FULL LENGTH ARTICLE

Phenol degradation by advanced Fenton process in combination with ultrasonic irradiation


Department of Petrochemicals, Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt

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Abstract In this study, a successful degradation of phenol was achieved by means of coupling nano-sized zero-valent iron (NZVI), H$_2$O$_2$ and 20 kHz ultrasound irradiation. The effect of H$_2$O$_2$ concentration, initial pH, ultrasonic irradiation time and NZVI addition on the degradation efficiency was investigated and the kinetics of the process was discussed. The results showed that the degradation rate increased by increasing the H$_2$O$_2$ concentration and the irradiation time but decreased with the increase of the initial pH value. These results clearly indicate that the degradation of phenol is intensified in the presence of NZVI and H$_2$O$_2$, which can be attributed to enhanced production of •OH radicals in the system. The degradation rate in the presence of NZVI was faster than in its absence. Thus, an appropriate selection of operating conditions will lead to an economical and highly efficient technology with eventual large-scale commercial applications for the degradation of organic pollutants in aqueous effluents.

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1. Introduction

Aromatic compounds such as phenol and its derivatives are persistent in the environment and are a potential hazard to human health and to the environment. These aromatic compounds are prevalent in industrial effluents and are major sources of water pollution. Traditional methods for removal of organic pollutants from wastewater such as ultrafiltration, extraction and incineration have their own limitations. Recently, there has been some interest in the use of ultrasound for water treatment. A large number of studies have been reported on the sonodegradation of organic pollutants in water [1–4]. As phenol is a very stable compound, decomposed mostly by the attack of hydroxyl radical, the rate of sonodegradation of phenol is relatively low. In the literature, there are some reports of this kind of combination with or without an additional oxidant to the solution [5–10]. Ultrasound assisted oxidation of phenol as a model compound is successfully harnessed in the presence of various heterogeneous catalysts such as zero-valent iron, and therefore attracts an increased attention as an effective, inexpensive and reliable method to decompose phenol in aqueous solutions [11–13]. Zero-valent iron (ZVI) has drawn great attention as an inexpensive and environmentally friendly strong reducing agent. The advanced Fenton process (AFP), which utilizes ZVI, has been studied as a potential technique to degrade different pollutants in wastewater [14]. Successful mineralization of phenol
was achieved by means of coupling ZVI particles, hydrogen peroxide and a short input of ultrasonic irradiation. This short sono-advanced Fenton process provided a better performance of ZVI in a subsequent silent degradation stage, which involves neither extra cost of energy nor additional oxidant [15]. Moreover, Bremner et al. [16,17] have reported the degradation of organic compounds using ultrasound combined with the Fe(0)/H₂O₂ system, although in these cases degradation had always been examined in the presence of excess hydrogen peroxide.

The present work describes phenol degradation studies by AFP using NZVI as a catalyst in conjunction with H₂O₂ and 20 kHz ultrasound irradiation. Degradation effectiveness of NZVI is investigated. The effect of H₂O₂ concentration, initial pH, ultrasonic irradiation time and NZVI addition on the degradation efficiency is investigated, and the kinetics of the process is discussed.

2. Materials and methods

2.1. Reagents

Phenol (99%) was obtained from Sigma–Aldrich, and hydrogen peroxide (30% W/W) was purchased from Fluka (USA). NaBH₄ was obtained from Sigma–Aldrich, FeCl₃·6H₂O and Sodium hydroxide (96%), were purchased from ADWIC, Cairo, Egypt. Sodium hydroxide (96%), were purchased from ADWIC, Cairo, Egypt. Sodium hydroxide (96%), were purchased from ADWIC, Cairo, Egypt.

2.1.1. Synthesis of Fe₀ nanoparticles

Fe₀ nanoparticles were synthesized by the reduction of ferric chloride with sodium borohydride using the method described by Wang and Zhang, 1997 [18]. 1:1 volume ratio of NaBH₄ (0.2 M) and FeCl₃·6H₂O solution (0.05 M) were vigorously mixed in a flask reactor for 30 min. Excessive borohydride (0.2 M) was applied to accelerate the synthesis and ensure uniform growth of iron crystals. A black precipitate of Fe₀ was obtained after addition of NaBH₄ according to Eq. (1) NZVI was filtrated and washed several times with deionized water to get rid of excessive borohydride. NZVI was dried by N₂ gas and was preserved from the oxidation by maintaining a thin layer of ethanol on the surface of NZVI.

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^{0} + 3H_2BO_3^- + 12H^+ + 6H_2$$  (1)

2.2. Experimental procedures

Sono-advanced Fenton process (Sono-AFP) reactions were performed in a glass reaction vessel with thin and indented bottom for ensuring efficient energy transmission using a commercial sonicator (VC-750, Sonics and Materials, Inc.) equipped with a titanium probe with 13 mm diameter, capable of operating continuously at a fixed frequency of 20 kHz with a variable electric output power up to 125 W, by dispersing 0.1, 0.3, 0.5, 0.7, 1 gm of the catalyst into 50 ml solution of 25 ppm phenol aqueous solution, followed by shaking for 15 min. to ensure a proper dispersion of the catalyst. The reactor was immersed in a water bath adjusted at 11 °C, with the help of an external cooling device, which was then elevated to 28 °C within 10 min. Thus, degradation of phenol was initiated by the rapid addition of the oxidizing agent (10, 20, 30, 40, 50 mM of H₂O₂) to the reactor and immediately turning on the ultrasonic for interval times (10, 20, 30, 40, 50, 60) min. Solution acidity was also investigated in detail by varying the solution pH value from 3.0 to 11.0 while keeping the tip of the titanium probe of the ultrasonic apparatus (2 cm) below the surface of the solution during sonication. Eventually, 20 ml aliquots of the reaction solution were sampled, immediately centrifuged at 14,000 rpm for 15 min. Using EBA-21 centrifuge, Hettich-Germany, catalysts were removed to make the solution ready for HPLC analysis. Samples were analyzed by an HPLC system equipped with a pump Waters 515 a sample injector and Waters 2489 UV–Visible detector. Column Waters (X Bridge™ C18 5 μm 4.6×250 mm) was used. A guard column was fitted before the analytical one. The mobile phase was acetonitrile/water of 30:70 with a flow rate equal to 1 ml/min.

2.3. Characterizations of the samples

In order to characterize the NZVI, several techniques were used. X-ray diffraction patterns were recorded in the 2θ range from 4° to 80°, using Philips Powder Diffractometer with Cu Kα radiation which is operated at 40 kV at scanning speed of 2°/min⁻¹. TEM images were obtained by using a Jeol 2010 named DV 300W1 system operating at 130 kV. The sample was ultrasonically suspended and deposited on a carbon film supported on a copper grid. TEM images were used to determine the particle size.

3. Results and discussion

3.1. XRD and TEM of nano-sized ZVI

Fig. 1 gives the XRD pattern of NZVI. The average size (D) of the particles can be determined according to the Scherrer equation: 

$$D = k\lambda / (β \cos θ)$$

Where k is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.154 nm, β is the full width at half maximum and θ is the half diffraction angle (18.14°). The calculated result indicates that the average size of NZVI is about 33.6 nm.

Transmission electron microscopy (TEM) was used to describe the size and shape of NZVI. From Fig. 2 it was found that the NZVI was at nanometer scale with the size around 20–50 nm. Hence, the crystallite size calculated by Scherrer equation (33.6 nm) was in a good agreement with the size of the particles observed by TEM.

3.2. Degradation using ultrasound solely

Initially, the extent of degradation was investigated using ultrasound induced acoustic cavitation phenomena at 25 mg/L initial concentration of the phenol pollutant and the obtained results have been shown in Fig. 3. It can be seen from the figure that the rate of degradation is 20% after 60 min. and this indicates that the sonolysis of aqueous solutions generates highly reactive hydroxyl radical (OH⁻) [19]. Applying sonolysis alone is not capable of full degradation of phenol, as shown in Fig. 3 this is because phenol is an extremely stable contaminant that can only be destroyed by a vicious radical attack. Therefore, to reach higher removal efficiency, the combination of the oxidants and ultrasound irradiation must be applied.
3.3. Degradation using a combination of ultrasound and hydrogen peroxide

The controlling mechanism of sonochemical degradation of phenol is the production of free radicals and their subsequent attack on the pollutant species. Considering this mechanism and knowing that hydrogen peroxide also dissociates in the presence of ultrasound giving hydroxyl radicals, a combination of ultrasound and hydrogen peroxide was investigated as a treatment strategy. On the sonolytic degradation of phenol, experiments were carried out with an initial phenol concentration of 25 mg/L and pH 7.0 by varying H$_2$O$_2$ concentration in the range 10–50 mM, Fig. 4. It can be observed from this figure that the rate of phenol degradation is substantially enhanced by the addition of H$_2$O$_2$ to the ultrasound system. The extent of degradation increased from 30% at 10 mM H$_2$O$_2$ to 40% at
30 mM after 60 min of sonication. However, the degradation decreased to 15% as the H₂O₂ increased to 60 mM. The addition of hydrogen peroxide enhances the degradation rate of phenol, due to the additional free radical generation, it can be concluded that the controlling mechanism of phenol degradation is the free radical attack. It should be noted here that the use of hydrogen peroxide in combination with ultrasonic irradiation resulted in an enhanced extent of degradation. On the one hand, hydrogen peroxide acts as a source of free radicals by the dissociation process, but it also acts at high concentration as a scavenger of the generated free radicals, which indeed retard the degradation of organic compounds by consuming more H₂O₂. This would indicate that when the system contains no other organic substances that can be oxidized by radical species, the radical species generated via the decomposition of H₂O₂ would be finally terminated to produce molecular oxygen and water [20–22] as follows:

\[ \text{OH}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]  \hspace{1cm} (2)

\[ \text{HO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^+ + \text{H}_2\text{O} + \text{O}_2 \]  \hspace{1cm} (3)

\[ \text{OH}^+ + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  \hspace{1cm} (4)

Similar trends have been observed in the literature for degradation of 2,4-dinitrophenol where H₂O₂ concentration was varied from 100 to 800 mg/L [23] and for phenol where H₂O₂ concentration was varied from 1 to 5 g/L [24]. Yalfani et al. reported that formic acid could also interact with H₂O₂ leading to better formation of hydroxyl radical for degradation of phenol by Fenton’s reaction [25]. Our results also suggest that the concentration of hydrogen peroxide must be kept at optimum levels in order to achieve high phenol decomposition efficiency.

3.4. Influence of ultrasound and the NZVI on the oxidative degradation of phenol (US + advanced Fenton process)

The extent of degradation was higher in the case of AFP as compared to the conventional Fenton process at equivalent loadings. Ultrasound in combination with AFP yielded more degradation than ultrasound combined with H₂O₂ and about 10% more degradation than ultrasound combined with conventional Fenton process [26]. As shown in Fig. 5, the obtained results reveal that maximum degradation of 75% was obtained at 1 g/L of NZVI dosage and 30 mM H₂O₂ after 60 min. The mechanism proposed by Weiss, 1952, for the decomposition at metal surfaces, is thought to be applicable for metal oxides [27]. Fe⁰ is corroded and gets converted to Fe²⁺ after that the mechanism is similar to the conventional Fenton process [26]. The different radical reactions taking part in the process are as follows:

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]  \hspace{1cm} (5)

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}_2^- \]  \hspace{1cm} (6)

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe} + \text{O}_2\text{H}_2^+ + \text{H}^+ \]  \hspace{1cm} (7)

\[ \text{Fe} - \text{O}_2\text{H}_2^+ \rightarrow \text{Fe}^{2+} + \text{HO}_2^- \]  \hspace{1cm} (8)

3.5. Influence of NZVI addition amount on the sonocatalytic degradation of phenol

The influence of the addition amount of NZVI on the sonocatalytic degradation efficiency of phenol is shown in Fig. 6. The experiments performed with different addition amounts showed that the sonocatalytic degradation efficiency of phenol increases with the increase of NZVI powder from 0.1 up to 1 g/L. The degradation efficiency of phenol reached up to 75% for 1 g/L NZVI as the number of active sites on the surface of NZVI increased which also enhance the adsorption of phenol on the surface of NZVI. Therefore, the degradation of phenol depends on the amount of NZVI.

3.6. Influence of solution acidity on sonocatalytic degradation of phenol

As well known, the chemical forms of many organic pollutants in aqueous solution and the surface properties of NZVI particles both depend on the solution pH value [28]. Here, the influence of varying the solution pH value from 3.0 to 11.0 on the sonocatalytic degradation of phenol was studied and the results are shown in Fig. 7. In general, the point of zero charge (PZC) of NZVI is about pH 8. Above these pH values, the surfaces of NZVI particles are negatively charged, while below these pH values they are positively charged. Hence, when the solution pH value is below the PZC, phenol anions should
be adsorbed on the surfaces of NZVI particles easily. It can be presumed that the degradation reactions can be accelerated under acidic conditions. By contraries, under strong alkaline condition, because of the repulsion force from the negatively charged surface, phenol anions in aqueous solution are mainly degraded through radical (\(\cdot\)OH) oxidation, which is a slow-motion degradation process.

### 3.7. Kinetic study

Prior to any kinetic studies, the effect of heat and mass transfer limitations during the oxidation process has to be established. The strong dependence between the conversion rate and the rate of ultrasonic irradiation is studied. Thus, the resistance to the mass transfer must have been negligible between the liquid bulk of the reactant and the outer surface of the catalyst particles [29]. Moreover, applying the ultrasound decreased both, the heat and mass transfer limitations due to the physical effects induced by cavitation [30]. The slope of a linear plot of \(\ln(C/C_0)\) versus time gives rate constant without catalyst Fig. 8. The reaction rate constants \(k(\text{min}^{-1})\) are given in Table 1. It is evident from Table 1 that in the presence of 30 mM H\(_2\)O\(_2\) and 1 g/L of NZVI the rate constant is much higher than the rate constant without catalyst. It was found that the reaction rate constant of phenol oxidation increased with increasing the catalyst amount in the presence of H\(_2\)O\(_2\) as shown in Fig. 9. This is attributed to the decrease in mass transfer in the presence of the catalyst. The calculated values of first order rate constants of phenol degradation are given in Table 1, which are consistent with previous studies [31].

### 4. Conclusions

The present work has clearly established the utility of using a combination of ultrasound induced cavitation reactors and advanced Fenton process for degradation of phenol at pilot scale operation. Advanced Fenton process is more efficient in degradation of pollutants than conventional Fenton process, which is attributed to the fact that the presence of solid
particles enhances the cavitational activity. Degradation efficiency of phenol increased with the increase of ultrasonic irradiation time, catalyst dosage and decreased with the increase of solution acidity and H₂O₂ concentration. In addition, the calculated values of first order rate constants of phenol degradation are given from the degradation ratio. The data presented here add useful information in terms of scale up strategies for large scale operation of the hybrid treatment schemes for industrial wastewater.

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References