



## Industrial wastewater treatment using hydrodynamic cavitation and heterogeneous advanced Fenton processing

Anand G. Chakinala<sup>a</sup>, Parag R. Gogate<sup>b</sup>, Arthur E. Burgess<sup>a</sup>, David H. Bremner<sup>a,\*</sup>

<sup>a</sup> School of Contemporary Sciences, University of Abertay Dundee, 40 Bell Street, DD1 1HG Dundee, United Kingdom

<sup>b</sup> Chemical Engineering Department, Institute of Chemical Technology, University of Mumbai, Mumbai 400 019, India

### ARTICLE INFO

#### Article history:

Received 21 November 2008

Received in revised form 2 May 2009

Accepted 14 May 2009

#### Keywords:

Hydrodynamic cavitation

Advanced Fenton process

Industrial wastewater treatment

Iron metal catalyst

Latent remediation

### ABSTRACT

A combination of hydrodynamic cavitation and heterogeneous advanced Fenton process (AFP) based on the use of zero valent iron as the catalyst has been investigated for the treatment of real industrial wastewater. The effect of various operating parameters such as inlet pressure, temperature, and the presence of copper windings on the extent of mineralization as measured by total organic carbon (TOC) content have been studied with the aim of maximizing the extent of degradation. It has been observed that increased pressures, higher operating temperature and the absence of copper windings are more favourable for a rapid TOC mineralization. A new approach of latent remediation has also been investigated where hydrodynamic cavitation is only used as a pre-treatment with an aim of reducing the overall cost of pollutant degradation. It has been observed that approach of latent remediation works quite well with about 50–60% removal of TOC using only minimal initial treatment by hydrodynamic cavitation.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Due to increasing awareness about the environment and more stringent environmental regulations, treatment of industrial wastewater has always been a key aspect of research. Much work has been done in developing and testing newer techniques and their combinations for wastewater treatment either individually or as a supplementary role to the conventional biological and chemical methods [1,2]. Cavitation is one such recent technique which has been found to be substantially beneficial in wastewater treatment [3]. Cavitation can be described as formation, growth and subsequent collapse of cavities releasing large magnitudes of energy locally, creating conditions similar to hot spots, and also generating strong oxidizing conditions by way of production of hydroxyl radicals and also hydrogen peroxide. The reactors, based on the use of ultrasonic irradiation for generation of cavities, have been categorized as sonochemical reactors whereas when cavities are generated using hydrodynamic means (interchange of flow energy and pressure energy) they are termed, hydrodynamic cavitation reactors. Considerable work has indeed focussed on the application of sonochemical reactors for wastewater treatment [3–10] for a variety of pollutants. However, very few studies have reported the use of the much more energy efficient hydrodynamic cavitation reactors for wastewater treatment [11,12]. It should also be

noted here that, though cavitation (particularly sonochemical) reactors have been reported to be highly successful on laboratory scale operation, these still have been not able to find application on an industrial scale mostly due to comparatively higher costs of treatment and problems associated with efficient operation at levels of power dissipation required for treatment [13]. The efficacy of cavitation reactors can be significantly enhanced by combining cavitation with other oxidation processes or by using catalysts and/or additives. With this intensification, cavitation can be a suitable technology for degradation of wastewater streams or at the minimum it can be used for lowering the toxicity levels of the effluent stream so that conventional biological oxidation can be readily applicable [14]. It may not be practical, especially considering the economics of the process, to use cavitation reactors for complete mineralization but it is strongly recommended as a pre-treatment strategy especially for high COD effluent streams as considered in the present work. In our earlier recent work, a novel combination of hydrodynamic cavitation reactors and the advanced Fenton process was applied to the destruction of real industrial wastewater procured from a commercial organization in UK at an operating capacity of 4 L [15]. We have also reported on hydrodynamic cavitation, generated using a liquid whistle reactor, and acoustic cavitation in conjunction with the advanced Fenton process (AFP) utilizing zero valent iron metal in the form of scrap iron pieces as the heterogeneous catalyst [16–18] with an aim of reduction in the overall cost of the treatment. It was observed that hydrodynamic cavitation was found to play a supplementary role in enhancing the efficacy of AFP and the combination of the two

\* Corresponding author. Tel.: +44 1382 308667; fax: +44 1382 308663.  
E-mail address: [d.bremner@abertay.ac.uk](mailto:d.bremner@abertay.ac.uk) (D.H. Bremner).

resulted in higher overall extents of degradation. The current work is in continuation of the earlier work and utilizes a newly constructed hydrocavitator for generation of hydrodynamic cavitation with a maximum operating capacity of 25 L. The paper presents an advancement over the earlier work in terms of experimental data on a larger scale of operation with an aim of enhancing the confidence among prospective users for commercial applications, use of additional oxidants with a possibility of reducing the treatment times and an investigation of the effect of operating temperatures which affects the efficacy of advanced Fenton oxidation. Also, as cavitation reactors have been found to be cost intensive [13], a novel approach of latent remediation has been investigated wherein the treatment time with hydrodynamic cavitation reactors has been kept at a minimum in order to achieve lower overall costs of treatment.

## 2. Materials and methods

### 2.1. Experimental setup

Hydrodynamic cavitation was generated using an in-house constructed unit termed a Hydrocavitator which has a feed vessel tank with maximum capacity of 25 L and operates in re-circulation mode. Effluent from the feed tank is pumped using a triplex plunger pump (SPECK NP25) with a maximum discharge pressure of 4500 psi (31,020 kPa) and passes through an orifice unit (orifice area about  $7.0 \times 10^{-2} \text{ m}^2$ ) followed by a catalyst bed and finally back to the feed tank. An external ice bath is used to control the temperature in the feed vessel tank, which is necessary as cavitation results in production of heat thereby increasing the temperature of the effluent stream. A schematic representation of the reactor assembly is shown in Fig. 1.

### 2.2. Characteristics of industrial wastewater

The experimental studies were performed to evaluate the efficacy of the combination technique for degradation of industrial wastewater effluent obtained from a local site (details not given due to confidentiality issues). The current investigation is very important in the context of the application to wastewater treatment as the majority of the reported literature deals with simulated effluents and the results may, or may not, be reproduced for real industrial applications due to the presence of trace components such as radical scavengers.

The effluent stream used in the present work consisted of a complex mixture containing substituted phenolic compounds with an initial pH of 1.7, initial COD of 42,000 mg/L and TOC of 14,000 mg/L. COD indicates the concentration of all organic compounds which can be fully oxidized using strong oxidizing agents whereas TOC

usually indicates the amount of all the organics present in the system.

### 2.3. Experimental methodology

All experiments were carried with 8 L of wastewater (25 times dilution with fresh water) with a reaction time of 150 min with zero valent iron pieces (150 g as 100 pieces with dimensions of  $1 \text{ cm} \times 2 \text{ cm} \times 0.10 \text{ cm}$ ) and  $\text{H}_2\text{O}_2$  (usually 1900 mg/L unless specified otherwise). The concentration of  $\text{H}_2\text{O}_2$  has been found to be the optimum concentration in our earlier investigations on a smaller scale of operation with an operating capacity of 4 L [15] as compared to an operating capacity of 8 L in the present work. Passage of the hydrogen peroxide through the iron bed results in generation of hydroxyl radicals and this has been described as advanced Fenton process [15–18]. Solutions of sulphuric acid (2 M) and sodium hydroxide (2 M) were used for the adjustment of pH. An operating pH of 2.5 was selected for all the experimental runs based on the fact that maximum efficacy of the cavitation reactors as well as Fenton chemistry is observed over an operating pH range of 2–3 [1]. The temperature was maintained constant using an external cooling ice bath.

At defined time intervals, samples were taken and analysed for TOC content present in the solution, as optimal mineralization of the effluent stream was the main objective of the investigation. The extent of mineralization was determined by direct injection of the filtered samples into the heated persulphate-type ( $100^\circ\text{C}$ ) TOC analyser (Model 700, OI Analytical).

In the current work, all the experiments were carried out in duplicate to estimate the repeatability of the obtained data which were analysed by statistics tools provided by Excel, MS Office 2003. The graphs were plotted using mean values obtained from the data and the standard deviation of the replicate values is shown as error bars in the values depicted on Y-axis. All the experimental errors were found to be within  $\pm 2\%$  of the mean reported value.

## 3. Results and discussion

The experimental results obtained by varying the parameters of inlet pressure into the system, operating temperature of the reactor and the role of additional copper windings on the AFP will be discussed.

### 3.1. Effect of initial pressure

Preliminary control experiments without the use of the advanced Fenton process indicated that hydrodynamic cavitation alone results in very little degradation and that using an iron catalyst in the presence of hydrogen peroxide is a definite requirement. The effect of different initial pressures of the hydrocavitator in conjunction with the AFP was investigated over the range of 500–1500 psi (3446.7–10,340 kPa) and the results are shown in Fig. 2, where it is clear that higher inlet pressures are effective in the rapid mineralization of the wastewater. Maximum TOC removal ratio (about 60% removal) was obtained at 1500 psi (10,340 kPa) whereas the extent of TOC removal is 52% and 50% at 1000 psi (6893.3 kPa) and 500 psi (3446.7 kPa) respectively under otherwise identical experimental conditions. The trends in the variation of TOC removal with inlet pressures are in close agreement with the reported literature [19–21]. The increase in the extent of degradation with increasing pressure can be attributed to the enhanced cavitation activity at higher pressures. Bubble dynamics studies [22] have indicated that the cavitation intensity generated at the collapse of the cavity increases with higher inlet pressure of the system. The increase in the cavitation collapse intensity generates

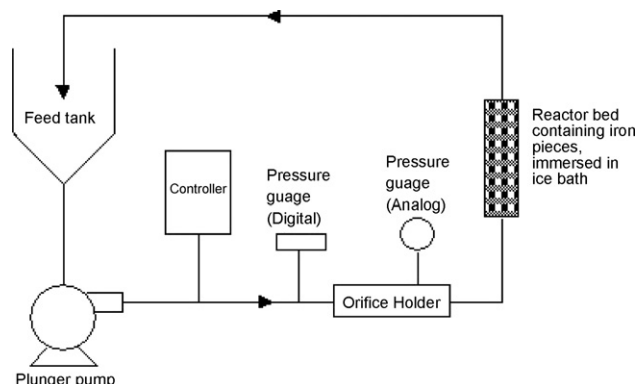


Fig. 1. Schematic representation of the experimental setup.

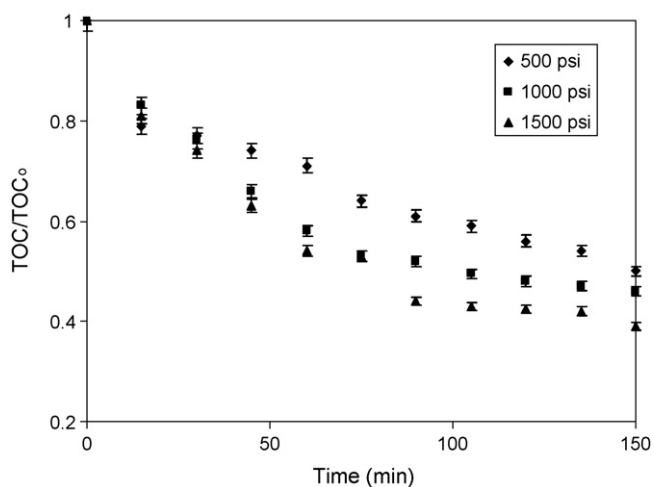


Fig. 2. Effect of different hydrocavitator pressures on the extent of mineralization (experimental conditions—initial pH: 2.5, sample volume: 8 L, iron pieces: 100, dilution factor: 25 times,  $H_2O_2$ : 1900 mg/L, temperature:  $30 \pm 5^\circ C$ ).

higher temperatures and pressures resulting in enhanced dissociation of the water molecules trapped in the cavity thereby leading to a higher concentration of hydroxyl radicals. Also higher cavitation activity is expected to have better activation effects on the advanced Fenton process in terms of greater particle size reduction leading to a larger surface area for enhanced rates of reactions.

It should be also noted here that applying 1500 psi (10,340 kPa) may not be feasible on an industrial scale where a modification in the design of the hydrodynamic cavitation setup (use of multiple orifice plates) is recommended to get similar effects at much lower inlet pressures and the work of Vichare et al. [20] provides more insight into optimization of hydrodynamic cavitation reactors.

### 3.2. Effect of operating temperature

Operating temperature is another key parameter which affects the intensity of hydrodynamic cavitation as well as efficacy of Fenton chemistry. Normally, cavitation intensity decreases with an increase in temperature due to the formation of vaporous cavities which collapse less violently [23–25]. However, the Fenton process, in terms of generation of hydroxyl radicals, is significantly enhanced at higher operating temperatures [26–29]. Sun et al. [26] have reported that the rate constant for degradation of p-nitroaniline increased by almost 100% with a rise in temperature from  $20^\circ C$  to  $30^\circ C$ . Kavitha and Palanivelu [27] have reported that the maximum extent of degradation of cresols occurs at an operating temperature of  $30^\circ C$  using conventional Fenton chemistry.

The effect of operating temperature was investigated at  $20^\circ C$  and  $30^\circ C$  and was performed with precise temperature control and the extent of variation in these sets was  $\pm 2^\circ C$ . The extent of mineralization at the end of 150 min was about 50% higher at  $30^\circ C$  as compared to an operating temperature of  $20^\circ C$ . The enhanced efficacy of the advanced Fenton process based on the use of iron metal combined with hydrodynamic cavitation at higher operating temperatures can be attributed to the controlling contributions from the AFP compared to hydrodynamic cavitation. Zhou et al. [30] have reported an improvement in the extent of degradation of 2,4-dichlorophenol using a combination of ultrasonic irradiation and a Fenton-like system based on the use of Fe/EDTA, with an increase in the operating temperature from  $10^\circ C$  to  $50^\circ C$ . Sun et al. [31] have also reported similar behaviour for the combined process of ultrasound assisted Fenton oxidation of acid black 1. The decolouration efficiency increased marginally from 92.39% to 99.14% as a consequence of raising the temperature from  $20^\circ C$  to  $40^\circ C$ .

In the current work, the study of the effect of operating temperature has enabled us to establish the controlling contribution from the AFP for the overall extent of mineralization, amongst the two opposite effects of temperature on cavitation and the Fenton process.

### 3.3. Effect of copper

As the advanced Fenton process was the controlling process, it was thought desirable to investigate the effect of the presence of additional zero valent metals, in the form of copper, on the otherwise optimized advanced Fenton process parameters such as iron and hydrogen peroxide loadings [15]. It has also been reported recently that use of copper results in generation of hydroxyl radicals [32] giving a similar mechanism of oxidation.

Fig. 3 shows the extent of mineralization in the presence and absence of copper windings on the iron pieces by the combination of the AFP and hydrodynamic cavitation. It is observed that the addition of copper has a negative impact on the mineralization of organic pollutants present in wastewater. From the figure, it can be seen that about 60% of TOC was removed in the presence of iron pieces alone and only 40% of TOC was removed with copper windings on iron pieces after 150 min of treatment. This can be explained on the basis of relative rates of hydroxyl radical generation due to the presence of iron and copper. It is well accepted that the rate of hydroxyl radical generation and hence the extent of TOC mineralization is much higher in the presence of iron as compared to copper metal. Dai et al. [33] have reported that degradation of pentachlorophenol was much faster in the presence of elemental iron as compared to copper metal. Guo et al. [34] have also confirmed the beneficial effects of iron based Fenton chemistry for 2,4-dinitrophenol removal. In the current scenario, the presence of copper windings on the iron pieces (with an aim of increasing the overall loading of metal loading and, potentially, any synergistic effects between the metals) blocks some surface of iron catalyst being exposed to hydrogen peroxide. Since the formation of hydroxyl radicals in the advanced Fenton process is a surface phenomenon [16–18], the blockage of the iron surface by copper results in decreased hydroxyl radical generation thereby lowering the overall extent of mineralization.

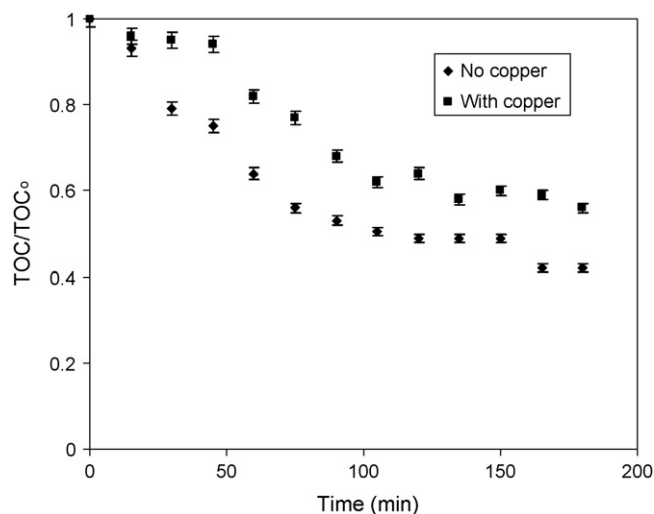
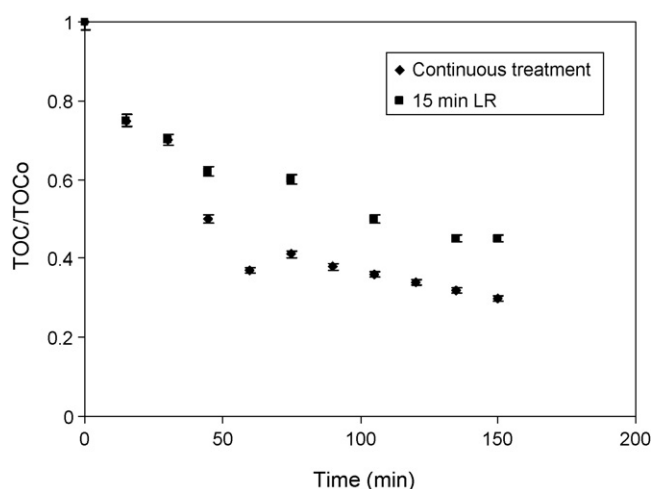


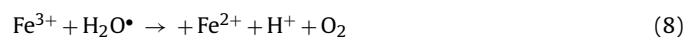
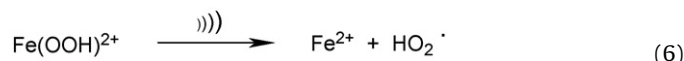
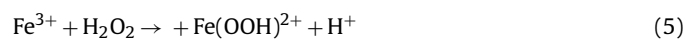
Fig. 3. Effect of copper windings on iron pieces on the extent of mineralization (experimental conditions—initial pH: 2.5, copper wire: 5.5 g, sample volume: 8 L, iron pieces: 50, pressure: 1500 psi (10,340 kPa), dilution factor: 25 times,  $H_2O_2$ : 1900 mg/L).



**Fig. 4.** Effect of the different treatment times on the extent of mineralization (experimental conditions—initial pH: 2.5, sample volume: 8 L, iron pieces: 100, pressure: 1500 psi (10,340 kPa), dilution factor: 25 times,  $\text{H}_2\text{O}_2$ : 1900 mg/L, temperature:  $30 \pm 5^\circ\text{C}$ ).

### 3.4. Latent remediation studies

Cavitation, though very effective in wastewater treatment, is often a cost intensive operation. To minimize the overall costs of treatment in the present combined advanced Fenton process and hydrodynamic cavitation, a new approach of latent remediation was tested where the treatment time of hydrodynamic cavitation was kept at a minimum. In this instance the waste effluent stream was circulated through the hydrocavitator unit fitted with the iron bed and cavitation chamber for an initial fixed time after which the effluent was left in the reactor undisturbed. The effect of different treatment times (continuous treatment and 15 min of treatment time) on the extent of mineralization is depicted in Fig. 4. It is evident from the figure that about 70% of the initial TOC was removed by the continuous treatment of the wastewater for a treatment time of 150 min. However, when the wastewater was treated for only 15 min using the hydrocavitator and the AFP, further analysis of the samples indicated that TOC mineralization did not cease. It can be seen from the figure that the initial TOC content was reduced to 53% after further 135 min of only storage, i.e. without any treatment. During the first 15 min of treatment, the extent of TOC reduction was 30% while the remainder occurred in storage which can be described as latent remediation. The process of latent remediation can be explained on the basis of the contributing actions of hydrodynamic cavitation and iron particles in the presence of hydrogen peroxide. During the first 15 min of treatment time, iron particles are corroded in the presence of water and hydrogen peroxide and generate oxidizing species in the system. Some amount of iron is also leached into the effluent mixture as observed in our earlier work [15]. These oxidizing species present in the effluent mixture along with the dissolved iron and remaining hydrogen peroxide initiate a series of radical reactions which ensures the presence of oxidizing species to continue TOC mineralization. The series of possible radical reactions that occur during the initial treatment and during latent remediation is illustrated below:



It should be also noted here that out of the initially added hydrogen peroxide in the system, some hydrogen peroxide will be utilized by Fenton chemistry and some due to thermal dissociation in the presence of cavitating conditions. The remaining hydrogen peroxide, along with some hydrogen peroxide generated due to hydrodynamic cavitation (the amount is expected to be substantially lower), contributes to the continuous formation of the oxidizing species according to the reaction scheme illustrated earlier. Credence to this hypothesis can be obtained from the results with variation of the treatment time with the combined advanced Fenton process and hydrodynamic cavitation. It has been observed that when the treatment time was increased to 30 min instead of 15 min, the efficacy of latent remediation decreased possibly due to lower availability of hydrogen peroxide. The extent of TOC mineralization using the latent remediation approach was only 47% when 30 min treatment (using hydrodynamic cavitation) was used as against 53% when only 15 min treatment (using hydrodynamic cavitation) was applied.

## 4. Conclusions

The combination of hydrodynamic cavitation generated by an in-house built hydrocavitator and the advanced Fenton oxidation can be effectively used for treatment of real industrial wastewater samples. Studies on the effect of different operating parameters and treatment approaches have enabled us to draw following important conclusions:

- Higher inlet pressures result in greater cavitation activity contributing to the enhanced hydroxyl radical generation and hence increased TOC mineralization of the effluent.
- Higher operating temperatures are preferred indicating that the controlling contribution between the two oxidizing mechanisms is due to advanced Fenton process.
- Presence of copper windings on iron pieces did not result in beneficial effects possibly attributed to the blockage of the iron surface for generation of hydroxyl radicals.
- A novel approach of latent remediation is substantially effective in overall mineralization. Short treatment times of 15 min are more beneficial than the 30-min treatment time thereby minimizing the energy costs.

The results achieved using the hydrocavitator and the advanced Fenton process are particularly beneficial and path-breaking due to the fact that the overall unit operates in a continuous mode and hence large volumes of contaminated water can be treated cost effectively using the approach of latent remediation.

It should also be noted here that in the present work the effluent stream received from industry was diluted by a factor of 25 before actual treatment using fresh water adding up to the total cost of treatment and also requires use of fresh water for dilution. Recent results indicate that previously treated water, in which the TOC has been reduced by around 60%, can be re-used as diluent. However, further work is indeed required to reduce the dilution ratio for treatment using a combination of hydrodynamic cavitation reactors and the advanced Fenton process and this is currently in progress.

## Acknowledgements

The authors, A.G. Chakinala and D.H. Bremner wish to acknowledge funding of Scottish Enterprise under the Proof Of Concept extension (POC+) award and P.R. Gogate wishes to acknowledge the support of Department of Science & Technology, India, and Royal Society, UK, for sponsoring the visit to University of Abertay Dundee under the India UK Science Networks Scheme (Part II).

## References

- [1] P.R. Gogate, A.B. Pandit, A review of imperative technologies for waste water treatment. I. Oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501.
- [2] P.R. Gogate, A.B. Pandit, A review of imperative technologies for waste water treatment. II. Hybrid methods, *Adv. Environ. Res.* 8 (2004) 553.
- [3] Y.G. Adewuyi, Sonochemistry: environmental science and engineering applications, *Ind. Eng. Chem. Res.* 40 (2001) 4681.
- [4] C. Petrier, Y. Jiang, M.-F. Lamy, Ultrasound and environment: sonochemical destruction of chloroaromatic derivatives, *Environ. Sci. Technol.* 32 (1998) 1216.
- [5] M. Sivakumar, A.B. Pandit, Ultrasound enhanced degradation of rhodamine B: optimisation with power density, *Ultrason. Sonochem.* 8 (2001) 233.
- [6] N.N. Mahamuni, A.B. Pandit, Effect of additives on ultrasonic degradation of phenol, *Ultrason. Sonochem.* 13 (2006) 165.
- [7] P.R. Gogate, S. Mujumdar, J. Thampi, A.M. Wilhelm, A.B. Pandit, Destruction of phenol using sonochemical reactors: scale up aspects and comparison of novel configuration with conventional reactors, *Sep. Purif. Technol.* 34 (2004) 25.
- [8] R. Kidak, N.H. Ince, Ultrasonic destruction of phenol and substituted phenols: a review of current research, *Ultrason. Sonochem.* 13 (2006) 195.
- [9] C. Petrier, A. Francony, Incidence of wave-frequency on the reaction rates during ultrasonic wastewater treatment, *Water Sci. Technol.* 35 (1997) 175.
- [10] M.H. Entezari, C. Pétrier, P. Devidal, Sonochemical degradation of phenol in water: a comparison of classical equipment with a new cylindrical reactor, *Ultrason. Sonochem.* 10 (2003) 103.
- [11] M. Sivakumar, A.B. Pandit, Wastewater treatment: a novel energy efficient hydrodynamic cavitation technique, *Ultrason. Sonochem.* 9 (2002) 123.
- [12] K.M. Kalumuck, G.L. Cahine, The use of cavitating jets to oxidize organic compounds in water, *J. Fluids Eng.* 122 (2000) 465.
- [13] T.J. Mason, Large scale sonochemical processing: aspiration and actuality, *Ultrason. Sonochem.* 7 (2000) 145.
- [14] P.R. Gogate, Treatment of wastewater streams containing phenolic compounds using hybrid techniques based on cavitation: a review of current status and the way forward, *Ultrason. Sonochem.* 15 (2008) 1.
- [15] A.G. Chakinala, P.R. Gogate, D.H. Bremner, A.E. Burgess, Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process, *Ultrason. Sonochem.* 15 (2008) 49.
- [16] D.H. Bremner, A.E. Burgess, D. Houllemare, K.C. Namkung, Mineralization of phenol by a heterogeneous ultrasound/Fe-SBA-15/H<sub>2</sub>O<sub>2</sub> process: multivariate study by factorial design of experiments, *Appl. Catal. B: Environ.* 63 (2006) 15.
- [17] K.C. Namkung, A.E. Burgess, D.H. Bremner, A Fenton-like oxidation process using corrosion of iron metal sheet surfaces in the presence of hydrogen peroxide: a batch process study using model pollutants, *Environ. Technol.* 26 (2005) 341.
- [18] 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.
- [19] P. Senthilkumar, M. Sivakumar, A.B. Pandit, Experimental quantification of chemical effects of hydrodynamic cavitation, *Chem. Eng. Sci.* 55 (2000) 1633.
- [20] N.P. Vichare, P.R. Gogate, A.B. Pandit, Optimisation of hydrodynamic cavitation using a model reaction, *Chem. Eng. Technol.* 23 (2000) 683.
- [21] K.K. Jyoti, A.B. Pandit, Water disinfection by acoustic and hydrodynamic cavitation, *Biochem. Eng. J.* 7 (2001) 201.
- [22] P.R. Gogate, A.B. Pandit, Engineering design methods for cavitation reactors. II. Hydrodynamic cavitation, *AIChE J.* 46 (2000) 1641.
- [23] K.S. Suslick, M.M. Mdeleleni, J.T. Ries, Chemistry induced by hydrodynamic cavitation, *J. Am. Chem. Soc.* 119 (1997) 9303.
- [24] M.H. Entezari, P. Kruus, Effect of frequency on sonochemical reactions. II. Temperature and intensity effects, *Ultrason. Sonochem.* 3 (1996) 19.
- [25] N.P. Vichare, P. Senthilkumar, V.S. Moholkar, P.R. Gogate, A.B. Pandit, Energy analysis in acoustic cavitation, *Ind. Eng. Chem. Res.* 39 (2000) 1480.
- [26] J.-H. Sun, S.-P. Sun, M.-H. Fan, H.-Q. Guo, L.-P. Qiao, R.-X. Sun, A kinetic study on the degradation of *p*-nitroaniline by Fenton oxidation process, *J. Hazard. Mater.* 148 (2007) 172.
- [27] V. Kavitha, K. Palanivelu, Destruction of cresols by Fenton oxidation process, *Water Res.* 39 (2005) 3062.
- [28] H. Zhang, H.J. Choi, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, *J. Hazard. Mater.* 125 (2005) 166.
- [29] F.J. Rivas, F. Beltran, O. Gimeno, F. Carvalho, Fenton-like oxidation of landfill leachate, *J. Environ. Sci. Health A: Environ. Sci. Eng.* 38 (2003) 371.
- [30] T. Zhou, Y. Li, F.-S. Wong, X. Lu, Enhanced degradation of 2,4-dichlorophenol by ultrasound in a new Fenton like system (Fe/EDTA) at ambient circumstance, *Ultrason. Sonochem.* 15 (2008) 782.
- [31] J.-H. Sun, S.-P. Sun, J.-Y. Sun, R.-X. Sun, L.-P. Qiao, H.-Q. Guo, M.-H. Fan, Degradation of azo dye Acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation, *Ultrason. Sonochem.* 14 (2007) 761.
- [32] J.K. Kim, I.S. Metcalfe, Investigation of the generation of hydroxyl radicals and their oxidative role in the presence of heterogeneous copper catalysts, *Chemosphere* 69 (2007) 689.
- [33] 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.
- [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.