Degradation of phenol and \textit{m}-cresol in aqueous solutions using indigenously developed microwave-ultraviolet reactor

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A MW-UV reactor was developed indigenously for degradation of aqueous phenol and \textit{m}-cresol (degradation efficiency, \textit{MW-UV-TiO}_2 > \textit{UV-TiO}_2 > \textit{MW-TiO}_2 > \textit{MW-UV} \geq \textit{UV} \geq \textit{MW}). Maximum degradation of phenol (85%) and \textit{m}-cresol (92%) by \textit{MW-UV-TiO}_2 and \textit{MW-UV-TiO}_2 was three folds faster in reaction time and catalyst requirement than \textit{UV-TiO}_2 method. Degradation of phenol and \textit{m}-cresol in reactor followed pseudo first order reaction and reaction rate (k) for \textit{MW-UV-TiO}_2 was 2.2 times greater than \textit{UV-TiO}_2 and greater (17 times for phenol and 22 times for \textit{m}-cresol) than other processes. \textit{MW-UV-TiO}_2 was 2.3 times more efficient in removal of TOC than conventional photocatalytic method.

\textbf{Keywords:} \textit{m}-Cresol, Microwave-ultraviolet treatment, Phenol, Photocatalytic degradation, Wastewater treatment

\textbf{Introduction}

Advanced oxidation processes (AOPs) such as UV, \textit{UV-TiO}_2 \textsuperscript{1}, \textit{UV-H}_2\textsuperscript{2}O\textsubscript{2} \textsuperscript{2}, \textit{UV-Fe-H}_2\textsuperscript{3}O\textsubscript{2}, \textit{O}_3 \textsuperscript{4}, \textit{UV-O}_3 \textsuperscript{5} etc., have been demonstrated as efficient treatment methods for recalcitrant pollutants like phenolic compounds. AOPs are destructive, non selective in nature and produce no sludge\textsuperscript{6}. Most AOPs use ferric or ferrous salts, which might cause secondary pollution\textsuperscript{7}, or ozone and hydrogen peroxide, which are costly. Moreover, their efficiencies need to be further improved from an economic point of view, especially when techniques are to be used for large-scale operations\textsuperscript{8}. Depending on targeted wastewater quality, extended treatment duration may involve unaffordable, high operating costs, mostly due to high energy and chemical requirements.

Combination of microwave irradiation with ultraviolet irradiation (MW-UV) is reported\textsuperscript{9} an efficient treatment method for destruction of organics in wastewater. Although MW accelerates photocatalytic reaction, it is reported\textsuperscript{10,11} that metal electrodes in conventional UV lamps in that reactors were easily damaged under MW irradiation and hence conventional UV lamps are not suitable for such reaction. Though microwave electrodeless lamp (MEL), which comprises an envelope or bulb containing plasma-forming medium, substitutes conventional lamp as light source, mechanism of photolytic degradation of organic pollutants under MEL irradiation is uncertain. In MELs, polar solvents absorb most of MW energy at a low power; lamp does not have enough power to operate, it is impossible to carry out photochemical reactions at temperatures below solvent boiling point and overheating causes lamp failure. Special attention is also required when working with flammable and toxic material with such reactors\textsuperscript{12}.

This study presents an indigenously developed MW-UV reactor for phenol and \textit{m}-cresol degradation in aqueous solutions in presence/absence of \textit{TiO}_2 under controlled temperature.

\textbf{Experimental Section}

\textbf{Development of MW-UV Reactor}

MW-UV reactor (Fig. 1) was developed using a domestic microwave oven (Kenstar-Ken chef, Model No. MWO 9807, Serial No. V807K00498, made in India; output power, 300W; frequency, 2450 MHz), a mercury lamp (SANKYODENKI 7B, made in Japan, supplied by Heber Scientific-India; 352 nm & 6 W; length, 24 cm) and a quartz cylinder [Air Blow Equipments Pvt Ltd, India; outer diam, 50 mm; height, 20 cm; inlet and outlet openings at opposite directions at top and bottom with a hole of 18 mm diam at center of cylinder (350 ml)]. Lamp was inserted into quartz tube and both

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are positioned in oven in such a way that electrode of lamp is not directly exposed to microwaves. Turntable, typically found in microwave cooking ovens, was removed to prevent rotation of reactor and to avoid damage to quartz cylinder and mercury lamp. One end of silicon tube (diam, 8 mm) was inserted at the bottom of quartz reactor and other end was connected with top of the quartz reactor through a peristaltic pump (Model–Watson Marlow 313S; made in England) and a condenser (supplied by Air Blow Equipments Pvt Ltd, India), which was cooled by a cooler (Model–LAUDA WK 1400; make-Germany) to prevent excess heat generated and damage to reactor during microwave heating. Reactor was checked for any possible leakages of microwave using an electrical field probe (C.A.43 Field Meter Model-CHAUVIN ARNOUX, make-France) - an antenna combined with high frequency detector (power, 0.1-200 V-m; sensitivity, 100 KHz to 2.5 GHz). Reactor set up was fully closed by an aluminum sheet to prevent any exposure of microwave through joints, door and especially from modified area to working environment. Microwave leakage was absolutely nil in all directions after reactor was closed by aluminum sheet.

**Estimation of Microwave Power and Control of Reacting Fluid Temperature**

Microwave power absorbed into water could be estimated as $P = mc\Delta T/t$, where $P$ is absorbed power of microwave (W), $m$ is mass of water (g), $c$ is heat capacity of water (4.184 J-g °C), $\Delta T$ is temperature rise (°C), and $t$ is irradiation time (s). It was found that water irradiated with input current (15 amp) presented 0.208°C-s of temperature rise ($\Delta T/t$) and 304.60 of absorbed power. Temperature of water or reacting fluid during experiments was measured by a temperature indicator with a sensor (range 1-199.9°C, type PT 100) immediately when stopping to irradiate microwave and maintained as 21°C.

**Chemicals**

Commercial reagents in analar (AR) were used for preparing samples without further purification. Phenol and $m$-cresol were purchased from Central Drug House Ltd., New Delhi, India. Titanium dioxide, Degussa P25 (mean particle size, 0.3µ; Anatase/rutile (3.6/1); crystalline form; surface area, 56 m²/g; band gap energy, 3.2 eV; procured from Germany) was used as photocatalyst. Phenol / $m$-cresol (Phm-C) degradation was carried out in following six phases: (i) Microwave irradiation in absence of TiO₂ (MW), (ii) Photodegradation with UV light (UV), (iii) Simultaneous microwave and ultraviolet radiations in absence of TiO₂ (MW-UV), (iv) Microwave irradiation in presence of TiO₂ (MW-TiO₂), (v) Photodegradation by UV and TiO₂ (UV-TiO₂) and (vi) Simultaneous MW and UV irradiations in presence of TiO₂ (MW-UV-TiO₂).
Results and Discussion

After 180 min of treatment, efficiencies of MW-TiO\(_2\) for degradation of phenol (12%) and \(m\)-cresol (17%) were found slightly more than that of MW, MW-UV and UV processes (< 10%) due to adsorption of P/\(m\)-C over surface of TiO\(_2\) particles. MW-UV-TiO\(_2\) was found superior to any other processes studied in degradation of P/\(m\)-C. It was also found that efficiency decreased with increase in initial concentration. Degradation efficiency of MW-UV-TiO\(_2\) at 180 min was found maximum at natural pH as follows: 0.1 mM of phenol (natural pH 6.9±0.1), 85% (1.4 times more than UV-TiO\(_2\) process) (Fig. 2a); and 0.1 mM of \(m\)-cresol (natural pH 5.0±0.1), 79% (1.6 times more than UV-TiO\(_2\) process) (Fig. 2b). With a low pH, surface of TiO\(_2\) is occupied with H\(^+\) ions. When pH increases, active hydroxyl groups on TiO\(_2\) surface increase and accelerate P/\(m\)-C oxidation. As pH value increases further, oxidation power of photogenerated holes decreased and so decrease of P/\(m\)-C degradation occurred in alkaline solution. It was also observed that MW-UV-TiO\(_2\) was 1.5-2.0 times higher than UV-TiO\(_2\) for any initial P/\(m\)-C concentration studied (Fig. 3).

Effect of MW-UV-TiO\(_2\) on P/\(m\)-C degradation was studied by varying TiO\(_2\) dosage (0.2-1.0 g) and compared with conventional UV-TiO\(_2\) photocatalytic method (Fig. 4). Degradation efficiency was found to increase with increase in catalyst dosage and attained maximum degradation at 0.6 g for phenol and 0.8 g for \(m\)-cresol. Amount of TiO\(_2\) affects both number of active sites on TiO\(_2\) and penetration of UV light through suspension. Excess TiO\(_2\) suspended in aqueous solution could cause a shielding effect on light, resulting in decrease of P/\(m\)-C degradation for higher TiO\(_2\) dosage. Phenol degradation efficiency of UV-TiO\(_2\) at 0.6 g of TiO\(_2\) was 59%, and that of \(m\)-cresol at 0.8 g TiO\(_2\) was 70%, whereas this was attained with only 0.2 g dose of TiO\(_2\) by MW-UV-TiO\(_2\). It was also observed that efficiency of UV-TiO\(_2\) in
3 h was achieved by MW-UV-TiO$_2$ within 1 h. Thus, effect of integrated MW-UV-TiO$_2$ method was three folds more effective in reaction time and catalyst requirement (four fold in case of m-cresol) when compared with conventional UV-TiO$_2$ method.

Degradation of phenol in MW-UV reactor follows pseudo first order reaction (Fig. 5). Reaction rate (k) of degradation due to MW-UV-TiO$_2$ was found more than double for phenol ($13.2 \times 10^{-3}$ min$^{-1}$; only $5.2 \times 10^{-3}$ min$^{-1}$ for UV-TiO$_2$) and m-cresol ($15.0 \times 10^{-3}$ min$^{-1}$; only $6.7 \times 10^{-3}$ min$^{-1}$ for UV-TiO$_2$) compared to conventional UV-TiO$_2$ method at same experimental conditions. Similarly, time requirement to reduce pollutant concentration to half of its initial concentration (half life $t_{0.5}$) by MW-UV-TiO$_2$ was less (60% for phenol and 56% for m-cresol) when comparing to UV-TiO$_2$. Sequence of reaction rate of degradation was: MW-UV-TiO$_2$ > UV-TiO$_2$ > MW-TiO$_2$ > MW-UV > UV > MW.

TOC was not influenced significantly by the effect of UV, MW, MW-UV and MW-TiO$_2$ (Fig. 6). However, 68% TOC of phenol and 76% TOC of m-cresol were removed by MW-UV-TiO$_2$ as against only 30-32% removal of TOC by UV-TiO$_2$. It was also found that TOC reduction obtained at 3 h by UV-TiO$_2$ method was achieved at 1 h by MW-UV-TiO$_2$ method.

After 3 h of irradiation, 30% and 68% of phenol was mineralized into CO$_2$ and H$_2$O by UV-TiO$_2$ and MW-UV-TiO$_2$ methods respectively. During degradation of phenol, aromatic compounds such as hydroquinone, benzoquinone and catechol were identified as main intermediates and evolution of intermediates confirms high efficiency of MW-UV-TiO$_2$ method. Hydroquinone, benzoquinone and catechol, which are OH adducts of phenol, are also toxic as well as phenol and are desirable to remove. These intermediates were detected from beginning of reaction upto 110 min for UV-TiO$_2$ method, whereas, they disappeared after 40 min of reaction for MW-UV-TiO$_2$. The intermediates detected can be rationalized assuming existence of an activation of phenol molecule by reaction with an *OH radical, forming an adduct that evolves to give a phenoxy radical and to form hydroxylated compounds such as catechol.
**Conclusions**

A MW-UV reactor, developed indigenously, was found to be effective in degradation of P/m- C at controlled temperature conditions (21°C) in order to avoid risks while handling such materials in microwave radiations and significant degradation could be obtained even at low reacting temperature in MW-UV reactor. Degradation efficiency was (MW-UV-TiO$_2$ > UV-TiO$_2$ > MW-TiO$_2$ > MW-UV > UV > MW). MW-UV-TiO$_2$ was three folds faster in reaction time and catalyst requirement when compared with conventional UV-TiO$_2$ method for P/m-C. Degradation of phenol in MW-UV reactor followed pseudo first order reaction. MW-UV-TiO$_2$ was 2.3 times more efficient in removal of TOC of P/m-C than conventional photocatalytic method. Unit operating time for MW-UV-TiO$_2$ was 50% less than UV-TiO$_2$.

**References**


