Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.982197

57 (2016) 2104–2112
January

Taylor & Francis
Taylor & Francis Group

Sonocatalytic degradation of phenol catalyzed by nano-sized zero valent Cu and Ni

F.Z. Yehia, Gh. Eshaq*, A.M. Rabie, A.H. Mady, A.E. ElMetwally

Department of Petrochemicals, Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt, Tel. +20 1 001403715; email: omy432@hotmail.com (F.Z. Yehia), Tel. +20 2 22747847; email: ghadaamer2002@yahoo.com (Gh. Eshaq), Tel. +20 1 228289661; email: abdo3040@yahoo.com (A.M. Rabie), Tel. +20 1 221004221; email: amr_mady@yahoo.com (A.H. Mady), Tel. +20 1 115025588; email: ahmed_ezzatt@msn.com (A.E. ElMetwally)

Received 28 May 2014; Accepted 23 October 2014

ABSTRACT

In this study, a successful degradation of phenol was achieved using nanosized zero-valent copper (NZVC) or nanosized zero-valent nickel (NZVN) in combination with H_2O_2 and 20 kHz ultrasound irradiation. The effect of H_2O_2 concentration, initial pH, catalyst amount, and ultrasonic irradiation time on the degradation efficiency was investigated, and the reaction kinetics was discussed. The results showed that the degradation extent increases with increasing catalyst amount and irradiation time, but decreases with increasing initial pH value. These results also revealed that the degradation of phenol is intensified in the presence of NZVC or NZVN and H_2O_2, which can be attributed to the enhanced production of $^{\cdot}OH$ radicals in the system. 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.

Keywords: Ultrasound; Phenol; Advanced Fenton process; Heterogeneous Fenton; Zero-valent metals

1. Introduction

Phenol is a common and an important pollutant as it is found in a variety of effluent streams from chemical industries (resins, plastics, textiles, pulp and paper, coal conversion, etc.) and is often used as a model pollutant in wastewater remediation studies [1]. Conventional chemical, physical, and biological treatments, such as adsorption using activated carbon particles and fibers or air stripping, have been used for "dephenolization" of industrial wastewater [2]. Recently, chemical treatment methods, based on the generation of hydroxyl radicals, known as advanced oxidation processes (AOPs), have been applied for pollutant degradation, due to the high oxidative power of the OH radical. The most widely studied AOPs include; heterogeneous photocatalytic oxidation [3], treatment with ozone [4], H_2O_2/UV systems [5], Fenton [6] and modified Fenton-type reactions [7].

In the last decades, several studies have focused on the use of ultrasound for the degradation of phenol and its byproducts [8]. Nucleation, growth, and finally implosion of the cavities generated by ultrasound irradiation lead to extremely high local conditions of temperature and pressure which allow the formation of reactive radicals, such as $H^{\cdot}$, $HO^{\cdot}$, and $O_2^{\cdot-}$, as well as

---

*Corresponding author.

the homolytic splitting of pollutant compounds [9–11]. However, ultrasound alone does not produce sufficient oxidizing species from water to carry out degradation. So, often it is utilized along with Fenton reactions (Fenton and Photo-Fenton) [12]. The application of Fenton-like system in combination with an ultrasound system has been of most interest. Since, the reaction between H_2O_2 and (either homogeneous or heterogeneous) Fenton-type catalysts referred to as a Fenton-like process is known to produce hydroxyl radicals capable of oxidizing a wide range of organic compounds. Fenton reagent (Fe^{2+}/H_2O_2) has also been widely studied. However, the use of stoichiometric quantities of ferrous ions is the major drawback of the traditional Fenton process, and so alternatives such as advanced Fenton process (AFP) which utilize zero-valent iron (ZVI) as a catalyst have been successfully applied [13,14]. The advantage of using a heterogeneous system is the ease of catalyst removal by filtration. Moreover, ultrasonic irradiation generates benefits in heterogeneous catalytic systems by decreasing mass transfer limitations and fragmentation of catalyst into small particles that provide a higher surface area [15]. ZVI has been applied due to the effectiveness, low cost, and benign environmental impact of the *in situ* remediation of groundwater. Over the last decade, several studies have demonstrated that ZVI effectively reduces the concentration of several organic and inorganic pollutants [16,17]. It has been reported that the combination of ultrasound with ZVI is a good alternative to enhance the oxidative capacity of ZVI due to the synergistic mechanism obtained with the combined system [18–20]. AFP using ZVI as a catalyst has been studied as a potential technique to degrade different pollutants in wastewater [21]. Moreover, Chakinala et al. [22] and Bremner et al. [23] have reported the degradation of organic compounds using ultrasound combined with the Fe^0/H_2O_2 system, although in these cases degradation had always been examined in the presence of excess hydrogen peroxide. Recently, the use of zero-valent metals (ZVMs), such as iron, copper, nickel, and zinc, have played a significant role in mineralizing the organic pollutants in wastewater [24].

The present work describes the phenol degradation by advanced Fenton-like processes using nanosized zero-valent copper (NZVC) or nanosized zero-valent nickel (NZVN) as catalysts in conjunction with H_2O_2 and 20 kHz ultrasound irradiation. These nanoparticles are fully characterized and their catalytic effectiveness is examined. The effect of H_2O_2 concentration, initial pH, ultrasonic irradiation time, and catalyst amount on the degradation efficiency is investigated, and the reaction kinetics is discussed. To the best of our knowledge, the use of these nanoparticles in the sonocatalytic degradation of phenol has yet to be published.

2. Materials and methods

2.1. Reagents

Phenol (99%) and $NaBH_4$ were obtained from (Sigma–Aldrich), and hydrogen peroxide (30% W/W) was purchased from Fluka (USA). $CuCl_2{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$, and sodium hydroxide (96%) were purchased from Merck, (Germany).

2.2. Synthesis of Cu^0 and Ni^0 nanoparticles

The nanoparticles were prepared according to the procedures described in the literature [25]. Briefly, $CuCl_2{\cdot}2H_2O$ (6.2 g) was dissolved in deionized water (100 mL). The pH was adjusted to 6.2–7 using NaOH (3.8 M) and then $NaBH_4$ (3.1 g) was added under vigorous stirring. The reaction was allowed until no bubbles were observed. No special precautions were taken to eliminate oxygen from the reaction vessel. The resulting black solid was washed with deionized water, and then washed with ethanol and acetone to eliminate water. The obtained particles were dried in a vacuum oven overnight [26]. For storage, a thin layer of ethanol was added to preserve the nanoparticles from oxidation. The same method was used to synthesize the NZVN, with the weight ratio of metal to borohydride adjusted appropriately.

2.3. Catalysts characterization

X-ray diffraction (XRD) patterns of the samples were recorded in the range $2\theta = 4–80^\circ$ using a Philips powder diffractometer with Cu Kα radiation ($k = 0.154$ nm). The instrument was operated at 40 kV and 40 mA. The spectra were recorded with a 2θ step of 0.02° at a scanning rate of $2^\circ\ \theta/\text{min}$. Surface area, pore volume, and average pore size were obtained from the N_2 adsorption–desorption isotherms determined at 196˚C using a Quantachrome Nova 3200 instrument (USA). Prior to measurements, the samples were perfectly degassed at 100˚C for 12 h under vacuum (10–5 mm Hg). TEM images were obtained using a JEOL JEM-2100 (Japan) operated at 200 kV.

2.4. Catalytic oxidation of phenol and analytical procedures

A standard aqueous solution of phenol was used in all the experiments with a concentration of 25-mg L^{-1} solution. A commercial sonicator, VCX-750

(Sonics and Materials, Inc.) equipped with a titanium probe (diameter 13 mm) capable of operating continuously at a fixed frequency of 20 kHz with a variable electric output power up to 125 W was used. Experiments were carried out in a glass reaction vessel with thin and indented bottoms for uniform and more efficient energy transmission. Ultrasound power output was set at 100 W for all the experiments. The power dissipated (P_{diss}) was estimated to be 6.3 W, and the Power density was found to be 0.126 W/mL.

Nanosized ZVMs of 0.1, 0.3, 0.5, 0.7, and 1 g L^{-1} were dispersed into phenol solution (25 mg L^{-1}) followed by shaking for 15 min to ensure a proper dispersion of the catalysts, then they were filled into the reactor. Afterward, this reactor was placed in an ultrasound apparatus and irradiated according to the experimental requirements. Sonication was applied in continuous mode and the tip of the titanium probe was placed about 2 cm below the surface of the phenol solution. During the degradation, the reactor was immersed in a water bath adjusted at 25 ± 2˚C. The reaction temperature was monitored by a thermocouple located inside the reactor.

The degradation of phenol was initiated by the rapid addition of the oxidizing agent (10, 20, 30, 40, and 50 mM of H_2O_2) to the reactor and immediately turning on the ultrasonic apparatus at regular time intervals (10, 20, 30, 40, 50, and 60 min). Eventually, 20-mL aliquots of the reaction solution were sampled, immediately centrifuged at 14,000 rpm for 15 min using EBA-21 centrifugal, Hettich, Germany, to remove the catalysts and then the solution was ready for HPLC analysis.

Samples were analyzed by an HPLC system equipped with pump Waters 515, sample injector, Waters 2489 UV–Visible detector set at 280 nm, Column Waters (X Bridge$^{\mathrm{TM}}$ C18 5 μm 4.6 × 250 mm), and guard column. A mixture of acetonitrile-Milli-Q water solution (30:70 by volume) at 1 mL $\min^{-1}$ was used as the mobile phase throughout the analysis.

3. Results and discussion

3.1. Characteristics of the prepared NZVC and NZVN

The XRD patterns of NZVC and NZVN are shown in Fig. 1. The average size (D) of the particles can be determined according to the Scherrer equation: $D = k(\lambda/\beta \cos \theta)$. 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 results reveal that the average size of NZVC and NZVN is approximately 20 and 52 nm, respectively.

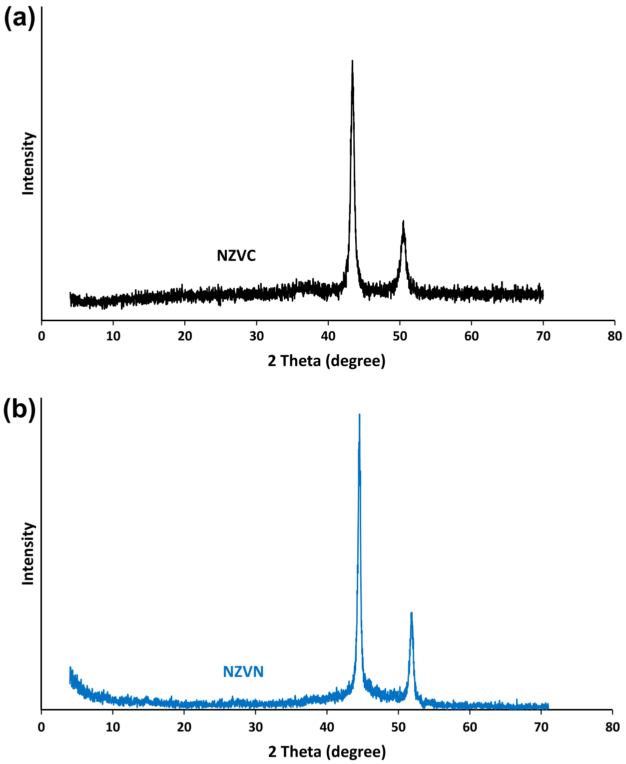

Fig. 1. XRD spectra of (a) NZVC and (b) NZVN.

TEM is used to describe the shape and determine the size of NZVC and NZVN. Fig. 2 shows that NZVC and NZVN are on the nanometer scale with sizes approximately (15–20 nm) and (20–50 nm), respectively, which are in good agreement with that obtained using XRD. The values of specific surface area are calculated using BET-equation, A_{BET}, are given in Table 1 together with the values of total pore volume, Vp, taken at P/P_{o} = 0.975 single point.

3.2. Silent mode system (without sonication)

To examine the role of sonication, the reaction was carried out in the system using catalyst and H_2O_2

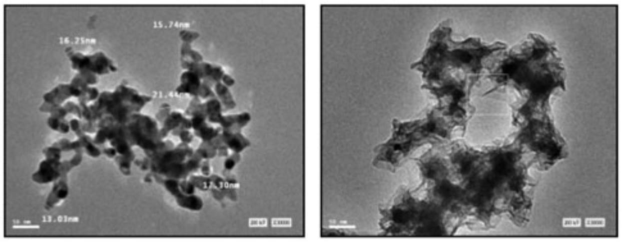

Fig. 2. TEM images of (a) NZVC and (b) NZVN.

Table 1
Texture data and crystallite size of NZVC and NZVN

Catalyst	A_{BET} (m^2/g)	Pore volume (cm^3/g)	Crystallite sizes (nm)
NZVC	52.5	0.143	15–20
NZVN	19	0.052	20–52

without ultrasound. The results show that the extent of phenol degradation in the silent mode reaction reached 8 and 5% with NZVC and NZVN, respectively, after 1 h as shown in Fig. 3. These results evidence a negligible impact in silent conditions.

3.3. Degradation of phenol using ultrasound solely

Initially, the extent of phenol degradation was investigated using ultrasound, and the obtained results are shown in Fig. 4. It is obvious that the extent of degradation is 20% after 60 min as shown in Fig. 4. Sonolysis alone (20 kHz) is not capable to entirely degrade the phenol. The sonolysis of aqueous solutions generates a highly reactive hydroxyl radical (·OH) and hydrogen atom (H·) that in the presence of oxygen forms $HO_2^{\cdot}$ radicals. Formation of hydrogen peroxide can take place via combination of two $HO_2^{\cdot}$ or two ·OH [27]. The value of the rate constant (k) for reaction of H· with oxygen is 2.1×10^{10} M^{-1} s^{-1}, and for the combination of two hydroxyl radicals is $5.2–6.2 \times 10^9$ M^{-1} s^{-1}. For the reactions between phenol and ·OH, k is 6.6×10^9 M^{-1} s^{-1} [28]. Thus, a great loss of formed ·OH and H· occurs before participation in the process of phenol degradation that explains the low efficiency of sonication alone under the used conditions. However, some studies have reported that a higher sonication frequency has resulted in increasing the extent of phenol degradation using 300 kHz US reactor with phenol being undetectable only within 25 min [29].

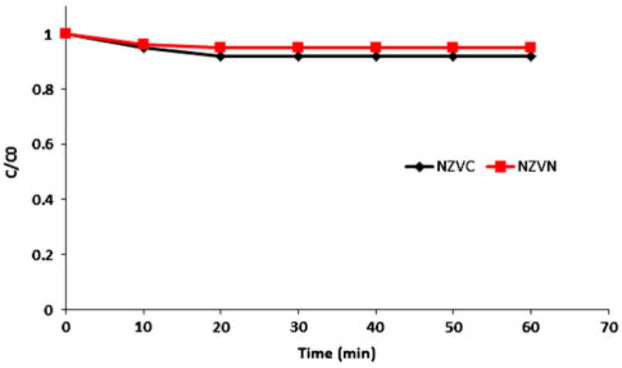

Fig. 3. Degradation of phenol (25 mg L^{-1}) using the catalyst and H_2O_2 without ultrasound (silent mode system). Reaction conditions: NZVC or NZVN (1 g L^{-1}), H_2O_2 concentration (65 mM), pH (7), and 25°C.

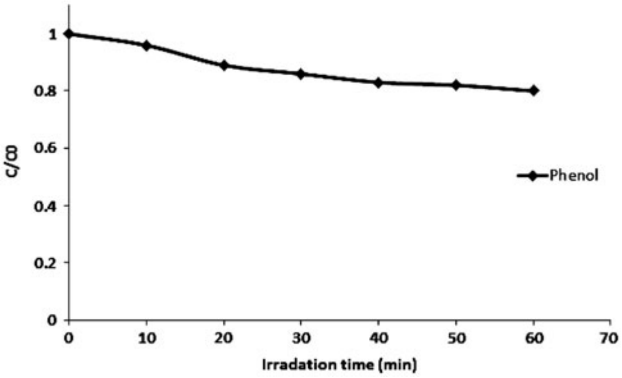

Fig. 4. Influence of ultrasonic irradiation time on phenol (25 mg L^{-1}) degradation ratios. Reaction conditions: pH (7) and 25°C.

3.4. Degradation of phenol 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. A simple mechanism for radical formation during sonication of an aqueous solution of hydrogen peroxide is given by:

$$H_2O \rightarrow {}^{\cdot}OH + {}^{\cdot}H \quad (1)$$

$$H_2O_2 \rightarrow {}^{\cdot}OH + {}^{\cdot}OH \quad (2)$$

The sonolytic degradation of phenol was investigated using the H_2O_2 concentration range of 10–50 mM. Fig. 5 reveals that the extent of phenol degradation is substantially enhanced by the addition of H_2O_2 to the ultrasound system. The enhancement in the degradation extent of phenol can be mainly due to the contribution of hydroxyl radicals that are produced from hydrogen peroxide since hydroxyl radicals can be also formed by the sonication of aqueous solutions of hydrogen peroxide. The bond energy of O–O in hydrogen peroxide (139 kJ mol^{-1}) is lower than the bond energy (463 kJ mol^{-1}) of O–H in water [30]. The degradation extent increased from 30% at 10-mM H_2O_2 to 40% at 20-mM H_2O_2 after 30 min of sonication. However, the degradation decreased to 15% when the H_2O_2 concentration increased to 60 mM. On the one hand, hydrogen peroxide acts as a source of free radicals by the dissociation process, but on the other hand, it acts as a scavenger of the generated free radicals at high concentration, which indeed retard the degradation of organic compounds by consuming more H_2O_2. Thus, when the system contains no other organic substances that can be oxidized by radical species, the radical species generated via the decomposition of H_2O_2 would be finally terminated to produce molecular oxygen and water [31–33] as follows:

$$OH^{\cdot} + H_2O_2 \rightarrow OH^{\cdot}_2 + H_2O \tag{3}$$

$$HO^{\cdot}_2 + H_2O_2 \rightarrow OH^{\cdot} + H_2O + O_2 \tag{4}$$

$$OH^{\cdot} + HO^{\cdot}_2 \rightarrow H_2O + O_2 \tag{5}$$

Similar trends have been observed for degradation of 2,4-dinitrophenol where H_2O_2 concentration was varied from 100 to 800 mg L^{-1} and for phenol, H_2O_2 concentration was varied from 1 to 5 g L^{-1} [34,35]. Our results also suggest that the concentration of hydrogen peroxide must be kept at optimum levels in order to achieve high phenol decomposition efficiency.

3.5. Degradation of phenol using ultrasound assisted with H_2O_2 and nanosized ZVMs

Advanced Fenton-like process was investigated for quantifying the degradation extent under different operating conditions. In this case, NZVC and NZVN were used in combination with H_2O_2 in the presence of ultrasonic treatment. Ultrasonic irradiation generates benefits in heterogeneous catalytic systems by decreasing mass transfer limitations and fragmentation of catalyst into small particles that provide a higher surface area [36]. Moreover, the additional generation of free radical species in ultrasound systems should enhance the overall catalytic performance [15]. The introduction of catalysts is another way to drive the decomposition of H_2O_2 for the oxidation of organic contaminants. It is obvious that the phenol degradation is markedly higher in the combined method (US and catalyst) than in the individual cases (US only).

The enhancement in the degradation extent of phenol can be mainly due to the presence of heterogeneous catalyst, which can promote the decomposition of H_2O_2 under ultrasonic irradiation and the generation of ·OH radicals. The increase in the efficiency can be attributed to the increase in the ·OH production due to the increased bubble explosion at particle crevices. As shown in Fig. 6, the obtained results reveal that the maximum degradation extent of 65 and 60% was achieved using 1 g L^{-1} of NZVC and NZVN, respectively, in the presence of 20-mM H_2O_2 after 60 min of sonication. The mechanism proposed by Weiss for the H_2O_2 decomposition at metal surfaces

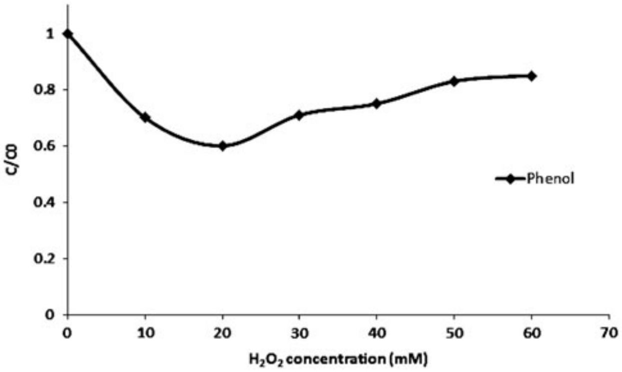

Fig. 5. Influence of H_2O_2 concentration on phenol (25 mg L^{-1}) degradation ratios. Reaction conditions: pH (7), 25˚C, and 30 min of sonication.

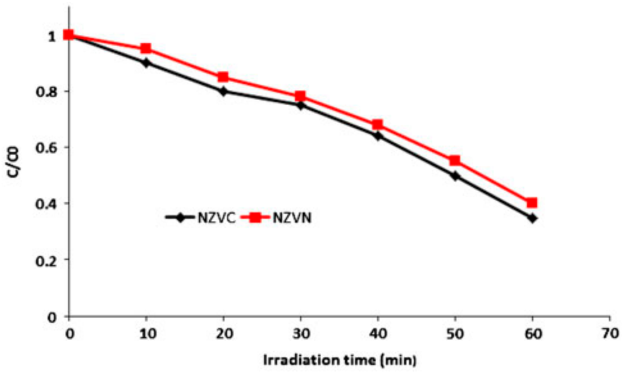

Fig. 6. Influence of ultrasonic irradiation time on phenol (25 mg L^{-1}) degradation ratios. Reaction conditions: NZVC or NZVN (1 g L^{-1}), H_2O_2 concentration (20 mM), pH (7), and 25˚C.

[37], is thought to be applicable for metal oxides. Petrier et al. [38] and Nosaka et al. [39] reported that both hydroxyl radicals ·OH and superoxide radicals $HO_2^{\bullet}/O_2^{\bullet}$ can be measured indirectly by chemiluminescence method. In addition, Drijvers et al. [40] concluded that during the decomposition of H_2O_2 by different catalysts, the most intensive luminescence was observed in the case of CuO and this might explain why NZVC has a higher catalytic activity than NZVN.

3.6. Influence of the catalyst amount on the sonocatalytic degradation of phenol

The influence of the catalyst amount on the sonocatalytic degradation efficiency of phenol is shown in Fig. 7. The results show that the sonocatalytic degradation efficiency of phenol increases with an increase in the catalyst amount. The degradation efficiency of phenol reached 65 and 60% for NZVC and NZVN, respectively, using 1 g L^{-1} of catalyst in the presence of 20-mM H_2O_2 after 60 min of sonication. NZVC has higher catalytic activity than NZVN because NZVC has large numbers of active sites on its surface, which can increase the chances to produce point of contact between cavities and phenol.

3.7. Influence of pH on sonocatalytic degradation of phenol

The influence of pH on the sonocatalytic degradation of phenol was studied and the results are shown in Fig. 8. As well known, the chemical forms of many organic pollutants in aqueous solution and the surface properties of NZVC and NZVN particles depend on the solution pH value [41]. In general, the point of zero charge (PZC) of NZVC and NZVN is approximately pH 8.5 and 8, respectively. Above these pH values, the surface of NZVC and NZVN is negatively charged, while below these pH values it is positively charged. Hence, when the solution pH value is below the PZC, phenol should be adsorbed on the surfaces of NZVC and NZVN particles easily, thus, phenol will be subjected to the higher number of generated ·OH radicals on the surface of the catalysts, accordingly increases the degradation efficiency. It is obvious that the degradation extent is enhanced under acidic conditions; however, the probability of metal dissolution cannot be ruled out. By contraries, under strong alkaline condition, because of the repulsion force due to the negatively charged surface, phenol anions in the aqueous solution are mainly degraded through radical (·OH) oxidation, which is a slow-motion degradation process due to the fast decomposition of H_2O_2 into H_2O and O_2 at strong basic conditions [11,42].

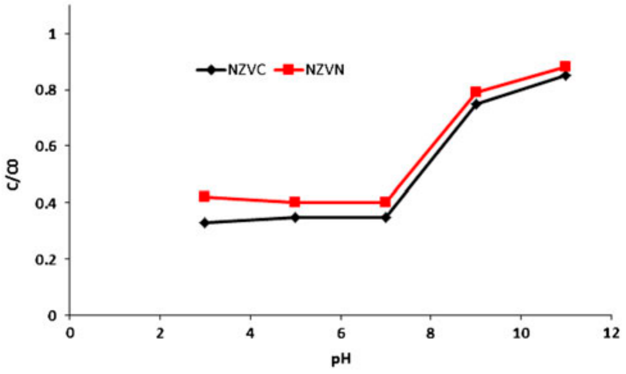

Fig. 8. Influence of pH value on phenol (25 mg L^{-1}) degradation ratios. Reaction conditions: NZVC or NZVN (1 g L^{-1}); H_2O_2 concentration (20 mM), 25˚C, and 60 min of sonication.

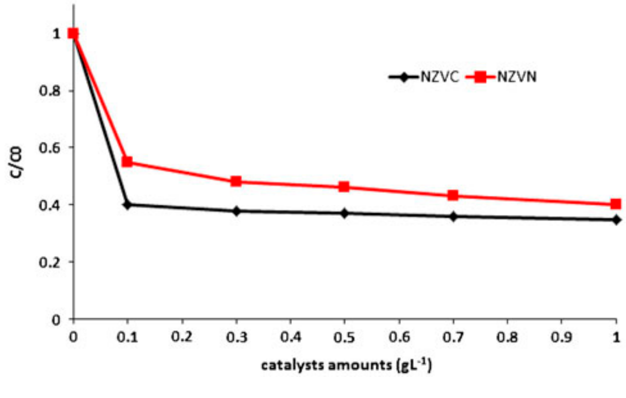

Fig. 7. Influence of catalyst amount on phenol (25 mg L^{-1}) degradation ratios. Reaction conditions: H_2O_2 concentration (20 mM), pH (7), 25˚C, and 60 min of sonication.

3.8. Influence of surface area on the catalytic efficiency

As heterogeneous catalysis is a surface phenomenon, it is well documented that the overall kinetics of the oxidation process is highly dependent on the surface area that participates in the reaction [43]. In practice, only some part, so-called active sites of the catalyst surface area are available for the reaction. However, it is quite difficult to estimate the number of active sites that are present in the catalytic system due to the catalyst deactivation processes, which lead to a low catalytic efficiency. When ultrasound irradiation is applied, the significant variation in the surface area occurs with the possible increase in the number of active "clean" sites and consequently, the increase in the reaction rates may be observed. Table 1 shows that BET surface area and pore volume of the NZVC catalyst are much higher than that of NZVN. This implies that high accessibility of reactants to copper active sites and/or a higher number of active sites. Nevertheless, the sites themselves could be less active.

3.9. Kinetic study

The rate constants in presence of 20-mM H_2O_2 and 1-g L^{-1} of NZVC are higher than the corresponding rates of NZVN. The calculated values of first-order rate constants of phenol degradation are listed in Table 2 and the plots of the linear representation of first-order equation are shown in Fig. 9. Prior to any kinetic studies, the effect of heat and mass transfer limitations during the oxidation process has to be established. 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 [44]. Moreover, applying ultrasound decreased the heat and mass transfer limitations due to the physical effects induced by cavitation [45]. Table 2 reveals that the reaction rate constant for NZVC is higher than NZVN. Thus, NZVC has higher catalytic activity than NZVN.

Table 2
The calculated values of first-order rate constants of phenol degradation using ultrasound in the presence of nanosized ZVMs[a]

Catalyst	k (min^{-1})	R^2
NZVC	0.012	0.9505
NZVN	0.010	0.9368

Note: [a]Reaction conditions: NZVC or NZVN (1 g L^{-1}), H_2O_2 concentration (20 mM), pH (7), and 25°C.

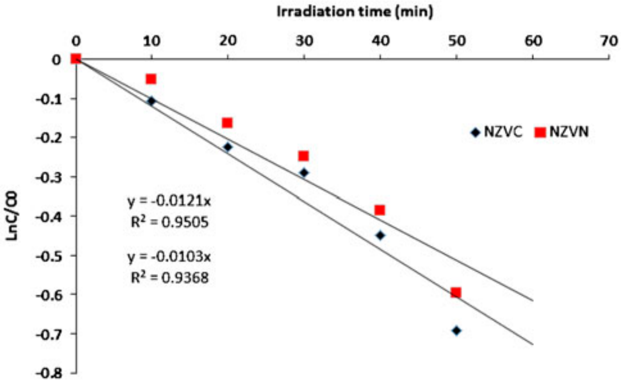

Fig. 9. First-order rate constant (min^{-1}) of phenol (25 mg L^{-1}) degradation ratios. Reaction conditions: NZVC or NZVN (1 g L^{-1}), H_2O_2 concentration (20 mM), pH (7), and 25°C.

4. Conclusions

The use of ultrasound for destroying phenol in water and wastewater is a promising approach as an environmental remediation. The combination of ultrasound and the AFP could effectively degrade phenol. The highest phenol oxidation was observed using NZVC under the US/NZVC/H_2O_2 system. Degradation efficiency of phenol increased with the increase in the ultrasonic irradiation time and catalysts amount, and decreased with the increase in the pH value. The reaction rate constant for NZVC is higher than NZVN. Thus, NZVC has higher catalytic activity than NZVN.

Acknowledgments

The authors wish to acknowledge the financial support of this research by Egyptian Petroleum Research Institute.

References

[1] K.C. Namkung, A.E. Burgess, D.H. Bremner, H. Staines, Advanced Fenton processing of aqueous phenol solutions: A continuous system study including sonication effects, Ultrason. Sonochem. 15 (2008) 171–176.

[2] M.H. Entezari, C. Pétrier, A combination of ultrasound and oxidative enzyme: Sono-biodegradation of phenol, Appl. Catal., B 53 (2004) 257–263.

[3] M. Pérez, F. Torrades, J.A. García-Hortal, X. Domènech, J. Peral, Removal of organic contaminants in paper pulp treatment effluents by TiO_2 photocatalyzed oxidation, J. Photochem. Photobiol., A 109 (1997) 281–286.

[4] M. Mare, G. Waldner, R. Bauer, H. Jacobs, J.A.C. Broekaert, Degradation of nitrogen containing organic compounds by combined photocatalysis and ozonation, Chemosphere 38 (1999) 2013–2027.

[5] K. Tanaka, K. Abe, T. Hisanaga, Photocatalytic water treatment on immobilized TiO_2 combined with ozonation, J. Photochem. Photobiol., A 101 (1996) 85–87.

[6] G. Ruppert, R. Bauer, G. Heisler, The photo-Fenton reaction—An effective photochemical wastewater treatment process, J. Photochem. Photobiol., A 73 (1993) 75–78.

[7] G.M.S. ElShafei, F.Z. Yehia, O.I.H. Dimitry, A.M. Badawi, Gh Eshaq, Degradation of nitrobenzene at near neutral pH using Fe_2^+–glutamate complex as a homogeneous Fenton catalyst, Appl. Catal., B 99 (2010) 242–247.

[8] S.T. Kolaczkowski, F.J. Beltran, D.B. McLurgh, F.J. Rivas, Wet air oxidation of phenol, Process Saf. Environ. Prot. 75 (1997) 257–265.

[9] N.H. Ince, G. Tezcanli, R.K. Belen, I.G. Apikyan, Ultrasound as a catalyzer of aqueous reaction systems: The

state of the art and environmental applications, Appl. Catal., B 29 (2001) 167–176.

[10] G.M.S. ElShafei, F.Z. Yehia, O.I.H. Dimitry, A.M. Badawi, Gh Eshaq, Ultrasonic assisted-Fenton-like degradation of nitrobenzene at neutral pH using nanosized oxides of Fe and Cu, Ultrason. Sonochem. 21 (2014) 1358–1365.

[11] F.Z. Yehia, Gh. Eshaq, A.E. ElMetwally, Role of surface modification of some metal oxides with amino acids in upgrading the sonocatalytic degradation of nitrobenzene, Desalin. Water Treat. (2014), doi: 10.1080/19443994.2014.958541.

[12] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, Chemosphere 55 (2004) 1235–1243.

[13] D.H. Bremner, S.D. Carlo, A.G. Chakinala, G. Cravotto, Mineralisation of 2,4-dichlorophenoxyacetic acid by acoustic or hydrodynamic cavitation in conjunction with the advanced Fenton process, Ultrason. Sonochem. 15 (2008) 416–419.

[14] H. Zhang, J. Zhang, C. Zhang, F. Liu, D. Zhang, Degradation of C.I. Acid Orange 7 by the advanced Fenton process in combination with ultrasonic irradiation, Ultrason. Sonochem. 16 (2009) 325–330.

[15] J.K. Kim, F. Martinez, I.S. Metcalfe, The beneficial role of use of ultrasound in heterogeneous Fenton-like system over supported copper catalysts for degradation of p-chlorophenol, Catal. Today 124 (2007) 224–231.

[16] S.H. Joo, A.J. Feitz, D.L. Sedlak, T. D. Waite, Quantification of the oxidizing capacity of nanoparticulate zero-valent iron, Environ. Sci. Technol. 39 (2005) 1263–1268.

[17] I.A. Katsoyiannis, T. Ruettimann, S.J. Hug, pH dependence of Fenton reagent generation and As(III) oxidation and removal by corrosion of zero valent iron in aerated water, Environ. Sci. Technol. 42 (2008) 7424–7430.

[18] H.M. Hung, F.H. Ling, M.R. Hoffmann, kinetics and mechanism of the enhanced reductive degradation of nitrobenzene by elemental iron in the presence of ultrasound, Environ. Sci. Technol. 34 (2000) 1758–1763.

[19] B. Chen, X. Wang, C. Wang, W. Jiang, S. Li, Degradation of azo dye direct sky blue 5B by sonication combined with zero-valent iron, Ultrason. Sonochem. 18 (2011) 1091–1096.

[20] Y. Dai, F. Li, F. Ge, F. Zhu, L. Wu, X. Yang, Mechanism of the enhanced degradation of pentachlorophenol by ultrasound in the presence of elemental iron, J. Hazard. Mater. 137 (2006) 1424–1429.

[21] M. Kallel, C. Belaid, T. Mechichi, M. Ksibi, B. Elleuch, Removal of organic load and phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron, Chem. Eng. J. 150 (2009) 391–395.

[22] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced Fenton processing, Chem. Eng. J. 152 (2009) 498–502.

[23] D.H. Bremner, A.E. Burgess, D. Houllemare, K.C. Namkung, Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide, Appl. Catal., B 63 (2006) 15–19.

[24] J. Rima, E. Aoun, K. Hanna, Q.X. Li, Degradation of phenol, into mineral compounds, in aqueous solutions using zero-valent iron powder (ZVIP), J. Phys. IV France 124 (2005) 81–89.

[25] S.M. Ponder, J.G. Darab, T.E. Mallouk, Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron, Environ. Sci. Technol. 34 (2000) 2564–2569.

[26] B. Schrick, J.L. Blough, A.D. Jones, T.E. Mallouk, Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel−iron nanoparticles, Chem. Mater. 14 (2002) 5140–5147.

[27] E.J. Hart, A. Henglein, Free radical and free atom reactions in the sonolysis of aqueous iodide and formate solutions, J. Phys. Chem. 89 (1985) 4342–4347.

[28] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons chemical kinetic data base for combustion chemistry. Part 3: Propane, J. Phys. Chem. Ref. Data 17 (1988) 513–886.

[29] R. Chand, N.H. Ince, P.R. Gogate, D.H. Bremner, Phenol degradation using 20, 300 and 520 kHz ultrasonic reactors with hydrogen peroxide, ozone and zero valent metals, Sep. Purif. Technol. 67 (2009) 103–109.

[30] A. Mehrdad, R. Hashemzadeh, Ultrasonic degradation of Rhodamine B in the presence of hydrogen peroxide and some metal oxide, Ultrason. Sonochem. 17 (2010) 168–172.

[31] H. Christensen, K. Sehested, H. Corfitzen, Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures, J. Phys. Chem. 86 (1982) 1588–1590.

[32] A.Y. Sychev, V.G. Isak, Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O_2 and H_2O_2 and of the oxidation of organic substrates, Russ. Chem. Rev. 64 (1995) 1105–1129.

[33] J.P. Sweet, J.K. Thomas, Absolute rate constants for H atom reactions in aqueous solutions 1, J. Phys. Chem. 68 (1964) 1363–1368.

[34] Z. Guo, Z. Zheng, S. Zheng, W. Hu, R. Feng, Effect of various sono-oxidation parameters on the removal of aqueous 2,4-dinitrophenol, Ultrason. Sonochem. 12 (2005) 461–465.

[35] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process, Ultrason. Sonochem. 15 (2008) 49–54.

[36] P.R. Gogate, Treatment of wastewater streams containing phenolic compounds using hybrid techniques based on cavitation: A review of the current status and the way forward, Ultrason. Sonochem. 15 (2008) 1–15.

[37] J. Weiss, The free radical mechanism in the reactions of hydrogen peroxide, Adv. Catal. 4 (1952) 343–365.

[38] C. Petrier, M.F. Lamy, A. Francony, A. Benahcene, B. David, V. Renaudin, N. Gondrexon, Sonochemical degradation of phenol in dilute aqueous solutions: Comparison of the reaction rates at 20 and 487 kHz, Phys. Chem. 98 (1994) 10514–10520.

[39] Y. Nosaka, Y. Yamashita, H. Fukuyama, Application of chemiluminescent probe to monitoring superoxide radicals and hydrogen peroxide in TiO_2 photocatalysis, J. Phys. Chem., B 101 (1997) 5822–5827.

[40] D. Drijvers, H.V. Van Langenhove, M. Beckers, Decomposition of phenol and trichloroethylene by the ultrasound/H_2O_2/CuO process, Water Res. 33 (1999) 1187–1194.

[41] J. Wang, Z. Jiang, Z. Zhang, Y. Xie, Y. Lv, J. Li, Y. Deng, X. Zhang, Study on inorganic oxidants assisted sonocatalytic degradation of Acid Red B in presence of nanosized ZnO powder, Sep. Purif. Technol. 67 (2009) 38–43.

[42] N. Wang, L. Zhu, M. Wang, D. Wang, H. Tang, Sono-enhanced degradation of dye pollutants with the use of H_2O_2 activated by Fe_3O_4 magnetic nanoparticles as peroxidase mimetic, Ultrason. Sonochem. 17 (2010) 78–83.

[43] V.A. Sakkas, I.M. Arabatzis, I.K. Konstantinou, A.D. Dimou, T.A. Albanis, P. Falaras, Metolachlor photocatalytic degradation using TiO_2 photocatalysts, Appl. Catal., B 49 (2004) 195–205.

[44] S.Z. Shamshuddin, N. Nagaraju, Liquid phase transesterification of methyl salicylate and phenol over solid acids: Kinetic studies, J. Mol. Catal. A: Chem. 273 (2007) 55–63.

[45] E.V. Rokhina, M. Lahtinen, M.C.M. Nolte, J. Virkutyte, The influence of ultrasound on the RuI_3-catalyzed oxidation of phenol: Catalyst study and experimental design, J. Appl. Catal., B 87 (2009) 162–170.