www.ijsc.info

Pankaj et al./Interdisciplinary Journal of Sciences

IJSC. Vol.1, No.1/ pp 022-039

March-May2012

EFFICACY OF DEGRADATION PROCESSES OF PHENOL IN WASTEWATER

Pankaj*, Mayank Verma and Shikha Goyal
Department of Chemistry, Dayalbagh Educational Institute, Agra, India 282 110
E-mail : pankaj2@bsnl.in

ABSTRACT

Studies for the degradation of phenol in aqueous solutions and effluents, using several techniques such as electromagnetic waves, bio-degradation, electrochemical, plasma assisted processes, use of fly ash, photocatalytic, advanced oxidative method and sonochemical processes have been summarized briefly in this review. The efficacy of each technique towards the total mineralisation of phenol has also been examined and discussed in terms of the mechanism involved. Overall, it appears that hybrid techniques are more effective compared to individual techniques in enhancing the mineralisation rate.

KEYWORDS

Phenol, degradation, advanced oxidative processes, waste water treatment, mineralisation

INTRODUCTION

On one side, the industrial growth, urbanization and increasing use of synthetic organic substances are essential for the development and progress of the society. The simultaneous production of toxic waste and end products, on the other hand, leads to a serious adverse impact on the environment, especially the quality of water[1]. Since the last reservoir of all these pollutants is water- whether it is through atmospheric contamination coming down to soil and water as precipitation or as a runoff from the crustal surface or percolation to underground water, the degradation of these toxicants in water is of utmost importance. Phenol is considered to be a hazardous[2] organic pollutant if present in water system above its permissible limit (1µg/l). The major sources are industries[3] and automobile exhaust and a minor contribution coming from the domestic sources. In spite of the industrial[4], laboratory[5] and medical[6] applications of phenol, it constitutes a major threat to the ecosystem[7], due to its toxicity[8] and carcinogenic nature[9-10]. The prolong use of phenol can cause severe health problems[11-16] to humans, animals and micro-organisms.

Therefore numerous attempts have been made and reported in the literature to remove or at least minimize phenol concentration by transforming to less polluting by-products before its release to the environment. The objective of this review is to summarise all such studies published during the past few years, involving different techniques. Different treatment methods of phenol have been categorised as advanced oxidative processes (AOPs) and non-AOPs. Different AOPs have been further classified as individual and combined methods. Different degradation methods can thus be discussed as under these two broad categories.

1. NON-AOPs

1.1 Biodegradation Methods

Phenols could be metabolized by micro-organisms like bacteria, yeast, algae and fungi. Biodegradation of phenol can be completed either by aerobic or anaerobic methods. Aerobic methods involve O_2, which acts as electron acceptor, while in anaerobic process the electron acceptor species could be inorganic as well such as CO_2, NO_3^-, SO_4^{2-} and Fe^{3+} etc. Since, the aerobic process had precedence over the anaerobic due to its capability of complete mineralization to CO_2, the biodegradation could, therefore, be discussed further on the basis of aerobic and anaerobic conditions and on the type of methods applied.

1.1.1 Aerobic biodegradation

Kryst investigated biodegradation of phenol by using an inverse fluidized-bed biofilm reactor and reported maximum degradation of 180 mg/hr. To augment aerobic biodegradation of phenol Jiang et al[18] improved aerobic granulation by selecting specific microbial groups co-aggregating the two bacterial strains *Propioniferax*- like PG-02 and *Comamonas* sp. PG-08. Phenol degradation rate was found maximum with the co-culture of both the bacterial strains PG-02 and PG-08 in comparison to monoculture of both the bacterial strains used separately. Mordocco et al[19] examined phenol degradation with immobilized micro-organisms and organic modified montmorillonite in a two-phase partitioning bioreactor (TPPB) to treat initially higher concentration of phenol and achieved high degradation rate by using organically modified montmorillonite containing polysulfone capsule (OMMT-PSF) and polyurethane foam- immobilized micro-organisms in TPPB. The method provided a better option due to reusability of the immobilized micro-organisms and OMMT-PSF capsules. Pai et al[20] investigated continuous phenol degradation using phenol degrading bacterium *Rhodococcus* sp. DCB-p0610, immobilized on granular activated carbon (GAC) and in calcium alginate beads separately. The phenol (100 ppm) removal rate on alginate beads was higher than that on GAC. Many filamentous fungal strains isolated from effluents of a stainless steel industry were examined by Santos to ensure their phenol biodegradation efficiency. Some of them like FIB 4, LEA 5, and AE 2 strains of Graphium sp. and FE 11 of Fusarium sp. showed the highest 75% degradation of phenol (initial concentration 10mM) in 168 hours for FIB 4. This work has been further extended through the studies involving the biodegradation of phenol with the combination of fungi and bacteria[22]. The fungus *M sarneyensis Mil΄ko,* amongst all, was found to be more efficient for phenol removal at 4°C.

1.1.2 Anaerobic biodegradation

Karlsson studied meso- and thermophillic anaerobic degradation of phenol and proposed the fermentation of phenol into acetate in their degradation pathway; in addition a part of the phenol was reductively converted to benzoate while the rest was oxidized to acetate as end product (Figure 1). Fang et al[24] investigated the biodegradation of phenol under thermophillic conditions and reported over 99% degradation of phenol (630mg/l) in an up flow anaerobic sludge blanket (UASB) reactor at 55°C with 40 hrs of hydraulic retention time. Analyzing the specific methanogenic activity data and phylogenetic analysis, the degradation pathway of phenol for thermophillic sludge was suggested to be probably through caprolate (Figure 2) and not by benzoate.

Figure 1. **Proposed Phenol degradation pathway [Ref 23]**

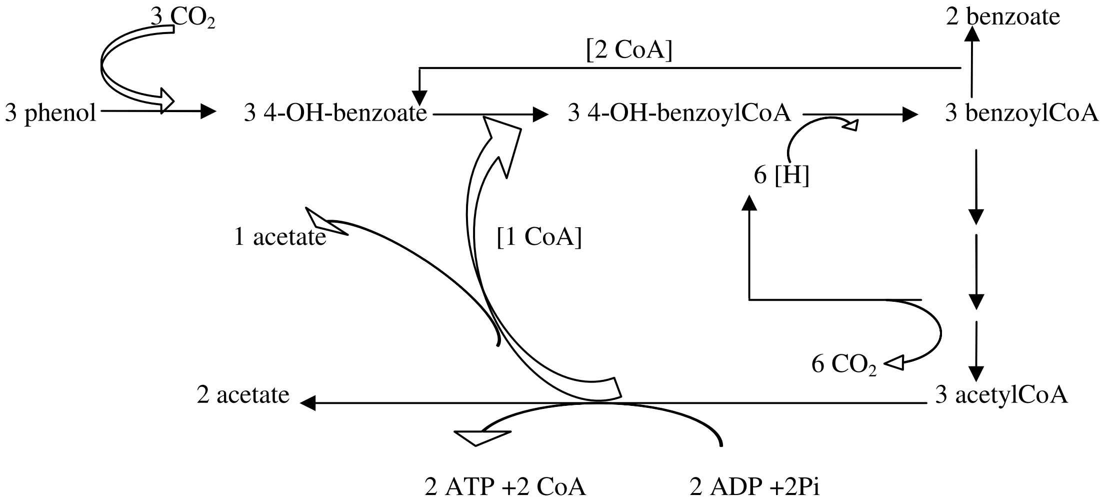
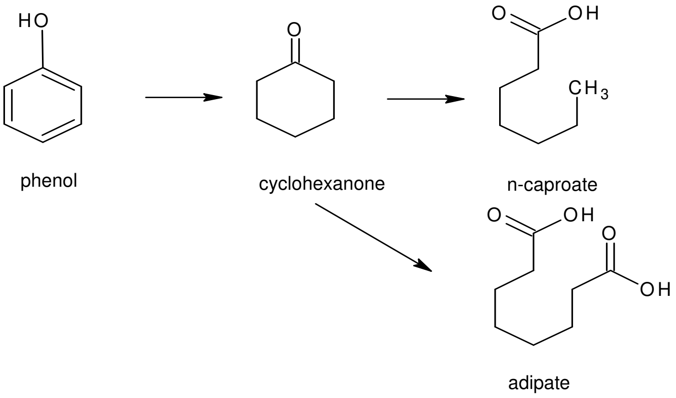


Figure 2. Phenol degradation pathway via cyclohexanone [Ref 24]



1.1.3 Enzyme immobilized membrane reactor

Akey used a cross-flow enzyme-immobilized membrane reactor to examine the phenol elimination from waste water. The highest phenol (500 mg/ml) degradation rate was found to be 1.3μg/m^2/s and the rate of removal was found linearly dependent on the flux rate.

1.1.4 Biodegradation by microbial fuel cell

The advancement of the use of microbial fuel cell (MFC), by Luo for phenol biodegradation, was its utility in the production of electricity directly from contaminant. They used MFC with aqueous air cathode and a packing type MFC using ferricyanide as the terminal electron acceptor. The phenol degradation rate in MFC increased about 15% compared to the open-circuit control. A shorter acclimation time was required with ferricyanide cathode (80 hours), used in the MFCs, than that in MFCs using aqueous air cathode (about 300 hours) with the maximum (>90%) phenol removal within 48 hours of each electrical cycle. The degradation efficiency of phenol in all MFCs was found to be above 95% within 60 hours.

1.1.5 Biodegradation using moving-bed sequencing batch reactor

The moving-bed sequencing batch reactor (MSBR), used by Moussavi demonstrated its effectiveness for the removal of higher concentration of phenol. The action of bio-film was found greater than the activity of suspended biomass in phenol removal. At optimum hydraulic retention time, the phenol with the initial concentration up to 3000 mg/L was effectively removed with efficiency greater than 90%.

1.1.6 Use of Fly ash

The greater adsorption capacity of fly ash in phenol removal was reported to be better due to the cost effectiveness of fly ash compared to the use of activated carbon[28]. Factors, such as the small particle size of fly ash, higher increased agitation time and dose of fly ash increased phenol degradation rate.

2. ADVANCED OXIDATION PROCESSES

Advanced oxidation process (AOP) is amongst the most efficient removal methods reported for the degradation of phenol. AOP is the course of action by which the oxidative aptitude of the parent compound could be amended to make redox reactions more speedy or complete. In most of such studies, the process oxidized the organic species completely into CO_2 and H_2O. These processes were suitable for effluents containing refractory, toxic or non-biodegradable materials. AOPs are beneficial over the biological or physical processes due to its highly automated process, the ability of handling fluctuating flow rates and compositions and easy operability.AOPs can be categorized as

(i) Chemical oxidation processes in which H_2O_2, O_3, combined H_2O_2 and O_3, HOCl, Fenton reagents etc. were used
(ii) UV enhanced oxidation like UV-O_3, UV- H_2O_2, UV- H_2O_2 and O_3, UV-air, and
(iii) Wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) processes. In the destruction of organic contaminants, AOP is dependent on aqueous phase oxidation reaction occurring due to involvement of $OH^{\bullet}$ radicals.

2.1 Individual Methods

A number of methods for the degradation of phenol under photocatalytic (in the presence of both natural sunlight and UV light), electrochemical, electromagnetic waves, plasma and ultrasonic waves, have been undertaken and are being reviewed in the following sections of this article.

2.1.1 Photocatalytic Methods

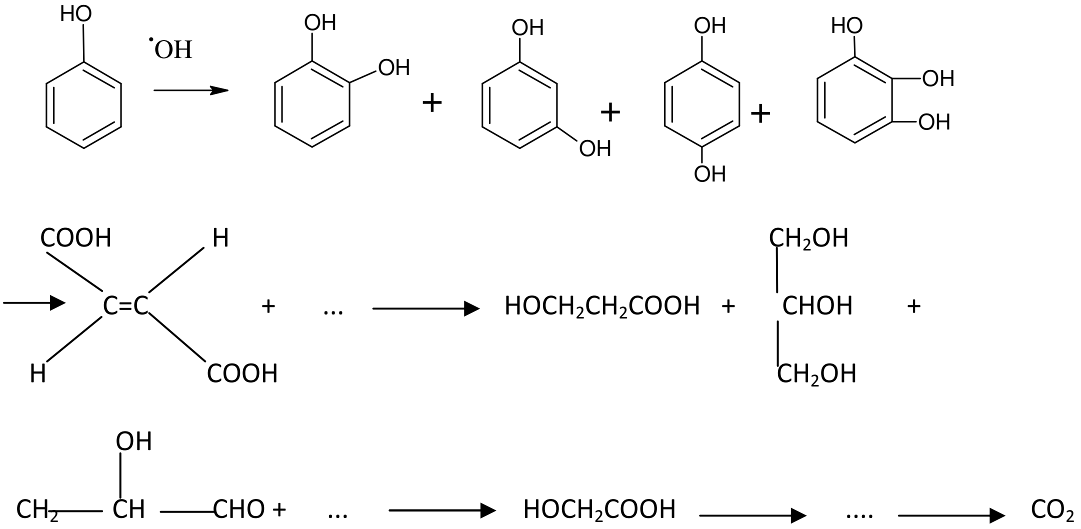
Almost all organic contaminants could be degraded by the use of photocatalyst TiO_2 with phenol being no exception. Photocatalysis generally depends upon the oxidation-reduction processes[29-31], which occur on the interface of semiconductor-solution interface[32]. Matthews[33] investigated the effect of natural sunlight as main illuminating source for phenol degradation with TiO_2 both in suspension and immobilized form using ordinary beach sand and silica gel as stationary support. The rate of degradation was three times faster in a freely suspended catalyst system compared to an immobilized catalyst surface under the same experimental condition (Table 1). During natural sunlight irradiation, 10 ppm phenol could be degraded to a level of 10 ppb in less than 80 minutes as maximum.

Table 1. Fractional disappearance times for 100 µM phenol solutions solar illuminated in the presence of immobilized and suspended TiO_2 (Ref. 33).

Conditions	**$t_{0.5}$ (min)**	**$t_{0.9}$ (min)**
250 mL solutions, 0.5g TiO_2/100g sand	30	130
500 mL solutions, 0.1% TiO_2	23	75
250 mL solutions, 0.1% TiO_2, estimated	11.5	37.5
$t_{0.5}$ or $t_{0.9}$ (250 mL, immobilized catalyst)/ $t_{0.5}$ or $t_{0.9}$ (250 mL, suspended catalyst)	2.6	3.5

Guo analysed the degradation of phenol (40ml of 100mg/l) in UV source in the absence and presence of 8.16 mg TiO_2 (20-30 nm particle size) and sonicated for 15 minutes before use[34]. The degradation products such as hydroquinone, resorcinol, catechol, 1,2,3-benzenetriol, (E)-2 butenedioic acid, 2-hydroxypropaldehyde, glycerol,3- hydroxypropyl acid, hydroxyacetic acid, malonic acid, maleic acid, oxalic acid, acetic acid and fumaric acid were confirmed by GC-MS. The photodegradation route explaining the formation of these products is given in the (Figure 3). Although $OH^{\bullet}$ radical was responsible for the initial degradation of organics, the role of intermediate products like oxalic acid, lactic acid etc. from o-, m- and p- disubstituted or 1,2,3-trisubstituted phenol, in combination with $H^{\bullet}$ radicals could not be ruled out in the degradation of organic contaminant mechanism[35].

Figure 3. Phenol photodegradation route showing mineralization of phenol [Ref 34]



The degradation of 100 μM phenol by anatase TiO_2 (Degussa P25, BET- 50 m^2 g^{-1}, particle size 30 nm) and Anjatox TiO_2[36] were compared under sunlight. The photocatalytic efficiency of Anjatox was found comparatively closer to Degussa P25. It showed high particle radii with non-uniform particle distribution. Anjatox TiO_2, compared to Degussa P25 had poor catalytic activity due to low BET surface area. Nano TiO_2 of different morphologies[35] synthesized by hydrothermal technique showed different photocatalytic efficiency for the degradation of the phenol. 400 ml of 50 mg/l phenol solution was degraded with 0.2 gm of TiO_2 using pyrex reactor (12 cm diameter and 5 cm height). TiO_2 (1-D rutile nanorods) and TiO_2 (3-D anatase nanoparticle-assembled microspheres) showed superior photocatalytic efficiency over TiO_2 (3-D rutile nanorods-assembled microspheres). Although TiO_2 itself was a good photocatalyst to degrade many organic pollutants but limited to its excitation only under UV region.

To bring down the excitation of TiO_2 in visible region doping of transition metals[37-42] alone and/or in combination of rare earths have been examined. The photocatalytic degradation of phenol using the polyaniline[43] doped TiO_2 was found to be more effective than the TiO_2 alone. Matosa et al studied[44] the synergistic effect in the photocatalytic degradation of phenol in a suspended mixture of titania and activated carbon and found an increase in the first order rate constant by a factor of 2.5. Scheck and Frimmel[45] studied UV induced H_2O_2 and O_2 catalyzed phenol degradation and reported the presence of hydroxylated phenols, benzoquinone and aliphatic acids up to 6 carbon atoms as reaction products confirming the involvement of the $OH^{\bullet}$ radicals. On the basis of the products, they proposed two mechanisms to explain the hydroxylation. Firstly, the $OH^{\bullet}$ radicals, produced upon UV-irradiation of H_2O_2 to phenolic ring giving cyclohexadienyl radical (intermediate) which upon abstraction of H atom, was converted into hydroxylated product. Secondly the abstraction of H atom of $OH^{\bullet}$ radical from phenolic compound produced phenoxyl radical (intermediate) and this in turn added hydroxyl radical giving hydroxylated product.

Santiago compared the different AOPs, involving O_3, O_3-H_2O_2, UV, UV -O_3 & UV- H_2O_2 -O_3, Fe^{2+}/H_2O_2, and photocatalysis, for the phenol degradation to find out the best. They reported that none of the ozone combinations (O_3- H_2O_2, O_3 - UV, and O_3 –UV & H_2O_2) compared to ozone alone got better degradation rate but might be a good choice due to its low cost for phenol removal. The degradation rate with UV-H_2O_2 process among all ozone combination processes was found 5 times more effective in degradation compared to photocatalysis and UV alone. Fenton's reagent showed the fastest degradation rate, 40 times higher than UV process and photocatalysis and 5 times higher than the ozonation. Karunakaran et al[47] reported the photocatalytic efficiency of various metal oxide and sulfide semiconductors for the treatment of phenol on sunlight exposure and found that with natural sunlight TiO_2 (anatase), Fe_2O_3, CuO, ZnO, ZnS, ZrO_2, CdO, HgO (yellow), PbO, PbO_2 and Al_2O_3 helped in catalyzing the reaction while MoO_3, Co_3O_4, CdS, SnO_2, Sb_2O_3, La_2O_3, CeO_2, Sm_2O_3, Eu_2O_3, Pb_2O_3 and Bi_2O_3 did not. Fe_2O_3, CuO, CdO, HgO, PbO and PbO_2 showed absorption in visible region confirming effective excitation by sunlight. Through another experiment, Karunakaran et al[48] further investigated the synergistic effect of photo-catalysis by using various semiconductors on Pr_6O_{11} insulated surface, varying illumination time of UV light, phenol concentration, photon flux and pH and reported that high energy UV radiation and photon flux increased the degradation rate while increasing pH reduced the rate. They again confirmed the absence of singlet oxygen in degradation pathway by observing no inhibition in degradation rate due to presence of singlet oxygen quencher azide ion. Pedro et al[49] investigated the kinetics of both phenol adsorption on activated carbon (AC) and their degradation by chemical reaction with oxygen.

2.1.2. Electrochemical methods

In electro-chemical methods the efficacy of electro-catalytic degradation depends on electrode materials. In this way anode with or without alteration could be prepared by layering the metal-oxide (M-O) mixtures[50-52] on titanium. Wang[53] studied electro-catalytic decomposition of phenol using Ti- based multilayered M-O anode (M= Sn, Sb, Pb, Mn and Ru) coated with SnO_2 + SbO_2 interlayer. Torres[54] et al studied the electro-catalytic degradation of substituted phenols with both electron donor (OH- and NH_2-) and electron withdrawing (NO_2-and COOH-) groups. Abaci et al[55] tried PbO_2 due to its good metal-oxide property[56] instead of TiO_2 for the electro-catalytic degradation of acidic aqueous solution of phenol and compared the efficacy of decomposition on different crystal structures of PbO_2 surfaces. The higher flux of $OH^{\bullet}$ radicals and therefore more oxygen evolution enhanced the phenol degradation, resulting into a better performance of highly crystalline β- PbO_2 over α-PbO_2. The better catalytic property of β- PbO_2 for the phenol decomposition was due to better conductivity[57], more stability[58], porosity[59] and crystallinity[55] of β- surface. Wu et al[60] reported that anodic oxidation of high saline and high acidic phenol using β-PbO_2/ceramic anode improved with fluorine resin and a Ni-Cr-Ti alloy cathode.

The method was improved further[61] by sparging air at cathodic region and adding ferrous ions in electrolyte concurrently. This method provided a proficient route of regeneration of Fe(II) ions compared to conventional Fenton's method. The percentage of phenol removal increased by about 12-15% in ferrous ion catalyzed anodic cathodic electro catalysis (FACEC) and 24-28% in anodic cathodic electro catalysis (ACEC) compared to conventional anodic electro-catalytic method (AEC). Pacheco et al[62] used boron-doped diamond electrodes and calculated the content of the combustion of phenol to accomplish complete combustion to CO_2. The electro-chemical method proved to be an excellent method for phenol removal due to its automated functionality, high efficiency and environmental compatibility[63] but only rarely difficult to further mineralize the intermediates produced[64]. Trabelsi et al[65] reported dimerization or polymerization of phenol radicals forming a layer on electrode surface passivating the electrode during electrolysis and observed that the grouping of high frequency (540 kHz) sonication with electrochemical method could degrade phenol in less than half an hour without any toxic aromatic intermediates formation and suggested one electron and two electron pathways respectively in the absence and presence of ultrasound.

2.1.3 Use of electromagnetic waves

Electromagnetic waves, such as γ–rays, microwaves and laser beams, of different frequencies have also been found to be effective in the degradation of phenol.

2.1.3.1 γ- irradiated degradation

The hydroxyl radicals generated by γ-irradiation, in the presence of dissolved oxygen, react with phenol to produce the degradation products e.g., hydroquinone, catechol etc. Sato reported γ- radiation (200 Ci ^{60}Co γ- rays) induced complete degradation of 100 ppm phenol in an oxygenated aqueous solution at room temperature through three possible mechanisms,

(i) Hydroxylation of benzene ring
(ii) dimerization and
(iii) ring-cleavage reaction.

2.1.3.2 Microwave irradiated degradation

The effect of microwave induction has been explained on the basis of its sufficient energy available to induce rotation and migration of polar molecules aggressively. These forceful movements result in greater molecular collisions, leading to faster degradation. Lai et al[67] investigated the microwave irradiated phenol degradation in the presence of a semiconductor, NiO, utilizing the uniform thermal effects of microwave over conventional heating and catalytic properties of semiconductor. The catalytic degradation in a temperature controllable microwave apparatus(2450 MHz and 100 W), phenol was degraded completely into non-hazardous products (CO_2 and malonic acid) by this method within 8 min under pH 7.0 and T = 40 °C over synthesized catalyst NiO_X. Activity of phenol degradation was found to be dependent on the oxidation state of nickel oxide, NiO_X, and the complete degradation was found within 8, 10 and 20 minutes at 40°C, 55°C and 70°C, respectively.

2.1.3.3 Laser irradiated degradation

Gondal have reported the laser-induced photocatalytic degradation of phenol using both n-type[68] and p-type[69] semiconductors. In both the experiments done for n-type and p-type semiconductor, the experimental setup consisted of UV laser and a glass cell. A 355 nm wavelength high power laser beam generated from Nd:YAG laser (Model GCR 250) with a pulsed width of ~8 ns as a light source was used and laser beam diameter was kept to 1.0 cm. The degradation influencing parameter i.e., stirring rate and laser beam diameter were kept constant to investigate the dependency of removal of phenol at laser exposure times ranging from 0 to 45 minutes which showed faster degradation in first 15 minutes (Figure 4). In a similar way the role of p-type NiO semiconductor[69] (Degussa P25, 70±15 m^2 g^{-1} BET surface area) was also investigated by Gondal for the degradation of phenol. More than 80% phenol degradation was attained during the first 45 min laser irradiation (Figure 5). The trend of the phenol removal was almost similar in both estimation methods. With an increase in irradiation time, the number of absorbed laser photons increased with the production of more and more hydroxyl radicals to facilitate more phenol removal.

Figure 4. Phenol concentration as a function of laser exposure time with n-type WO_3 semiconductor [Ref 68]

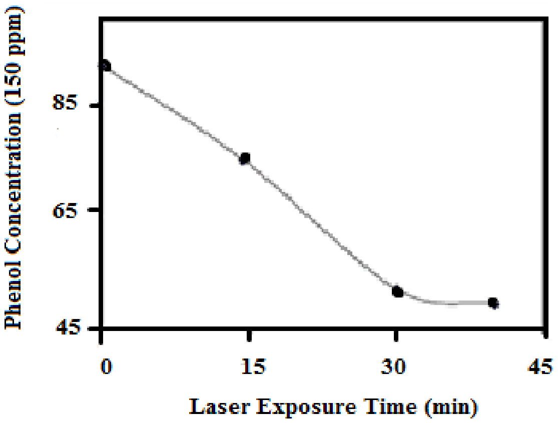
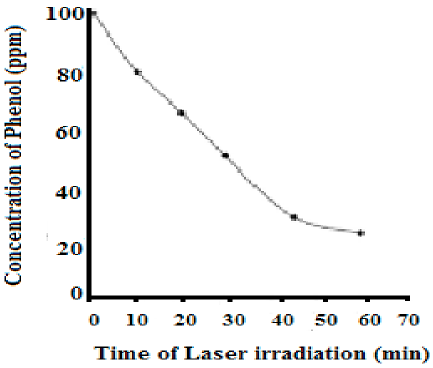


Figure 5. Phenol concentration as a function of laser exposure time with p-type NiO semiconductor [Ref 69]



2.1.4 Plasma-assisted method

Plasma- assisted techniques are effective to remove phenols from waste water because of their high removal efficiency and environmental compatibility. Many processes, such as pulsed corona discharge (PCD) perform best in water with lower conductivity while glow discharge electrolysis (GDE) can be operated under high-salt containing water and diaphragm glow discharge (DGD) could be operated in an electrolytic solution with no electrode erosion. Sano et al[70] used gas-phase corona discharge process with catalyst supported with mesoporous carbon gels and found better results with the simultaneous use. Li et al[71] used gas-liquid phase pulsed discharge plasma reactor for the efficient degradation of phenol. The degradation efficiency was found better with O_2 compared to argon, increase of pulsed peak voltage, energy input and treatment time. Liu et al[72] used diaphragm glow discharge process and found enhancement in the degradation of phenol on increasing the applied voltage, addition of Fe^{2+} or Fe^{3+} ions to the solution and at lower pH. The method has been found to be a better option over the high voltage corona discharge as this process has a simple technology with high energy efficiency, easy scale up, and applicable to saline water with no electrode erosion.

2.1.5 Sonochemical methods

The reactivity of chemical reactions undergoing ultrasonic irradiation is principally due to acoustic cavitation which essentially involves the free radical formation. The ultrasound would produce highly reactive species like $H^\bullet$ and $OH^\bullet$ free radicals from the homolytic cleavage of water. Further these could react with any other free radical/s present or with neutral molecules like O_2 and O_3 to produce peroxy, superoxide, hydrogen peroxide or hydrogen[73]. Sonochemical reactions are dependent upon the rate of scavenging of these radicals[74]. Higher the concentration of the scavenging radicals in the system, lower is the recombination and higher the degradation. Therefore, generation of free radicals and the rate of scavenging of radicals were the main causes of degradation of the species at higher rate. The complete removal of phenol was achieved when sonicated with 300 kHz frequency with zero valent iron compared to zero valent copper. The mechanism proposed for this reaction initiates with the erosion of iron metal in the presence of hydrogen peroxide under acidic conditions, leading to the oxidation of Fe^o to Fe^{2+},which on further reaction with H_2O_2 produces $OH^\bullet$ radicals and Fe^{3+}. The Fe^o finally reduces the Fe^{3+} back to Fe^{2+} and thus the chain continues.

2.2 Combined Methods

This section is classified in two parts. In the first part methods are based upon the photons with mechanical, electro-catalytic/chemical and biological methods while the other part explains the combination of ultrasonic waves with microwave.

2.2.1 Photo-mechanochemical methods

Mechanochemical processes are those reactions in which the reactions are either initiated by some mechanical action or by the participation of the reagents which were activated by prior mechanochemical actions. Cotto et al[76] used mechanically activated rutile TiO_2 for phenol degradation. Analysis has shown the efficacy of the catalyst used, since there was no decomposition of phenol in the absence of catalyst. The pressure and shear generated due to boundary frictions produced high energy and thereby heat and localized flash high temperature with lifetime of 1μs[77]. Therefore mechanical activation reduced the requirement of high heat or temperature[78] for such degradation process. Besides, this activation increased free radicals, surface area of catalysts/solids, and creation of lattice defects. The formation of defects in semiconductor catalysts is important as it would modify electronic properties of the catalyst[78-79]. The enhanced decomposition of phenol using TiO_2 doped with non-metals such as N, S and C have also been reported[80-81]. The doping of carbon nanotube (CNT) to TiO_2 shifted the photo-absorbance towards longer wavelength. Increase of the CNT content led to an increase in photo-absorbance towards visible region[82]. The TiO_2 doped with 10% CNT, calcined at 400°C, exhibited the maximum synergistic effect for phenol decomposition. Liao investigated the catalytic effect of multi-walled carbon nanotube (MWCNT) supported Fe_2O_3 in comparison to undressed Fe_2O_3 for phenol degradation. MWCNT supported Fe_2O_3 showed positive effect with 20% more removal than with the naked Fe_2O_3 after 200 minutes of treatment which was attributed to the increased surface area of Fe_2O_3/MWCNTs nearly four times as that of unsupported samples.

2.2.2 Photo-electrocatalytic/chemical methods

The photo-electrocatalytic degradation of phenol through highly ordered TiO_2 nanotube array[84] has also shown some potential of improving the transport of the photo-generated electrons in the TiO_2 films. It has been presumed that highly ordered architecture of TiO_2 array would provide an unidirectional electric channel and reduction in grain boundaries. The photo-electro-catalytic (PEC) activity depended on the length of the nanotube arrays. The arrays length could be controlled by the electrolyte media, anodization time or both. Therefore by controlling these parameters the photo-electro-catalytic degradation of phenol could be optimized.

2.2.3 Photochemical – biological Method

For the significant degradation of the phenol, both photocatalytic and biological methods have been used but in different ways. Edalatmanesh et al[85] investigated and optimized the retention time, power consumption and the total cost of the degradation of phenol by applying the combination of photochemical and biological methods respectively. A combination of UV/H_2O_2 and activated sludge bioreactor was used for this purpose. They found that the least retention time for the system was 99 hours and the optimal electrical energy consumption occurred at a photochemical retention time of 15 hours with the biological retention time of 92 hours. The incurred cost by the photochemical unit was found considerably higher than that for the biological unit.

2.2.4 Ultrasound assisted microwave method

Wu et al[86] used both the methods individually and in combination to examine the combined effect. The rapid thermal effect of microwave (MW) could be seen on polar chemicals and more $OH^{\bullet}$ radicals were produced due to ultrasound (US). Microwave irradiations have shown enhanced degradation effect when applied with sonication in the absence of additional catalyst though the rate increased more in presence of H_2O_2. The rate order in different conditions has been found to be MW-US > MW > US.

CONCLUSION

Phenol and its derivatives contaminate the environment through their natural and anthropogenic sources. They have toxic and hazardous effects, if the concentration limits are exceeded. Therefore, it is essential that the excess amount of phenol is degraded before it is discharged into the environment. This review on the degradation of phenol in wastewater highlights remediation processes, reaction pathways and kinetic studies which are already available in the literature. The use of biological treatment is limited to low phenol concentration because of its biorefractory nature. Advanced oxidation processes (AOPs) including ozonation, electrochemical, photocatalytic, ultrasonic and radiolytic decomposition represent an alternative treatment and based upon the generation of highly reactive hydroxyl radicals providing better option for the complete degradation of phenol. Using combinative AOP methods such as photo-mechanochemical, photo-electrocatalytic and ultrasound assisted microwave give excellent results as compared to all of the individual techniques and is certainly a positive step towards achieving quick mineralisation[87]. So, the future research should be concentrated in evaluating the efficacy of these hybrid methods in terms of cost and feasibility for variety of pollutants.

ACKNOWLEDGEMENT

Authors are grateful to DAE-BRNS for funding and Prof. M. Ashokkumar, Melbourne University, Australia for valuable discussion. MV is grateful to UGC for SRF and SG to CSIR for JRF.

REFERENCES

1) Barcelona M, Wehrmann A, Keely JF, John WAP. Contamination of ground water: prevention,assessment, restoration, Pollution Technology Review. ISSN 0090-516X; no 184: United States of America: Noyes Data Corporation; 1990**.**
2) Jagannathan K, Damodar AR , Swaminathan T. Versatile technique for removal of hazardous pollutants:Heterogenous photocatalytic oxidation. Chemical Engineering world.2004; 39(12): 47-54.
3) Duijvenbooden WV, Glasbergen P,Van IH. Quality of Ground water, Proceedings of an International Symposium.Studies in Environmental Science. 1981; 17: 208-209.
4) Hernandez P, Hernandez L, Velasco V. Carbon felt electrode design application to phenol electrochemical determination by direct oxidation .Anal Bioanal Chem.2003 Jun; 377(2):262-66.
5) Bryant SL , Bartosek M, Lockhart TP. Laboratory evaluation of phenol formaldehyde /polymer gelants for high temperature application. Journal of Petroleum Science and Engineering.1997 May; 17(3-4): 197-209.
6) Kayaalp C, Olmez A, Aydin C, Piskin T, Kahraman L. Investigation of a one- time phenol application for pilonidal disease. Med Princ Pract. 2010 Mar; 19(3): 212-15.
7) Cardenas SA, Velazquez TG, Revilla GO, Cortez MSL, Perea BG. Adsorption of Phenol
and Dichlorophenols from Aqueous solutions by porous clay Heterostructure (PCH). Journal of Mexican Chemical Society. 2005; 49(3):287-91.
8) Kuhn R, Pattard M, Pernak KD, Winter A. Results of the harmful effects of selected water pollutants (anilines, phenols, aliphatic compounds) to Daphnia magna. Water Res. 1989 Apr; 23(4): 495-99.
9) Kim JH, Oh KK, Lee ST, Kim SW, Hong SI. Biodegradation of phenol and chlorophenols with defined mixed culture in shake-flasks and packed bed reactor. Process Biochemistry. 2002 Jul; 37(12): 1367-73.
10) Iurascu B, Siminiceanu I, Vione D, Vicente MA, Gil A. Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite. Water Res. 2009 Jan; 43(5): 1313-22.
11) Shailubhai K. Treatment of petroleum industry oily sludge in soil. Trends Biotechnol.

1986 Aug; 4(8): 202-06.

12) Salonen, Middeldorp P, Briglia M, Valo R, Haggblom M, Bain A.Mc., in Biotechnology and Biodegradation, D.Kamely, A. Chakrabarty, G.S.Omenn. (Eds.). Portfolio Publishing Co., The Woodlands, Tx, 347-365 (1989).
13) Sharma H, Barber JT, Ensley HE , Polito MA. A comparison of the toxicity of phenol and chlorinated phenols by Lemna gibba with reference to 2,4,5-trichloorophenol. Environ Toxicol Chem. 1997 Feb; 16(2): 346-50.
14) Warner MA, Harper JV. Cardiac dysrhythmias associated with chemical peeling with phenol. Anesthesiology.1985 Mar; 62(3) : 366–67.
15) Budavari S. The Merck index: an encyclopedia of chemicals, drugs and biological. 12th ed. Whitehouse Station, NJ: Merck ;1996.