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# The beneficial role of use of ultrasound in heterogeneous Fenton-like system over supported copper catalysts for degradation of *p*-chlorophenol

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**Abstract**

A heterogeneous sono-catalytic system with addition of hydrogen peroxide ($US_{H_2O_2+Cat.}$) was employed for the degradation of 200 ppm of *p*-chlorophenol (4-CP) at 25 °C and 100 W of ultrasound power. One thousand and six hundred parts per million of initial hydrogen peroxide ($H_2O_2$) concentration and 1 g/L of catalyst loading over three heterogeneous copper catalysts, CuO, $Cu/Al_2O_3$ (Cu/Al) and $CuO{\cdot}ZnO/Al_2O_3$ (Cu/Zn) was used. The benefits of ultrasound in a heterogeneous catalytic system were evaluated. A considerable synergistic effect of the $US_{H_2O_2+Cat.}$ system was only achieved with supported catalysts (Cu/Al and Cu/Zn) possibly due to good dispersion of catalysts as a result of catalyst size reduction during ultrasound irradiation. Moreover, between the two supported copper catalysts, the Cu/Al provided promising catalytic performance by giving higher 4-CP and TOC removal accompanied with efficient $H_2O_2$ consumption. Experiments with a homogeneous copper catalyst revealed that use of ultrasound in a homogeneous system shows an adverse effect on decomposition of 4-CP.


*Keywords:* Ultrasound; Copper; Heterogeneous catalyst; Fenton; Chlorophenol

## 1. Introduction

Over the last few years, great attention has been paid to the use of ultrasound as one of many potential wastewater treatment technologies since this method is easy to operate. However, total mineralization of organic pollutants by means of ultrasound irradiation alone still remains a difficult task especially for refractory organic compounds and thus application of ultrasound for an industrial plant is still impractical. To overcome the limitation of low degradation efficiency, many efforts have been made on investigation of various combined ultrasound systems in order to reach a desired efficiency of substrate and total carbon degradation and reduce the reaction time required for removing the pollutants [1]. These methods include ultrasound coupled with oxidants such as hydrogen peroxide ($H_2O_2$) [2,3] and ozone [4], electrochemical method [5], Fenton reagent [6–10] and photocatalysis [11–13].

Of these, application of the Fenton-like system coupled 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 oxidising a wide range of organic compounds, it is believed that addition of the Fenton reagent may accelerate the ultrasonic degradation of organic compounds. It has been reported that ferrous ions added into the ultrasound system ($US/Fe^{2+}$) could react with $H_2O_2$ produced via aqueous ultrasound irradiation and consequently increase degradation rates higher than for ultrasound alone for chlorophenols [14], 1,4-dioxane [15], and 4-*n*-nonylphenol [16]. However, Neppolian et al. [6] pointed out that the $US/Fe^{2+}$ system did not improve degradation rate efficiency of metyl-tercbutyl ether (MTBE) due to insufficient generation of $H_2O_2$ which would react with $Fe^{2+}$. Several researchers have also investigated the application of sonication coupled with a homogeneous Fenton-like method ($H_2O_2$ and $Fe^{2+}$ or $Cu^{2+}$) for various aromatic compounds. Indeed degradation of organic pollutants by means of sonication coupled with the homogeneous Fenton-like method has been remarkably improved compared to the use of ultrasound alone or with only homogeneous catalyst.

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However, it is still controversial as to whether ultrasound has a beneficial role in the homogeneous Fenton system ($H_2O_2/Fe^{2+}$) for treating organic pollutants. Lin and Ma [8] and Neppolian et al. [6] reported that a substantial enhancement of degradation efficiency for MTBE and 2-chlorophenol was found in the US/$H_2O_2/Fe^{2+}$ system compared to a Fenton method without ultrasound (henceforth referred to as a silent Fenton system), whereas lower degradation efficiencies for phenols [17] in US/$H_2O_2/Fe^{2+}$ system and 2,4-dinitrophenol [9] in US/$H_2O_2/Cu^{2+}$ were observed in comparison to those in the silent Fenton mode. Moreover, Visscher and Langenhove [10] demonstrated that the degradation rate of the US/$H_2O_2/Cu^{2+}$ system for 2-chlorophenol was nearly the sum of those from the US alone and silent Fenton modes, indicating no synergistic effect of the coupling of the systems.

Few works regarding application of a heterogeneous Fenton-like catalyst with $H_2O_2$ and ultrasound have been reported despite three potential effects of ultrasound on a heterogeneous system such as an increase of active catalyst surface area, promotion of cavitation bubble formation and removal of impurities deposited on the catalyst [18]. Neppolian et al. [19] reported that a heterogeneous Fenton system coupled with ultrasound using a heterogeneous iron catalyst (FeOOH) appeared to be a promising method, showing relatively high degradation rates of *para*-chlorobenzoic acid compared to ultrasound alone or silent Fenton mode. Drijvers et al. [20] also studied the degradation of phenol and trichloroethylene in US/$H_2O_2$/catalyst processes using various metal oxides such as $Al_2O_3$, ZnO, $Ni_2O_3$ and CuO. They demonstrated that although the copper oxide (CuO) showed the highest activity of tested metal oxides, the degradation rate of phenol using the CuO was lower than the sum of those obtained from ultrasound alone and silent Fenton mode and a detrimental effect of ultrasound was observed for degradation of trichloroethylene. Despite previous research on ultrasound irradiation of the heterogeneous Fenton-like reaction for degradation of organic compounds, a comprehensive understanding of the system such as the beneficial effect of ultrasound and comparison with the homogeneous system has not yet been conducted. Furthermore, investigations of supported copper catalysts with respect to enhancement of the sonochemical effect, which was not observed with CuO previously, have not been attempted in the combination of sonication and Fenton-like reaction.

This paper focuses on developing a fundamental understanding of a heterogeneous $US_{H_2O_2+Cat.}$ system over heterogeneous copper catalysts such that an assessment of the benefit of the ultrasound system over the silent system can be made. In addition, the benefits of using a heterogeneous catalyst in comparison to a homogeneous catalyst in the $US_{H_2O_2+Cat.}$ system are discussed.

## 2. Methods

### 2.1. Experimental set-up

A standard aqueous *para*-chlorophenol (4-CP) solution supplied by Aldrich, UK was used in all of the experiments with an initial concentration of 200 mg/L solution. This resulted in a 4-CP solution with the following properties: TOC 115 mg/L; pH 7.2.

A commercial sonicator, VC-750 (Sonics and Materials, Inc.) equipped with a titanium probe (diameter 13 mm) capable of operating either continuously or in a pulse mode at a fixed frequency of 20 kHz with a variable electric output power up to 125 W was used for ultrasound experiments. 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. Typically, 170 mL of 200 ppm 4-CP solution was filled in the reactor, which was immersed in a water bath adjusted at 11 °C with the help of an external cooling device. The reaction temperature was monitored by a thermometer located inside the reactor. Due to the heat dissipation caused during the ultrasound run, the temperature of 4-CP aqueous solution that was initially cooled at 11 °C increased rapidly to 27 °C after 5 min, 28 °C after 1 h and remained constant at 28 °C up to 240 min of sonication. Initial $H_2O_2$ concentration of 1600 ppm and catalyst loading of 1 g/L were used when those conditions were required for combined systems. In order to study the impact of ultrasound on the system, silent experiments were carried out at identical conditions with an axial stirring device instead of the sonicator. Since impact of ultrasound on the heterogeneous catalytic system is the main aim of this study, other ultrasonic effects, which may happen in both of homogeneous and heterogeneous systems, must be ruled out to avoid making erroneous conclusions. Increase of reaction temperature and mixing are known to occur during ultrasound irradiation in aqueous media. Thus, a steady state temperature (28 °C) and maximum stirring speed (500 rpm) were used in the silent experiments to offset those ultrasonic effects and highlight the impact of ultrasound in the heterogeneous system. Samples were periodically withdrawn and filtered by means of 0.45 μm cellulose nitrate membrane filter papers (Whatman, UK) before being analysed.

### 2.2. Catalysts

Three heterogeneous copper catalysts were used in this study: (i) powder copper oxide (CuO) received from Aldrich, UK, (ii) CuO supported over γ-alumina (Cu/Al) purchased from Aldrich, UK and (iii) CuO·ZnO supported on γ-alumina (Cu/Zn) supplied from ICI Katalco, UK. Nitrogen adsorption–desorption measurements were carried out at 77 K using a micrometritics Tristar 3000. Surface area was calculated using the BET equation. With the purpose of comparison, for all the samples, pore volume ($V_p$) was taken at $P/P_o = 0.975$ single point, using the data analysed with BHJ model. The chemical composition, BET surface area and pore volume of the materials are listed in Table 1. Copper sulphate pentahydrate (99.999%) from Aldrich was used as a metal source for the homogeneous catalytic experiments. For those experiments carried out in the presence of copper ions, the appropriate amounts of copper (II) sulphate (Aldrich, UK) were dissolved in the solution to give a metal concentration of 10 and 20 mg/L, respectively.

Table 1
Physical–chemical properties of the heterogeneous copper catalysts

| Material | CuO content (wt%) | $S_{BET}$ ($m^2$/g) | Pore volume ($cm^3$/g) |
|---|---|---|---|
| CuO | 99 | 0.64 | 0.002 |
| Cu/Al | 13 | 306.8 | 0.617 |
| Cu/Zn | 60 | 56.9 | 0.184 |

### 2.3. Analytical methods

Quantification and identification of residual 4-CP were monitored by high performance liquid chromatography (HPLC) on a Varian Prostar HPLC using a photodiode array detector. A reverse phase Phenomenex C18 column of 250 mm × 4.6 mm, which consists of octadecylsilane (ODS) covered spherical silica gel as a stationary phase was used for the analysis. A gradient method with an ultra-pure water solution and a 30:70 water:methanol solution (total flow rate 1 mL/min) as mobile phases were used. Both mobile phases were acidified with sulphuric acid at pH 1.8. UV absorbency at 228 permitted 4-CP to be detected. Quantification of 4-CP was achieved using an external standard calibration method. Both the standards and the samples were periodically analysed in duplicate to test the reproducibility of the measurements, which is within ±2.5% difference. Total organic carbon (TOC) was measured by means of Shimadzu TOC-V CSH analyser based on combustion and subsequent non-dispersive infrared (NDIR) $CO_2$ detector. Repetitive measurements of both standards and sample of reaction did not exceed 1% difference for the range of TOC concentrations measured. $H_2O_2$ concentration was determined by using the titanium spectrophotometric method [21] using titanyl sulphate in acid solution and measuring the resultant absorbance from yellow complex at 410 nm with UV spectrophotometry. Particle size distribution was carried out by means of Malvern Mastersizer 2000 (Malvern, UK) equipped with Hydro 2000MU sample dispersion unit in the applicable measuring range of 0.1–3000 μm, based on laser diffraction method. Samples were also analysed by Zetasizer 3000HSa (Malvern, UK) capable of detecting particles less than 0.1 μm and it was confirmed that particle size of the samples was in the range 0.1–3000 μm in all cases. Leaching of noble metal catalysts was measured using inductively coupled plasma-optical emission spectrophotometry (ICP-OES) (Varian-Vista MPX Axial CCD-simultaneous ICP-OES). Carbonaceous deposits on the fresh and used catalysts were quantified by a Carlo Erba 1108 elemental analyser, based on dynamic flash combustion, GC separation with thermal conductivity detector.

## 3. Results and discussion

### 3.1. Investigation of the $US_{H_2O_2+Cat.}$ system over heterogeneous copper catalysts

Table 2 shows 4-CP and TOC removal after 4-h reaction at 28 °C, 100 W of ultrasound power, 1600 ppm of initial $H_2O_2$ concentration and 1 g/L of catalyst loading in various separate systems of the $US_{H_2O_2+Cat.}$. Only 9.5 and 2.1% of 4-CP and TOC removal, respectively were obtained using ultrasound alone. It has been generally reported that due to its hydrophilic and non-volatile properties, degradation of 4-CP takes place mainly at the interface of cavitation bubbles or in the bulk solution via a free radical reaction rather than inside of the bubbles via a pyrolysis reaction [14,22]. Relatively small amounts of $H_2O_2$ (7.9 ppm) were produced during ultrasound irradiation of deionised water under the same conditions (700 ppm of $H_2O_2$ is necessary for complete oxidation of 200 ppm of 4-CP). Therefore, the poor performance of ultrasound alone may be due to the scarcity of oxidising species and this justifies the use of an additional oxidant and/or catalysts in order to enhance the degradation efficiency. Addition of $H_2O_2$ or three heterogeneous copper catalysts to the ultrasound system modestly enhanced degradation of 4-CP. Addition of $H_2O_2$ in the ultrasound system showed higher conversion of 4-CP than addition of the catalysts. However, ultrasound coupling with the heterogeneous catalysts exhibited higher 4-CP and TOC degradation efficiencies as compared to the silent runs while degradation efficiency in ultrasound with $H_2O_2$ was marginally improved, which highlights potential impact of ultrasound on a heterogeneous system. Nevertheless, in all cases 4-CP and TOC removal never exceeded 18 and 12%, respectively.

Fig. 1 shows normalised 4-CP and TOC removal (%) and $H_2O_2$ conversion (%) in the $US_{H_2O_2+Cat.}$ over the three heterogeneous copper catalysts, while the corresponding silent Fenton runs are given as references. In general, use of the heterogeneous copper catalysts and $H_2O_2$ together in the ultrasound system provided greater degradation of 4-CP and TOC than its separated systems such as the $US_{H_2O_2}$ and $US_{Cat.}$. Of the three heterogeneous copper catalysts used, a CuO catalyst appeared to be the least active, showing lower 4-CP and TOC removal and negligible $H_2O_2$ conversion in the $US_{H_2O_2+Cat.}$ as compared to the supported copper catalysts (Cu/Al and Cu/Zn). From Table 1, it can be seen that BET surface area and pore volume of the CuO catalyst are much lower than those of Cu/Al and Cu/Zn. This implies that limited

Table 2
4-CP and TOC removal (%) in separate systems of the $US_{H_2O_2+Cat.}$ at 28 °C, 100 W of ultrasound power, 1600 ppm of initial $H_2O_2$ concentration and 1 g/L of catalyst loading after 4-h reaction over CuO, Cu/Al and Cu/Zn

| | $US_{alone}$ | $H_2O_2$ | | Catalyst | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | With US | w/o US | CuO | | Cu/Al | | Cu/Zn | |
| | | | | With US | w/o US | With US | w/o US | With US | w/o US |
| 4-CP removal | 9.5 | 18.2 | 15.3 | 15.6 | 2.1 | 11.7 | 0.0 | 13.6 | 6.4 |
| TOC removal | 2.1 | 6.9 | 5.3 | 5.1 | 1.6 | 11.2 | 0.0 | 11.7 | 0.0 |

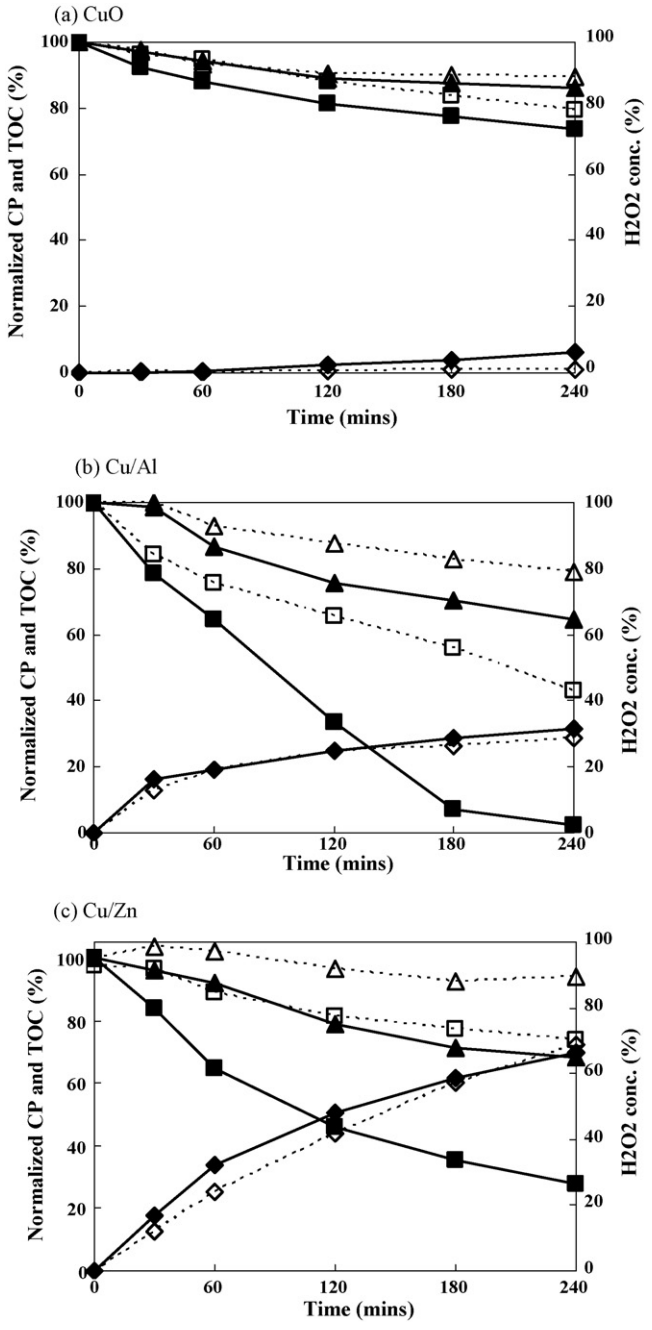


Fig. 1. Normalized 4-CP (■, □) and TOC (▲, △) (%) and $H_2O_2$ conversion (%) (◆, ◇) profiles during 4-h reaction at 28 °C, 100 W of ultrasound power, 1600 ppm of initial $H_2O_2$ concentration and 1 g/L of catalyst loading in $US_{H_2O_2+Cat.}$ modes (closed symbol) and silent Fenton (open symbol) over CuO, Cu/Al and Cu/Zn.

accessibility of reactants to copper active sites and/or a lower number of active sites. Nevertheless, the sites themselves could be less active. Compared to the CuO, the supported copper catalysts showed higher 4-CP and TOC removal accompanied with substantial $H_2O_2$ conversion. However, we must ask if ultrasound has a significant impact on enhancement of system efficiency in the $US_{H_2O_2+Cat.}$. For this reason, the synergism on ultrasound coupling with the Fenton-like reagent was assessed for three copper catalysts by using a synergistic index ($f$) as

Table 3
Synergistic index of the $US_{H_2O_2+Cat.}$ system for the heterogeneous copper catalysts in terms of 4-CP and TOC removal

| Synergstic index | CuO | Cu/Al | Cu/Zn |
|---|---|---|---|
| $f_{CP}$ | 0.9 | 1.5 | 2.0 |
| $f_{TOC}$ | 1.1 | 1.5 | 4.1 |

expressed below

$$f_{\text{CP or TOC}} = \frac{r_{f(US+H_2O_2+Cat.)}}{r_{f(US)} + r_{f(H_2O_2+Cat.)}} \quad (1)$$

where $f_{CP}$ and $f_{TOC}$ are synergistic indexes in terms of 4-CP and TOC degradation respectively and $r_f$ is 4-CP or TOC removal (%) after 4 h of reaction in ultrasound alone, silent Fenton-like and $US_{H_2O_2+Cat.}$ modes. Table 3 shows synergistic indexes of 4-CP and TOC for the three copper catalysts. For the CuO catalyst, although final 4-CP and TOC removal from the $US_{H_2O_2+Cat.}$ is marginally greater than those obtained from the silent Fenton system, it is equal to or less than sum of those obtained from ultrasound alone and the silent Fenton system, indicating no beneficial effect of ultrasound over the CuO. This result is in good agreement with that reported by Drijvers et al. [20], who found a negative effect of ultrasound when the CuO is used in a sono-catalystic system with $H_2O_2$ for phenol removal. Unlike the CuO catalyst, a marked improvement in 4-CP and TOC removal by ultrasound irradiation was observed over the supported copper catalysts. Therefore, beneficial synergistic effects of ultrasound coupling with the heterogeneous Fenton-like system were observed when the supported copper catalysts were used.

Interestingly, when 4-CP and TOC removal is considered with respect to $H_2O_2$ consumption, the benefit of ultrasound in the heterogeneous Fenton-like system over the two supported catalysts is more evident. Although $H_2O_2$ conversions are similar in both of the $US_{H_2O_2+Cat.}$ and silent Fenton-like systems, the $US_{H_2O_2+Cat.}$ showed higher degradation of 4-CP and TOC than the silent Fenton-like system, which implies that more efficient $H_2O_2$ utilization for degradation of 4-CP and TOC occurs when ultrasound is employed in the Fenton-like system. This could be explained by catalyst particle reduction associated with productive reaction of OH radical in the $US_{H_2O_2+Cat.}$. Fig. 2 depicts the particle size distribution of fresh catalyst and used catalysts after reactions with and without ultrasound for the supported catalysts. Significant size reductions as a result of ultrasound irradiation were observed for the supported catalysts. The size reduction of the catalysts indicates that the catalysts are broken into smaller particles due to ultrasound irradiation and the fragmented particles are then well distributed throughout the reactor, which was confirmed by visual observation. A good distribution of the fragmented catalyst particles leads to an increase in the accessibility of 4-CP to the catalyst surface and thus increases the collision probability between 4-CP and active radicals that are produced as a result of reaction of $H_2O_2$ with the catalyst active sites. Besides attack of active radicals on organic compounds, the

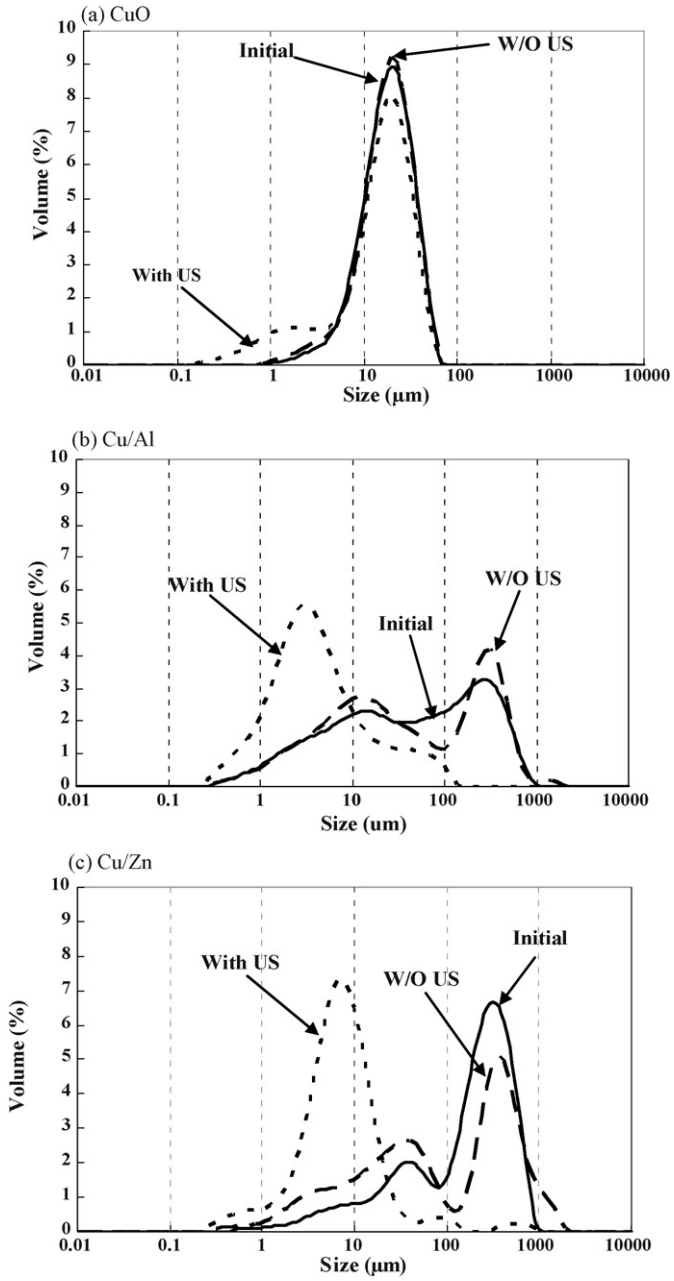


Fig. 2. Particle size distribution (PSD) of initial catalysts and used catalysts after 4-h reaction in the $US_{H_2O_2+Cat.}$ and silent Fenton modes at 28 °C, 100 W of ultrasound power, 1600 ppm of initial $H_2O_2$ concentration and 1 g/L of catalyst loading over CuO, Cu/Al and Cu/Zn.

active radicals may also undergo non-productive reactions for oxidation of organic compounds [20,23,24]. Table 4 shows possible non-productive reactions for active radical species. Active radical species generated via a Fenton reaction mechanism such as $OH^\bullet$ and $HO_2$ radicals can take part in radical–radical reactions [25–30] or hydrogen peroxide scavenging reactions [31–33], which indeed retard degradation of organic compounds by consuming more $H_2O_2$. This would indicate that when the system contains no other organic substances that can be oxidised by radical species, the radical species generated via the decomposition of $H_2O_2$ would be finally terminated to produce molecular oxygen and water. Hence, we may expect that probability of the non-productive reactions will increase when smaller amounts of organic compounds are available for oxidation via a radical attack. Moreover, it should be noticed that in Fig. 2, a negligible change in catalyst particle was observed after the reaction in both $US_{H_2O_2+Cat.}$ and silent Fenton-like modes over CuO. This catalyst exhibited no synergistic effect for decomposition of 4-CP. This is further evidence to support the importance of a good distribution of fragmented catalyst particles achievable through ultrasonic irradiation in the case of decomposition of 4-CP. In addition to the above benefit, the catalyst size reduction may also result in an increase of active metal surface area. However, since the supported copper catalysts possess high porosity, as copper oxides are impregnated throughout the entire catalyst surface, fragmentation of the supported copper catalysts is not thought to increase active surface area significantly.

Besides the effect of catalyst size reduction, promotion of cavitation bubble formation due to the presence of solid particles has been suggested as a potential benefit of ultrasound in a heterogeneous solid–liquid system. According to Mason [18], presence of solid particles in the ultrasound system can induce trapped vapour gas nuclei in the crevices of the solid particles leading to more cavitation bubble formation. To check the possibility of this effect, experiments with alumina particles (1 g/L) were conducted in ultrasound alone with deionised water and the amount of $H_2O_2$ generated during ultrasound irradiation was monitored to compare with that measured in the run without alumina. Seven parts per million of $H_2O_2$ was generated during 4-h sonication in presence of alumina particles, which is slightly lower than the amount from the

Table 4
Possible non-productive reactions of active radical species

| Reaction | References |
|---|---|
| $OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$ | [31] |
| $HO_2^\bullet + H_2O_2 \rightarrow OH^\bullet + H_2O + O_2$ | [32] |
| $H^\bullet + H_2O_2 \rightarrow H_2O + OH^\bullet$ | [33] |
| $OH^\bullet + OH^\bullet \rightarrow H_2O_2$ | [25] |
| $OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$ | [26] |
| $OH^\bullet + OH^- \rightarrow H_2O + O^{-\bullet}$ | [27] |
| $OH^\bullet + H_2 \rightarrow H_2O + H^\bullet$ | [28] |
| $OH^\bullet + O_2^{-\bullet} \rightarrow OH^- + O_2$ | [26] |
| $HO_2^\bullet + O_2^{-\bullet} + H^+ \rightarrow H_2O_2 + O_2$ | [29] |
| $HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$ | [29] |
| $O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet$ | [30] |

run without alumina particles (7.9 ppm). In addition, experiments in presence of alumina particles with 1600 ppm of initial $H_2O_2$ concentration showed lower 4-CP removal than that in absence of alumina particles (8.2 and 18.2% with and without alumina particles, respectively). Therefore, the presence of alumina particles is not likely to promote formation of cavitation bubbles leading to the generation of active radicals in this study.

According to Suslick and coworkers [34,35], ultrasound irradiation could also remove impurities such as reaction intermediates deposited on a catalyst surface, thus preventing catalyst deactivation. They have reported that enhanced sonocatalytic activity is likely due to the removal of the surface oxide layer on nickel and zinc powder. From the 4-CP and TOC removal in the $US_{Cat}$ mode (see Table 2), percentage removal of TOC was nearly same as that of 4-CP for Cu/Al and Cu/Zn. Since oxidative degradation of 4-CP via radical species generally produces rate-limiting intermediates such as carboxylic acids, higher substrate removal than TOC removal is expected. On the other hand, adsorption of organic compounds on the catalyst surface results in similar 4-CP and TOC removal. Moreover, nearly zero removal of 4-CP and TOC was observed in the corresponding silent runs, indicating incapability of the catalyst itself for degradation of 4-CP. It may thus hint that ultrasound may not have a beneficial role on removal of impurities deposited on the catalyst and even it may increase adsorption of organic compounds on the catalyst surface by increasing the surface area for adsorption of 4-CP due to the catalyst particle fragmentation. In order to quantify carbonaceous deposits on the catalysts, elemental analysis was carried out for fresh and used catalysts after the $US_{H_2O_2+Cat.}$ and silent Fenton-like modes (see Table 5). Noticeable amounts of carbon were deposited on the catalysts (less carbon was deposited on the CuO catalyst probably due to its lower surface area) after 4 h of reaction in the $US_{H_2O_2+Cat.}$ mode; ratios of mass of carbon deposited on catalysts to mass of total organic carbon removed after 4-h reaction were 0.41 and 0.31 over Cu/Al and Cu/Zn, respectively in the $US_{H_2O_2+Cat.}$ runs, which are higher than those obtained in the silent Fenton-like system. This probably indicates that use of ultrasound is not likely to have the benefit on removal of carbonaceous impurities deposited on the catalyst surface. However, it should be pointed out that since greater TOC removal was obtained in the $US_{H_2O_2+Cat.}$ compared to the silent Fenton-like mode, we cannot overlook that greater TOC removal may result in larger amount of carbons deposited on the catalyst. Thus, a firm conclusion could not be reached on the surface cleaning effect of ultrasound. Also from Table 5, it should be noted that there is no significant difference between mass of carbon deposited on Cu/Zn before and after the reaction in the silent Fenton-like system; this is compounded with uncertainties in the elemental analysis. The maximum uncertainty in the measured mass of carbon in the catalysts was ±0.2 mg. This was obtained by measuring each mass at least twice. Hence, the uncertainty associated with the data is the reason for the apparent negative value for the mass of carbon deposited on Cu/Zn for the reaction in the silent Fenton-like system.

Of the supported copper catalysts providing the benefit of ultrasound in the heterogeneous catalytic system, Cu/Al provides higher degradation of 4-CP and TOC with more efficient $H_2O_2$ conversion than Cu/Zn. For instance, with 32.0% $H_2O_2$ consumption over Cu/Al and Cu/Zn, nearly complete 4-CP conversion and 35.2% TOC removal were obtained over Cu/Al compared to only 35.2% 4-CP conversion and 7.9% TOC removal over Cu/Zn possibly because of an inhibitory effect of zinc oxide on active radical attack to organic compounds. The results obtained by Bahranowski et al. [36] also reveals that in most cases decomposition of $H_2O_2$ seemed to provide a very small contribution to the degradation of toluene and *p*-xylene and at certain composition ratios of copper and zinc, almost zero decomposition was accompanied by complete $H_2O_2$ utilization in a Fenton-like experiment over Zn, Cu, Al layered double hydroxides. Therefore, Cu/Al appears to be the most promising catalyst, exhibiting the highest activity for 4-CP and TOC removal associated with efficient $H_2O_2$ utilization.

Table 5
Percentage of carbon deposited on the fresh and used catalysts and mass ratio of actual carbon deposited on the catalysts to removed total organic carbon after 4-h reaction over Cu/Al and Cu/Zn in the $US_{H_2O_2+Cat.}$ and silent Fenton-like modes

| | Percentage of carbon deposited on catalyst (w/w) | Mass of carbon deposited on fresh and used catalysts (MCD) (mg) | Mass of actual carbon deposited on catalysts (difference of MCD between fresh and used catalysts) (mg) | Mass of removed total organic carbon (ΔTOC) (mg) | Mass ratio of actual carbon deposited on catalysts to ΔTOC (mg/mg) |
|---|---|---|---|---|---|
| CuO | | | | | |
| Fresh | 0.18 ± 0.00 | 0.31 ± 0.2 | – | – | – |
| With US | 0.33 ± 0.09 | 0.55 ± 0.2 | 0.25 ± 0.4 | 2.89 | 0.09 ± 0.14 |
| w/o US | 0.41 ± 0.02 | 0.69 ± 0.2 | 0.38 ± 0.4 | 2.23 | 0.17 ± 0.18 |
| Cu/Al | | | | | |
| Fresh | 0.42 ± 0.02 | 0.71 ± 0.2 | – | – | – |
| With US | 2.04 ± 0.02 | 3.54 ± 0.2 | 2.83 ± 0.4 | 6.90 | 0.41 ± 0.06 |
| w/o US | 1.16 ± 0.17 | 2.00 ± 0.2 | 1.29 ± 0.4 | 4.11 | 0.31 ± 0.10 |
| Cu/Zn | | | | | |
| Fresh | 4.02 ± 0.01 | 7.11 ± 0.2 | – | – | – |
| With US | 5.06 ± 0.08 | 9.05 ± 0.2 | 1.94 ± 0.4 | 6.17 | 0.31 ± 0.06 |
| w/o US | 3.79 ± 0.11 | 6.69 ± 0.2 | −0.42 ± 0.4 | 1.16 | −0.36 ± 0.35 |

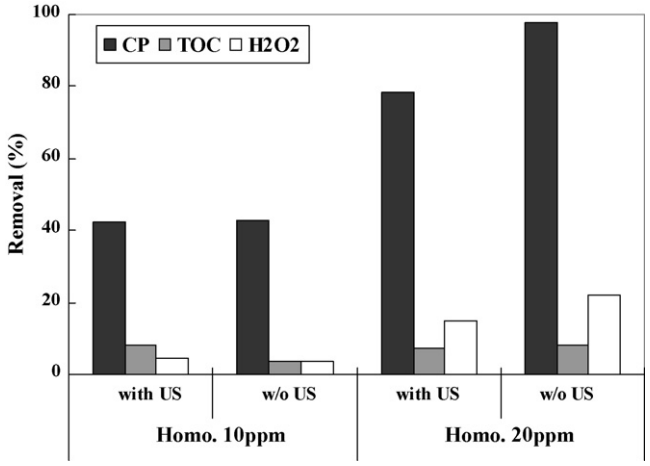


Fig. 3. 4-CP, TOC and $H_2O_2$ removal (%) in the $US_{H_2O_2+Cat.}$ and silent Fenton-like modes at 28 °C, 100 W of ultrasound power and 1600 ppm of initial $H_2O_2$ concentration for different concentration of homogeneous copper catalyst after 4-h reaction.

### 3.2. *Homogeneous* $US_{H_2O_2+Cat.}$ *system*

As insignificant beneficial effect of ultrasound was observed in the case of ultrasound with $H_2O_2$, the effect of ultrasound on a homogeneous catalytic system was investigated. Moreover, since a considerable amount of copper ions was leached out during the $US_{H_2O_2+Cat.}$ runs over Cu/Al and Cu/Zn, respectively (Cu/Al leached 25 ppm or 24% of the total copper present, Cu/Zn leached 10 ppm or 2% of the copper present) the impact of dissolved copper on degradation of 4-CP should be assessed. Therefore, experiments with a homogeneous copper catalyst were performed for different concentrations of copper ion (10 and 20 ppm) at the same conditions as in the heterogeneous catalytic systems, while the corresponding silent Fenton runs were also conducted as references. As seen in Fig. 3, the presence of ultrasound does not show better enhancement of the catalytic performance in terms of 4-CP and TOC removal and $H_2O_2$ conversion for the $US_{H_2O_2+Cat.}$ with copper ions ($Cu^{2+}$) as compared to the silent mode. Even at higher concentration, the silent Fenton system displays a slightly better performance than the $US_{H_2O_2+Cat.}$. Since increase of reaction temperature and mixing caused by ultrasound irradiation, which typically increase degradation rates of organic compounds in Fenton-like reactions, were offset in the silent experiments, it can thus be concluded that ultrasound irradiation has an adverse effect in homogeneous system when those effects are ruled out and this further emphasises the benefit of ultrasound in a heterogeneous catalytic system.

The presence of $Cu^{2+}$ in the solution seems to be important for the disappearance of 4-CP under the $US_{H_2O_2+Cat.}$. 43.5 and 78.3% of 4-CP removal were obtained at 10 and 20 ppm of initial $Cu^{2+}$ concentration. However, despite considerable reduction of 4-CP, only relatively low TOC degradation was observed and even an increase of catalyst concentration from 10 to 20 ppm did not improve TOC removal. Since 25.3 and 10.0 ppm of $Cu^{2+}$ were leached out after 4-h reaction in the $US_{H_2O_2+Cat.}$ over Cu/Al and Cu/Zn, respectively, the synergistic indexes were recalculated by incorporating the corresponding 4-CP and TOC removal obtained from the runs with 10 and 20 ppm of $Cu^{2+}$ into Eq. (1) (see Table 6). While synergistic indexes ($^{homo.}f_{CP}$) in terms of 4-CP degradation for both of the catalysts are less than 1 due to the high reactivity of the leached copper ion for conversion of 4-CP, a positive synergistic effect of ultrasound in terms of TOC degradation was still obtained. Moreover, real synergistic indexes are expected to higher than the calculated values as the concentration of leached copper ions in the heterogeneous catalytic system increases gradually from zero with reaction time. Therefore, although considerable impact of leached $Cu^{2+}$ on 4-CP conversion exists, a noticeable positive synergistic effect of ultrasound is still observed in total carbon mineralization, indicating a meaningful impact of ultrasound on the heterogeneous Fenton-like system.

Table 6
Synergistic index of the $US_{H_2O_2+Cat.}$ system for the heterogeneous copper catalysts in terms of 4-CP and TOC removal considering the contribution of leached copper ion

| Synergistic index | Cu/Al | Cu/Zn |
|---|---|---|
| $^{Homo}f_{CP}$ | 0.7 | 0.9 |
| $^{Homo}f_{TOC}$ | 1.1 | 2.0 |

## 4. Conclusions

Ultrasound coupling with the heterogeneous Fenton-like reagent over copper oxide and two supported copper catalysts were investigated for the abatement of 4-CP aqueous solutions. The conclusions that can be drawn from the results are summarised as follows:

- Synergistic effects in the $US_{H_2O_2+Cat.}$ system over the supported copper catalysts (Cu/Al and Cu/Zn) verified the benefits of ultrasound in the heterogeneous Fenton-like system. Efficient $H_2O_2$ utilization accompanied with higher 4-CP and TOC reductions as compared to the silent Fenton system is possibly due to good dispersion of fragmented catalysts caused by catalyst size reduction during ultrasound irradiation, leading to greater degradation efficiency. The impact of the presence of solid particles (alumina particles) resulting in formation of more cavitation bubbles appeared to be negligible in this study. Of the supported copper catalysts, Cu/Al provided a more promising catalytic performance by giving higher 4-CP and TOC removal accompanied with efficient $H_2O_2$ consumption.
- Use of ultrasound in a homogeneous system with either $H_2O_2$ or Fenton reagent appeared to be detrimental; this emphasises the beneficial use of ultrasound in a heterogeneous catalytic system.

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