



Degradation of Phenol in Water Using Light Induced ZnO Photocatalysis

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KEYWORDS: phenol degradation, photocatalysis, ZnO photocatalyst, U.V absorption spectroscopy

1. Introduction:

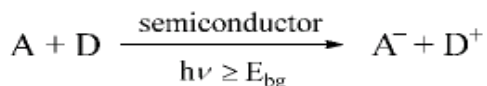
Photocatalysis can be defined as a change in the rate of chemical reactions or their generation under the action of light in the presence of substances, called photocatalysts, which absorb light quanta and are involved in the chemical transformations of the reactants. Flash photolysis provides a technique for the study of rapid chemical reactions. It involves the breakup of a molecular species by an intense flash of light (Luxon & Parker, 1992). Then, the absorption lines of the resulting products are monitored to determine the identities and concentrations of the reaction products as a function of the time after the flash. In this way, the course of the chemical reactions may be monitored.

Flash photocatalysis has been used to generate photochemically, and to study spectroscopically, a wide variety of free radicals and excited molecules (John E. T. et al., 1998).

Semiconductor photo-catalysis aimed to effectively detoxify noxious organic pollutants. UV light is used to create electron hole pairs in the semiconductor (Xu W. & Raftery D., 2001, Hoffmann M. R. et al., 1995).

A semiconductor has a manifold of electron energy levels filled with electrons, the valence band (VB), and also many higher energy levels that are largely vacant, the conduction band (CB). The energy difference between these two bands is called the band gap energy (E_{bg}). A general photocatalytical reaction can be summarized by the equation:

After excitation with UV light the band gap energy has created an electron-hole pair, the following reactions can occur:



- Reduction of an electron acceptor A at the surface by a photo-generated electron.
- Oxidation of an electron donor D at the surface by a photo-generated hole.
- Electron-hole recombination in the bulk or at the surface, which generates heat (Hagen J., 2006).

In this study we tried to achieve phenol degradation in water by irradiation of mixtures of zinc oxide (ZnO) and phenol with UV light source. Widespread contamination of water by phenol has been recognized as an issue of growing importance in recent years. The effect of light irradiation time and ZnO amount on the phenol degradation were studied here.

2 – Materials and methods:

2 -1 Materials

The materials used in this work were:

Zinc oxide (ZnO)

ZnO semiconductor has several favorable properties like: high electron mobility and a relatively large band gap of ≈ 3.3 eV at room temperature (Klingshirn C., 2004).

Phenol

Phenols are compounds that have one or more hydroxyl groups attached directly to an aromatic ring. Phenol structure is the structure upon which the entire group is based. The aromatic ring in this case is benzene (Chemguide Co., 2004). Phenol is moderately soluble in water – about 8 g of phenol will dissolve in 100 g of water. Phenol is known as human carcinogen and is of considerable health concern, even at low concentration. Phenol can remain in the air, soil, and water for long periods of time if a large amount of it is released at one time, or if it is constantly released to the environment from a source.

2 – 2 Equipments, tools and setup

The following equipments and tools were used in this work:

U.V Light Emitting Diode (LED) with a wavelength of 395 nm and output power of 1W.

Quartz cell used to contain the samples.

Magnetic stirrer with speed between 60 to 1500 rpm was used for mixing the semiconductor and the solution of phenol in water in the liquid all. This enables molecules exposure to UV radiation. This device was manufactured by Scott Science & Healthcare Limited Co.

UV/Visible spectrophotometer manufactured in U.K. by Jenway Company, its response is ranged from 190 to 1100nm with a resolution of 1 nm.

Figure (1) shows a sketch diagram of the setup used in this work.

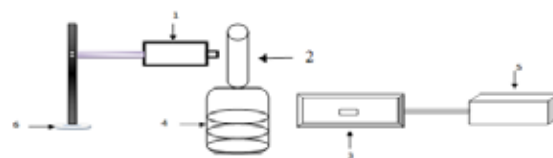


Figure 1: Block diagram of the two setups used in this work

(1) UV light source. (2) Quartz cell.
(3) UV/Visible spectrophotometer. (4) Magnetic stirring.
(5) Printer. (6) Stand.

2.3 Methods:

The experimental work was done in steps as follows:

- Two mg from phenol crystals was added to 100 ml distilled water and its spectrum was recorded.
- Two mg of phenol crystals was added to 400 mg of ZnO, and then 50 ml of water was added to the mixture and stirred for ten minutes by the magnetic stirrer.
- The solution was then topped up to 100 ml by distilled water in a volumetric flask.
- A small portion of the solution was filtered off and its spectrum was then recorded.
- The rest of the solution was placed in the quartz cell and was irradiated by a LED beam of 2.3 cm diameter for 20 minutes.
- A small portion of the irradiated solution was quickly filtered off and its absorption spectrum was recorded.

- The above steps were repeated with irradiation for 30 minutes.
- The whole process was repeated with 600 mg of ZnO.

The degradation of phenol was deduced from the comparison of its absorption intensity in the spectra before and after irradiation where the decreasing in the intensity of the absorption bands after irradiation indicates the phenol degradation.

3 - Results and discussion

Figure 2 shows the absorption spectrum of pure phenol in 100 ml water, where two absorption peaks can be distinguished in 210 and 275 nm, respectively.

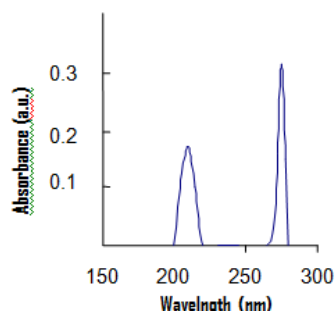


Figure 2: The absorption spectrum of pure phenol in 100 ml water without any irradiation or semiconductor addition.

The absorption spectra of phenol mixed with 400 mg of ZnO were recorded after irradiation by LED with different exposure times. Figure 3 shows the obtained spectra.

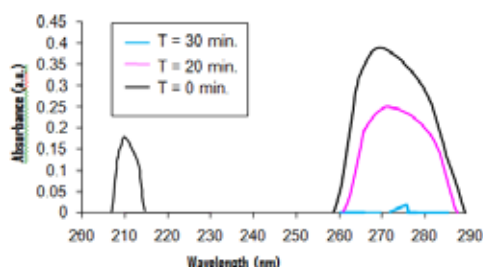


Figure 3: The absorption spectra of phenol mixed with 400 mg ZnO irradiated by LED with exposure times of: 0, 20 and 30 minutes

As can be seen from figure 3, the absorption band of phenol at 210 nm was disappeared after irradiation for 20 min while the intensity of the band at 275 nm was decreased significantly with increasing the exposure time. Phenol was disappeared almost totally after 30 minutes of irradiation. This result agrees with previous study done by Gondal et.al. (Gondal et.al., 2005).

The peak disappearance was due to the increase in the carrier charges. When the ZnO particles exposed to the UV LED, the production of electron-hole pairs was increased and these were capable to reduce or oxidize the organic compounds in solution.

The absorption spectra of phenol were recorded after addition of different amounts of ZnO to investigate the effect of semiconductor amount on the phenol degradation process. Figure 4 shows the obtained results, the exposure time was 20 minutes.

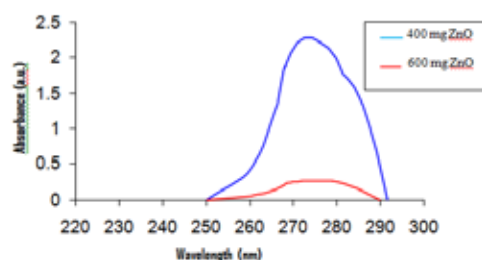
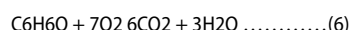
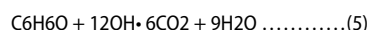
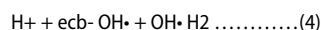
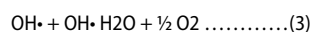
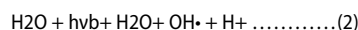
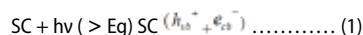


Figure 4: The absorption spectra of phenol mixed with 400 and 600 mg of ZnO after irradiation for 20 minutes

From figure 4 it can be seen that the intensity of the absorption peak at 275 nm was decreased significantly with increasing ZnO weight. Increasing ZnO weight led to more production of electron-hole pairs, which react with the materials in the solution and increase the rate of phenol degradation.

The mechanism is based on the decomposition of the phenol rather than its removal from water (Devipriya S. P. & Yesodharan S., 2010). The overall process of phenol degradation by this technique can be briefly described by the following equations:



where:

SC: the semiconductor catalyst.

Eg: energy gap of the semiconductor.

h ν + : Hole in the valence band of semiconductor.

ecb- : Electron in the conduction band of semiconductor.

Equation 1 illustrates the reaction of semiconductor with phenol and water during the exposure to UV light and the production of holes (valence band) and electron (conduction band). Equation 2 shows that water reacts with the holes to produce radicals ($OH^\bullet$) and hydrogen. Equation 3 indicates that water reacts with $OH^\bullet$ in solution to produce H_2O and O_2 . Equation 4 illustrates that $H^\bullet$ produced from equation (2) is reacted with electrons to produce H_2 . Equation 5 shows that phenol is interacted with $OH^\bullet$ to produce CO_2 , H_2O . Equation 6 illustrates that phenol is interacted with O_2 to produce CO_2 and H_2O .

The last two equations proved the efficiency of this method for phenol degradation as they illustrate the decomposition of phenol into harmless compounds and hence eliminating the hazardous effects. This can be described as very useful and practical approach since the phenol is entirely decomposed.

4. Conclusions

From the results obtained in this work the followings can be concluded that:

- Degradation of phenol increases with increasing U.V exposure time.
- The degradation of phenol increases with the increase of the semiconductor catalyst amount.

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