

HFO Supported Polymeric Material Using for the Photocatalytic Degradation of Phenol

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Abstract

The process of phenol degradation using UV irradiation has been investigated using polystyrene-divinylbenzene polymeric hybrid ion exchange (HIX) resin as a catalyst. The polymeric material was modified with iron cations and thermally treated at 60°C to produce nano FeOOH species (HFO) supported on the HIX polymer and denoted as Fe-HIX. The obtained material was characterized using X-ray diffraction (XRD) and scanning electron microscope (SEM). The data obtained for the degradation of phenol indicate that the addition of Fe-HIX material to the degraded phenol solution greatly enhance the rate of degradation in the presence of H₂O₂. Since the rate of degradation was found to be governed by the adsorption mechanism, so the adsorption isotherms were established in dark at different pH values and different doses from resin correlated with the obtained data of degradation.

Keywords: Phenol; HFO; Photocatalytic degradation; HPLC; IC

Introduction

At present, a large part of the pollution in the public water system is caused by industry [Marhaba and Washington, 1998]. Phenol is a toxic organic component often found in wastes from oil refining, plastics, coke, petroleum refining, and pharmaceutical processing. Being water-soluble, phenolic effluents contaminate nearby watersheds. The fate of phenol and its derivatives is of serious environmental concern since they persist as toxic species

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. The U.S. Environmental Protection Agency (EPA) has listed phenol as a major pollutant [Korzhenovich et al., 1995] with toxicity to aquatic microorganisms and malodors imparted at very low concentrations (0.005 mg/L) [Santos et al., 2009].

Phenol is toxic upon ingestion, contact or inhalation and it is recommended that human exposure to phenol does not exceed 20 mg in an average day [Saha et al., 1999]. Phenol and its derivatives may often cause the breakdown of wastewater treatment plants by inhibition of microbial growth [Ren et al., 2003].

Phenols and phenolic compounds are main contaminants in the industrial wastewater. The effluents discharged by industries such as petroleum refining, coal tar, steel, dyestuff, synthetic resins, coal gasification and liquefaction, surface runoff from coal mines and steel plant etc. contain considerable amounts of phenolic waste which are ultimately released to the environment. Phenolic derivatives are also widely used as intermediates in the synthesis of plastics, colors, pesticides, insecticides, etc [Robert et al., 2002; Lathasree et al., 2004].

Phenol and phenol derivatives used as raw materials in petrochemical and chemical industries are considered one of the most common organic water pollutants because of its high toxicity, even at low concentrations. Several technologies are available to remove industrial organic wastes, such as biological, thermal and chemical treatments and the named advanced oxidation processes (AOPs) [Hadj Salah et al., 2004; Esplugas et al., 2002; Seftel et al., 2008; Regina et al., 2000].

Recent studies have demonstrated the effectiveness of a simple chemical-thermal technique to disperse hydrated iron (III) [Fe (III)] oxide (HFO) particles and magnetite nanocrystals within commercially available ion-exchange resins and polymeric sorbents [Leun and Sengupta, 2000; Li and Sengupta, 1998]. Such hybrid polymeric-inorganic particles combine the durability of the robust polymer beads with the unique sorption and magnetic properties of iron oxide-based nanoparticles.

The earlier investigation also revealed that HFO particles are irreversibly encapsulated within the gel phase of the ion exchangers but accessible to dissolved solutes from the aqueous phase [Leun and Sengupta, 2000; Li and Sengupta, 1998]. On

the basis of these observations, it was conceptualized that a single hybrid polymer bead, if appropriately synthesized in accordance with the experimental protocol developed in Sengupta's laboratory, can be (I) magnetically active, (II) selective toward a host of diverse group of regulated contaminants, and (III) amenable to efficient regeneration and reuse.

We will try in this work to use a new technique have been used extensively in past for the removal of both organic and inorganic contaminants from polluted water. The mechanism of this technique based on the adsorption of such contaminants on the surface of a certain types of resins. In this paper we will benefit from the excess amount of loaded Fe on the polymeric material to achieve the photo-degradation of phenol in a similar way to Fenton process.

- **The advantage of this method**

1. Fe ions can react as a Fenton reagent while it holding the HIX surface, hereby there is no iron in solution.
2. Fe HIX is durable, resistant to sustainable frictions and amenable to efficient regeneration and reuse.

Experimental

Materials

The following chemicals were analytical reagents and were purchased from Fluka chemical and were used without further purification. Hydrogen peroxide (50%). Acetonitrile (CH₃CN). phenol [C₆H₅(OH)]. C-145 cation exchange resin was purchased from Puroite, Inc., Philadelphia

Catalyst preparation

The process of magnetization for the polymeric sorbent particles was carried out as that of [Leun and Sengupta, 2000]. The obtained materials were dried at 50–60°C.

Adsorption Isotherms

All batch equilibrium experiments were conducted in the dark. Measurements were made on suspensions prepared by 200 ml solution of phenol at natural pH and different pH. The equilibrium concentrations were determined using HPLC, after filtration. The concentration of phenol and the intermediates in the clear filtrate was determined by HPLC analysis.

The amount of adsorbate per gram of phenol (Q_{ads} mol/ g) and the maximum number of adsorbed molecules Q_{max} were determined according to the derived Langmuir equation [14] after linearization:

$$Q_{ads} = \frac{Q_{max} K_{ads} C_{eq}}{1 + K_{aeq}} \quad (1)$$

The Freundlich parameters K and n were calculated classically using the results in all the studied of concentrations ($C_{eq} = K C_0^n$)

Photocatalytic Degradation Experiments

Photocatalytic degradation cell

The photoreactivity experiments were carried out in a 200 ml cylindrical quartz glass reactor. A 6 W UV light lamps (Cole Palmer E-09815-55, $\lambda_{max} = 254$ nm) was immersed in the photoreactor where the total radiant flux amount (20 m W cm^{-2}) was measured using UV radiometer (Digital, UV X 36).

Procedure

200 ml of the solution to be investigated which could be phenol of different concentrations or phenol with the proper catalyst of known concentrations is placed in the container of the cell. The starting time of the experiment was determined as soon as the addition of the catalyst is completed. A 5 ml aliquot was then withdrawn after specific interval which is reported for each experiment and its value was 15 min when no light was used and 2 min when UV light is used.

The Collected aliquots at the different intervals were then analyzed using the High Performance Liquid chromatography (HPLC) and Ion Chromatograph (IC) instruments.

Analytical Methods

High Performance Liquid Chromatography (HPLC)

The concentration of phenol and the photodegradation produced intermediates of aliquots of each experiment were identified and followed using HPLC Dionex 202TP™ C18 column (4.6 x 250 mm). The mobile phase used was a mixture of acetonitrile: water (60:40), by a pump at a flow rate of 1 ml/min (Dionex p580 pump). This HPLC type has a UV detector and the wave length at which measurements were carried out was 290 nm.

Ion Chromatography (IC)

The acetates as an intermediate were measured using ion chromatography (Dionex Ion Pac(R)) attached with AS14 column with eluent consisted of 2:7 sodium carbonate: sodium bicarbonate mixture, and the flow rate was 1.2 ml/min. In all cases, air was bubbled through the reaction mixture to ensure a constant dissolved O₂ concentration.

pH measurement

pH values of the samples were measured using Multimeter; WTW (Wissenschaftlich – Technische Werkstätten GmbH) Inolab Multi Levll, be 12237de,(Germany).

Results and Discussion

Catalyst characterization

XRD

XRD patterns of the Hybrid Ion Exchange HIX samples which have been modified with Fe cations was presented in Figure (1b) in comparison with that modified by Sengupta et. al. Figure (1a). The data obtained indicate that the Hybrid Ion Exchange samples possess an amorphous structure due to the absence of any diffraction line characteristic of the crystalline phase and/or Fe- oxide species, this may be due to that the formed FeOOH particles are smaller than the detection limit of the instrument and located in the nano range which can not be detected by XRD.

Scanning Electron microscope

Figure (2) shows Hybrid Ion Exchange particles modified with Fe cations; note that the spherical geometry is retained after processing. A number of macropores in the sizes of 20–300 nm can be readily observed. The obtained SEM picture for Hybrid Ion Exchange particles and close physical observation suggest that HFO agglomerates are accessible to dissolved solutes through a network of pores.

Mechanism of phenol adsorption

No one can deny the important role of adsorption in the catalytic removal of both organic and inorganic contaminants. The adsorption process depends mainly on the surface functional groups which will attract the contaminant molecules. In our case the surface of the Fe modified resin contains FeOOH functional group which may be negatively or positively charged depending on the pH of the medium [Leun and Sengupta, 2000; Li and Sengupta,1998].

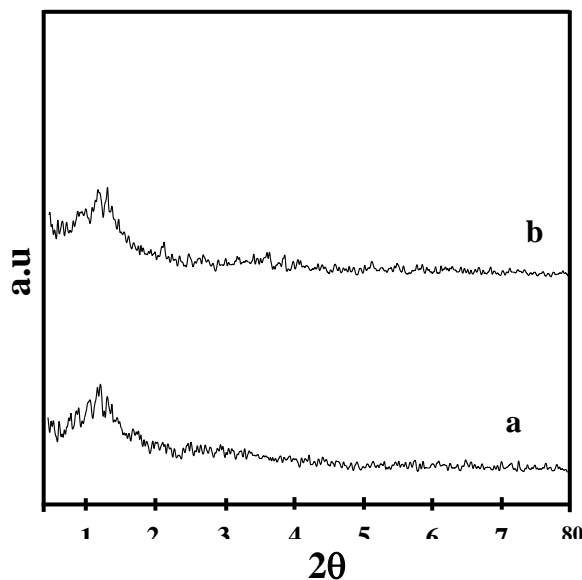


Figure (1): XRD patterns of different cations modified HIX
a) Home (Sengupta et. al.) b) Fe-HIX

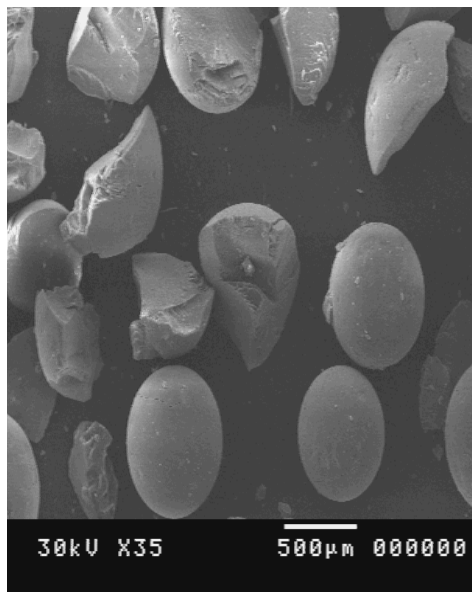


Figure (2): Scanning Electron Micrograph of the Iron modified polymeric material (C-145)

Adsorption of phenol over Fe loaded Hybrid Ion Exchange (Fe-HIX)

Since the rate of most catalytic reactions generally depends on the amount of adsorbed molecules, a series of experiments were carried out in the dark to study the adsorption of HQ on Fe-HIX surface at different doses of the catalyst (0.05, 0.1, 0.15 and 0.2 g/l). It was found that an equilibrium adsorption of a Langmuire type was observed.

According to the Langmuire model, the coverage θ varies as

$$\theta = \frac{Q_{ads}}{Q_{max}} = \frac{KC_{eq}}{1+KC_{eq}} \quad (2)$$

Where Q_{ads} is the number of adsorbed molecules at the adsorption equilibrium, Q_{max} the maximal adsorbable quantity, K the Langmuire adsorption constant of phenol on Fe-HIX and C_{eq} the concentration of phenol at the adsorption equilibrium.

Equation (3) represents the linear transformation of Eq. (1) which is expressed by the following equation:

$$\frac{1}{Q_{ads}} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}KC_{eq}} \quad (3)$$

Plotting the linear transformation indicate that the ordinate at the origin is equal to the reciprocal of Q_{max} , whereas K can be calculated from the slope (slope = $1/Q_{max}K$).

The adsorption process have been carried out using 200 ml phenol solution with different concentration of catalyst in dark and kept under constant stirring for different time periods. The data obtained indicate that the increase of catalyst dose will increase the amount of adsorption. Figure (3) illustrates the adsorption data of 300 ppm phenol over different amounts of HFO material (0.05, 0.10, 0.15 and 0.20 gm). It is clear that the adsorption process follows the following order $0.20 > 0.15 > 0.10 > 0.05$

Degradation of phenol

Photolysis of different concentration of phenol

Direct photolysis is efficiently applied for the removal of phenolic compounds chlorinated hydrocarbons, including hydroquinone amino aramoatic compound, trihalomethanes [Cunningham et al.,1990], chlorinated compounds [Nicole et al.,1991; Cesareo et al.,1986], nitroaromatic compounds [Guittonneau et al.,1988] and certain pesticides [Hessler et al.,1992].

The data obtained in figure (4.a) indicated that phenol is stable in the absence of light and in absence of any added catalyst. In the presence of light in figure (4.b), low concentrations (50 to 100 ppm) of phenol degraded completely in less than 300 min. However, for solution containing 200-300 ppm of phenol the degradation process is very slow and consumes about 300 min for the removal of 53% of the initial concentration (300 ppm).

Photocatalytic degradation of phenol with H₂O₂

In this series of experiment 300 ppm phenol concentration was examined with five different concentrations of H₂O₂ (0.001 M, 0.005 M, 0.01 M and 0.05 M) were found to increase the degradation process in UV light Figure (5.a) when compared with that in the absence of UV light Figure (5.b).

The data obtained indicated that the rate of degradation increase for 0.001 and 0.005 M H₂O₂ solution which means that the addition of any further amount of H₂O₂ has no effect on the irradiation time more than that obtained with 0.005 M H₂O₂. For example complete degradation of the 300 ppm phenol with 0.005 M H₂O₂ took place within 90 minutes while it took 110 minutes for 0.05 M H₂O₂. The data showed that 0.005 M H₂O₂ is the optimum concentration for the degradation of 300 ppm phenol in presence of UV light.

Photocatalytic degradation of phenol over Fe-HIX

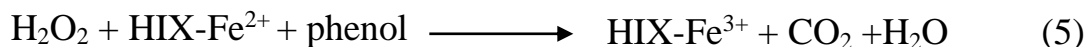
Photo catalytic degradation of phenol has been investigated using a newly generated and modified type of polystyrene-divinyl benzene polymer. The modification of polymeric material was made using iron cation due to its catalytic activity and photosensitivity toward organic contaminants.

Since the degradation process in this case is based on Fenton's Reagent, which uses H₂O₂ and iron salts for producing hydroxyl radicals by reaction of H₂O₂ and ferrous ion (Fe²⁺). Hydroxyl radicals are very powerful, effective and nonspecific oxidizing agents.

In our case the iron species held to the surface of HIX material in form of FeOOH and can react as follows:



The formed hydroxyl radicals will attack the phenol molecules to produce water and carbon dioxide.



- During the optimum reaction sequence with an iron catalyst, ferrous ion (Fe²⁺) is converted to ferric iron (Fe³⁺).

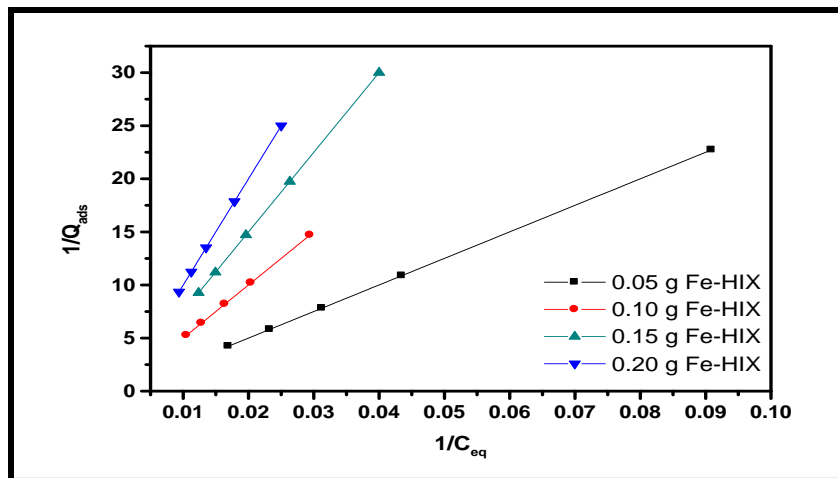


Figure (3): adsorption of 300 ppm phenol at different doses of Fe- HIX.

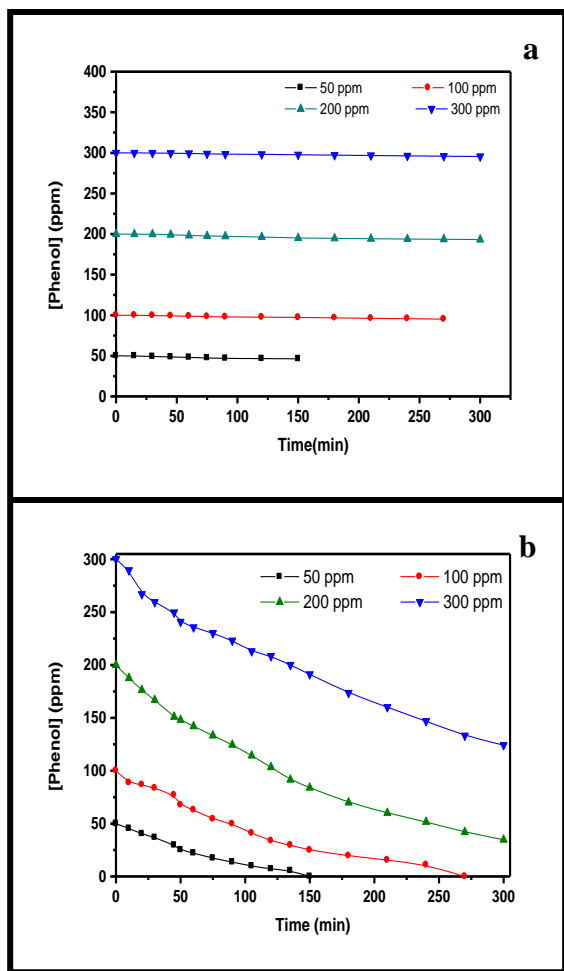


Figure (4): Degradation of different concentrations of phenol
 a) In absence of UV light (Dark)
 b) In presence of UV light

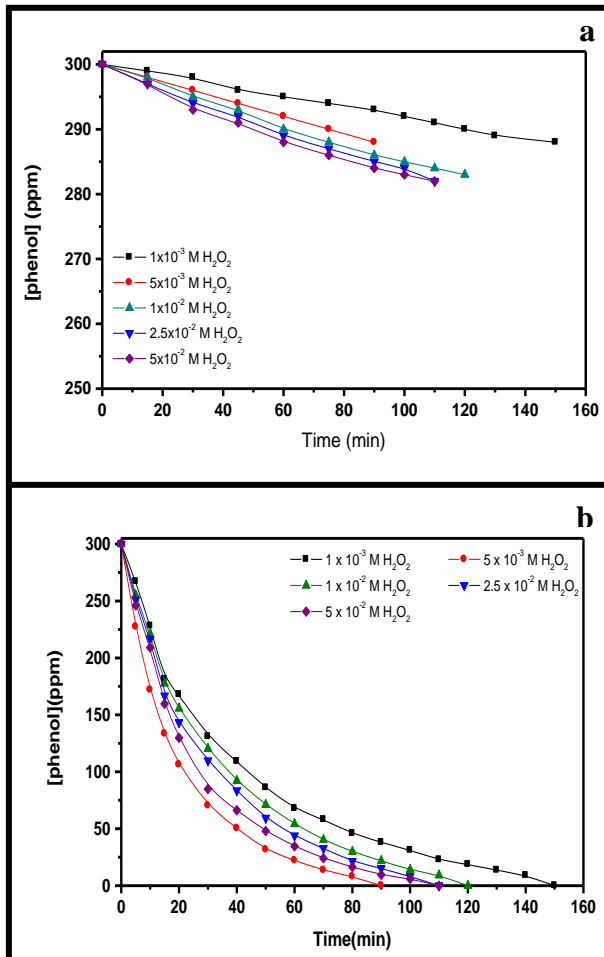
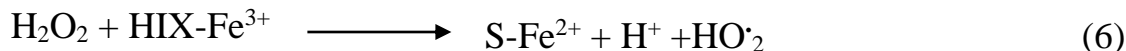


Figure (5): Degradation of 300 ppm phenol in presence of different concentrations of H₂O₂
 a) In absence of UV light (Dark)
 b) In presence of UV light

- Ferric ion will not generate the hydroxyl radical but it can be regenerated back to ferrous iron by a subsequent reaction with an additional molecule of H_2O_2 and hereby the degradation reaction will goes on as in equation 6.



Effect of catalyst dose

Investigation of the effect of Fe modified HIX polymeric material dosage has been carried out under different experimental conditions both in the absence and the presence of UV light. The data obtained in figure (6) indicated that the addition of different concentration of HIX polymeric material dosage (0.05 - 0.20 gm) has increased the rate of degradation with increase the catalyst doses in presence of UV light only.

The addition of H_2O_2 to the degraded solution in the absence or the presence of UV irradiation was found to greatly enhance the degradation rate. The data obtained in figure (7) and figure (8) indicated that the rate of degradation was faster in UV light than in absence of UV light.

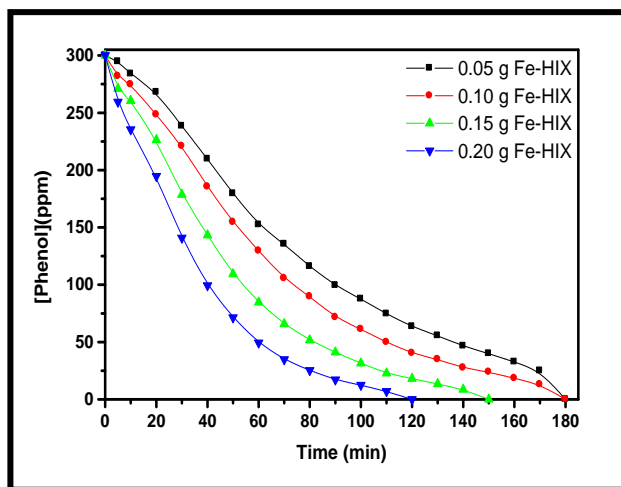


Figure (6): Effect of Fe-HIX amount on degradation of 300 ppm phenol (UV)

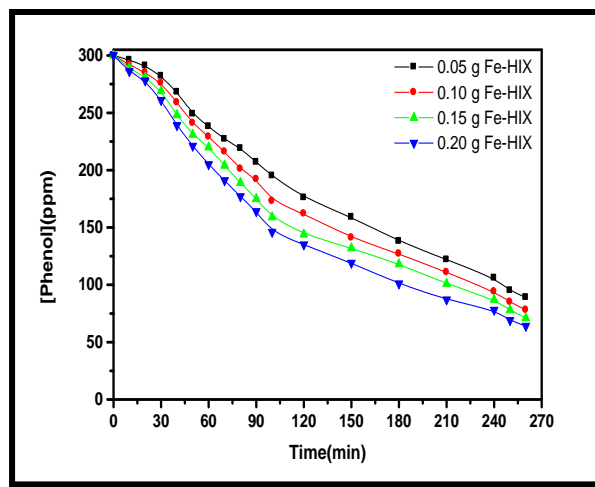


Figure (7): Effect of Fe-HIX amount on degradation of phenol at fixed 0.005 M

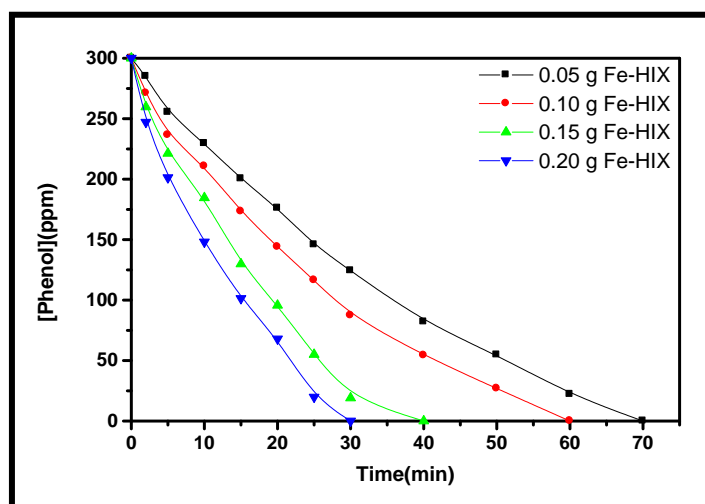


Figure (8): Effect of Fe-HIX amount on degradation of phenol at fixed 0.005 M H₂O₂ (UV)

The effect of degradation of phenol (300 ppm) on pH of medium and vice versa

One important feature in photocatalytic degradation reaction is the pH change which should either be followed up during the reaction (which will be the effect of degradation on pH) or adjusted at different values to evaluate the effect of its change on the degradation process.

Effect of degradation on pH

In this study we monitored the pH in all experiments of degradation of aqueous phenol under all conditions. These results are shown in Figures 9 → 12. The variation of pH of the solutions depends on the starting pH of the experiment and the values depend on the mixture and type of degradation experiment. For example pure aqueous phenol (300 ppm) has a pH value of 6.66 at room temperature; this value did change within 300 minutes under dark condition to 6.61 while it changed to 3.66 under UV light irradiation (Figure 9).

For degradation of phenol in presence of H₂O₂ (0.001 M → 0.05 M) under UV light irradiation, the pH started 6.65 and became 3.01 for 0.001 M H₂O₂ after 150 minute, while it became 2.26 for 0.005 M H₂O₂ after 90 minute, 2.5 for 0.01 M H₂O₂ after 120 minute, (2.27 → 2.12) for (0.025 → 0.05 M H₂O₂) after 110 minute (Figure 10).

For degradation of phenol (300 ppm) using different concentration of Fe-HIX under UV light the pH started at 6.65 and became (3.67→ 3.26) for (0.05→ 0.10g) after 180 minute, while it became 3.05 for 0.15 g after 150 minute, 2.9 for 0.20 g after 120 minute (Figure 11).

For degradation of phenol (300 ppm) using different concentration of Fe-HIX under UV light at fixed concentration of 0.005 M H₂O₂ the pH started at 6.65 and became 2.58 for 0.05 g after 70 minute, 2.4 for 0.10 g after 60 minute, 2.25 for 0.15 g after 40 minute, 2.04 for 0.20g after 30 minute (Figure 12).

From the above mentioned results, it is seen that the pH of the phenol (300 ppm) under these variable degradation conditions decreased as the process proceeded indicating that the medium become more acidic which also suggests that there are some acidic intermediate species before any possible complete mineralization of phenol. The pH change depends on the rate by which degradation takes place as well as on the concentrations and types of these intermediates.

Effect of different pH on the degradation of phenol

In this section the pH will be adjusted by adding the proper concentrations of hydrochloric acid to bring it down to the values 2 and 4, then adding the proper concentrations of sodium hydroxide to higher the values 8 and 10.

The role of pH on the rate of degradation phenol was studied in the pH range 2-10. Figure (13) indicate that the pH change strongly affected not only the adsorption but also the degradation rate of phenol. It is clear that the maximum adsorption was observed with pH 8. Figure (14) show that the rate of degradation is faster in lower acidic and basic medium than in higher acidic and basic medium. The higher rate of degradation occurs at pH 8.

Upon the addition of catalyst and H₂O₂ at different pH values the degradation of phenol was observed in absence and presence of UV light. Figures (15, 16) the obtained data indicate that the rate of degradation is faster in presence of UV light than absence. The data also indicate that the maximum degradation took place at pH 8.

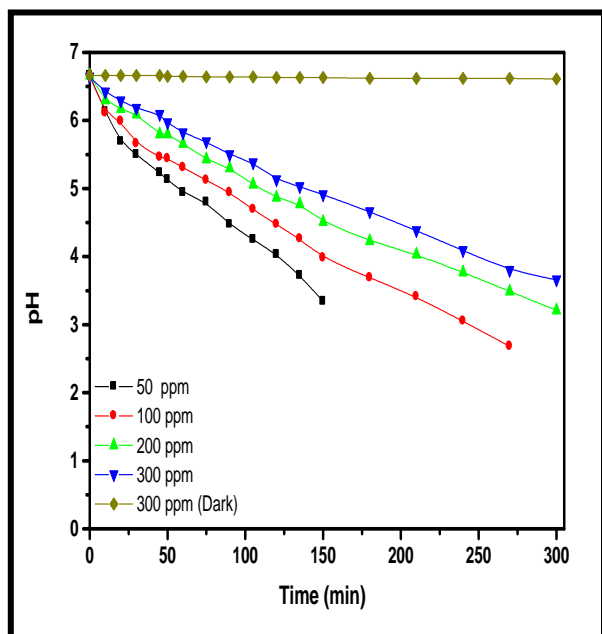


Figure (9): Variation of pH during using different concentrations of phenol (UV)

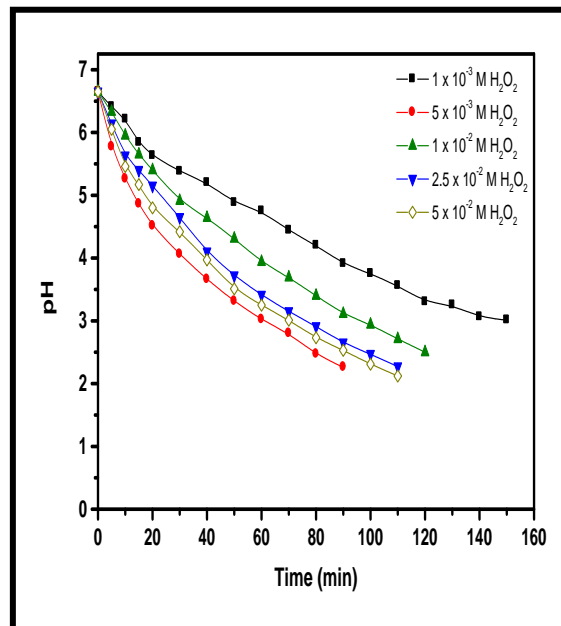


Figure (10): Variation of pH during the degradation of phenol using different concentrations of H₂O₂ (UV)

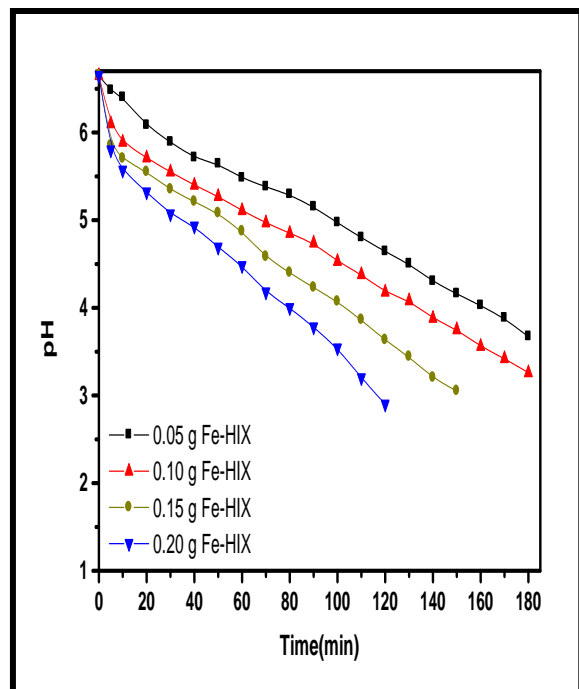


Figure (11): Variation of pH during the degradation of phenol using different concentrations of resin (UV)

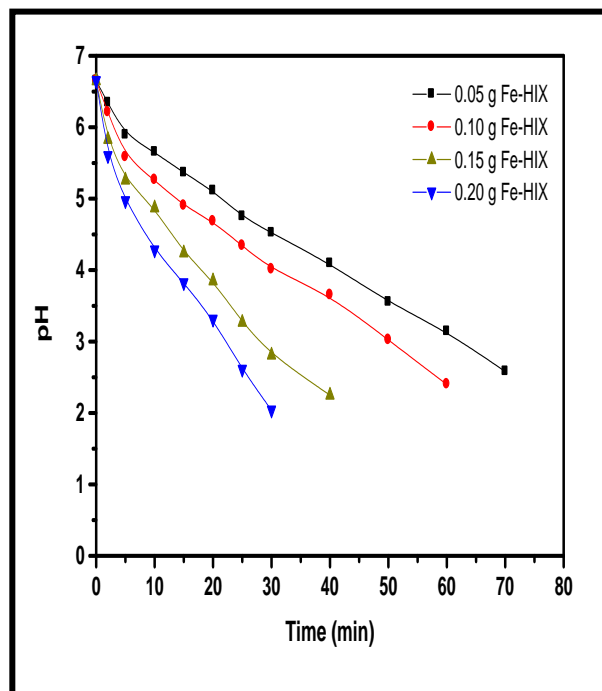


Figure (12): Variation of pH during the degradation of phenol using different concentrations of resin at fixed 0.005 M H₂O₂ (UV)

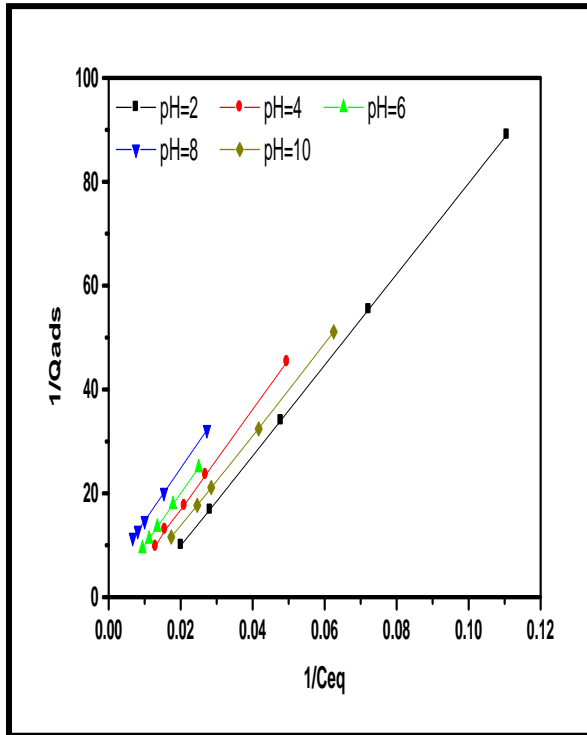


Figure (13): Effect of different pH on adsorption of 300 ppm phenol at fixed 0.20 g Fe-HIX

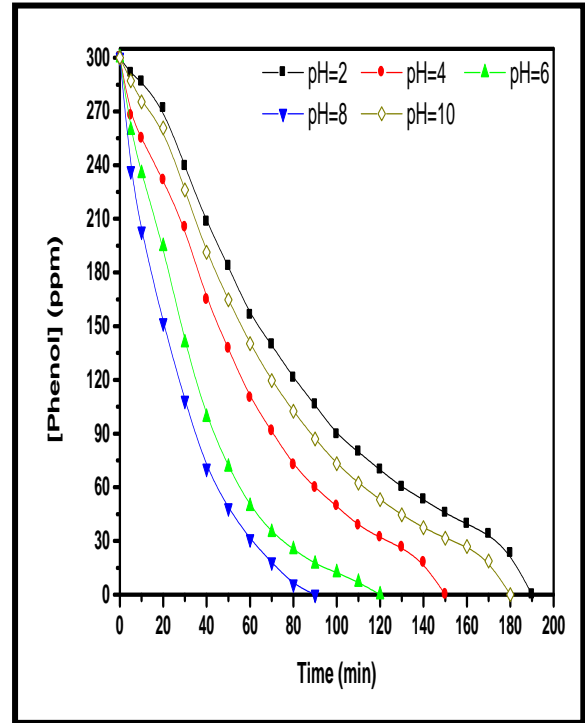


Figure (14): Effect of different pH on degradation of 300 ppm phenol at fixed 0.20 g Fe-HIX (UV)

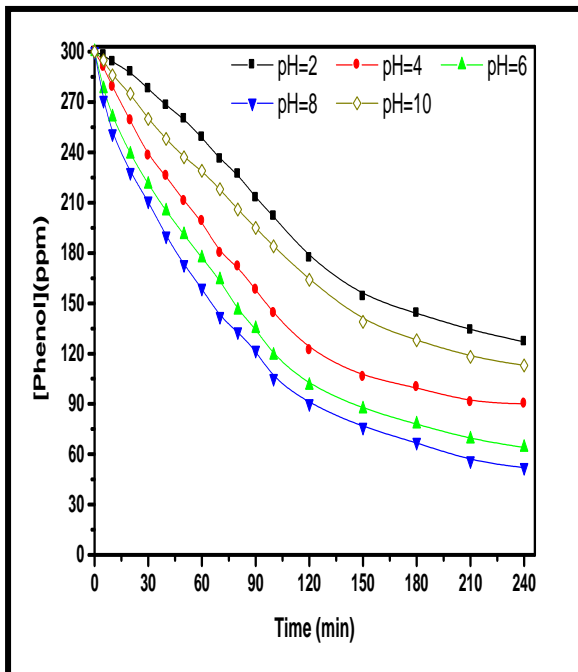


Figure (15): Effect of different pH on degradation of 300 ppm phenol at fixed 0.005 M H₂O₂ and 0.20 g Fe-HIX (Dark)

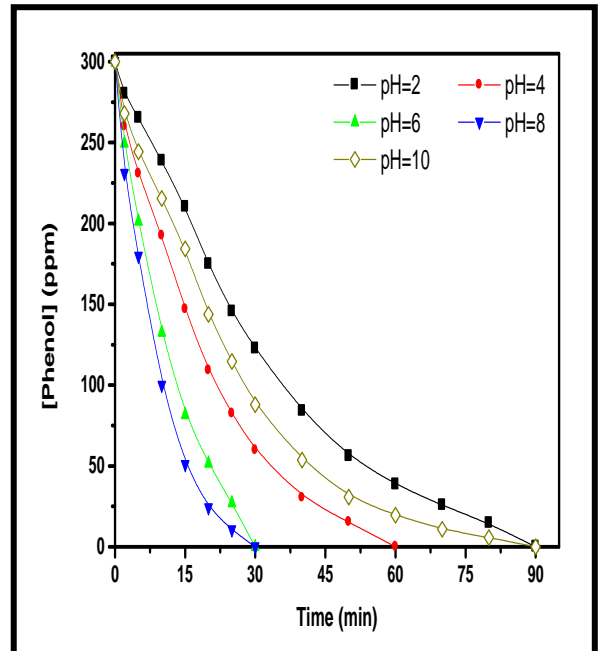


Figure (16): Effect of different pH on degradation of 300 ppm phenol at fixed 0.005 M H₂O₂ and 0.20 g Fe-HIX (UV)

Kinetics studies of Degradation of Phenol

Phenol degradation can probably proceed through two pathways: complex oxidation and HO· oxidation. Figure (17) may represent the principal pathways of phenol degradation.

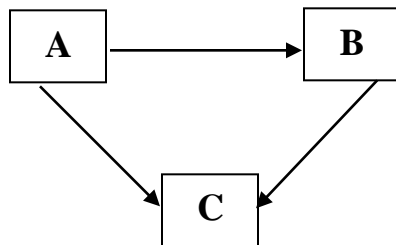


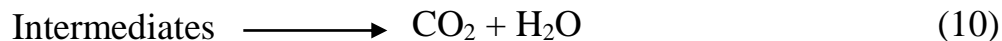
Figure 17: The principal pathways of phenol degradation

In the above reaction pathways (Figure 17), A represents the original organic compound (phenol), B is the organic intermediates such as acetic acid, etc., and C is the final substrates, CO₂ and H₂O. K is the rate constant (min⁻¹). The pathway from A to C represents the complex reaction; that from A to B to C represents the radical reaction.

If we assume that HO· is produced as a consequence of the following primary process.



This can either be used in the phenol degradation as follows:



If we now assume that the degradation process is either first order or pseudo-first order kinetics, thus the rate expression can be written as follows:

$$\frac{-d [\text{Phenol}]}{dt} \propto [\text{Phenol}] [\text{HO}\cdot] \quad (11)$$

$$\frac{-d [\text{Phenol}]}{dt} = k_{\text{obs}} [\text{Phenol}] [\text{HO}\cdot] \quad (12)$$

If make use of the fact that $[\cdot\text{OH}]$ is practically constant, therefore, equation (12) becomes

$$-\frac{d [\text{Phenol}]}{dt} = k_{\text{obs}} [\text{Phenol}] \quad (13)$$

Where $[\text{Phenol}]$ is the concentration of Phenol at time t and k_{obs} is the observed rate constant included into it the constancy of $\text{HO}\cdot$ and the intensity of the UV light. If equation (11-13) is integrated between initial condition at $t = 0$ and any time at $t = t$ where $[\text{Phenol}]$ is equal $[\text{Phenol}]_0$ and $[\text{Phenol}]$ respectively we get:

$$\text{Ln} \frac{[\text{Phenol}]_0}{[\text{Phenol}]} = k_{\text{obs}} t \quad (14)$$

Or

$$\frac{C_0}{C} = k_{\text{obs}} t \quad (15)$$

Where $C_0 = [\text{Phenol}]_0$ at $t = 0$ time and $C = [\text{Phenol}]$ at $t = t$ time. If our degradation process does follow this equation (11-14), thus when plot $\text{Ln } C_0/C$ versus time in every experiment must lead to a straight line whose slope is k_{obs} . When this was done using the results obtained in this investigation under all experimental conditions reported here in this paper, fortunately we did obtain straight lines as can be seen from Figures (18 → 23), and k_{obs} is calculated from the corresponding slope. k_{obs} is shown in Figures (24→ 27) as a function of the proper condition reported with the corresponding figures.

For example, figure 18 shows this plot for experiments where the intensity of the UV light and initial concentration of H_2O_2 and HIX were constants and phenol concentration was varied. As it can be seen, points lie satisfactory in straight lines with correlation coefficients greater than 0.95.

Effect of the various parameters on K_{obs}

We have established the fact that the rate expression of the kinetic model by degradation of phenol as a pollutant in water, is first order or pseudo-first order. This simply indicates that the rate - determining step does follow this model. However, the possible or plausible mechanism through which this process proceeds is not yet clear and

we shall through some light on it in a coming section. Also the behavior of k_{obs} with some of the experimental variables need to be looked at and explained. This also might help in elucidating the mechanistic pathway of the degradation reaction.

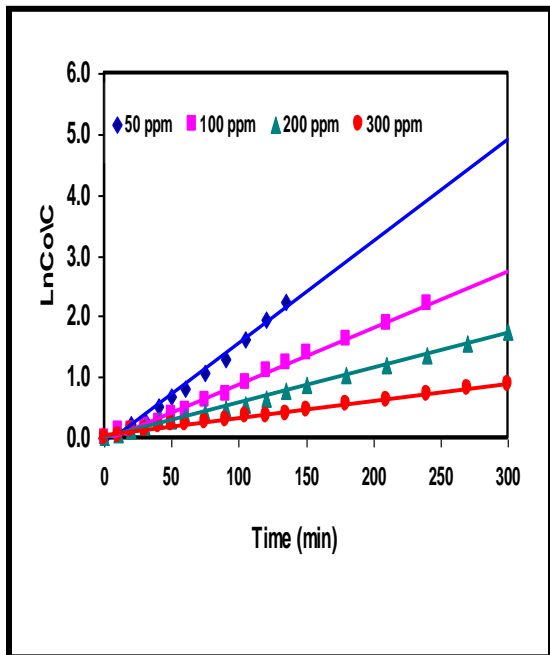


Figure (18): Ln Co\C v.s time for the photo-degradation of different concentrations of phenol (UV)

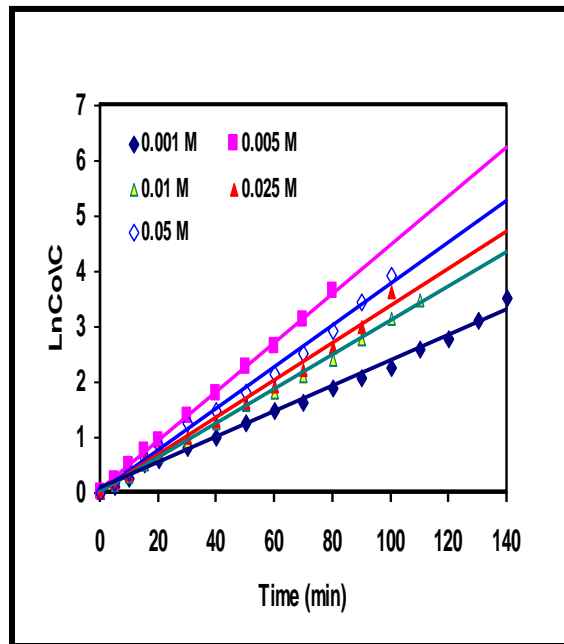


Figure (19): Ln Co\C v.s time for the photodegradation of different concentrations of H_2O_2 (UV)

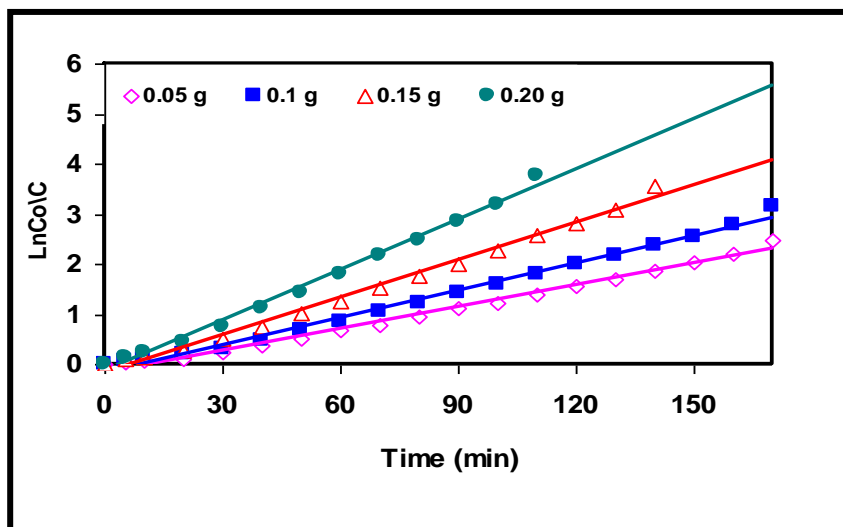


Figure (20): Ln Co\C v.s time for the photodegradation of different concentrations

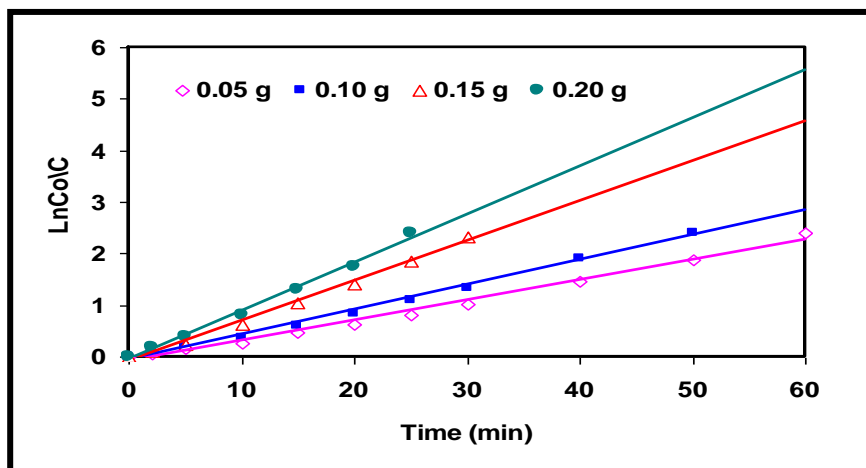


Figure (21): Ln Co\C v.s time for the photodegradation of different concentrations of Fe-HIX at fixed H₂O₂ (UV)

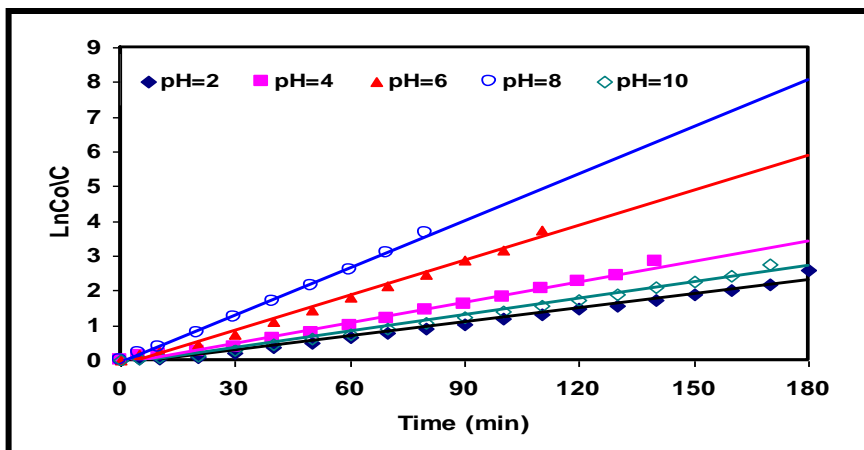


Figure (22): Ln Co\C v.s time for the photodegradation of phenol at fixed 0.20g Fe-HIX at different pH of different (UV)

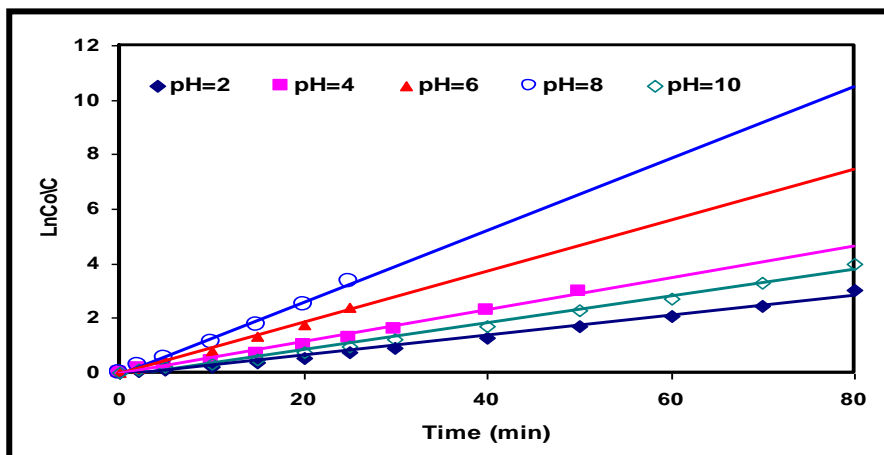


Figure (23): Ln Co\C v.s time for the photodegradation of phenol at fixed 0.20g Fe-HIX and 0.005 M H₂O₂ at different pH (UV)

Effect of phenol initial concentration

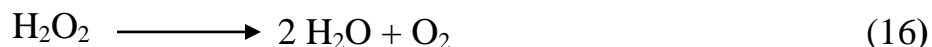
When the k_{obs} are plotted vs different concentrations of phenol we find that the behavior varies greatly. Figure (24a) shows that k_{obs} decrease as phenol increases from 50 to 300 ppm. The decrease of k_{obs} as [phenol] increased may be explained on the basis that HO^\bullet radicals which is the initiator responsible of oxidizing phenol to either intermediates or complete mineralize

tion. The extent of HO^\bullet radicals is dependent on the UV intensity, which is constant for all initial concentrations of phenol (50 \rightarrow 300 ppm), thus the availability of HO^\bullet radicals to the phenol molecules in lower concentrations will be higher than in case of higher concentrations, which is very consistent with the observed results.

Effect of H_2O_2 initial concentration

As shown in figure (24b) a significant enhancement of the mineralization efficiency was observed when the H_2O_2 concentration was increased from 0 to 0.05 M (the continuous line does not mean any fitting but only a way of showing the tendency).

Above this H_2O_2 concentration, the oxidation rate seems to be negatively affected by the increase of H_2O_2 up to 0.005M. This is probably due to both the auto- decomposition of H_2O_2 into oxygen and water (eq.16) and the scavenging effect of hydroxyl radicals by H_2O_2 (eq.17) as follows:



Excess of H_2O_2 will react with HO^\bullet competing with organic pollutants and consequently reducing the efficiency of the treatment.

Effect of Fe-HIX

Figure (24c) shows k_{obs} as a function of [Fe- HIX] in presence of UV light only. It is seen that k_{obs} increases almost linearly with [Fe- HIX].

Figure (25) shows k_{obs} as a function of [Fe- HIX] at fixed H_2O_2 (0.005 M). It is seen that k_{obs} increased almost linearly with [Fe- HIX] than in UV light only.

Effect of pH

We showed the effect of the variation of pH of the aqueous phenol (300 ppm) on the rate of degradation. The pH ranged from 2 \rightarrow 10 and it was found that the rate of degradation did increase with the increase in the pH value. This of course should be reflected in the k_{obs} value for these same experiments under the same conditions (Figures 12 and 13) show the behavior of k_{obs} as a function of pH (2 \rightarrow 10) under photocatalysis condition.

In Figures 26 where HIX fixed at 0.2g was used as a catalyst under photocatalytic condition the k_{obs} increased as the pH increased from (2 \rightarrow 8), above this k_{obs} decreased.

In Figures 27 shows the k_{obs} as a function of pH when HIX fixed at 0.2g and 0.005 M H_2O_2 is used as a catalyst in presence of UV light. It is seen here that k_{obs} increase as the pH increases (2 \rightarrow 8) above this k_{obs} decreased.

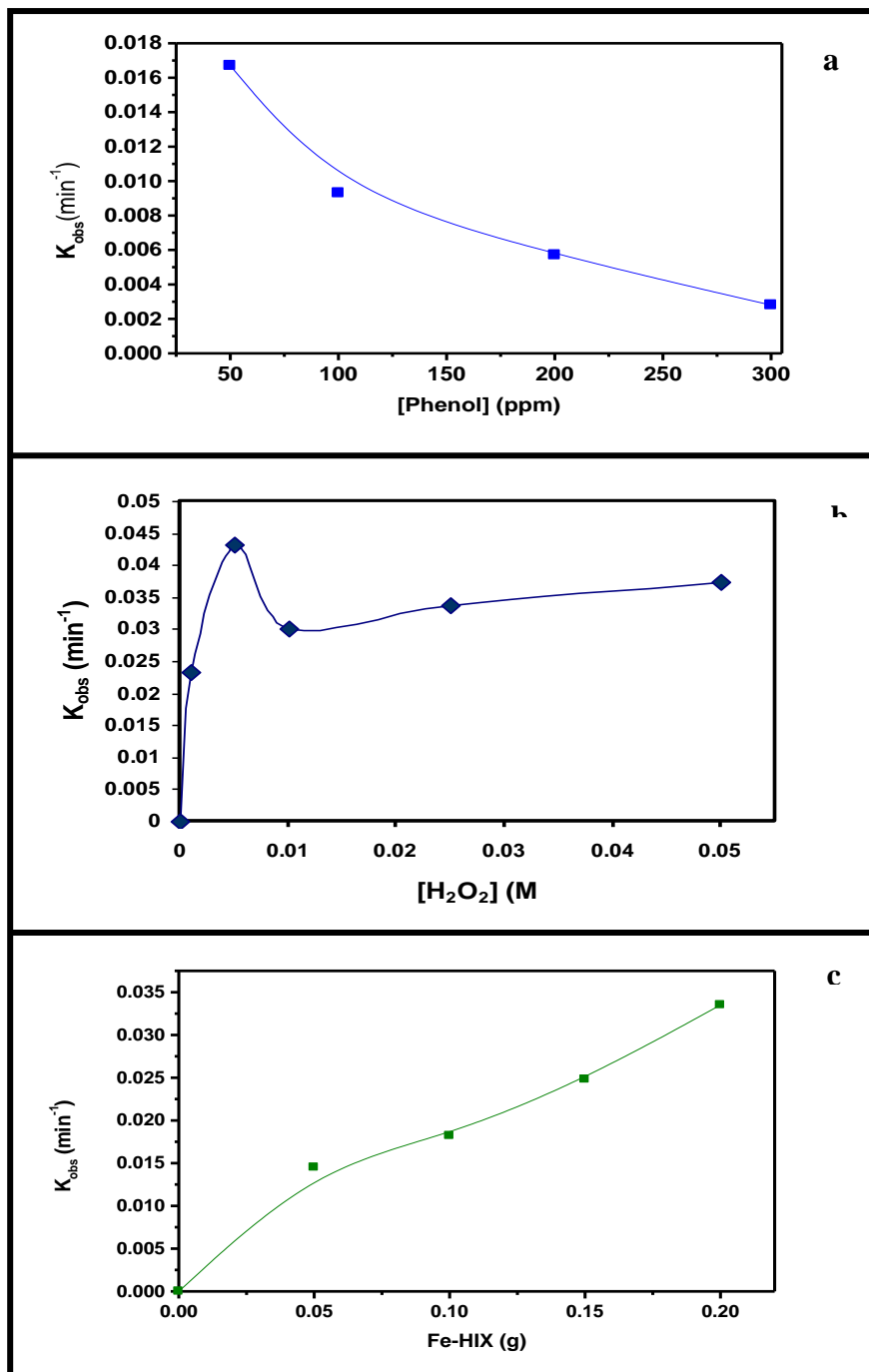


Figure (24): k_{obs} against concentration for the photodegradation of phenol a) At different concentrations of phenol
 b) At different concentrations of H₂O₂
 c) At different concentrations of Fe-HIX IX

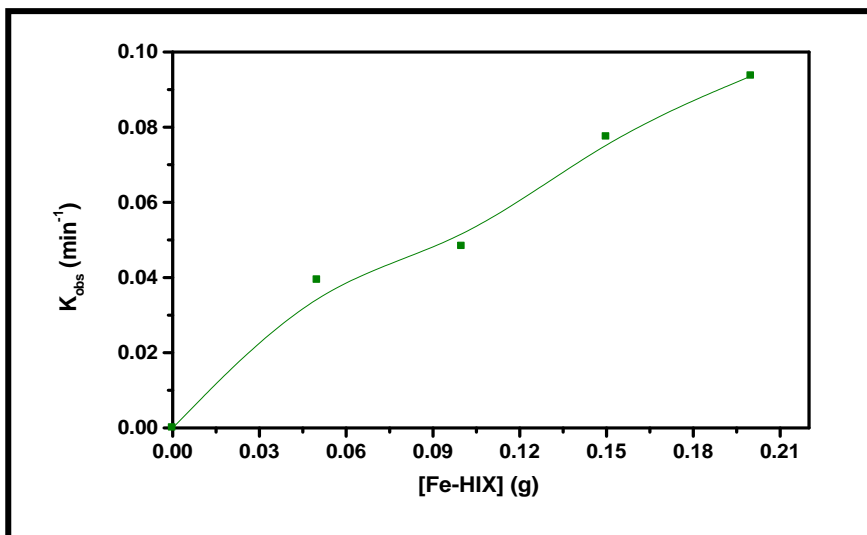


Figure (25): k_{obs} against [Fe- HIX] for the photodegradation of phenol at fixed 0.005M H_2O_2

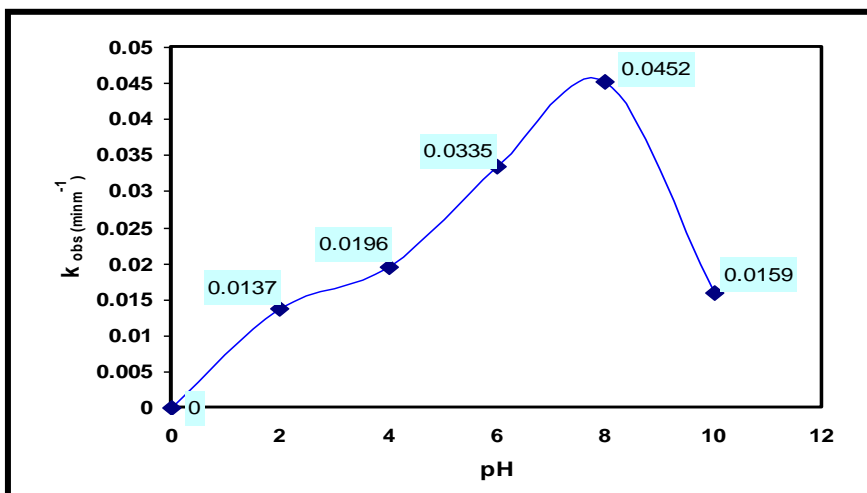


Figure (26): k_{obs} against pH for the photodegradation of phenol at fixed 0.02g Fe-HIX

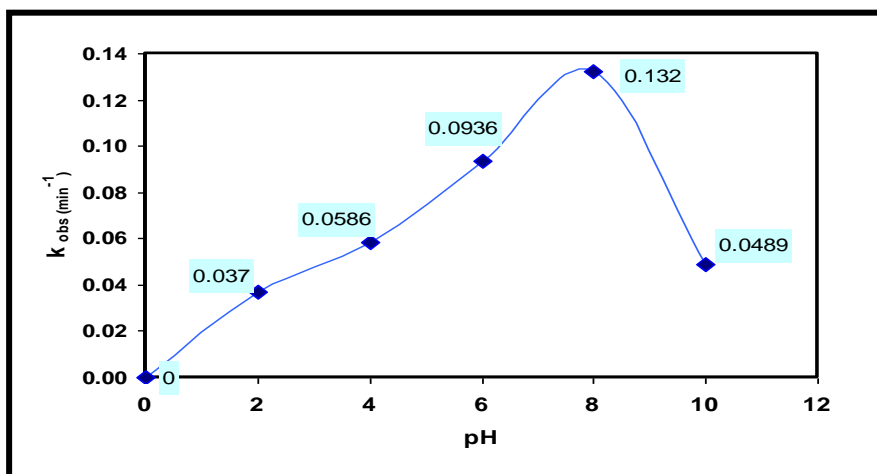


Figure (27): k_{obs} against pH for the photodegradation of phenol at fixed 0.02g Fe-HIX and 0.005M H_2O_2

Mechanism of phenol degradation

The degradation products of phenol might in theory be classified as primary products (such as catechol and hydroquinone), more oxidized products (such as maleic acid, benzenzene and oxalic acid), and the final products to CO₂ and water [Walling, 1998; Okamoto et al., 1985]. In our study, only several main products were detected. The primary products (such as catechol and hydroquinone) were detected possibly because their concentrations were detection by HPLC after all very easily further oxidize them. Some other intermediate products, such as malic acid and benzenzene were unsaturated organic substances with double-carbon bonds easily attacked by HIX. So these products that would be further oxidized to more steady species, such as oxalic acid. Oxalic acid should be a certain degradation product of phenol. The oxalic acid molecule is symmetrical, with each of its carbon atoms stabilized by carboxyl. A high quantity of oxalic acid was detected as expected; with the amount increasing with the reaction time.

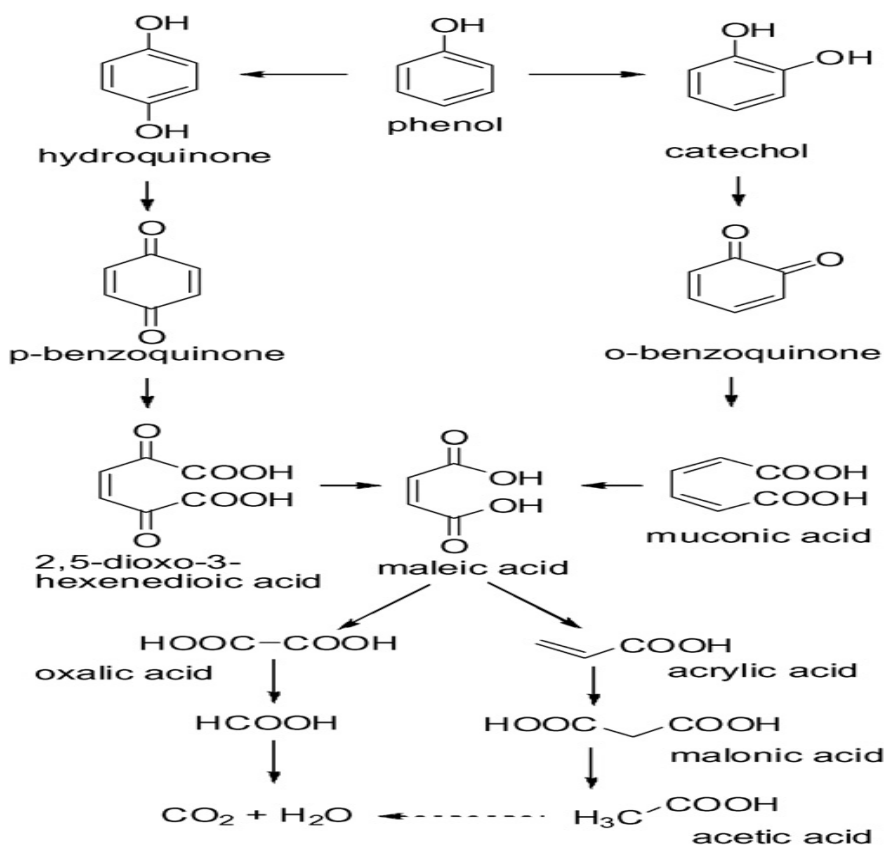


Figure (28): Simplified scheme for phenol

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