

Microwave enhanced catalytic decomposition of carbetamide and chlorotoluron

George Chi-Tangye and Katherine Huddersman

School of Pharmacy, Faculty of Health and Life Sciences, De Montfort University

Abstract

Growing population and industrial activities mean that fresh and potable water resources are declining at an alarming rate with the generation of vast amounts of wastewater and subsequent release of contaminants into water courses. Heterogeneous advanced oxidation processes constitute a promising technology for the treatment of wastewaters containing non-easily removable organic compounds. However, some reaction rates are very slow, thereby limiting the scope of application especially with regards to throughput. In this paper we report a method for the treatment of toxic and recalcitrant contaminants such as carbetamide and chlorotoluron in wastewater by enhancing the rate of a heterogeneous catalytic treatment process using microwave (MW) energy. The use of 80W CW microwave power (2.45GHz) in a multimode cavity under atmospheric pressure increased the rate of decomposition of the organic pollutants (100mL of 20mg/L carbetamide and chlorotoluron solutions, pH 4.6, 300mg/L H₂O₂, and 4g catalyst) by 2.6 fold in comparison to conventional isothermal reactions performed at 32°C. Most significantly, a 32% rate improvement was observed when microwave energy was used in comparison to conventional heating under the same temperature profile.

1. INTRODUCTION

The demand for fresh water is on a constant rise due to growing human population. This results in the release of toxic and recalcitrant contaminants such as pesticides into water courses. To this day many wastewater streams containing toxic and recalcitrant pollutants are treated only by dilution. The ever-increasing volume and diversity of pollutants offer a significant challenge to conventional wastewater treatment systems. Moreover, individual treatment technologies are not effective in removing these recalcitrant pollutants owing to their toxicity, shock loads, selectivity and slow reaction rates. As a result of increasing environmental awareness and more stringent legislation, most conventional wastewater treatment technologies cannot meet discharge standards.

Advanced oxidation processes (AOPs) characterised by the production of hydroxyl radicals constitute a promising technology for the treatment of wastewaters containing non-easily removable organic compounds. Amongst the AOPs, Fenton's Chemistry has gained renewed attention in the past decade because of relatively simple means of generating the very reactive hydroxyl radicals (E_o = 2.8V) from non-toxic and very abundant iron, and easy to handle environmentally safe H₂O₂. The production of hydroxyl radicals (HO[•]) proceeds according to the following two principal equations^{1,2}.





Despite the numerous advantages of the Fenton's systems, homogeneous processes are pH limited (pH between 3 and 4) and still require the removal of iron (present as iron oxide sludge contaminated with non-degraded pollutant) post-treatment. Our recently developed heterogeneous modified PAN catalysts system involving the ligation of iron on a support has eliminated the need for iron removal post treatment and has broadened the pH range of application ^{3,4}, whilst enabling continuous flow processes favoured by industry. Although this heterogeneous system has been shown to be very effective in the removal of toxic contaminants from a variety of waste streams, some reactions rates are very slow, thereby limiting the scope of application especially with regards to throughput.

Microwave (MW) radiation has found its niche in several domestic, industrial and medical applications. Research studies have explored applications of microwave radiation (a) in organic syntheses, as well as in polymerization and dehydration processes; (b) in inorganic syntheses; (c) in environmental water treatments; (d) in safety and biological aspects; (e) in analyses and extraction processes; and (f) in food sterilization⁵⁻⁷.

Microwaves energy is insufficient to disrupt the chemical bonds of many organic compounds ⁸, its oscillating electric and magnetic fields have an effect on any material that can be electrically or magnetically polarised at certain frequencies – resulting in heating. Therefore, microwave radiation coupled with adsorbents, catalysts and AOPs could increase treatment efficiencies of pollutants and shorten reactions times. The principal heating mechanisms of MW are dipolar polarization, conduction mechanism and interfacial polarization. MW can provide rapid heating of materials with power conversion per unit volume (in Gaussian units):

$$P = \frac{\omega \epsilon''}{8\pi} |\vec{E}|^2 \quad \dots 5.$$

Depending on the distribution of electric field \vec{E} and relative loss factor (ϵ'') of the material characterized by complex dielectric constant:

$$\epsilon = \epsilon' + i\epsilon'' = \epsilon' + i(\epsilon_d'' + \epsilon_\sigma'') = \epsilon' + i\epsilon_d'' + i \frac{4\pi\sigma}{\omega} \quad \dots 6.$$

Here, it is assumed that: \vec{E} is a complex amplitude of real electric field $\bar{e} = \text{Re}\{\vec{E}e^{-i\omega t}\}$; ϵ' - relative dielectric constant; ϵ_d'' and ϵ_σ'' - parts of relative dielectric loss factor ϵ'' due to contribution of polarization mechanism and conduction mechanism, respectively; σ - electrical conductivity; $i = \sqrt{-1}$; $\omega = 2\pi f$, f - the frequency of microwaves.

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 ⁹ and theoretically evaluated ¹⁰.

In recent years, a reasonable number of reports have demonstrated the use of microwaves to promote the oxidative degradation of bio-refractory wastes due to its advantages of speeding up the reaction, high-efficiency with no pollution to the environment ⁶. These investigations

suggest that microwaves could promote the degradation efficiency of traditional and advanced treatment methods. Microwaves have been combined with a Fenton-like system for the treatment of Persistent Organic Pollutants (POPs) in soil ^{11,12}. Some researchers proposed a treatment technology for highly concentrated and bio-refractory wastewater and reported superior treatment efficiency of the microwave enhanced Fenton-like combined process compared to the Fenton-like reaction for the removal of organic contaminants in pharmaceutical wastewater ⁷.

In this work, we investigated the potential of using microwave energy to enhance the rates of a heterogeneous catalytic system towards the removal of organic contaminants from agricultural wastewater – case of carbetamide and chlorotoluron.

2. MATERIALS AND METHODS

All reagents were of analytical grade, purchased from Sigma Aldrich, Dorset UK. Double distilled water was used for all the experiments. Table 1 shows the physicochemical properties of the pesticides – carbetamide and chlorotoluron. The modified PAN catalyst used was prepared as described in our previous work ¹³.

Carbetamide and chlorotoluron concentrations were analysed by reversed phase high performance liquid chromatography (HPLC), using a Perkin Elmer series 200 HPLC with ultra-violet (UV) detection at 234 nm. Optimised HPLC conditions were: Germini C-18 (4.6 mm × 150 mm, 5 µm) column supplied by Supelco, mobile phase 60% acetonitrile, 40% water, flow rate 1 ml min⁻¹ and column temperature 25°C.

The reactions were performed using 100 mL solutions of carbetamide and chlorotoluron in a round bottom reaction vessel. The required amount of catalyst (3g) was added to the reaction vessel followed by the required dose of hydrogen peroxide (8.8 mM H₂O₂). The CEM Mars 6 reactor with capacity of 1800W (two 900 W magnetrons at 2.45GHz), equipped with a fibre optics temperature sensor and magnetic stirrer was used for the microwave enhanced reaction (see Fig 1 for experimental setup). Conventional heating experiments were performed on a temperature controlled Radleys six reaction station carousel. To compare the effect of microwaves and conventional heating, reactions were performed under same conditions (initial reagent concentrations and stirring) and similar heating profiles for both microwaves and conventional heating experiments. The temperature of the reaction media were measured using the same fibre optics sensor system. Experiments were performed in triplicates.

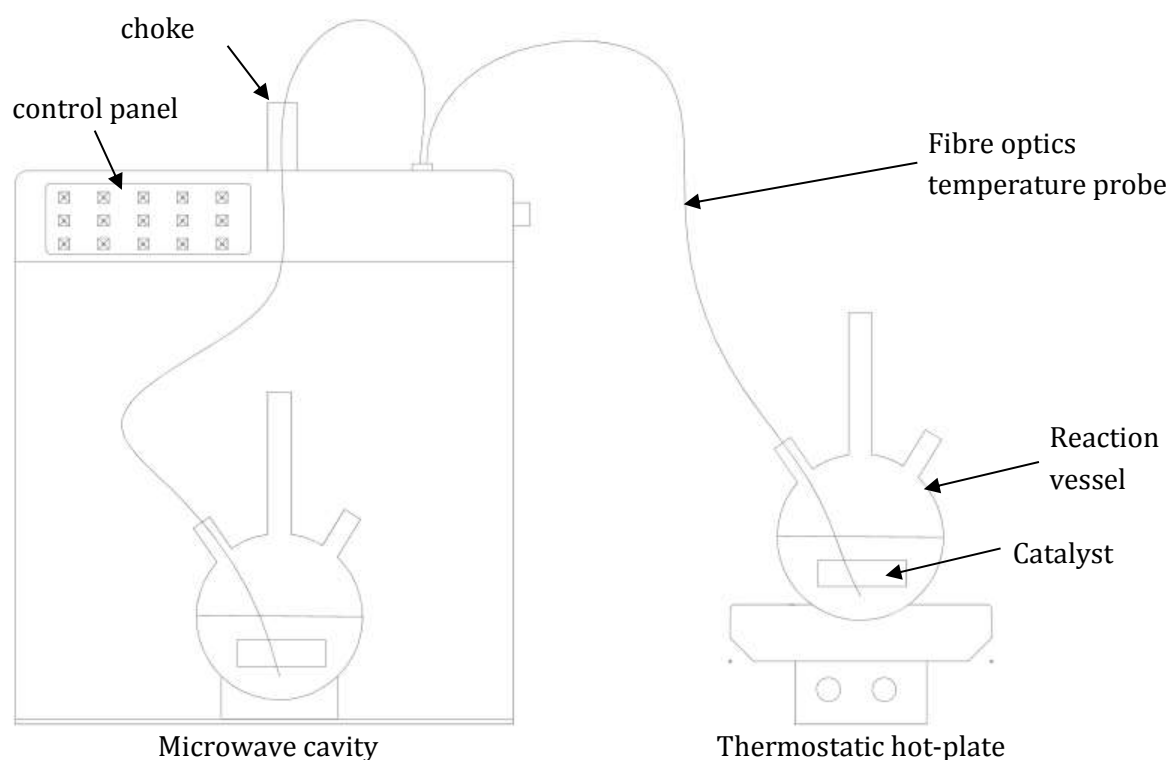


Fig. 1 Experimental setup for microwave assisted catalysis and conventional heating catalysis

Table 1. Physico-chemical properties of carbetamide and chlorotoluron

Structure	Uses	Molecular weight (g mol^{-1})	Water solubility (mgL $^{-1}$ at 25 °C)	log Kow
<p>chlorotoluron</p>	<p>Phenylurea herbicides pre- or early post-emergence herbicide widely used to control annual grasses and broad-leaved weeds in winter cereals.</p> <p>DT(50) = 45 days - moderately persistent in soil, very persistent in water, High leachability, Koc = 196 - moderately mobile</p>	212.7	74	2.29
<p>Carbetamide</p>	<p>carbamate herbicides Soil herbicide, DT50 in soil = 10 days - non persistent in soils High leachability</p>	236.27	3270	1.78

3. RESULTS AND DISCUSSION

3.1 Comparing microwave assisted catalysis with conventional heating assisted catalysis

The effectiveness of microwave in processing is well substantiated as exemplified by the widely used domestic microwave ovens, in which many different products with various electromagnetic properties are heated efficiently. However, in most of the work reported in the literature, a modified domestic microwave oven (2450 MHz) is generally used for the aqueous phase MW-assisted degradation experiments. As a result, there is lack of proper control of the microwave power, pulses, field distribution and measurement of temperature. Our use of an optical fibre temperature sensor, continuous wave source and power control facility means that the probe can reside in the reaction medium enabling in-situ monitoring and control and the microwave power can be accurately controlled. As shown in Figure 2, 16 % and 35 % of carbetamide and chlorotoluron were removed respectively in 35 minutes at a constant temperature of 32°C (performed on the hot plate). This suggests that the removal of these contaminants under ambient temperature conditions will require much longer residence times as temperatures are generally significantly lower.

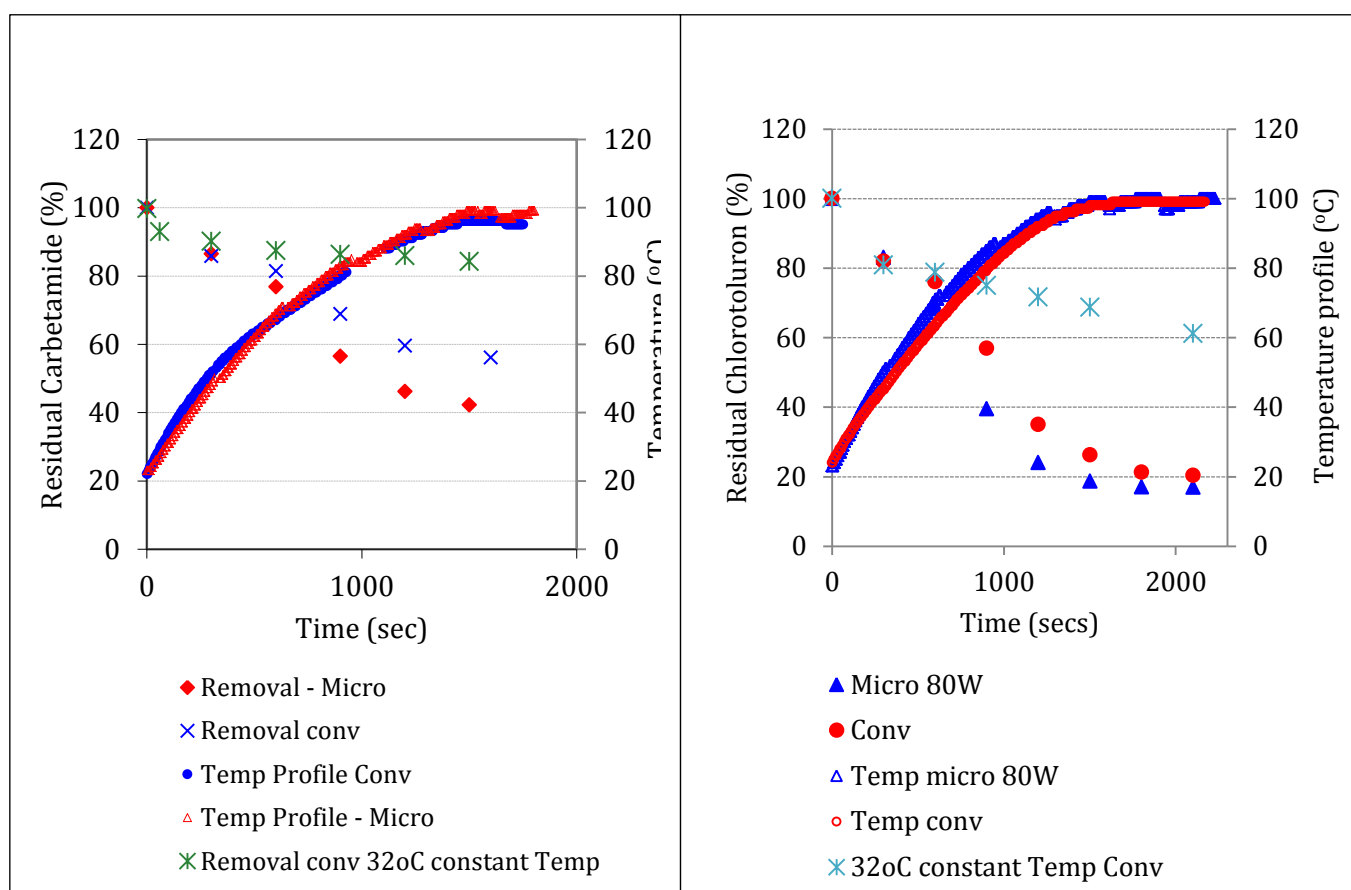


Figure 2, Removal of (a) carbetamide and (b) chlorotoluron using 3g of modified PAN catalyst and 8.8 mM H₂O₂.

A microwave power of 80 W was applied to the system and the temperature profile of the 100 mL solution recorded. This temperature profile was successfully replicated on the conventional hot plate system as shown in Figure 2. Decomposing the contaminants using similar temperature profiles, there was a 32% improvement in the rate of removal of carbetamide in comparison to the conventional heating system. In addition, there was a 2.6 fold improvement by microwaves in comparison to conventional heating at 32°C. In such a heterogeneous catalytic system, the improved degradation efficiency could be attributed to the interfacial polarization mechanism. Although both temperature profiles are similar, hot-spots possibly formed at reaction sites could cause thermal or temperature gradients resulting to differences between the temperature at the reaction site and temperature in the medium or reactor system, thereby decreasing the activation energy, hence facilitating the destruction of the chemical bonds and increasing the rate of reaction. Regardless, the ability to selectively heat materials is one of the unique advantages of using microwaves in processing.

3.2 Effect of temperature on the removal rates

As seen in Figure 3, reactions at constant temperatures also show faster rates in the microwave enhanced process in comparison to conventional heating process. The half-lives at 32, 40, 50 and 60°C reaction temperatures using the microwaves were 350, 250, 190 and 80 min respectively. This could be attributed to the selective heating of peroxide as well as catalytic sites at molecular level resulting in increasing the energy of the reaction. The MW effects are mainly classified as thermal or non-thermal effects. The thermal effects due to rapid heating, volumetric heating, superheating, hotspots and selective heating are considered to be the most prominent ⁶. On the other hand, the concept of non-thermal effect mainly associated with surface polarisation resulting from non-thermal interaction between the substrate and MW are more pronounced in solvent free or biphasic reaction systems for example in heterogeneous catalysis ^{9,14,15}.

It was observed that the time required to heat the solution using the conventional heating system was significantly longer as heating is mainly by conduction and convection. The use of microwaves therefore eliminates significant long heating periods, thereby potentially increasing throughput.

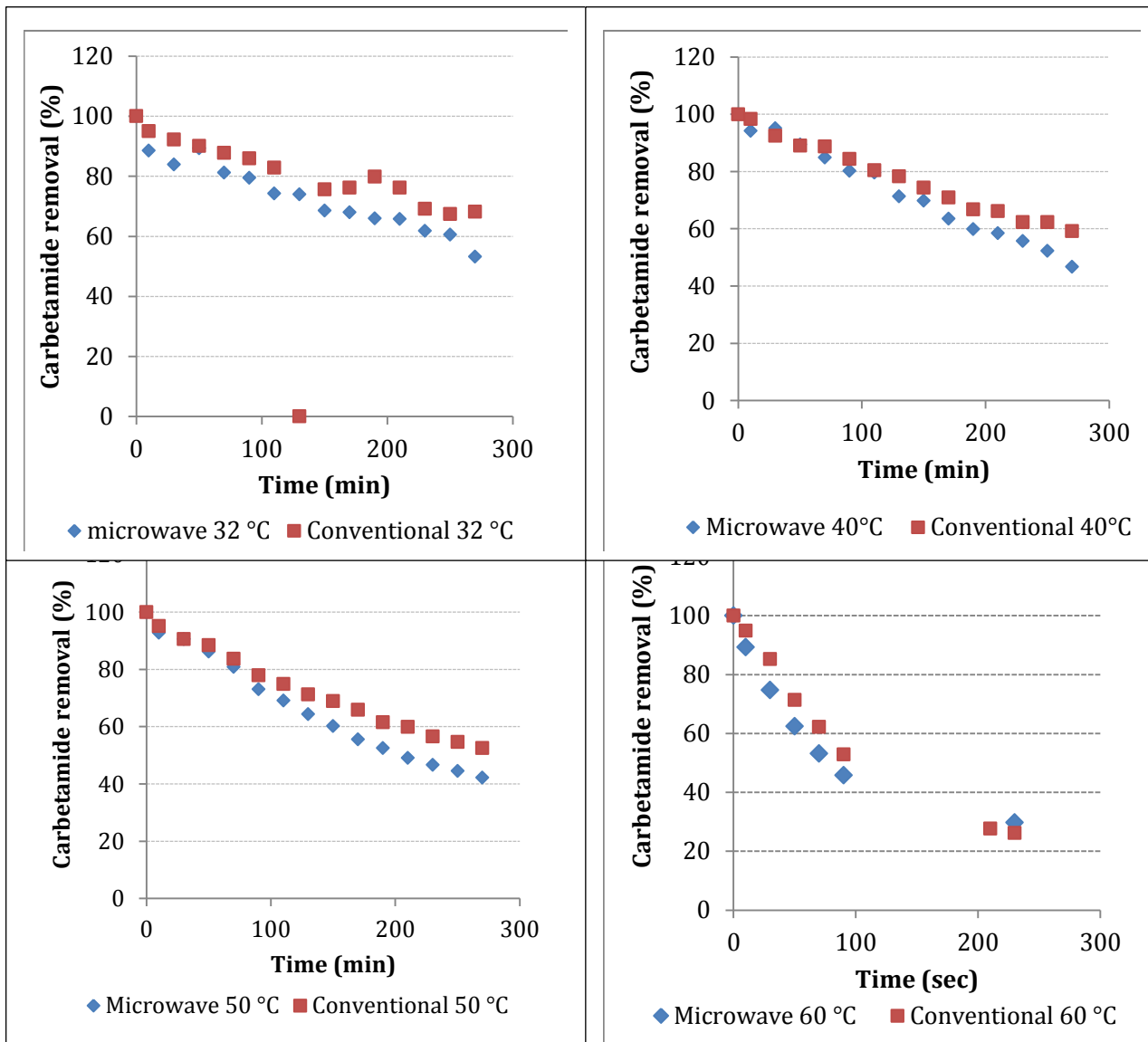


Figure 3 Effect of temperature on the removal of carbetamide

CONCLUSION

In this work, we have shown that the microwave assisted heterogeneous catalytic decomposition of carbetamide and chlorotoluron is superior to conventional heating when using the same temperature profile, by a factor of 30%. This shows the advantages of microwave energy over thermal heating and justifies the microwave “special effect”. On comparing the reaction rate at 32°C the addition of microwave energy improved the reaction rate by a factor of 2.5. In addition, the time taken to raise the temperature of the process water in the conventional thermal process is much slower than that of the microwave process. Effectively incorporating microwave energy

to the modified PAN catalyst system offers real potential towards the treatment of wastewater contaminated with pesticides.

REFERENCES

1. Barb WG, Baxendale JH, George P, Hargrave KR. Reactions of ferrous and ferric ions with hydrogen peroxide. part II.-the ferric ion reaction. - *Trans Faraday Soc.* 1951;47:591-616.
2. Walling C, Goosen A. Mechanism of the ferric ion catalyzed decomposition of hydrogen peroxide. effect of organic substrates. *J Am Chem Soc.* 1978;95(9):2987-2991.
3. Chi GT, Churchley J, Huddersman KD. Pilot-scale removal of trace steroid hormones and pharmaceuticals and personal care products from municipal wastewater using a heterogeneous fenton's catalytic process. *Int J Chem Eng.* 2013;760915:1-10.
4. Ishtchenko VV, Huddersman KD, Vitkovskaya RF. Part 1. production of a modified PAN fibrous catalyst and its optimisation towards the decomposition of hydrogen peroxide. *Appl Catal A: Gen.* 2003;242(1):123-137.
5. Horikoshi S, Serpone N. Photochemistry with microwaves: Catalysts and environmental applications. *Journal of Photochem and Photobiol C: Photochem Reviews.* 2009;10(2):96-110.
6. Remya N, Lin J. Current status of microwave application in wastewater treatment—A review. *Chem Eng J.* 2011;166(3):797-813.
7. Yang Y, Wang P, Shi S, Liu Y. Microwave enhanced fenton-like process for the treatment of high concentration pharmaceutical wastewater. *J Hazard Mater.* 2009;168(1):238-245.
8. Horikoshi S, Miura T, Kajitani M, Serpone N. Microwave discharge electrodeless lamps (MDEL). III. A novel tungsten-triggered MDEL device emitting VUV and UVC radiation for use in wastewater treatment. - *Photochem Photobiol Sci.* 2008;7:303-310.
9. Nüchter M, Müller U, Ondruschka B, Tied A, Lautenschläger W. Microwave-assisted chemical reactions. *Chem Eng Technol.* 2003;26(12):1207-1216.
10. Bhattacharya M, Basak T, Senagala R. A comprehensive theoretical analysis for the effect of microwave heating on the progress of a first order endothermic reaction. *Chem Eng Sci.* 2011;66(23):5832-5851.
11. Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ Int.* 2009;35(2):402-417.
12. Serpone N, Horikoshi S, Emeline AV. Microwaves in advanced oxidation processes for environmental applications. A brief review. *J Photochem and Photobio C: Photochemistry Reviews.* 2010;11(2-3):114-131.
13. Chi GT, Huddersman KD. Maleic acid oxidation using A heterogeneous modified polyacrylonitrile (PAN) fibrous catalyst. *J Adv Oxi Technol.* 2011;14(2):235-243.
14. Kuhnert N. Microwave-assisted reactions in organic synthesis—Are there any nonthermal microwave effects? *Angewandte Chemie Int Ed.* 2002;41(11):1863-1866.
15. Kappe CO. Microwave dielectric heating in synthetic organic chemistry. - *Chem Soc Rev.* 2008;37(6):1127-1139.