Experimental and Kinetic Study of Phenol Oxidation Using Ni-oxide Catalysts

Lecturer. Dr. Usama Akram Saeed *M. Sc. Israa Shaker M. Ali*
M. Sc. Huda Dhiaa Abdulkader
Nahrain University /College of Engineering/Chemical Engineering Dept.

Abstract :

The current study focuses on the investigation of Nickel Oxide in advanced oxidation process of phenol. The removal of phenol from aqueous phase continues to be an important environmental issue. In this work, the oxidation of phenol in aqueous solutions in a batch reactor using nickel oxide was studied. The efficiency of the system was evaluated with respect to reaction time, pH, feed concentration of reactants, catalyst load. The concentrations of phenol after reaction were determined by UV visible. The results showed that the optimum conditions (≅100% conversion at 90 min) were obtained at a neutral pH, with 0.5 g of Nickel Oxide and 18°C. However, decreasing of efficiency was observed for pH in the range of 2–12. The results showed that increasing temperature from 18°C to 50°C lead to decrease the conversion from 80% to 62%. Analytical profiles on phenol transformation were consistent with the best line fit of the Eley-Rideal Mechanism. Moreover, the degradation rate constants k and K_e ***were found*** $1.1*10^{-3}$ ***(***cm^3***.liter/gcata) and 4.9889 respectively with*** $R^2=0.99522$***. Finally, the results of mineralization studies indicated that dechlorination was better accomplished but more time was required to completely mineralize phenol into water and carbon dioxide.***

Keywords: Catalytic oxidation, Nickel Oxide, Phenol

دراسة عملية ونظرية لعملية تحول الفينول بطريقة الأكسدة بوجود أكسيد النيكل كعامل مساعد

م.د.أسامة أكرم سعيد م.م. أسراء شاكر محمود م.م. هدى ضياء عبد القادر
جامعة النهرين/كلية الهندسة قسم الهندسة الكيمياوية

الخلاصة :

تركز الدراسة الحالية على استخدام أكسيد النيكل في عملية الأكسدة المتقدمة للفينول. إزالة الفينول من الماء لا تزال قضية بيئية هامة. في هذا العمل، تم دراسة أكسدة الفينول في المحاليل المائية في مفاعل Batch باستخدام أكسيد النيكل. تم حساب نسبة الإزالة من خلال زمن التفاعل، درجة الحموضة، تركيز المواد المتفاعلة، وكمية العامل المساعد. استخدمت الأشعة فوق البنفسجية لقياس تركيز الفينول بعد التفاعل. أظهرت النتائج التي تم الحصول عليها في الظروف

المثلى (100٪ تحول في 90 دقيقة) في الرقم الهيدروجيني المعتدل، مع 0.5 غ من أكسيد النيكل و18 درجة مئوية. ومع ذلك، انخفضت كفاءة التفاعل عند الاس الهيدروجيني في حدود 2-12. أظهرت النتائج أن زيادة درجة الحرارة من 18 درجة مئوية إلى 50درجة مئوية تؤدي إلى تقليل التحول من 80٪ إلى 62٪. تم نمذجة تحول الفينول بما يتفق مع أفضل خط مناسبا Eley-Rideal Mechanism. وعلاوة على ذلك، تم حساب ثابت التفاعل $1.1*10^{-3}$ (cm^3.liter/gcata) and 4.9889 على التوالي مع $R^2 = 0.99522$. ***وأخيرا، أشارت نتائج الدراسات التي تؤدي الى إزالة جزيئه الكلور أفضل ولكن مع وقت أكثر ليتحول الفينول تماما إلى الماء وثاني أكسيد الكربون.***

1. Introduction

The spread of a wide range of contaminants in surface water and groundwater has become a critical issue worldwide, due to population growth, rapid development of industrialization and long-term droughts [1-3]. It is thus of necessity to control the harmful effects of contaminants and improve the human living environment. Contaminants persisting in wastewater include heavy metals, inorganic compounds, organic pollutants, and many other complex compounds [4-6].

Phenols belong to a class of organic compounds with aromatic functional groups and are similar in structure to the more common herbicides and insecticides, which resist biodegradation. The main sources of phenols are in the wastewaters of chemical and allied industries. In addition, phenolic compounds are often found in wastewaters from coal gasification, coke-oven batteries, refinery and petrochemical plants [7], and other industries, such as synthetic chemicals, herbicides, pesticides, antioxidants, pulp-and-paper, photo-developing chemicals, etc. [8,9]. The level of phenol in some of the effluents from these industries can be as high as 6,000 mg/l [10]. Young and Rivera [9] found that phenol could be stoichiometrically converted to methane and carbon dioxide by anaerobic sludge from a municipal digester.

There are different methods for the separation of phenols such as steam distillation [11], Separation by extraction [12], Separation by membrane [13,14], Destruction of phenol by air oxidation [15-19], electrochemical oxidation [20-22], Biochemical abatement [23]. Many problems associated with the above mentioned methods have been reported in the literature such as high cost, low efficiency and generation of toxic products [24]. Various processes such as adsorption, biodegradation, solvent extraction, incineration, reverse osmosis and adsorption have been proposed to remove phenolic compounds from contaminated waters, among which oxidation is one of the most effective techniques in either laboratory or industrial scale.

The oxidation of dilute aqueous solutions of refractory organic pollutants using air or oxygen as an oxidizing agent over a catalyst, so-called catalytic wet air oxidation (CWAO), has already largely demonstrated its effectiveness in removing toxic terminates [25].

In catalytic oxidation process, the reaction follows a specific oxidation pathway resulting in contaminant degradation. The oxidation is initiated due to the formation of free radicals in the presence of a catalyst. These radicals are extremely reactive and readily attack organic pollutants, thereby transforming them into harmless end products. The type and strength of the active radicals depends on the oxidant employed in the process.

The oxidation process of phenol using Ni-oxide makes the process more attractive by achieving high conversion and this process was carried out using batch technique at temperatures (18-60^{o}C) and atmospheric pressure. The concentration of phenol in aqueous solution was measured by UV-visible spectrophotometer (Shimadzu UV-160A) at wavelength 269 nm, except where otherwise specified.

This study was conducted to demonstrate that phenol could also be effectively removed from wastewater by using oxidation of aqueous phenol solutions even at ambient temperature by using Ni-oxide as a catalyst under different growth conditions, including pH, temperature, and different concentrations of phenol.

2. Chemicals

Phenol (analytical grade; Fluka) Nickel Oxide (NiO) (M.wt.=165.42 g/mol.) from Sigma Aldrich

2.1 Experimental Work

The phenol degradation characteristics were analyzed in batch process by monitoring the residual phenol content in each run by using (UV-visible type shmadzw) at a wave length of 269nm. A 250 ml. round bottom flask with three nicks was used for all oxidation runs, one for sampling, second for the source of air and the third for thermometer to control the temperature. The flask which placed on a magnetic hot plate with stirring was filled with 100 ml. of solution of phenol (which exhibited a pH value of 6) at the desired initial concentration (100-300 ppm) then the compressed air valve and the stirring were open for 30 min., after this time, Nickel oxide (0.1-0.7 g) was added to start the reaction and heated to the desired temperature (starting with ambient temperature 25 ^{o}C). Also the pH value of phenol solution was examined to get the optimum value (2-12). Liquid sample was withdrawn after 30min of reaction, heating and magnetic stirred were turned off and the air flow was interrupted to stop the reaction. The above procedure was repeated to get the optimum conditions of concentration of phenol, weight of catalyst, working temperature and the pH value.

The main parameter to compare the results in the results section is the percent conversion of the organic compound, Xorg. defined as:-

$$\%X_{org.}=\frac{[org]0-[org]}{[org]0}\times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Where [org]0 is the initial concentration and [org] the sample concentration after 30min of reaction.

3. Results and Discussion

3.1 Effect of Catalyst Load

A set of reactions was carried out by increasing the catalyst load (NiO) from 0.1 to 0.7 g/L while keeping the phenol concentration (50ppm) and reaction time 1 h (half hour for bubbling and half hour for reaction). For the range of catalyst loads, the conversion increased from 22.7 to 76.1%, which is quite remarkable **Figure. (1)**. The oxidative degradation of phenol was carried out subsequently at a constant catalyst load of 0.70 g/L. The conversion of phenol was decreased after 0.5g/L of catalyst as shown in figure 1, where at 0.5g/L of NiO the conversion of phenol is 76.1% and decrease to 74.1% for 0.6g/L and still decrease to 65.8% when adding 0.70g/L of catalyst. All reactions were carried out with a constant catalyst load of 0.50 g/L as it was found that this was sufficient to bring about very large conversion of phenol and its derivatives.

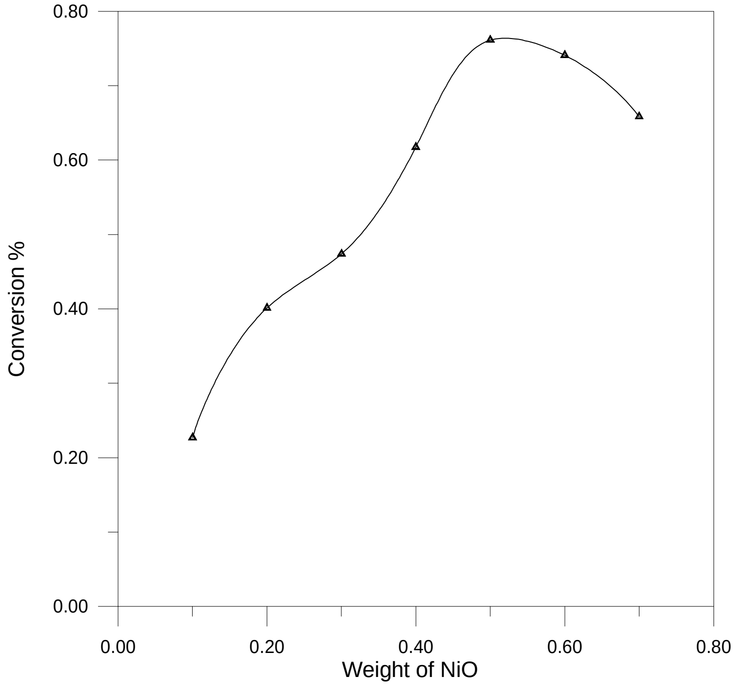

Fig . (1): The effect of Weight of Catalyst on the conversion of Phenol for 18^{o}C, pH=6

3.2 Effect of Time of Reaction

Reaction time had considerable influence in degradation of phenol. The conversion of phenol was quite reasonable at 41% even when the reaction time was only15min for a reactant feed of phenol and NiO load of 0.50 g/L **(Figure. 2)**. The conversion increased to 94.1% after 90 min and then it slowly increased with further increase in reaction time.

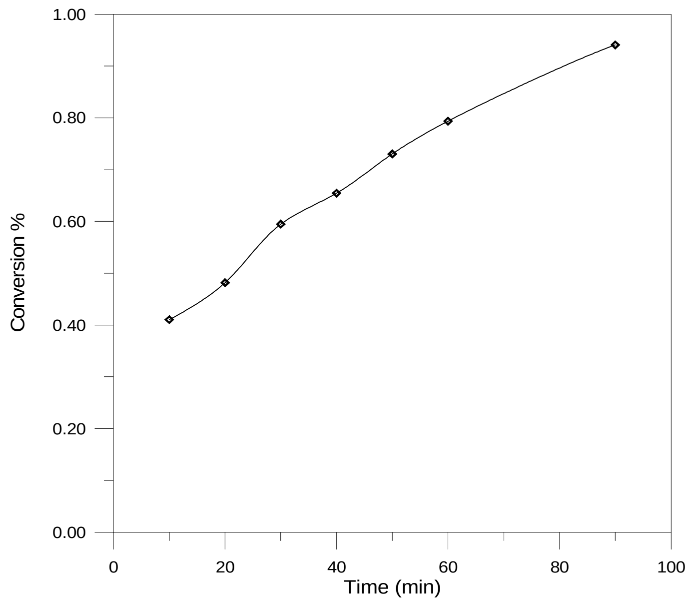

Fig. (2): The effect of Time on the conversion of Phenol for 18^{o}C, pH=6 and 0.5g of NiO

3.3 Effect of Initial Concentration

The experimental results of catalytic oxidation of phenol at various concentrations (50, 100, 150, and 200 mg/L) with conversion are shown in figure 3. This reveals that conversion decreased with increase in initial phenol concentration. This means that the conversion is highly dependent on initial concentration of the phenol because at lower concentration, the ratio of the initial number of phenol molecules to the available surface area is low. However, at high concentration the available sites of catalysts become fewer.

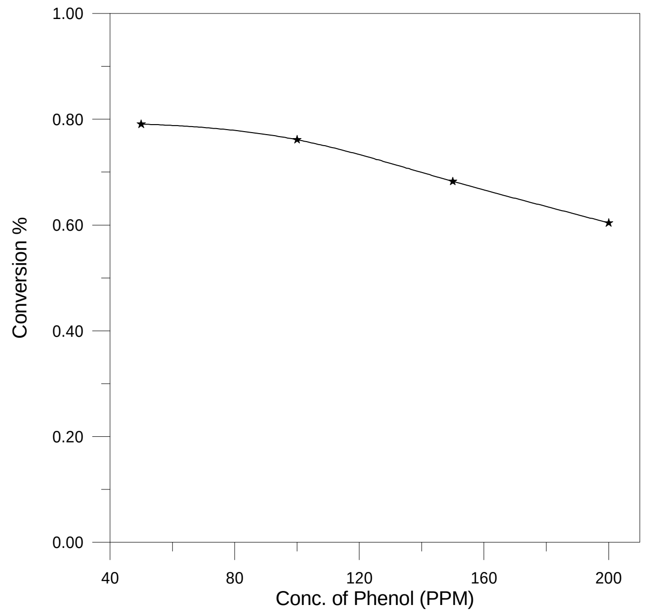

Fig .(3): The effect of Initial Concentration of Phenol on the conversion for 18^{o}C, pH=6 and 0.5g of NiO

3.4 Effect of pH

It is clearly shown in Figure 4 that the performance of system is dependent of pH and no significant effect was observed in the range of 6–8. Although, decreasing was observed in acidic and base pH (2 and 12), at pH=12 no significant reaction was indicated. Best results were obtained at neutral pH.

3.5 Effect of Temperature

To study the degradation pathway of phenol oxidation four experiments were conducted at different temperatures (18, 30, 40 and 50ºC), in the presence of 50 mg/l of phenol, 0.5g of NiO, and air.

As it can be seen in a previous work [9], the increase of the temperature leads to decrease of the reaction rates. The phenol oxidation profile Figure.(5) shows that even at the lower temperature (18°C), the catalytic oxidation process could still remove phenol after 1.5hours. However, the effect of the temperature on the phenol removal rates is not as significant.

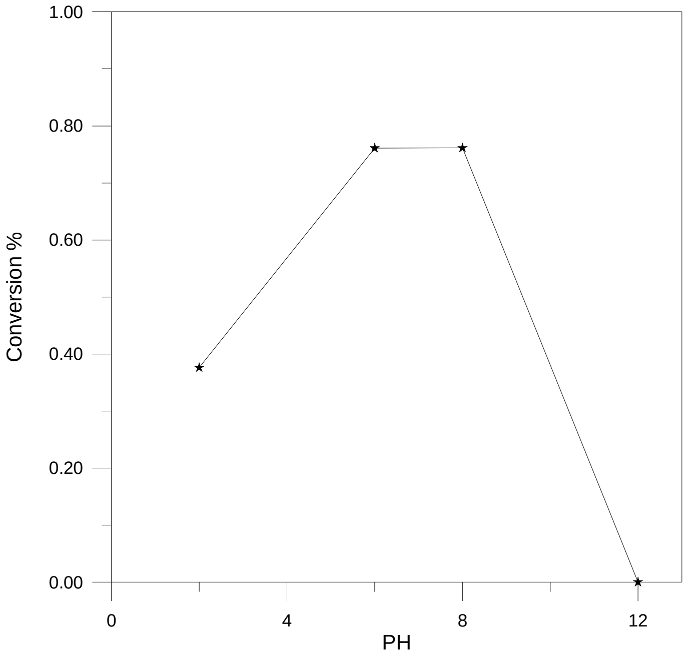

Fig. (4): The effect of pH on the conversion of phenol for 18^{o}C, and 0.5g of NiO

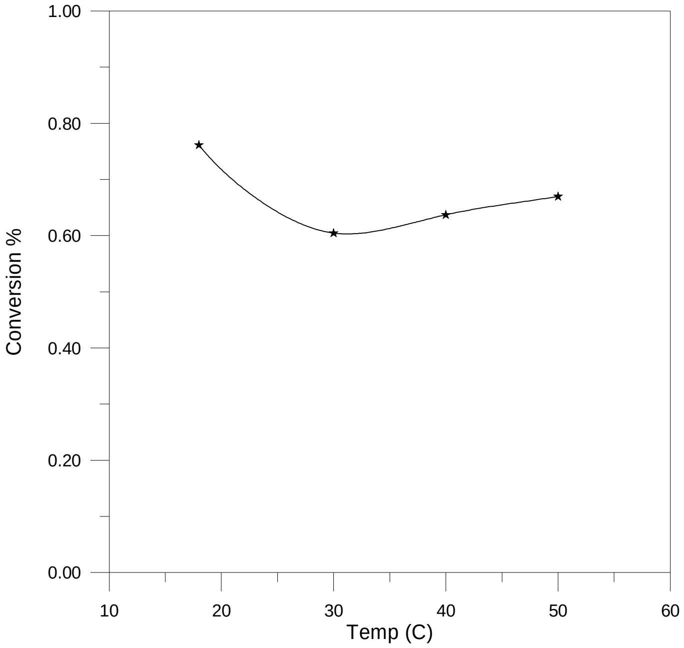

Fig. (5): The effect of Temperature on the conversion of phenol for pH=6 and 0.5g of NiO

4. Kinetic Modeling

4.1 Reaction Kinetics

The objectives of our kinetics analysis were to determine the reaction rate constant (k), its associated Arrhenius parameters, and the reaction orders for phenol (a), oxygen (b) for the power-law rate expression in Eq. 2:

$$rate = k\,[phenol]^a\,[O_2]^b \qquad ....(2)$$

When it was used as catalyst in the oxidation of phenol, exhibited high catalytic activity, as shown in Fig. 2. It was seen that phenol could be completely oxidized within 1.5 h at 25 °C in the coexisting system of catalyst. On the contrary, in the presence of single catalyst all evidenced that the partially oxidized aromatic product of phenol in our experiments was only p-benzoquinone, . It was inconsistent with the results obtained by some previous researchers [26] who showed that catechol and hydroquinone or o-benzoquinone and p-benzoquinone, as intermediate oxidized aromatic products of phenol, coexisted in the reaction systems as shown in **Figure .(6)**.

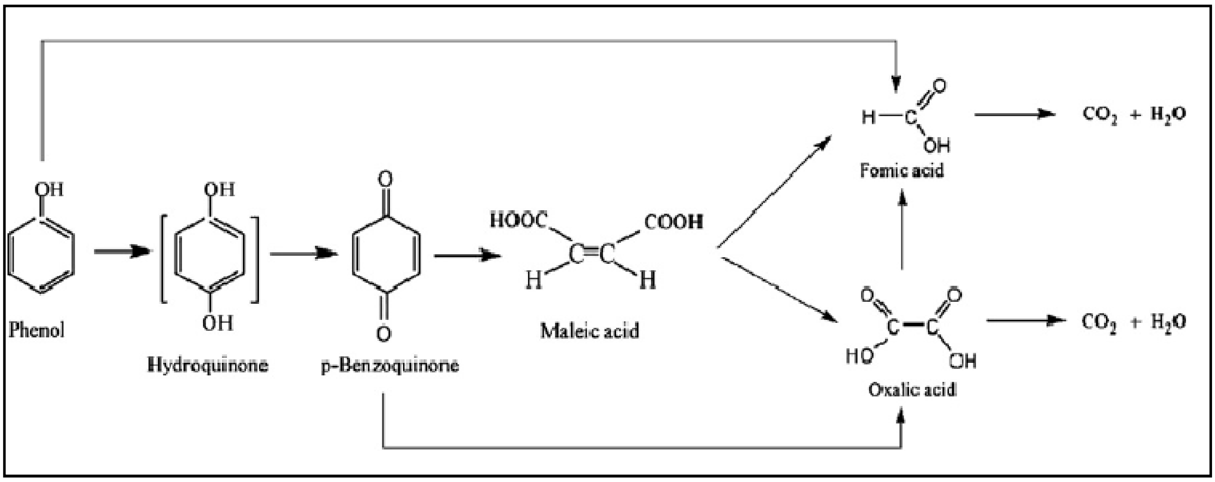

Fig. 6: The Mechanism of oxidation of Phenol with intermediates product [26]

Description of the above reaction would be:

$$C_6H_5OH \xrightarrow{+rO_2} Intermediat\ \mathrm{Pr}\, oduct \xrightarrow{+sO_2} 6CO_2 + 3H_2O$$

where *r* and **s** are stoichiometric coefficients with unspecified values. Thus, the presence of these intermediates and the multiple reaction pathways renders invalid the simple stoichiometric relation $[O_2] = [O_2]_0 - 7X[\mathrm{Phenol}]_0$, which describes the overall reaction.

$$C_6H_5OH + 7O_2 \longrightarrow 6CO_2 + 3H_2O$$

Additionally, all of the data used in the kinetics analysis were obtained from experiments that were conducted with a large excess of oxygen (>200% excess in all cases) so that the concentration of oxygen could be approximated as being roughly equal to its initial concentration.

The method to determine the reaction kinetic is the Eley-Rideal Mechanism; there are some assumptions to make the reaction model.

1- Phenol was adsorbed on the surface of catalyst and oxygen still in the gas phase.
2- The reaction is irreversible.
3- All intermediate products were converted to the CO_2 and H_2O.
4- The effect of mass transfer was neglected.
5- Isothermal operation.

Adsorption Rate

$$ph + s \rightleftharpoons ph.s$$

$$-r_{Aph} = k_A \left(P_{ph} C_v - \frac{C_{ph.s}}{Ke_A} \right) \qquad ......(3)$$

Where:

s:is the vacant site

$-r_{Aph}$ -rA=the rate of Adsorption

k_A=forward rate constant of adsorption

P_A=partial pressure of phenol

$\boldsymbol{C_v}$: The molar concentration of vacant sites

$\boldsymbol{C_{ph\bullet s}}$: Surface concentration of sites occupied by species ***ph*** (mol/g • cat)

Surface Reaction

$$ph.s + 7O_2 \uparrow \longrightarrow 6CO_2 \uparrow + 3H_2O \uparrow$$

$$-r_{sph} = k_s C_{ph.s} P_{O_2}^7 \qquad ....(4)$$

Site Balance

$$C_t = C_v + C_{ph\bullet s} \qquad ....(5)$$

Where

$\boldsymbol{C_t}$ (mol/g • cat) : Total molar concentration of active sites per unit mass of catalyst

We assume surface reaction is rate limiting step.

From equation 3: at equilibrium $-r_{Aph} / k_A \cong 0$,

$$\boldsymbol{C_{ph\bullet s}} = P_{ph} C_v \; Ke_A \qquad ....(6)$$

Sub. In eq. 4 and 5 and rearrange to give

$$-r_{sph} = k_s P_{ph} Ke_A P_{O_2}^7 \left(\frac{C_t}{1 + P_{ph} Ke_A} \right) \qquad ....(7)$$

Sub. k=$k_s Ke_A C_t$, eq.7 becomes:

$$-r_{sph} = k \left(\frac{P_{ph} P_{O_2}^7}{1 + P_{ph} Ke_A} \right) \qquad ....(8)$$

This is non-elementary equation described the catalytic oxidation of phenol. Equation (8) was solved using statistical package in comparison with experimental data. The parameters k and Ke_A in equation (8) were predicted as $1.1*10^{-3}$ (cm^3.liter/gcata.) and 4.9889 respectively and the correlation coefficient of the predicted equation is (R^2=0.99522). The results of equation derived above plotted in **Figure .(7)**.

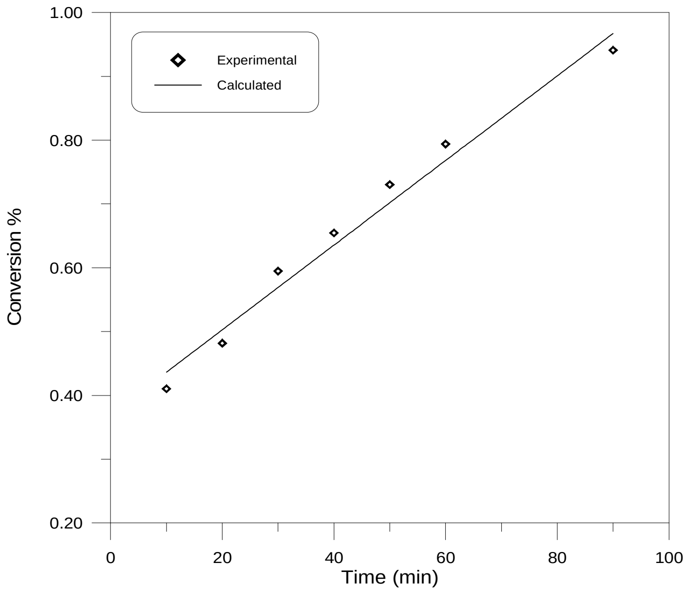

Fig. (7): Experimental and Calculated data for oxidation of phenol at 18°C, pH=6 and 0.5g of NiO

This demonstrate that the time required for phenol removal is less than that needed for phenol mineralization, showing clearly that phenol oxidation takes place in multiple steps and results in several byproducts rather than CO_2 an H_2O. It is obvious that the removal of phenol occurs much more quickly than the degradation of short-chain organic acids, which are formed from the phenol oxidation and are stable and refractory to further oxidation into CO_2 and H_2O as in others oxidation processes.

5. Conclusion

The results have indicated that oxidative degradation of phenol depended on phenol and also on the catalyst load. 76.1% conversion could be achieved with a catalyst load of 0.50 g/L. It was found that the oxidation could be carried out with atmospheric oxygen by shaking phenol solution with the catalyst. Optimization of the reaction conditions and other relevant considerations will require systematic experiments under various environmental conditions, which are being pursued. There is no oxidation reaction at increasing temperature and pH value. It is also proved in this research that phenol removal using this process follows the Eley-Rideal Mechanism. Moreover, results of mineralization and chloride ions studies showed that dechlorination was better accomplished but more time was required to completely mineralize phenol into H_2O and CO_2. It could be concluded that this process is a novel and effective for the degradation of phenol from aqueous phase and appears to be a promising technique for phenol remediation.

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