Study the Application of Ultrasonic Technology for Phenol Removal in Petroleum Industry

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ABSTRACT

In this study, the sonochemical degradation of phenol in water was investigated using two types of ultrasonic wave generators; 20 kHz ultrasonic processor and 40 kHz ultrasonic cleaner bath. Mineralization rates were determined as a function of phenol concentration, contact time, pH, power density, and type of ultrasonic generator. Results revealed that sonochemical degradation of the phenol conversion was enhanced at increased applied power densities and acidic conditions. At 10 mg/L initial concentration of phenol, pH 7, and applied power density of 3000 W/L, the maximum removal efficiency of phenol was 93% using ultrasonic processor at 2h contact time. Whereby, it was 87% using and ultrasonic cleaner bath at 16h contact time and 150 W/L power density. Kinetic models applied to the sonolysis of phenol was evaluated for the first-order, pseudo-first-order, second- order, and pseudo-second-order kinetic models. The experimental data fitted very well the first-order kinetic model.

Key words: ultrasonic, son chemical degradation, phenol, petroleum industry, wastewater

دراسة تطبيق تقنية الموجات فوق الصوتية لإزالة الفينول في الصناعة النفطية

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الخلاصة

في هذا البحث، تم دراسة إمكانية إزالة الفينول من المياه بتسليط الموجات فوق الصوتية بأستخدام نوعين من أجهزة توليد الموجات فوق الصوتية؛ الأول جهاز المعالج بتردد 20 كيلو هرتز والجهاز الثاني هو الحمام الحوضي وبتردد 40 كيلو هرتز. تم دراسة معدلات تحلل الفينول كدالة للتركيز الأولي للفينول , فترة التماس، الدالة الحامضية، ومقدار الطاقة المسلطة، إضافة إلى نوع الجهاز المولد للموجات فوق الصوتية. بينت النتائج إن معدل تحلل الفينول يرتفع بزيادة الطاقة المسلطة في الوسط الحامضي. عند تركيز أولي للفينول 10مقداره ملغم/ لتر ووسط متعادل الحامضية وعند طاقة 3000 واط/ لتر كانت أعلى كفاءة إزالة 93 % باستعمال جهاز المعالج خلال ساعتين . أما عند استخدام جهاز الحمام الحوضي ساعة وبتسليط طاقة مقدارها 150 واط/ لتر كانت الإزالة 87% خلال 16ساعة. كما وتم دراسة حركية تفاعلات تحلل الفينول بواسطة الموجات فوق الصوتية ولوحظ إن انسب موديل لوصف حركية التحلل بالموجات فوق الصوتية يتمثل بالموديل من الدرجة الأولى .

الكلمات الرئيسية: فوق الصوتية، التحلل الكيمياوي فوق الصوتي، فينول، الصناعة النفطية، المياه العادمة.

1. INTRODUCTION

Water pollution is the discharge of some undesirable materials into water in high amounts exceeds the allowable limits. In other words, water pollution is an issue that comes true by artificial effects, that constraint or prevents and that destroys ecological balance **,Abd.Razak, et al., 2013**. Many chemicals are released into the environment through waste streams. These chemicals are released by various industries mainly petroleum refineries and processing plants, pharmaceutical production, and petrochemical plants. Among many released hazardous chemicals, phenol is frequently found in effluent from refineries, chemical, and petrochemical industries **, Leili, et al., 2013**.

Treatment of industrial wastewater is a problem of major concern. Recently, stricter regulations are being imposed, which persevere on the need to develop and employ treatment technologies capable to deal with the hazardous pollutants in many industrial waste streams. Wastewaters containing phenols and other toxic petroleum derivatives need careful treatment before discharge into the receiving bodies of water. Biological treatments, activated carbon adsorption, incineration and chemical oxidation are the most widely used methods for treating synthetic organic compounds from industrial wastewaters including petroleum refinery wastewater **,Dìaz et al ., 2007 , Abdelwahab et al ., 2009 ,** and **Kulkarni** and **Kaware , 2013**.

Biological methods have little or no harmful effects on the environment, because this technique does not involve the use of harmful reagents. However, high concentration of phenol may cause declining of the process. Adsorption is a simple and efficient method to remove organics from wastewater. Activated carbon is the most widely used adsorbent due to its large specific surface area and predominant proportion of micro-pores. However, high regeneration cost and poor mechanical rigidity of activated carbon limit its wider applications. In addition, this technique as well solvent extraction do not degrade the synthetic organics but rather remove it from wastewater and pass it to another phase, which result in the formation of hazardous by products **, EI-Naas et al ., 2010.**

Advanced oxidation processes (AOPs) have appeared in recent decades as a viable alternative for the treatment of effluents containing toxic refractory organics. These processes are able to degrade a large number of organic compounds by reduction-oxidation and free-radical reactions to CO_2 and H_2O. Among these AOPs, the once that use ozone (O_3) , ultra-violet radiation (UV) , ozone combined UV, ozone with H_2O_2 , Hydrogen peroxide with UV , as well as Fenton and photo-Fenton processes , **Pham et al., 2009** and **Ricardo et al ., 2010.**

In recent years, considerable interest has been shown in the application of ultrasound power as a promising type of advanced oxidation process for the treatment of hazardous organic contaminants in water. The chemical consequences of high-intensity ultrasound do not arise from an interaction of acoustic waves and matter at a molecular or atomic level. Instead, in liquids irradiated with high-intensity ultrasound, acoustic cavitations (the formation, growth, and collapse of bubbles) provide the primary mechanism for sonochemical effects. During cavitations, bubble collapse produces intense local heating, high pressures, and very short lifetimes; these transient, localized hot spots drive high-energy chemical reactions. These hot spots have temperatures of ≈ 5000°C, pressures of about 1000 atmo, as well as heating and cooling rates above 10^{10} K/s **,Suslick and Price, 1999,** and **Ingole and Khedkar, 2012**. There are no additives introduced into the ultra-sonic system and no byproducts generated by ultrasonic technology. Therefore, there are no anticipated environmental concerns associated with this technology. In contrast to many other processes which are negatively affected when suspended solids of effluent increase, ultrasonic efficiency may even improve by increase of turbidity or suspended solids **,Mahvi, 2013**.

The aim of this study was to examine the application of ultrasound waves as a new clean technology for phenol destruction in aqueous solutions. Also, study and examine the suitable kinetic model that best describes the experimental results of the sonochemical degradation of phenol.

2. MATERIALS AND METHODS

2.1. Sonolysis Equipments

Stock solution of concentration 10 mg/L phenol was prepared by dissolving a purified grade phenol in double distilled water. Experimental solutions of the desired concentration were obtained by successive dilution.

The sonication experiments were carried out using two types of ultrasonic wave generators; ultrasonic processor and ultrasonic cleaner bath. Using ultrasonic processor type Sonics Vibracell VCX-750 operating at constant frequency of 20 kHz, sonication reactions were carried out using (300) mL Pyrex beaker **Fig. 1**, alternatively loaded with (50, 100, and 250) mL synthetic wastewater samples. This part of experimental work was performed at different power densities including 600, 1500 and 3000 W/L taking into consideration examining the degradation of contaminants under various pH conditions of 2, 5, 7, 9, and 11. The sonochemical degradation of phenol was evaluated using 5 different initial concentrations of phenol including 1, 2, 5, 8, and 10 mg/L.

Figure1. Ultrasonic processor.

Using ultrasonic cleaner bath Model VGT-1860 QT at a frequency of 40 kHz, sonochemical degradation of phenol was carried out in 50 mL-volumetric flasks loaded with phenol aqueous solution **Fig.2**. Effects of the applied power densities (50, 75, and 150 W/L), initial concentration of phenol (1, 2, 5, 8, and 10 mg/L), pH (2, 5, 7, 9, and 11), and contact time up to 24 h on the sonolysis of phenol were considered in this part of the experimental work. pH of solutions was adjusted by 0.1 M sulfuric acid (H_2SO_4) and 0.1 M sodium hydroxide (NaOH).

Figure2. Ultrasonic cleaner bath.

2.2. Analysis

Ultra Violet spectrophotometer (Model: T80 UV/VIS Spectrometer PG Instruments Ltd., Australia) was used to measure concentrations of phenol at wavelength (λ) of (270) nm. Solution pH was measured using a pH meter (Model: WTW, Inolab 720).

3. RESULTS AND DISCUSSION

3.1 Effect of Initial Concentrations and Contact Time

Sonochemical degradation of phenol was studied under various initial concentrations of phenol which were 1, 2, 5, 8, and 10 mg /L. The experiments were conducted using ultrasonic processor at pH 7, contact time 180 min, and power density 3000 W/L. As given in **Fig.3**, it is well observed that by increasing the initial concentrations of phenol from 1 to 10 mg /L, the sonochemical degradation decreased. This could be attributed to the fact that phenol is hydrophilic in nature. Phenol is moderately soluble compound with a solubility in aqueous solution of 83 g/L with a relatively low vapor pressure (4.60×10^{-4} atmo). These physiochemical properties preclude significant concentrations of phenol molecule diffusing into the vapor phase of the acoustic cavitation bubbles, so it remains in the bulk of the solution during cavitation. Most of the hydroxyl free radicals formed within the cavity during the sonication might be recombined before they attack phenol molecules in the bulk liquid **,Shawabkeh, et al., 2010**.

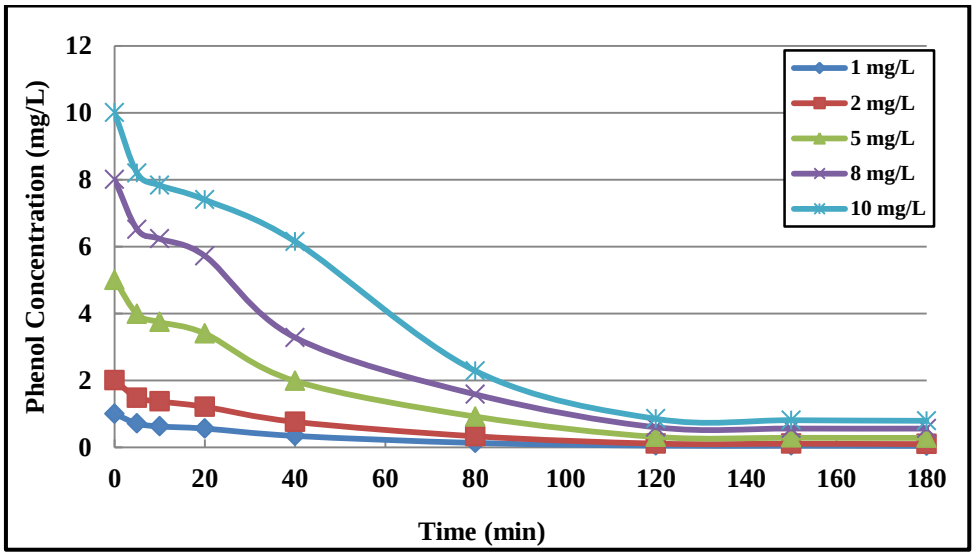

Figure 3. Profiles of phenol removal by ultrasonic processor at different initial concentrations.

3.2 Effect of pH

The pH of aqueous solutions is a primary parameter that affects and controls the sonochemical degradation process for organics sequestering from aqueous solution due to the influence of pH on the formation of the free radicals (OH^{o}), the major contributor to the sonolysis process. In this study, the effect of pH on phenol removal was studied at a pH range of 2.0 to 11.0 keeping their initial concentrations at 10 mg /L, power density 600 W/L, and contact time of 180 min. **Fig. 4** illustrates the effect of pH on the removal of phenol by sonolysis process.

The effect of pH on the sonolytic degradation of phenol compounds almost drops to zero at higher pH values, more specifically at pH value greater than the pKa value for the phenol compounds dissociation, **Tauber, et al., 2000**.

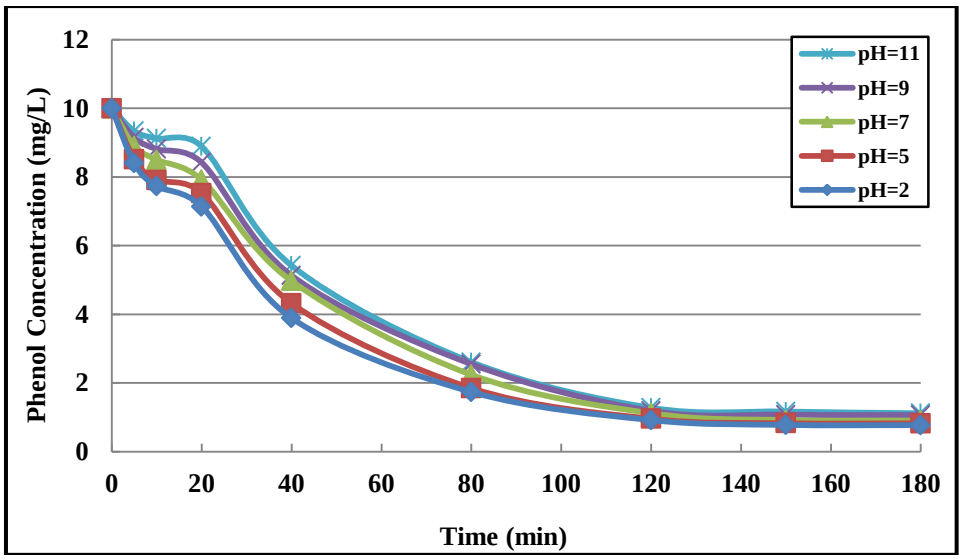

Figure4. Effect of pH on phenol removal using ultrasonic processor.

3.3 Effect of Power Density

The most important parameter for the application of ultrasonic waves is the power input. Increasing the ultrasonic power will increase the energy of cavitations, lower the threshold limit of cavitations, and enhance the quantity of the cavitation bubbles. The destruction of volatile compounds more likely occurs inside the cavitation bubbles thus the rate of sonochemical degradation should be related to the number of bubbles present if each bubble releases enough energy to ‘‘burn’’ the volatile pollutant **, Jiang, et al., 2002** and **Ye, et al., 2010**. In this study, a set of experiments were carried out to examine the effect of power density on sonochemical degradation of phenol at initial concentrations of 10 mg/L using the ultrasonic processor. Three different power density values were applied which were 600, 1500, and 3000 W/L. **Fig. 5** presents the effect of different power densities on the profiles of phenol removal at constant ultrasonic frequency of 20 kHz. However, as given in this Figure, a relatively limited increase of phenol sonolysis rate was observed with increasing the applied power.

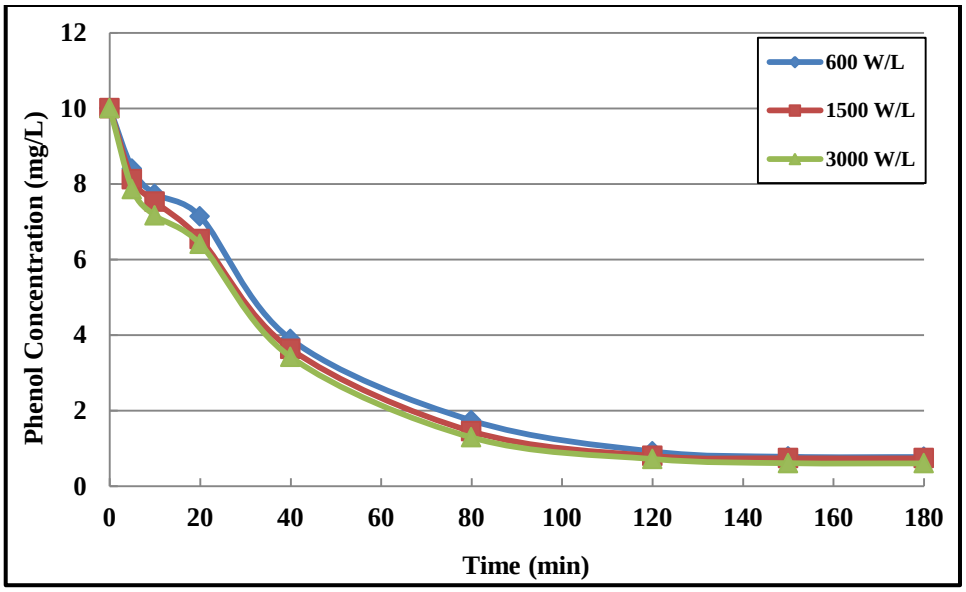

Figure 5. Effect of power density on phenol removal using ultrasonic processor at 20 kHz.

3.4 Effect of the Type of Ultrasonic Waves Generator

Additional sets of experiments were carried out to examine the efficiency of ultrasonic cleaner bath for phenol removal as an alternative type of ultrasound wave generator.

The effects of initial concentration and contact time, as well as power density on phenol sonochemical degradation were taken into consideration to evaluate the performance of the ultrasonic cleaner bath as shown in **Figs. 6** and **7.**

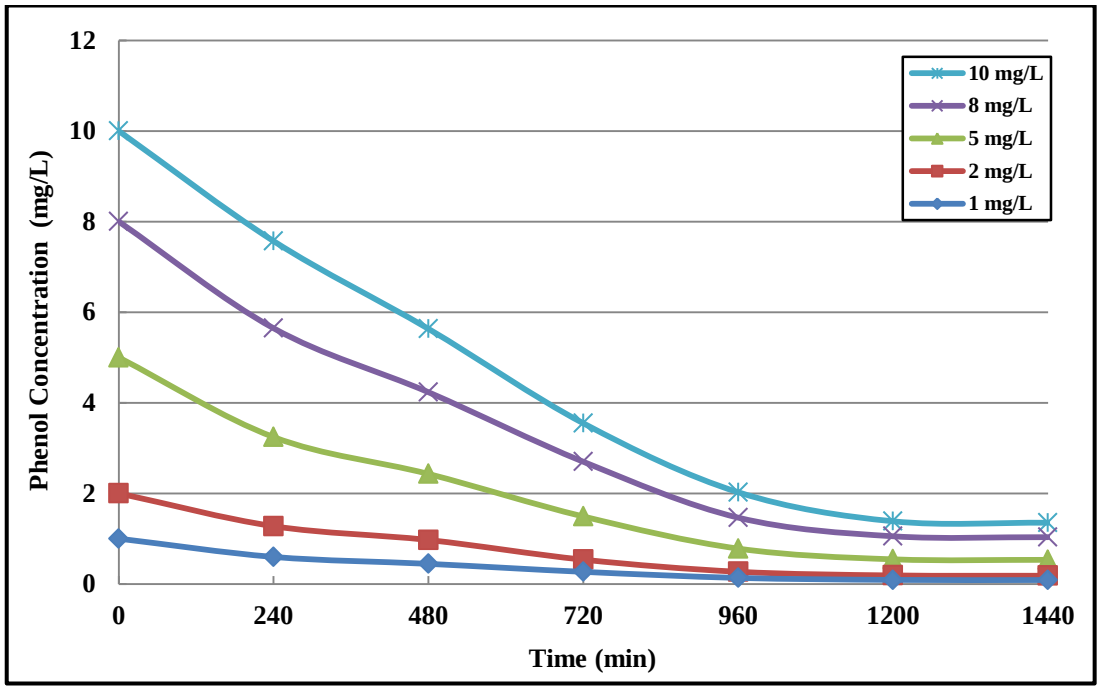

Figure 6. Phenol removal profiles by ultrasonic cleaner bath at 40 kHz.

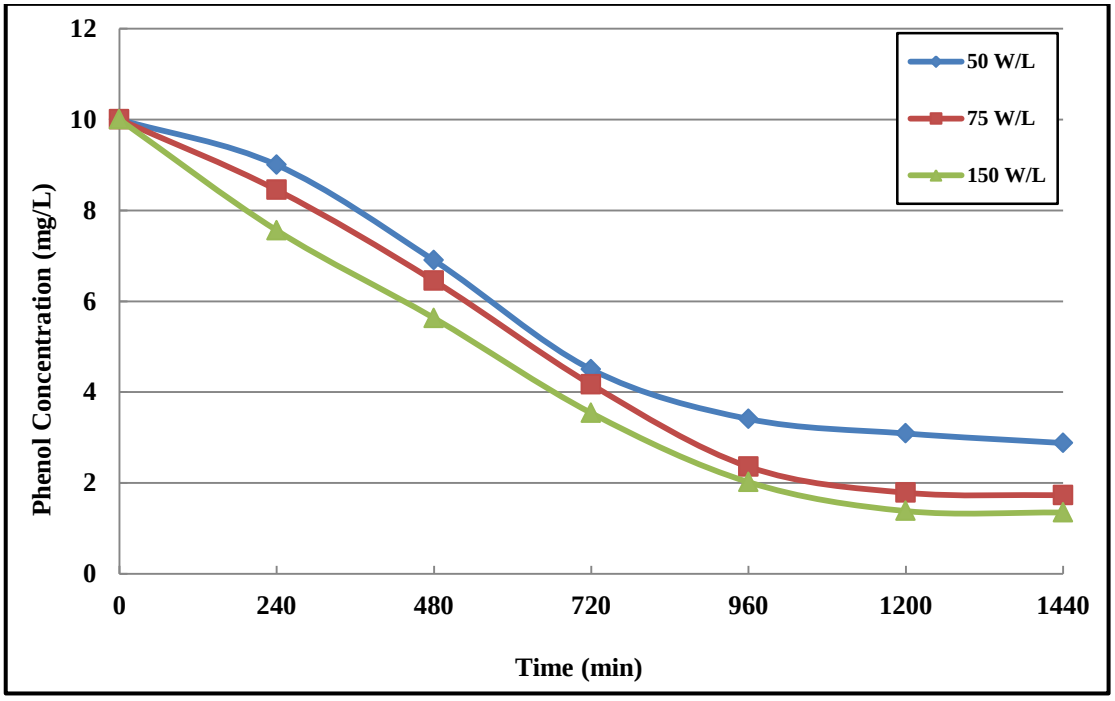

Figure 7. Effect of power density on phenol removal by ultrasound cleaner bath at 40 kHz.

3.5 Ultrasound Treatment of Actual Samples of Refinery Wastewater

A set of experiments were carried out using actual samples of refinery wastewater in order to investigate the reliability and effectiveness of the suggested approach of using ultrasonic treatment for phenol removal.

Samples of actual wastewater were freshly collected from the influent of Al-Daura petroleum refinery in Baghdad on a monthly basis for the purposes of the present study. **Fig. 8** illustrates the profile of phenol removal efficiency in real refinery wastewater. **Table 1** presents the quality of the actual samples of wastewater with respect to phenol and COD before and after the ultrasound treatment.

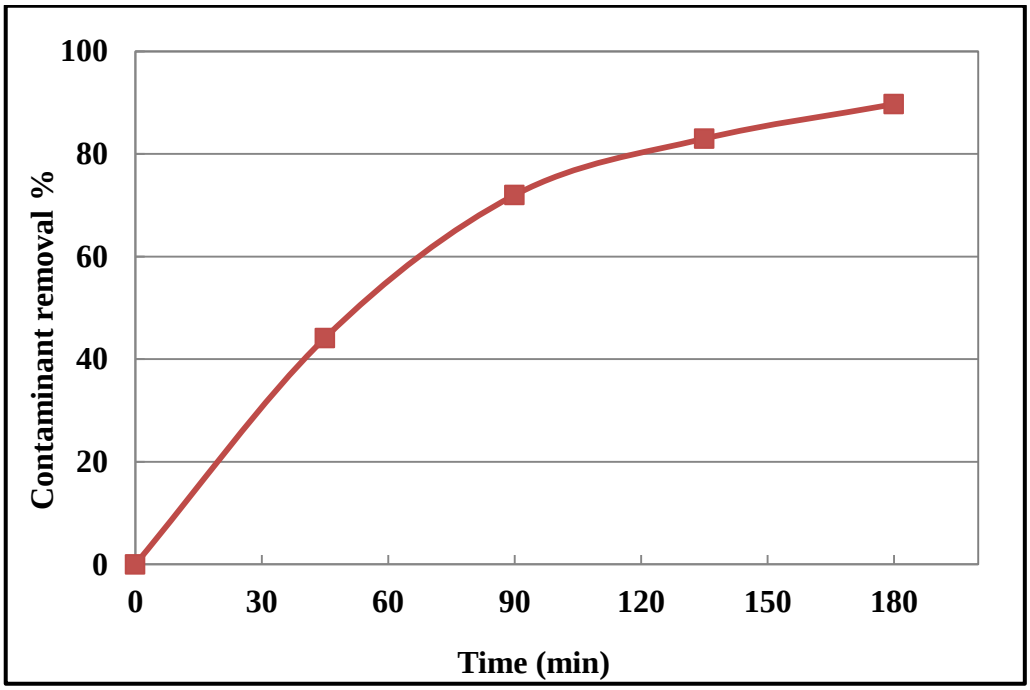

Figure 8. Profile of phenol removal in real samples of refinery wastewater at pH 7 and power density of 3000 W/L.

Table 1. Concentrations of phenol and COD in the actual samples wastewater before and after sonication treatment process

Constituent	Maximum Concentration (mg/L)		% removal
	Before ultrasonic treatment	After ultrasonic treatment	
COD	120	8.40	93
Phenol	7.50	0.53	93

3.6 Sonication Kinetics

Four well known kinetic models were applied in this study to test the experimental data in order to describe the behavior of sonochemical degradation process for further scale-up. The kinetic models are first order, pseudo-first order, second order, and pseudo-second order as follows:

1. First-order kinetics model

The experimental data were fitted according to simple first-order rate as shown in Eq. (1):

$$C_t = C_o e^{-k_1 t} \qquad (1)$$

Where:
C_o = the initial concentration of pollutant, mg/L
k_1 = first-order constant rate, min^{-1}
t = time, min
C_t = the concentration of pollutant at any time, mg/L

k_1 is estimated from the slope by plotting ln C_t versus time t, as shown in **Fig.9** for phenol removal efficiencies using ultrasonic processor.

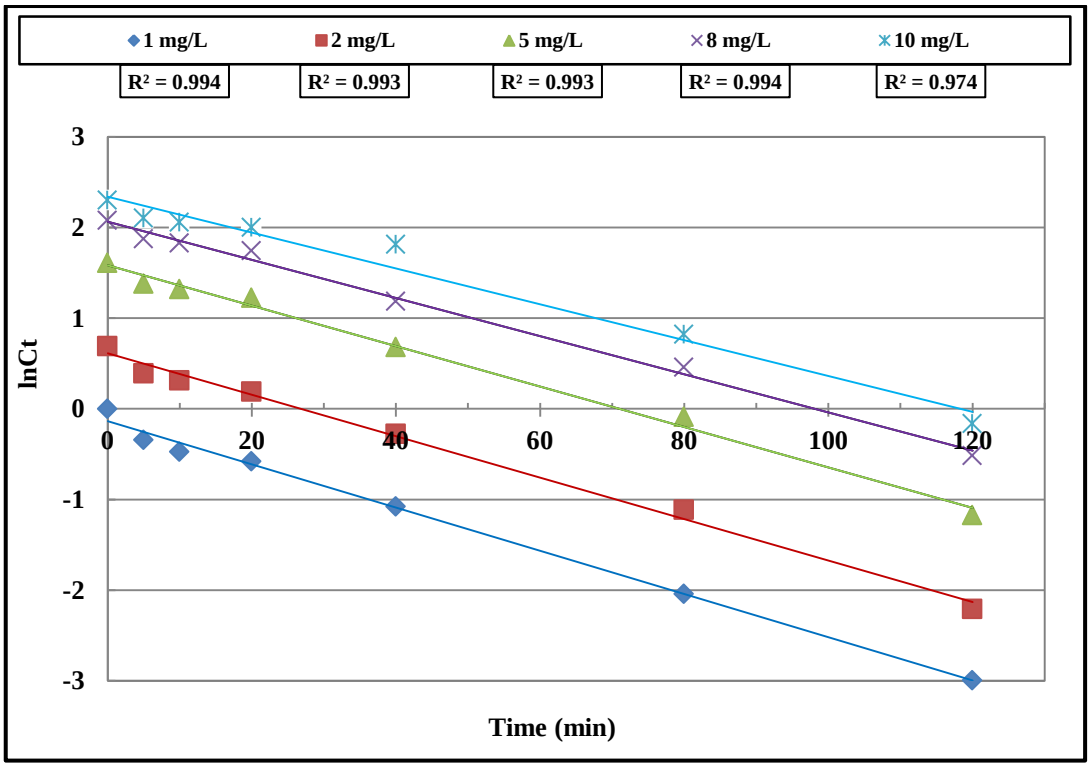

Figure 9. First-order kinetic of phenol degradation.

2 Pseudo-first-order kinetics

The second proposal is to assume a pseudo-first order kinetic model which is described by Eq. (2) as follows:

$$\frac{t}{C_t} = \frac{t}{C_e} + \frac{1}{k\ C_e^2} \qquad (2)$$

Where:

C_t = the concentration of pollutant at time t, mg/L

C_e = the equilibrium pollutant concentration, mg/L

t = time, min.

k = the pseudo-first-order rate constant, L/mg.min.

k is estimated from the slope after plotting $\ln(C_e-C_t)$ versus t, as shown in **Fig. 10**.

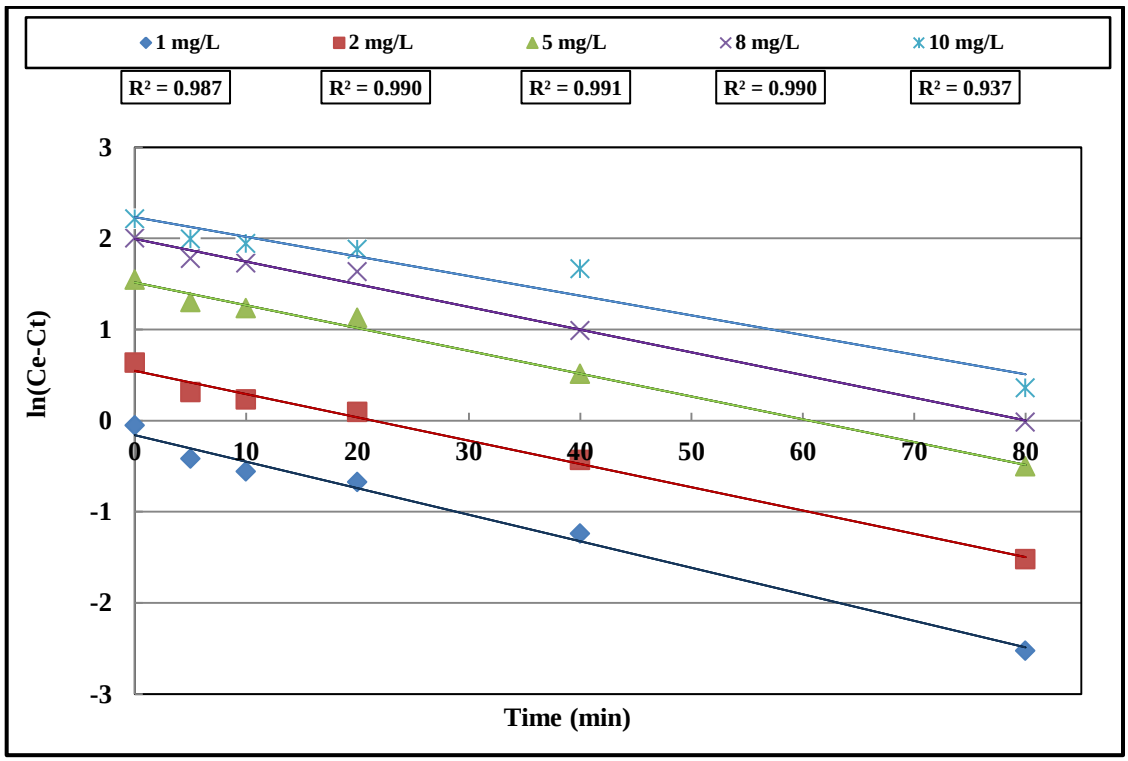

Figure 10. Pseudo-first-order kinetic of phenol degradation .

3 Second-order kinetics model

The proposal of having a second-order kinetic model will be examined here. The second-order kinetic equation model as in Eq. (3):

$$\frac{1}{C_t} = \frac{1}{C_0} + K\ t \qquad (3)$$

Where:

C_o = the initial pollutants concentration, mg/L
k = the second-order degradation rate constant, L/mg.min.
t = time, min.
k can be estimated from the slope after plotting 1/C versus t, as demonstrated in **Fig.11**.

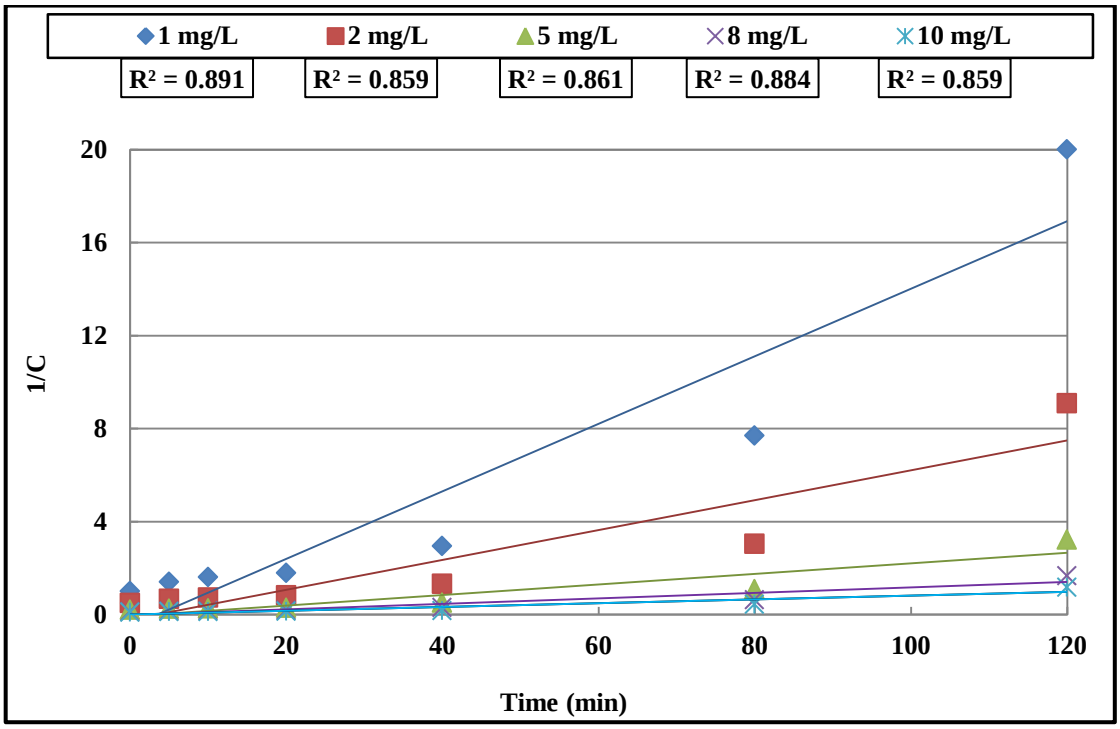

Figure 11. Second-order kinetic of phenol degradation.

4. Pseudo-second-order kinetics

The fourth proposal is to assume a pseudo-second order kinetic model which is described by Eq. (4) as follows:

$$\frac{t}{C_t} = \frac{t}{C_e} + \frac{1}{k\ C_e^{\,2}} \qquad (4)$$

Where:

C_e = the equilibrium pollutants concentration, mg/L
k = the pseudo-second-order degradation rate constant, L/mg.min.
t = time, min.
C_t = the concentration of pollutant at time t, mg/L
k can be estimated from the slope after plotting t/C_t versus t as shown in **Fig. 12**.

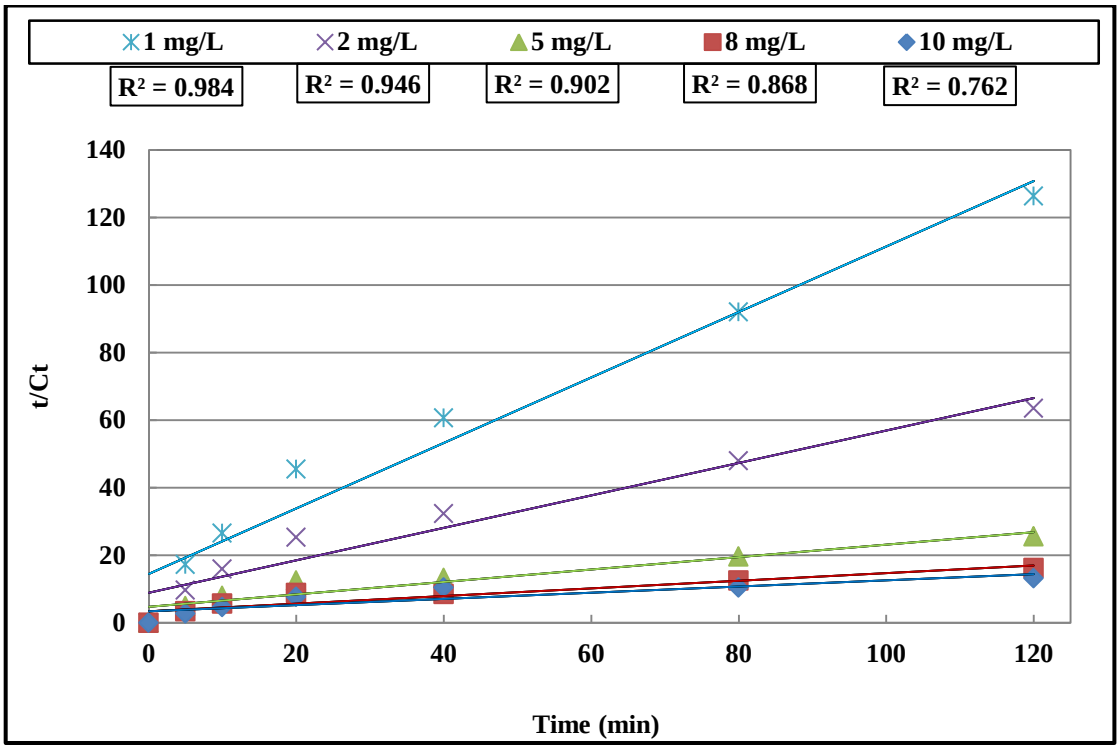

Figure 12. Pseudo-second-order kinetic of phenol degradation.

Table 1. summarizes the correlation coefficients of the kinetic study of ultrasonic process for phenol sonochemical degradation.
Fig.13 summarizes the effect of initial concentrations on degradation rate constants for phenol.

Table 1. Correlation coefficients (R^2) of phenol kinetic model.

Type of Kinetic model	Initial Concentration (mg/L)				
	1	2	5	8	10
First-order	0.994	0.993	0.993	0.995	0.974
Pseudo-first-order	0.987	0.990	0.991	0.990	0.937
Second-order	0.891	0.859	0.861	0.884	0.859
Pseudo-second-order	0.984	0. 946	0.902	0.868	0.762

The sonication kinetic study indicated that the degradation kinetics of phenol follows the first-order kinetics with correlation coefficients up to 0.995.

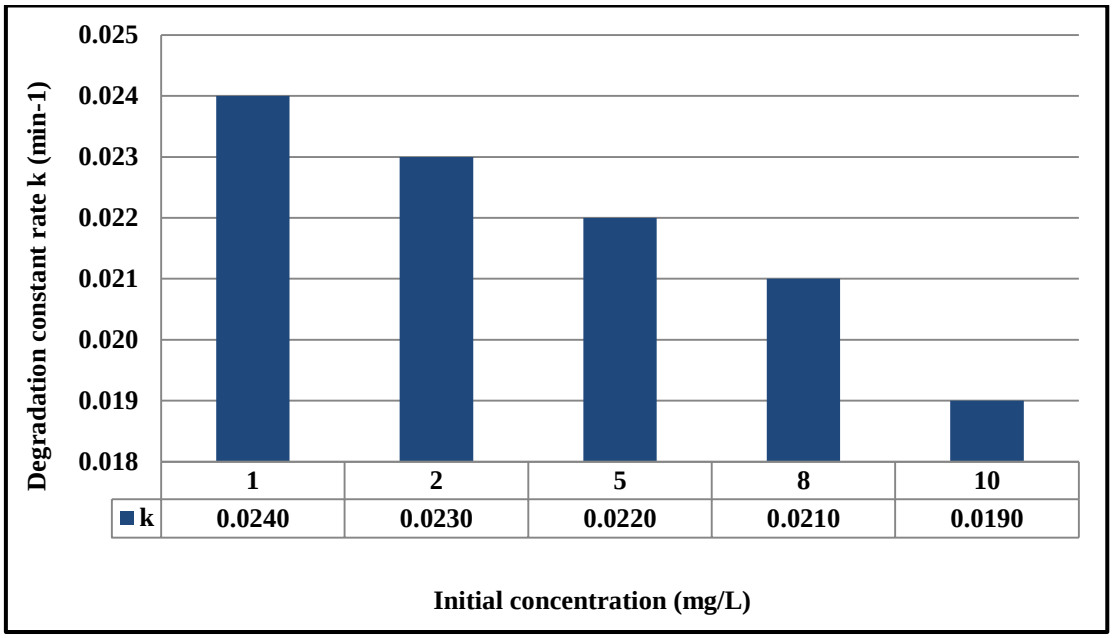

Figure 13. Effect of initial concentrations on the degradation rate constants of phenol for the first order kinetic model .

From **Fig. 13**, it is evident that the sonochemical degradation rate depends on the initial concentration of the phenol. Since the life time of hydroxyl radicals is very short (only a few nanoseconds), they can only react at or near the location where they are formed. A low phenol concentration logically the percentage of reduction in pollutant concentration was enhanced, comparing with high concentration at the same time, leading to an increase in the degradation rate constant.

4. CONCLUSSIONS

In this study, the maximum removal efficiencies were 93 and 87% using ultrasonic processor and ultrasonic cleaner bath, respectively at pH 7, 10 mg/L initial concentration of phenol, applied power densities of 3000 W/L for ultrasonic processor and 150 W/L for ultrasonic cleaner bath. Results revealed that equilibration times for sonolysis of phenol were achieved at 2 and 16 h for ultrasound processor and ultrasound cleaner bath.

Results showed that the removal efficiencies of phenol increased with increasing power density up to 93% using 20 kHz ultrasonic processor at pH 7 and power density of 3000 W/L. Similar behavior was observed using 40 kHz ultrasonic cleaner bath. However, the removal effeciency of phenol using the ultrasonic cleaner bath was 87% at pH 7 and power density of 150 W/L. Kinetic study revealed that the sonochemical degradation rate increased with decreasing the initial concentrations of phenol.

This study demonstrated that the phenol sonochemical degradation can be described by first-order model with R^2 of 0.995 using 20 kHz ultrasound processor.

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