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Laser enhanced photo-catalytic removal of phenol from water using p-type NiO semiconductor catalyst

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Abstract

Phenol is a carcinogen to humans and is a serious health concern, even at low concentrations. The efficient removal of phenol inside waste water is highly desirable. Laser induced photo-catalysis has been applied for removal of phenol from waste water using p-type NiO semiconductor catalyst for the first time. The characteristics of phenol removal using laser induced photo-catalytic process were investigated. The dependence of phenol removal on laser energy (100–250 mJ) and laser irradiation time (0–60 min) was studied. The rate of phenol removal process was characterized using UV absorption spectrometry, Raman spectroscopy and gas chromatography. In addition, the role of pH changes during the removal process was also investigated. Laser induced photo-catalytic process is highly efficient in removal of phenol in water over a short period of time (in minutes) as compared to conventional methods using lamps (hours). The phenol removal process pursued the first order kinetics with decay constant = 0.0125 min^{-1}.

1. Introduction

Phenol is being used in many industries, such as textile, paper mills, herbicides and fungicides production [1]. Phenolic compounds such as polyphenols, quinones are among the foremost ground water contaminants. Widespread contamination of water by phenol has been recognized as an issue of growing concern in recent years. Phenol is a carcinogen to humans and is of considerable health concern, even at low concentrations [2]. The efficient photo-transformation of phenol inside waste water is highly beneficial for safe environment. As phenol compounds are relatively stable and soluble in water, their degradation to reach safety levels in the range of 0.1–1.0 mg L^{-1} is not an easy task. Several advanced oxidation processes (AOPs) are currently being investigated to remove hazardous chemicals from contaminated water and are considered to be good alternatives for the treatment of organic pollutants such as phenol [3–9]. These processes include ultraviolet (UV) photolysis [10], direct ozonation

[11], high-energy electron irradiation [12], supercritical oxidation [13] and ultrasonification [14] and pulsed corona discharge in gas or liquid phase [15].

Heterogeneous photo-catalysis using semiconductor catalyst under UV irradiation is highly successful in mineralization of phenol. Photo-catalysis process depends on redox reactions taking place on the surface of the semiconductor catalyst/solution interface upon irradiation of semiconductor particles with light of specific energy (wavelength), higher than the band-gap [15–22]. The production of electron–hole pairs induced by photo-catalytic process is essential since these species are capable to reduce or oxidize different organic compounds in an aqueous solution. The oxidizing radicals formed upon reaction of holes with water attack and break phenol molecule. The photo-catalytic process breaks down phenol into different by-products such as catechol, hydroquinone, ring opening compounds and simple molecules like carbon dioxide and water depending on the laser irradiation time and efficiency of the catalyst. Due to the production of less toxic compounds, there is no further requirement for secondary disposal methods which is major advantage of photo-catalysis process [16]. Other treatment methods such as adsorption by activated carbon and air stripping merely

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concentrate the chemicals present by transferring them to the adsorbent or air and they do not convert them to non-toxic wastes. Furthermore, photo-catalysis is relatively inexpensive as ambient oxygen is used. One of the challenging tasks in the photo-catalysis is to improve the rate of reaction. A semiconductor applied for photo-catalysis has to be (a) photoactive, (b) able to absorb visible or near-UV light, (c) biologically and chemically inert, (d) photo-stable, and (f) acquired at a reasonable low cost.

It should be noteworthy that all previous work on phenol removal from waste water using heterogeneous photo-catalysis has been carried out using broad spectral radiation sources such as lamps and TiO_2 as a catalyst. Several problems are associated with the use of lamps emitting over broad spectral wavelength range. For example, the long term power stability due to over heating of lamps during the operation, low photonic efficiency, longer exposure time (hours) for complete mineralization of phenol are the major drawbacks associated with UV lamps as source of irradiation.

In order to overcome these problems, unique source of radiation such as laser was employed in this work. Very little work has been carried out, on photo-catalysis, with lasers using semiconductor catalyst and to the best of our knowledge no work has been reported on phenol removal with lasers using NiO as a photo-catalyst. NiO is a greenish black crystalline powder with density of 6.67 g/cm^3 and has melting point 1984 °C. It has a band gap = 3.5 eV while TiO_2 = 3.2 eV. NiO conduction band [−0.5 V] and valence band [+3.1 V] are highly suitable for splitting of water and photo-catalytic process [23,24]. In addition, NiO is the least studied catalyst for heterogeneous photo-catalytical processes but has been well studied as hydrogenation catalyst [25–27] while TiO_2 has been studied extensively for photo-catalytic applications in different fields (environment, waste water treatment, water splitting, etc). The main reason for the large scale use of TiO_2 in heterogeneous catalysis is the suitability of its band gap for conventional light sources like UV lamps commercially available. These are the main reasons

which motivated us to use this catalyst for phenol removal in water using lasers.

Since laser light has unique properties like monochromaticity, high intensity, and low beam divergence, it is of great interest to use laser radiations as an excitation source to study the activity of photo-catalysts. Laser induced photo-catalytic degradation of phenol using NiO semiconductor catalyst was investigated for the first time using 355 nm laser radiation generated by third harmonic of Nd:YAG laser. In this study, it is proved experimentally that Laser based photo-catalysis is an efficient and effective method for waste water treatment for removal of phenol as compared to conventional UV lamp based methods reported in the literature.

2. Experimental

2.1. Materials and methods

All chemicals used in this study were reagent grade and were used as received, except for phenol that was distilled under reduced pressure and the middle fraction collected for the experiments. NiO (Degussa P25, $70 \pm 15\,m^2\,g^{-1}$ BET surface area) was used as photo-catalyst. Solutions were prepared with distilled water of high purity.

2.2. Photo-catalytic experiments

Fig. 1 depicts the set up applied for the photo-catalytic removal of phenol and is discussed in detail in our previous publications on laser induced photo-catalysis applications for water splitting and hydrogen generation [21–25,29–33]. In brief, a 355 nm wavelength high power laser beam generated from the third harmonic of a Spectra Physics Nd:YAG laser (Model GCR 250), with a pulse width of ∼8 ns, was employed as a radiation source. During this study, it was noticed that the important parameters which significantly affects the reaction rate (removal of phenol) are: laser energy, amount of catalyst (particle density),
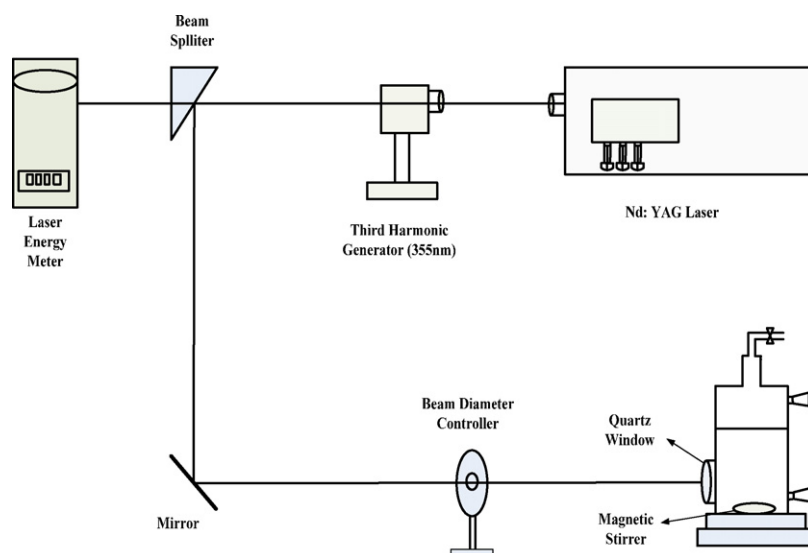

Fig. 1. Experimental setup for removal of phenol using laser induced photo-catalysis process.

stirring rate and laser beam diameter. The two parameters, i.e. stirring rate and laser beam diameter were kept constant for all the studies reported in this paper. However, the dependence of phenol concentration on laser energy and amount of catalyst, to identify the maximum removal of phenol was studied carefully for NiO catalyst using three analytical techniques. The destructive effects of focused laser beam were minimized by expanding the diameter of the beam to 1 cm by using set of lenses and mirrors.

2.3. Analyses and experimental procedure

The photo-catalytic removal of phenol over NiO was studied by suspending an optimized amount (300 mg) of above-mentioned semiconductor powder in 80 ml of distilled water. The pH changes in the solution during laser irradiation were measured using a pH meter that was calibrated by using the buffers of pH 4, 7 and 10.

The concentration of the phenol was estimated by analyzing the laser exposed samples at regular interval of ten minutes by using two independent analytical techniques such as gas chromatography (GC) and UV spectrophotometry. The GC analysis was done on Agilent HP 6890 plus, equipped with capillary column HP-1 (methyl siloxane) and flame ionization detector (FID). As aqueous solution is harmful to the specified column of the GC, extraction of phenol from water sample was carried out using the following procedure. 1.0 ml dichloromethane was added to 1 ml of aqueous phenol solution in a separatory funnel. After the solution was shaken for some time, the organic layer was separated and similar procedure was repeated with additional 1.0 ml of CH_2Cl_2. The combined organic phase was dried with magnesium sulphate and bubbled with nitrogen to concentrate to 1.0 ml. The temperature of the GC oven was held at 50 °C for 2 min, then heated at the rate of 10 °C/min to 140 °C, then 20 °C/min to 250 °C and held at this temperature for 10 min. The temperature of the injector was 250 °C.

3. Results and discussion

The photo-catalytic degradation of phenol is the hydroxylation of the phenyl ring in aqueous solution. The possible process of photo-reduction of phenol inside water is based upon the formation of hydroxyl radical ($OH^{\bullet}$) and H^+ ions through water oxidation by the valence band holes produced due to laser irradiation having photon energy ($h\nu$) ≥ band gap of a semiconductor catalyst (SC, NiO for example in our case) in an aqueous suspension [11–15,17,18]. The hydroxyl radicals generate oxygen while H^+ ions form hydrogen by capturing conduction band electrons in a de-oxygenation solution. In order to get rid of dissolved oxygen in aqueous solution, the solution was purged with argon gas for at least one hour prior to each experiment. The production of hydrogen and oxygen by water splitting using different semiconductor catalysts (WO_3, NiO, ZnO, TiO_2 and Fe_2O_3) has been studied well by our group [21–25,29–32]. The OH radicals and oxygen generated due to photo-catalytic process are responsible for reduction
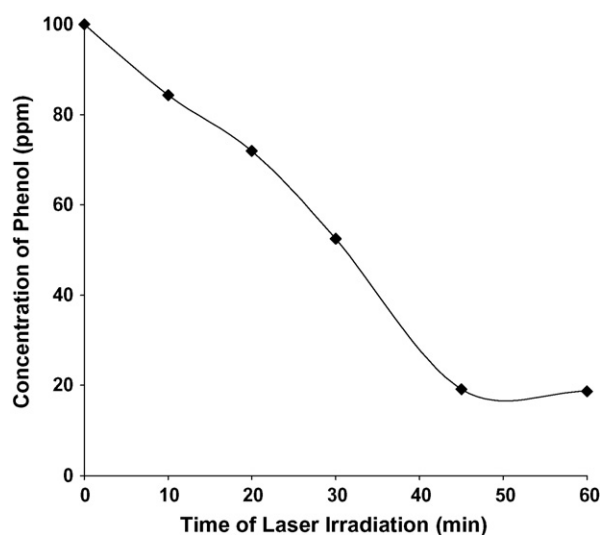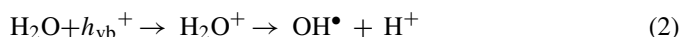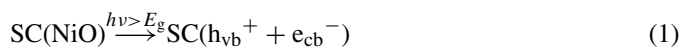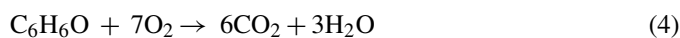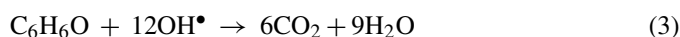

Fig. 2. Phenol concentration plotted as a function of laser exposure time. The concentration of phenol was estimated with GC analysis.

of phenol, i.e.

$$SC(NiO) \overset{h\nu > E_g}{\longrightarrow} SC(h_{vb}^+ + e_{cb}^-) \quad (1)$$

$$H_2O + h_{vb}^+ \rightarrow H_2O^+ \rightarrow OH^{\bullet} + H^+ \quad (2)$$

The $OH^{\bullet}$ radicals generated by water splitting then react with phenol (C_6H_6O) to generate CO_2 and water, i.e.

$$C_6H_6O + 12OH^{\bullet} \rightarrow 6CO_2 + 9H_2O \quad (3)$$

$$C_6H_6O + 7O_2 \rightarrow 6CO_2 + 3H_2O \quad (4)$$

The removal of phenol in water was estimated by measuring the concentration of phenol using two independent techniques such as GC analysis, UV absorption spectrophotometer and results are presented in following sections.

3.1. Gas chromatography (GC)

Fig. 2 depicts the trend of phenol removal using the GC analysis. using the NiO catalyst for 100 ppm of phenol concentration mixed in water. Here one can see, the strong phenol removal dependence on laser irradiation time.

The percentage degradation of phenol from the GC analysis, was estimated using the following relation:

$$phenol\ degradation\ (\%) = \left\{ \frac{C_0 - C_t}{C_0} \times 100 \right\} \quad (5)$$

Here, C_0 = initial concentration of phenol; C_t = concentration of phenol at any time 't'.

A plot of percentage phenol removal is depicted in Fig. 3 As clear from Fig. 3, more than 80% removal of phenol was achieved during first 45 min laser irradiation using NiO semiconductor catalyst which is reasonably high. It was observed that with the increase in laser irradiation time, the percentage of phenol degradation increases. This increase in phenol degradation with time could be due to the fact that with increase
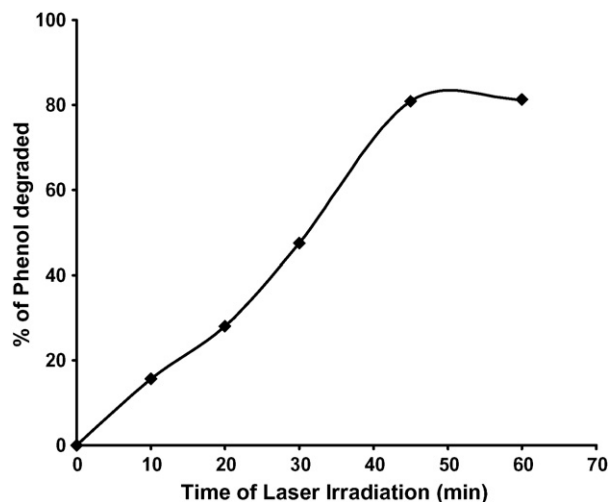
Fig. 3. %Degradation of phenol as a function of laser irradiation time for NiO catalyst calculated by using Eq. (5) where phenol concentration was estimated using the GC analysis.

in the irradiation time, the number of absorbed laser photons increases, producing more amount of $OH^\bullet$ radicals, thereby facilitating more degradation of phenol. The data on phenol removal using GC was utilized in estimating the reaction kinetic (rate of reaction) for removal of phenol and is presented in Section 3.5.

3.2. UV spectrophotometry

For estimation of the phenol removal progress, UV absorption spectrum of the degradation of phenol at different laser exposure times ranging from 0 to 60 min was measured by using a quartz cuvette. The concentration of phenol was estimated by measuring the intensity of UV light absorption at the phenol resonant absorption peak at ~269 nm as shown in Fig. 4. For this purpose, all samples irradiated at different laser exposure time were scanned from 230 to 330 nm and the disappearance of phenol height intensity at 269 nm was estimated. The peak
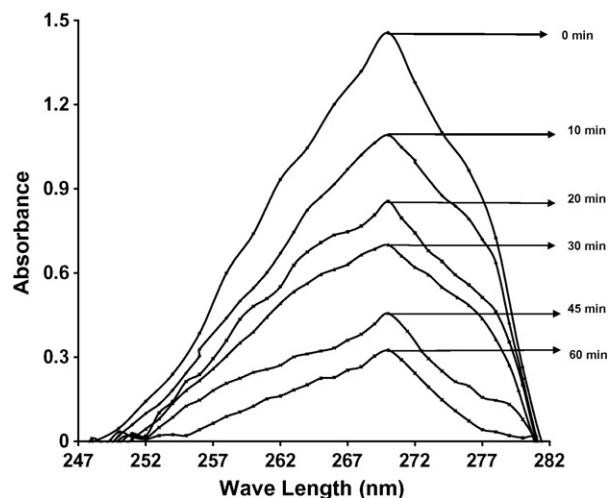

Fig. 4. Typical UV absorption spectra of the degradation of phenol at laser exposure times ranging from 0 to 60 min recorded with UV spectrometer.
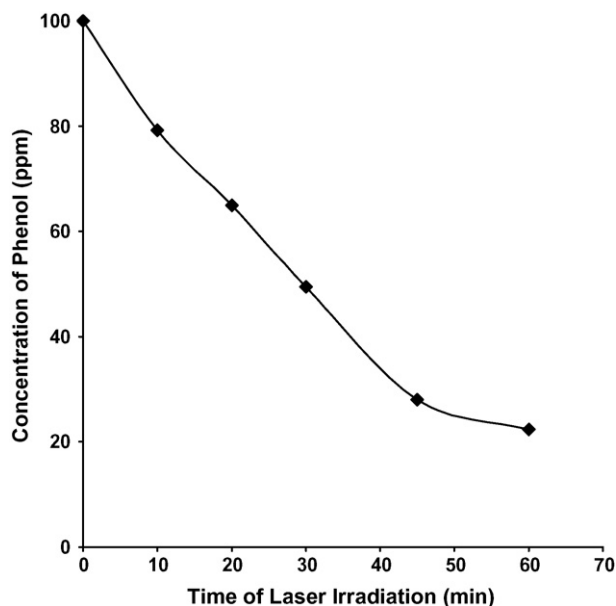

Fig. 5. Phenol concentration plotted as a function of laser exposure time. The concentration of phenol was estimated with UV spectrophotometry.

intensity was estimated at the peak height instead of peak area under the UV spectrum.

The trend of the phenol removal measured by UV absorption spectra for 269 nm phenol peak is presented graphically in Fig. 5 for first 60 min. The effect of laser irradiation time on photo-catalytic degradation of phenol is clear from Fig. 5 and a considerable degradation of 100 ppm phenol after exposure to about 60 min was achieved using laser.

It is worth noting that the phenol concentration at different laser irradiation time follows almost same trend as the concentration estimated by GC analysis. A minor discrepancy in phenol concentration was noticed between GC and UV analysis after laser exposure beyond 30 min. The concentration measured with UV spectrophotometry is little higher than GC at 45 and 60 min. This is due to the interference of by products of phenol which could not be isolated in spectrum recorded with UV spectrophotometer while in GC one can isolate these by products easily. The comparison of phenol concentration estimated with UV and GC techniques at different laser exposure time is presented in Table 1.

Table 1
Comparison of phenol concentration at different laser irradiation times analyzed by gas chromatography and UV spectrophotometry

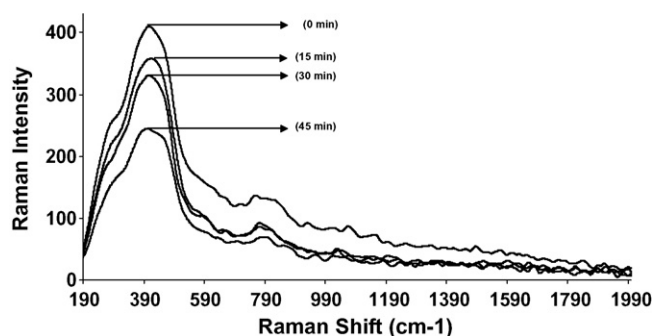| Laser irradiation time (min)	Phenol concentration (ppm) with gas chromatography	Phenol concentration (ppm) with UV spectrophotometry
0	100	100
10	84.3	79.2
20	72	64.9
30	52.53	49.4
45	19.15	28
60	19	21

Fig. 6. Typical Raman spectra of the degradation of phenol at different laser exposure times ranging from 0 to 45 min recorded with Raman spectrometer.

3.3. Raman spectrometry

For the recording of Raman spectrum of phenol, the medium resolution Raman spectrum of aqueous phenol was recorded using Occeans Optics Raman spectrometer having resolution of $10\,cm^{-1}$. This system includes a linear CCD-array spectrometer; a 785 nm diode laser to irradiate the sample, a fiber optic sampling probe for liquids, solids, powders and gels. Fig. 6 depicts the typical Raman spectrum of phenol at different irradiation time. Characteristic Raman shifts (peak) for phenol were determined by comparing their relative positions and intensities with the reported literature values [20]. The Raman shift peak was recorded at around $415\,cm^{-1}$ which is probably an overtone of an out-of-plane vibration at $503\,cm^{-1}$ in resonance with a nearby a^s fundamental band of phenol. The estimation of the concentration with Raman spectrometry is not trivial as there is interference due to by products of phenol in the Raman spectrum. Hence, the estimation of phenol removal based on Raman spectrum is not presented in this work.

3.4. Optimization of laser energy

The dependence of phenol removal on the laser energy was also carried out. A strong dependance of phenol degradation was observed with the increase in laser energy (photon flux) for a fixed amount (300 mg) of NiO. Fig. 7 depicts the removal of phenol versus the laser energy for NiO catalyst at 355 nm laser irradiation. During these experiments, the optimized amount of the catalyst from the previous step, i.e. 300 mg of the catalyst was suspended in 80 ml of deionized water and the yield of phenol concentration was measured for different laser energies ranging from 100 to 240 mJ/pulse. The strong dependence of phenol removal on the incident photon flux (laser energy) could be understood that with the increase in photon flux, the number of exposed catalyst particles increases causing a significant increase in the removal of phenol.

3.5. Measurements of pH and its role in NiO catalyst activity in phenol removal

The pH of a system is a measure of the concentration of H^+ ions and considered as a valuable tool in evaluating the mechanism of various chemical reactions. pH changes play a vital role
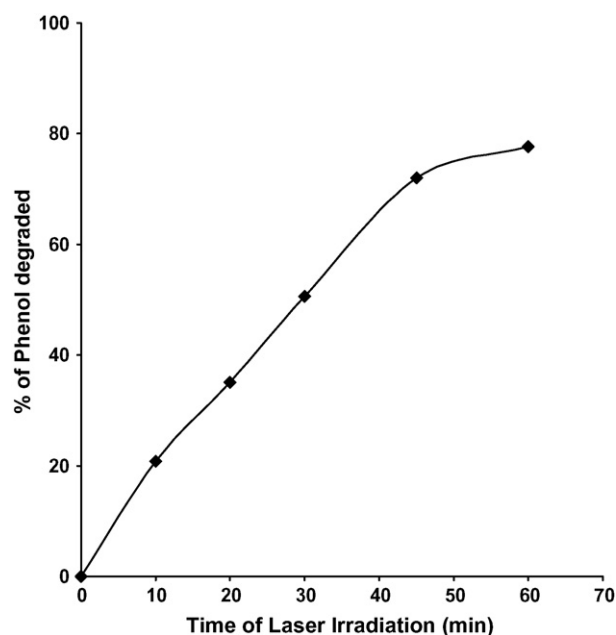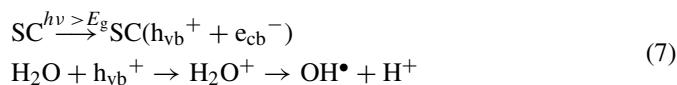

Fig. 7. %Degradation of phenol as a function of laser irradiation time for NiO catalyst calculated by using Eq. (5) where phenol concentration was estimated using the UV spectrophotometry.

in understanding of heterogeneous photo-catalysis. To oxidize water, the potential of valence band (V_{vb}) should be more positive than +1.23 V. The position of both conduction and valence bands, in aqueous medium, is pH dependent and the change in the pH of the semiconductor/electrolyte system by one unit shifts the position of the flat-band potential of the semiconductor by 59 mV. The change in the pH of a photo-catalytic system shifts the position of valence band and conduction band edge, which in turn affects the ability of the semiconductor to photo-oxidize or photo-reduce, i.e.

$$
\begin{aligned}
E_{vb} &= E_{vb}^0 - 0.059\,pH \\
E_{cb} &= E_{cb}^0 - 0.059\,pH
\end{aligned}
\tag{6}
$$

where E_{cb}^o and E_{vb}^o are the conduction and valence band potentials at zero pH.

When a photo-catalyst is illuminated in aqueous medium, H_2O splits into its components over the surface of a photo catalyst by donating the electrons to the photo-generated holes, with the formation of hydroxyl radicals ($OH^\bullet$) and H^+. This is possible when the valence band edge of the catalyst is positive than +1.23 V.

$$
\begin{aligned}
&SC \xrightarrow{h\nu > E_g} SC(h_{vb}{}^+ + e_{cb}{}^-) \\
&H_2O + h_{vb}{}^+ \rightarrow H_2O^+ \rightarrow OH^\bullet + H^+
\end{aligned}
\tag{7}
$$

The combination of an hole ($h_{vb}{}^+$) with water molecule generates hydroxyl radicals and oxygen because of water oxidation.

The capture of conduction band electrons by H^+ ions leads to the formation of hydrogen if the potential of the conduction band edge of the semiconductor photo-catalyst is more negative than 0.0 V
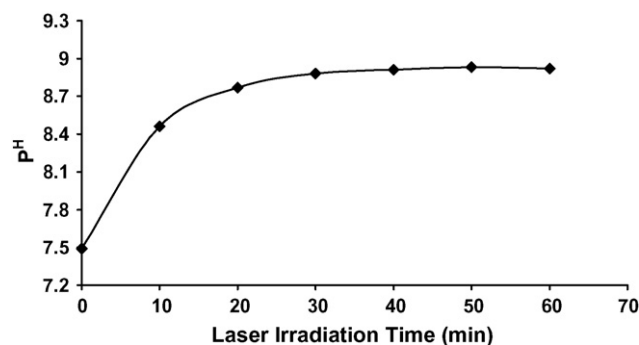
$$
H^+ + e_{cb}{}^- \rightarrow H^\bullet + H^\bullet \rightarrow H_2
\tag{8}
$$
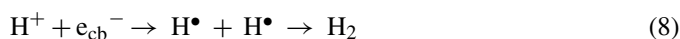
Fig. 8. Plot of pH versus laser irradiation time for phenol removal using NiO catalyst.

Fig. 9. Reaction rate for removal of phenol using NiO catalyst.

In this study, the role of pH changes for the photo-catalytic degradation of phenol in water over NiO catalyst has been investigated. The valence and conduction band edge potentials of NiO are +3.0 and −0.5 V, respectively. Fig. 8 depicts the trend of the pH changes during the removal of phenol. During 60 min laser irradiation of phenol in water, pH changes from 7.5 to 8.9 with the reduction of the NiO catalyst. Due to large shift in the pH, the valence and conduction band edges can be shifted to +2.32 V and −1.18 V, respectively. The value of +2.32 V for valence band edges shows a considerable decrease in the over potential [28] associated with the oxidation of water by the valence band holes which suggests an appreciable increase in the rate of water oxidation with the reduction of the NiO. In contrast, the catalyst NiO has the conduction band edges suitable for the conversion of H^+ ions to $H^\bullet$ radicals to form hydrogen which increases the pH of the system. The sharp rise in pH value during the first 20 min of the laser illumination of suspended catalyst indicates that NiO activated immediately. A stable pH value afterwards (beyond 20 min) reflects a steady state in the production and consumption of hydroxyl ions. It is also clear from graph (Fig. 8) that significant fraction of H^+ ions reacts with hydroxyl ions to generate water.

3.6. Kinetics of phenol degradation

In order to calculate the rate of removal of phenol (or the reaction rate), the experimental data on phenol concentration obtained from GC at various irradiation times was fitted to pseudo-first order kinetics [16]:

$$-\frac{dC_t}{dt} = k_{obs}C_0 \tag{9}$$

where C_0 and C_t are the concentrations at the beginning of the reaction and any time t, respectively where k_{obs} is the first order reaction rate constant. Solving the Eq. (9), we get

$$-\frac{dC_t}{C_0} = k_{obs}\, dt$$

$$-\ln \frac{C_t}{C_0} = k_{obs}t \tag{10}$$

By plotting the $-\ln(C_t/C_0)$ versus time, one can get the value of k_{obs}. A plot of $-\ln C_t/C_0$ versus time for our data is depicted in Fig. 9 which represents a linear fit having least square
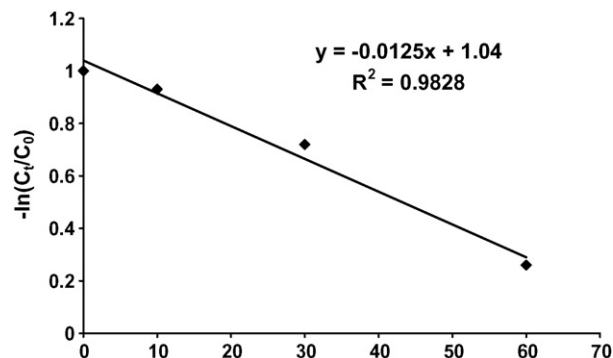
value = 0.99. A k_{obs} value of $0.0125\,min^{-1}$ has been estimated from the slope of $-\ln C_t/C_0$ versus time plot (Fig. 9). This value of reaction rate is higher by a factor of 1.6 than the value reported with conventional lamps and other methods [16]. Hence, it could be concluded that UV laser induced photo-catalytic degradation is highly efficient and much faster ($\sim$ in minutes) than the conventional lamps (hours and days) for the removal of phenol from water reported in previous studies. This is due to the fact that the average power delivered to the reaction zone using laser is $0.63\,W/cm^2$ which is higher than the typical average power ($0.015\,W/cm^2$ delivered to the reaction zone by UV lamps) [34]. The low power delivery of average power to reaction zone could be attributed to the fact that UV lamps are considered as broad band spectral sources having high divergence while lasers are coherent, monochromatic and very low beam divergence devices.

4. Conclusion

The photo-catalytic degradation of phenol using NiO semiconductor catalyst was investigated via laser induced photo-catalysis process. Laser induced photo-catalysis is much faster as compared with the conventional sources such as broad UV spectral lamps. Photo-catalysis was capable of removing phenol toxicity, generating a effluents which are not toxic. The removal of phenol obeyed the first order kinetics with decay constant = $0.0125\,min^{-1}$ which is quite high as compared with rates reported for conventional sources like UV lamps.

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