 (2009) 519–525.

[68] G. Zhao, J. Gao, W. Shi, M. Liu, D. Li, Electrochemical incineration of high concentration azo dye wastewater on the in situ activated platinum electrode with sustained microwave radiation, Chemosphere 77 (2009) 188–193.

[69] C.F. Gromboni, M.Y. Kamogawa, A.G. Ferreira, J.A. Nóbrega, A.R.A. Nogueira, Microwave-assisted photo-Fenton decomposition of chlorfenvinphos and cypermethrin in residual water, J. Photochem. Photobiol. A 185 (2007) 32–37.

[70] Y. Yang, P. Wang, S. Shi, Y. Liu, Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater, J. Hazard. Mater. 168 (2009) 238–245.

[71] N. Ta, J. Hong, T. Liu, C. Sun, Degradation of atrazine by microwave-assisted electrodeless discharge mercury lamp in aqueous solution, J. Hazard. Mater. 138 (2006) 187–194.

[72] J. Hong, N. Ta, S. Yanga, Y. Liu, C. Sun, Microwave-assisted direct photolysis of bromophenol blue using electrodeless discharge lamps, Desalination 214 (2007) 62–69.

[73] X. Zhang, Y. Wang, G. Li, J. Qu, Oxidative decomposition of azo dye C.I. Acid Orange 7 (AO7) under microwave electrodeless lamp irradiation in the presence of H_2O_2, J. Hazard. Mater. 134 (2006) 183–189.

[74] D.H. Han, S.Y. Cha, H.Y. Yang, Improvement of oxidative decomposition of aqueous phenol by microwave irradiation in UV/H_2O_2 process and kinetic study, Water Res. 38 (2004) 2782–2790.

[75] S. Horikoshi, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV illumination technique VI. A simple modified domestic microwave oven integrating an electrodeless UV–Vis lamp to photodegrade environmental pollutants in aqueous media, J. Photochem. Photobiol. A 161 (2004) 221–225.

[76] J. Hong, C. Sun, S.G. Yang, Y.Z. Liu, Photocatalytic degradation of methylene blue in TiO_2 aqueous suspensions using microwave powered electrodeless discharge lamps, J. Hazard. Mater. 133 (2006) 162–166.

[77] S. Horikoshi, A. Tokunaga, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV illumination method VII. Thermal/non-thermal effects in the microwave-assisted photocatalyzed mineralization of bisphenol-A, J. Photochem. Photobiol. A 162 (2004) 33–40.

[78] X. Zhang, G. Li, Y. Wang, Microwave assisted photocatalytic degradation of high concentration azo dye Reactive Brilliant Red X-3B with microwave electrodeless lamp as light source, Dyes Pigments 74 (2007) 536–544.

[79] X. Zhang, Y. Wang, G. Li, Effect of operating parameters on microwave assisted photocatalytic degradation of azo dye X-3B with grain TiO_2 catalyst, J. Mol. Catal. A: Chem. 237 (2005) 199–205.

[80] G. Zhanqi, Y. Shaogui, T. Na, S. Cheng, Microwave assisted rapid and complete degradation of atrazine using TiO_2 nanotube photocatalyst suspensions, J. Hazard. Mater. 145 (2007) 424–430.

[81] V. Církva, H. Žabová, M. Hájek, Microwave photocatalysis of mono-chloroacetic acid over nanoporous titanium(IV) oxide thin films using mercury electrodeless discharge lamps, J. Photochem. Photobiol. A 198 (2008) 13–17.

[82] Z. Ai, P. Yang, X. Lu, Degradation of 4-chlorophenol by a microwave assisted photocatalysis method, J. Hazard. Mater. 124 (2005) 147–152.

[83] S. Yang, H. Fu, C. Sun, Z. Gao, Rapid photocatalytic destruction of pentachlorophenol in F–Si-comodified TiO_2 suspensions under microwave irradiation, J. Hazard. Mater. 161 (2009) 1281–1287.

[84] H. Zhong, Y. Shaogui, J. Yongming, S. Cheng, Microwave photocatalytic degradation of Rhodamine B using TiO_2 supported on activated carbon: mechanism implication, J. Environ. Sci. 21 (2009) 268–272.

[85] Z. He, C. Sun, S. Yang, Y. Ding, H. He, Z. Wang, Photocatalytic degradation of rhodamine B by Bi_2WO_6 with electron accepting agent under microwave irradiation: mechanism and pathway, J. Hazard. Mater. 162 (2009) 1477–1486.

[86] Y. Liu, S. Yang, J. Hong, C. Sun, Low-temperature preparation and microwave photocatalytic activity study of TiO_2-mounted activated carbon, J. Hazard. Mater. 142 (2007) 208–215.

[87] S. Kataoka, D.T. Tompkins, W.A. Zeltner, M.A. Anderson, Photocatalytic oxidation in the presence of microwave irradiation: observations with ethylene and water, J. Photochem. Photobiol. A 148 (2002) 323–330.

[88] S. Horikoshi, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV-illumination technique IV. Non-thermal effects in the microwave-assisted degradation of 2,4-dichlorophenoxyacetic acid in UV-irradiated TiO_2/H_2O dispersions, J. Photochem. Photobiol. A 159 (2003) 289–300.

[89] S. Horikoshi, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV-illumination method. 1. Microwave-assisted degradation of rhodamine-B dye in aqueous TiO_2 dispersions, Environ. Sci. Technol. 36 (2002) 1357–1366.

[90] S. Horikoshi, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV-illumination method II. Characteristics of a novel UV–VIS–microwave integrated irradiation device in photodegradation processes, J. Photochem. Photobiol. A 153 (2002) 185–189.

[91] S. Horikoshi, H. Hidaka, N. Serpone, Hydroxyl radicals in microwave photocatalysis. Enhanced formation of OH radicals probed by ESR techniques in microwave-assisted photocatalysis in aqueous TiO_2 dispersions, Chem. Phys. Lett. 376 (2003) 475–480.

[92] D.A. Jones, T.P. Lelyveld, S.D. Mavrofidis, S.W. Kingman, N.J. Miles, Microwave heating applications in environmental engineering—a review, Resour. Conserv. Recycl. 34 (2002) 75–90.

[93] J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, J.M. Bermúdez, Review: microwave heating processes involving carbon materials, Fuel Process. Technol. 91 (2010) 1–8.

[94] S. Horikoshi, N. Serpone, Review: photochemistry with microwaves. Catalysts and environmental applications, J. Photochem. Photobiol. C 10 (2009) 96–110.

[95] T.V.C.T. Chan, H.C. Reader, Understanding Microwave Heating Cavities, Artech House, London, 2000.

[96] C.E. George, G.V.N. Rao, V. Thalakola, Thermal desorption of contaminants using microwave heated rotary mixture, in: Proceedings of the 29th Microwave Power Symposium, Chicago, IL, 1994.

[97] M. Nuchter, U. Muller, B. Ondruschka, A. Tied, W. Lautenschlager, Review: microwave-assisted chemical reactions, Chem. Eng. Technol. 26 (2003) 1207–1216.

[98] M. Hájek, Microwave catalysis in organic synthesis, in: A. Loupy (Ed.), Microwaves in Organic Synthesis, Wiley–VCH/Verlag, Germany, 2006, pp. 615–652.

[99] M.A. Herrero, J.M. Kremsner, C.O. Kappe, Nonthermal microwave effects revisited: on the importance of internal temperature monitoring and agitation in microwave chemistry, J. Org. Chem. 73 (2008) 36–47.

[100] M. Abrantes, P. Neves, M.M. Antunes, S. Gago, F.A. Almeida Paz, A.E. Rodrigues, M. Pillinger, I.S. Goncalves, C.M. Silva, A.A. Valente, Microwave-assisted molybdenum-catalysed epoxidation of olefins, J. Mol. Catal. A: Chem. 320 (2010) 19–26.

[101] S. Gopalakrishnan, J. Munch, R. Herrmann, W. Schwieger, Effects of microwave radiation on one-step oxidation of benzene to phenol with nitrous oxide over Fe-ZSM-5 catalyst, Chem. Eng. J. 120 (2006) 99–105.

[102] M. Irfan, M. Fuchs, T.N. Glasnov, C.O. Kappe, Microwave-assisted cross-coupling and hydrogenation chemistry by using heterogeneous transition-metal catalysts: an evaluation of the role of selective catalyst heating, Chem. Eur. J. 15 (2009) 11608–11618.

[103] K.E. Haque, Microwave energy for mineral treatment processes—a brief review, Int. J. Miner. Process. 57 (1999) 1–24.

[104] P. Müler, P. Klán, V. Církva, The electrodeless discharge lamp: a prospective tool for photochemistry. Part 4: Temperature- and envelope material-dependent emission characteristics, J. Photochem. Photobiol. A 158 (2003) 1–5.

[105] E. Cigdem, P. Audrey, M. Juan, Synergetic pretreatment of sewage sludge by microwave irradiation in presence of H_2O_2 for enhanced anaerobic digestion, Water Res. 42 (2008) 4674–4682.

[106] P. Klán, V. Církva, Microwaves in photochemistry, in: A. Loupy (Ed.), Microwaves in Organic Synthesis, Wiley–VCH/Verlag, Germany, 2006, pp. 860–897.

[107] P. Müler, P. Klán, V. Církva, The electrodeless discharge lamp: a prospective tool for photochemistry. Part 5: Fill material-dependent emission characteristics, J. Photochem. Photobiol. A 171 (2005) 51–57.

[108] V. Církva, L. Vlková, S. Relich, M. Hájek, Microwave photochemistry IV. Preparation of the electrodeless discharge lamps for photochemical applications, J. Photochem. Photobiol. A 179 (2006) 229–233.

[109] V. Církva, H. Žabová, Thin nanoporous titania films on the electrodeless discharge lamps for photocatalysis, in: G.K. Castello (Ed.), Handbook of Photocatalysts: Preparation, Structure and Applications, Nova Science Publishers, New York, 2010, pp. 103–151.

[110] X. Quan, Y. Zhang, S. Chen, Y. Zhao, F. Yang, Generation of hydroxyl radical in aqueous solution by microwave energy using activated carbon as catalyst and its potential in removal of persistent organic substances, J. Mol. Catal. A: Chem. 263 (2007) 216–222.

[111] C.C. Wong, W. Chu, The direct photolysis and photocatalytic degradation of alachlor at different TiO_2 and UV sources, Chemosphere 50 (2003) 981–987.

[112] A.G. Rincón, C. Pulgarin, Photocatalytical inactivation of E. coli: effect of (continuous–intermittent) light intensity and of (suspended–fixed) TiO_2 concentration, Appl. Catal. B: Environ. 44 (2003) 263–284.

[113] P. Klán, M. Hájek, V. Církva, The electrodeless discharge lamp: a prospective tool for photochemistry. Part 3: The microwave photochemistry reactor, J. Photochem. Photobiol. A 140 (2001) 185–189.