Cu-doped $\text{Bi}_2\text{O}_3/\text{Bi}^0$ composite as an efficient Fenton-like catalyst for degradation of 2-chlorophenol

Lili Zhang, Lai Lyu, Yulun Nie, Chun Hu *

Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

ARTICLE INFO

Article history:

Received 31 October 2014

Received in revised form 12 November 2015

Accepted 14 November 2015

Available online 14 November 2015

Keywords:

Cu-doped $\text{Bi}_2\text{O}_3/\text{Bi}^0$

Fenton-like

$\cdot\text{OH}$ radicals

2-Chlorophenol

ABSTRACT

Cu-doped BiO_x composites were prepared with and without citric acid. In the presence of citric acid, Bi^0 and $\text{Cu}^{2+}/\text{Cu}^+$ were confirmed to coexist in the composite (BiCu9/Bi^0) by X-ray diffraction and X-ray photoelectron spectroscopy. The catalyst showed high Fenton activity and stability for the degradation and mineralization of 2-chlorophenol in the pH range of 6–8. H_2O_2 was predominately converted into $\cdot\text{OH}$ radicals in BiCu9/Bi^0 suspension, as assessed by the electron spin resonance technique. In the composite, Bi^0 inhibited the oxidation of H_2O_2 by Cu^{2+} into O_2 and $\cdot\text{OH}$ by reducing Cu^{2+} , enhancing the reaction of H_2O_2 with Cu^+ to produce $\cdot\text{OH}$. Intermediate determination showed that 2-chlorophenol was decomposed mainly by $\cdot\text{OH}$ radicals into hydroxylation products, subsequently decomposed into short-chain organic acids, and eventually decomposed into CO_2 and H_2O .

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Iron-catalyzed hydrogen peroxide (H_2O_2) decomposition for generation of highly aggressive hydroxyl radicals ($\cdot\text{OH}$) has been extensively developed as Fenton oxidation processes for environmental applications. A variety of catalytic iron species, including Fe^{2+} and Fe^{3+} salts [1,2], iron oxides [3–6], and iron-immobilized zeolites [7], have been exploited for degradation and mineralization of recalcitrant organic pollutants, as well as for disinfection. However, the widespread use of iron-based Fenton oxidation for pollution abatement and disinfection is still limited by the requirement for strict acidic conditions, the requirement for UV irradiation to accelerate the reductive generation of Fe^{2+} and the uncontrolled leaching of iron ions from the catalyst's surface [4,8]. Therefore, non-iron Fenton catalysts, such as Au [9], carbon materials [10], cerium oxides [11], manganese oxides [12], and Cu-containing catalysts [13–16], and their reactivity towards H_2O_2 activation have been explored to overcome these problems.

Among these non-iron catalysts, Cu-containing catalysts have attracted considerable attention because the redox properties of copper are similar to those of iron. Importantly, a Cu-based Fenton-like system could work over a broader pH range than the Fe-based redox system [13,14]. In particular, $\text{Cu}^{2+}/\text{Cu}^+$ cycling has been found to result in the generation of reactive oxygen species in the presence of H_2O_2 [17–19]. Compared to $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycling,

which is usually limited by the reduction of Fe^{3+} due to the low rate constants [20], the reduction of Cu^{2+} by H_2O_2 occurs more easily than that of Fe^{3+} , and Cu^+ can react efficiently with H_2O_2 to form $\cdot\text{OH}$ with a higher reaction rate than Fe^{2+} [21,22]. However, the mobilization of Cu^+ limits its application due to its instability in water. The homogeneous reaction between Cu^+ and H_2O_2 is severely inhibited by O_2 in water because Cu^+ is quantitatively oxidized by O_2 to Cu^{2+} , which decreases the effective $[\text{Cu}^+]$ available for reaction with H_2O_2 [22]. Therefore, the immobilization of Cu^+ is required to overcome this problem. Two different methods for preparing copper-containing catalysts have been proposed: one yielding copper-doped samples and the other yielding copper supported on a porous solid substrate. Bismuth oxide (Bi_2O_3) is considered to be a good choice for a solid matrix because of its excellent catalytic, electrical, optical, and conducting properties [23,24]. Moreover, some reactions can proceed through a $\text{Bi(III)}/\text{Bi(0)}$ or $\text{Bi(III)}/\text{Bi(I)}$ redox couple in the presence of molecular oxygen [25]. Therefore, the aim of this work was to develop a highly active and stable heterogeneous Fenton-like catalyst by fixing Cu^+ and Cu^{2+} in a Bi_2O_3 structure.

In this paper, a composite catalyst with $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Bi}^0/\text{Bi}^{3+}$ was successfully synthesized by a citric acid-based sol–gel route. The performance of the catalyst was evaluated by degrading 2-chlorophenol (2-CP), which is a common model contaminant for the advanced oxidation process, a germicide/disinfectant, and an important precursor for synthesizing pesticides and other chlorophenols [26]. The Fenton-like degradation pathway of 2-CP was also investigated. The catalytic mechanism of Cu-doped

* Corresponding author.

E-mail address: huchun@rcees.ac.cn (C. Hu).

$\text{Bi}_2\text{O}_3/\text{Bi}^0$ was systematically studied on the basis of the effect of multivalent Cu and Bi^0 on the generation of $\cdot\text{OH}$ from H_2O_2 decomposition.

2. Experimental

2.1. Materials

Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), ethylene glycol, citric acid, 2-methoxyethanol, and H_2O_2 (30%, w/w) were purchased from Sinopharm Chemical Reagent Co., Ltd. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was supplied by Sigma. 2-CP was obtained from Acros. All chemicals were at least analytical grade and were used as received without further purification. Deionized water was used throughout this study.

2.2. Preparation of catalysts

Cu-doped $\text{Bi}_2\text{O}_3/\text{Bi}^0$ was prepared by a citric acid-based sol-gel route. The synthesized samples were designated as $\text{BiCu}_x/\text{Bi}^0$, where x indicated the Bi/Cu molar ratio. In the following, synthesis description for $\text{BiCu}_9/\text{Bi}^0$ is given. Typically, 9 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 1 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 20 mL of 2-methoxyethanol, followed by adding 20 μL of 0.1 M HNO_3 , 10 mmol citric acid (as a complexant) and 10 mL ethylene glycol (as a dispersant). After stirring for 1 h at 60 °C, the synthesis medium was incubated at 100 °C for 10 h to form the gel. Finally, the gel was calcined at 500 °C for 2 h in air. As a reference, BiO/Bi^0 was prepared as described above without $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ added. Cu_2O was also synthesized using a previously reported process [27]. To clarify the formation and effect of Bi^0 , BiO and BiCu_9 were prepared as described above without the addition of citric acid.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Scintag-XDS-2000 diffractometer with Cu K α radiation ($\lambda = 1.540598 \text{ \AA}$). The generator voltage and tube current used were 40 kV and 40 mA, respectively. The X'Pert HighScore Plus software (version 2.2.4) was used to semi-quantitatively determine the weight fraction of constituents. X-ray photoelectron spectroscopy (XPS) data were measured via an AXIS-Ultra instrument from Kratos using monochromatic Al K α radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, binding energies were calibrated using the C1s hydrocarbon peak at 284.8 eV. Electron spin resonance (ESR) spectra were obtained using a Bruker model ESP 300E electron paramagnetic resonance spectrometer.

2.4. Procedures and analysis

Unless indicated otherwise, 0.07 g of catalyst powders was dispersed in 50 mL of a 0.078 mM 2-CP solution at natural pH (approximately 6.0). The solution pH was not adjusted or controlled because it did not vary by more than 0.2 pH units during the catalytic reaction. The suspensions were stirred for approximately 20 min to establish an adsorption/desorption equilibrium between the solution and catalyst. Afterwards, the reaction was started by adding 20 mM H_2O_2 as an oxidant. At given time intervals, part of the suspension sample was withdrawn and filtered to remove catalyst powders for analysis. The concentrations of 2-CP and the intermediates catechol, p-benzoquinone and phenol were measured using high-performance liquid chromatography (1200 series; Agilent) with a Zorbax SB-Aq column (5 μm , $4.6 \times 250 \text{ mm}$; Agilent). The analysis was carried out at 275 nm

using a 60/40% v/v mixture of methanol/ultrapure water as the mobile phase. The total organic carbon (TOC) of the solution was analyzed using a TOC-V_{CPH} analyzer (Shimadzu). The measurements of chloride ions (Cl^-) and short-chain organic acids were conducted using a Dionex model ICS 2000 ion chromatograph (IC) equipped with an IonPac AS11-HC analytical column ($4 \times 250 \text{ mm}$) and using 40 mM KOH as an eluent.

In addition, the possible cation leaching (Bi, Cu) was monitored by inductively coupled plasma optical emission spectrometry (ICP-OES) on an Optima 2000 (PerkinElmer, Inc.) instrument. To test the stability and recyclability of $\text{BiCu}_9/\text{Bi}^0$, the catalyst was filtered, washed with water, dried at 70 °C and used again in the second cycle. This process was repeated several times.

All of the above experiments were repeated in triplicate, and the data are presented as the average of the triplicates, with a standard deviation of less than 5%.

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns of the synthesized samples were shown in Fig. 1. The characteristic peaks of $\alpha\text{-Bi}_2\text{O}_3$ (JCPDS 71-0465) and Bi^0 (JCPDS 85-1329) were present in all of the samples prepared in the presence of citric acid. The lattice parameters decreased with increasing copper content in Bi_2O_3 up to a Bi/Cu ratio of 9:1 as shown in Table 1, indicating that Cu^{2+} was incorporated into the Bi_2O_3 structure to replace Bi^{3+} , due to the smaller ionic radius of Cu^{2+} (72 pm) than that of Bi^{3+} (96 pm) [28]. However, further increase in Cu content resulted in the occurrence of the impurities Bi_2CuO_4 (JCPDS 80-1906) and Cu_2O (JCPDS 78-2076) in $\text{BiCu}_3/\text{Bi}^0$ (Fig. 1). Therefore, there was an upper limit of Cu content that could be incorporated inside the Bi_2O_3 structure. When citric acid was not added in the preparation process of BiO and BiCu_9 , pure $\alpha\text{-Bi}_2\text{O}_3$ was produced and no Bi^0 was found (e, f in Fig. 1), indicating that the formation of Bi^0 depended on the presence of citric acid in the course of synthesis.

XPS analysis was used to confirm the oxidation states of the Bi and Cu elements on the surface of $\text{BiCu}_9/\text{Bi}^0$. The binding energy of Bi 4f_{7/2} was 158.4 eV, which was assigned to Bi^{3+} [29]. Surface Bi^0 was not observed, but it appeared in the XRD patterns of $\text{BiCu}_9/\text{Bi}^0$, indicating that Bi^0 was in the interior of the catalyst and coated with Bi_2O_3 . Peaks corresponding to Cu 2p_{3/2} were observed at 932.4 and 934.2 eV for reduced copper species and Cu^{2+} ,

Fig. 1. XRD patterns of (a) BiO/Bi^0 , (b) $\text{BiCu}_{19}/\text{Bi}^0$, (c) $\text{BiCu}_9/\text{Bi}^0$, (d) $\text{BiCu}_3/\text{Bi}^0$, (e) BiO and (f) BiCu_9 . Some characteristic peaks in the patterns: (*) Bi^0 , (◆) Bi_2CuO_4 , (▼) Cu_2O .

Table 1
Lattice parameters and crystallite size of different samples.

Sample	Lattice parameters				Crystallite size (nm)
	a (Å)	b (Å)	c (Å)	β (°)	
BiO/Bi ⁰	5.8638	8.1677	7.5213	112.88	63.4
BiCu19/Bi ⁰	5.8498	8.1656	7.5169	112.89	58.0
BiCu9/Bi ⁰	5.8487	8.1518	7.5016	112.96	64.4

respectively, in Fig. 2 [30]. Reduced copper species, i.e., Cu⁰ and/or Cu⁺, were further identified by auger electron spectroscopy (AES). The auger parameter of the element Cu was 1849.4 eV, confirming the existence of Cu⁺ [31]. The surface concentration ratio of Cu²⁺ to Cu⁺ was 2.32:1 for BiCu9/Bi⁰. However, the Cu 2p_{3/2} peak for BiCu9 was only observed at 934.1 eV (Fig. S1), indicating that only Cu²⁺ was present on the surface of BiCu9 prepared without the addition of citric acid. All of the above results indicated that in the preparation process, the oxidation of citric acid led to the reduction of Bi³⁺ and Cu²⁺, inducing the formation of Bi⁰ and Cu⁺ in the composite.

3.2. Catalytic activity of catalysts in fenton-like reaction

The catalytic activity of different catalysts was evaluated based on the oxidation of 2-CP with H₂O₂ at natural pH (approximately 6.0) in Fig. 3. Less than 52% of the 2-CP was degraded by BiO/Bi⁰, BiCu9 or BiO in the presence of H₂O₂ within 120 min, while the coexistence of Cu and Bi⁰ in the Bi₂O₃ structure strongly increased

Fig. 2. XPS spectra of BiCu9/Bi⁰: (A) Cu 2p_{3/2}, (B) Cu LMM X-ray induced Auger parameter.

Fig. 3. The degradation and mineralization of 2-CP (0.078 mM) in the presence of H₂O₂ (20 mM) and catalysts (1.4 g L⁻¹): (a) BiO/Bi⁰, (b) BiCu19/Bi⁰, (c) BiCu9/Bi⁰, (d) BiCu3/Bi⁰, (e) BiO, (f) BiCu9 and (g) Cu₂O.

the Fenton catalytic activity of the oxides. The degradation rate of 2-CP increased with increasing Cu content in the catalysts from BiCu19/Bi⁰ to BiCu9/Bi⁰, but the presence of excessive Cu in the BiCu3/Bi⁰ did not significantly increase the degradation of 2-CP. Complete removal of 2-CP was achieved within 120 min in the BiCu9/Bi⁰-H₂O₂ system. Similarly, BiCu9/Bi⁰ had the highest TOC removal rate, over 75% within 360 min. In the presence of Cu₂O and H₂O₂, only 24% of the 2-CP was degraded after 120 min, indicating that the Fenton activity of Cu₂O with only Cu⁺ was reduced. This result suggested that the enhanced Fenton catalytic efficiency stemmed from the coexistence of Cu⁺, Cu²⁺ and Bi⁰ in the Bi₂O₃ structure. In addition, BiCu9/Bi⁰ could be reutilized for at least six cycles and exhibited no significant activity loss (Fig. 4). Moreover, no significant leaching of Bi and Cu ions was found in the BiCu9/Bi⁰ suspension after stirring for 120 min. It is possible that the multivalent metal state on the surface of BiCu9/Bi⁰ enhanced interfacial electron transfer, inhibiting the release of metal ions. These results indicated that BiCu9/Bi⁰ had high Fenton catalytic activity and excellent long-term stability.

Fig. 5 shows the degradation of 2-CP in the BiCu9/Bi⁰ suspension with H₂O₂ at different initial pHs. BiCu9/Bi⁰ exhibited similarly high activity at the tested pHs (6–8), suggesting that the catalyst could function in a wide and non-extreme pH range, which is well-suited for real application in wastewater treatment.

The changes of some intermediates were followed by the degradation of 2-CP in Fig. 6. The concentration of Cl⁻ increased with time, and more than 85% of the total chlorine content was converted into Cl⁻ at 120 min. The primary aromatic products were

Fig. 4. Cycling runs in the degradation of 2-CP (0.078 mM) with BiCu9/Bi⁰ and H₂O₂.

Fig. 5. Effect of initial pH on the degradation of 2-CP (0.078 mM) in the presence of BiCu9/Bi⁰ suspensions (1.4 g L⁻¹) and H₂O₂ (20 mM): (a) 6.0, (b) 7.0, (c) 8.0.

Fig. 6. Evolution of chloride ion and organic intermediates during 2-CP (0.078 mM) oxidation in the presence of BiCu9/Bi⁰ (1.4 g L⁻¹) and H₂O₂ (20 mM).

catechol, phenol and p-benzoquinone. The concentration of these products increased and reached a maximum at 10 min, 30 min and 60 min, respectively, and then gradually decreased and completely disappeared within 120 min. Furthermore, maleic acid and succinic acid were detected in trace amounts, showed a peak concentration and then disappeared within 240 min, while oxalic

acid continuously increased and tended to have a stable concentration. In summary, 2-CP was oxidized into hydroxylation products, subsequently into short-chain organic acids and eventually into CO₂ and H₂O.

3.3. Reaction mechanism

According to the XPS data of BiCu9/Bi⁰, the surface concentration ratio of Cu²⁺ to Cu⁺ was approximately 2.32:1 before the reaction and remained at a similar ratio of 2.17:1 after the catalytic runs (Fig. S2). The concentration of Bi³⁺ on the surface of the catalyst did not change before or after the reaction. Moreover, Bi⁰ was still present in the XRD pattern of BiCu9/Bi⁰ after the reaction (Fig. S3). The concentration ratio of Bi⁰ to Bi³⁺ was approximately 0.0465 in BiCu9/Bi⁰ after reaction for 120 min, which is more than the ratio 0.0113 before the reaction. The Bi⁰ to Bi³⁺ ratio returned to 0.0345 after reaction for 720 min based on the semi-quantitative analysis of XRD (Table S1). The results indicated that electron cycling involving Cu⁺/Cu²⁺ and Bi⁰/Bi³⁺ occurred during the reaction. The characteristic peaks of DMPO-·OH and DMPO-HO₂/O₂⁻ adducts were monitored in aqueous and methanolic suspensions [32] of different catalysts with H₂O₂ by the ESR spin-trapping technique (Fig. 7). Reduction of H₂O₂ will produce ·OH, while the oxidation of H₂O₂ will generate HO₂/O₂⁻, based on the characteristics of Fenton chemistry. In BiO suspensions, H₂O₂ was mainly converted into HO₂/O₂⁻ with the formation of a small amount of ·OH. However, more ·OH radicals were formed in BiO/Bi⁰ suspension than in BiO suspension, and the generation

Fig. 7. ESR spectra recorded in suspensions of different samples with H₂O₂ in aqueous dispersion (A) for DMPO-·OH and in methanol dispersion (B) for DMPO-HO₂/O₂⁻.

Scheme 1. Proposed mechanism for the effective generation of $\cdot\text{OH}$ during the interaction of BiCu9/Bi 0 with H_2O_2 .

of HO_2/O_2^- was greatly reduced. The results showed that Bi 0 could reduce H_2O_2 to $\cdot\text{OH}$ and was oxidized either to Bi $^+$ or to Bi $^{3+}$, which was reduced to Bi 0 again during the pollutant oxidation [33], inhibiting the oxidation of H_2O_2 into HO_2/O_2^- . With the introduction of Cu, the amount of $\cdot\text{OH}$ slightly increased, while the formation of HO_2/O_2^- did not change in BiCu9 suspensions compared with in BiO suspension, indicating that the reaction between Cu^{2+} and H_2O_2 occurred as follows [18,19]:

It is worth noting that the formation of $\cdot\text{OH}$ was greatly enhanced in BiCu9/Bi 0 suspension, while the amount of HO_2/O_2^- was not changed from that in BiO/Bi 0 suspension. Based on the characterization of BiCu9/Bi 0 , $\text{Cu}^{+/2+}$ and Bi $^{0/3+}$ coexisted in the composite. Moreover, Cu^+ is able to react easily with H_2O_2 to produce $\cdot\text{OH}$ and Cu^{2+} , and the formed Cu^{2+} can be reduced into Cu^+ by Bi 0 [25], inhibiting the oxidation of H_2O_2 by Cu^{2+} to O_2 and $\cdot\text{OH}$. Therefore, H_2O_2 was predominantly converted into $\cdot\text{OH}$ by the reaction of Cu^+ with H_2O_2 in BiCu9/Bi 0 suspension.

All of the above results suggest that an interfacial electron cycle process occurred as shown in Scheme 1. The presence of Bi 0 in the Bi $_2\text{O}_3$ structure promoted the reduction of H_2O_2 into $\cdot\text{OH}$ and inhibited the oxidation of H_2O_2 into HO_2/O_2^- . Moreover, Cu^+ interacted with H_2O_2 , producing $\cdot\text{OH}$, which was strongly enhanced by a fast reduction of Cu^{2+} by Bi 0 . Therefore, the synergetic effect of multivalent Cu and Bi 0 in the Bi $_2\text{O}_3$ structure facilitated the effective decomposition of H_2O_2 into $\cdot\text{OH}$, resulting in the high catalytic activity of BiCu9/Bi 0 .

4. Conclusions

Cu-doped Bi $_2\text{O}_3$ /Bi 0 was successfully prepared by a citric acid-based sol–gel route. The catalyst exhibited high activity and stability for the degradation and mineralization of 2-CP with H_2O_2 in the pH range of 6–8. The use of 1.4 g L^{-1} BiCu9/Bi 0 and 20 mM H_2O_2 led to the complete removal of 2-CP (0.078 mM) within 120 min at natural pH. The excellent catalytic performance was due to the coexistence of Bi $^{0/3+}$ and $\text{Cu}^{+/2+}$ in the catalyst structure. The interaction of multivalent Cu and Bi greatly enhanced the conversion of H_2O_2 into $\cdot\text{OH}$ radicals under natural conditions. 2-CP was decomposed mainly by $\cdot\text{OH}$ radicals into hydroxylation products, subsequently decomposed into short-chain organic acids and eventually decomposed into CO_2 and H_2O . These promising results suggest potential for the proposed heterogeneous Fenton process to be applied in actual wastewater treatment.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21407165, 51278527, 21125731, 51138009, 51538013), the National 863 Project of China (Grant No. 2012AA062606) and Key Laboratory of Drinking Water Science and Technology, Chinese Academy of Sciences (15Z04KLDWST).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2015.11.021>.

References

- [1] J.A. Zazo, J.A. Casas, A.F. Mohedano, M.A. Gilarranz, J.J. Rodríguez, Chemical pathway and kinetics of phenol oxidation by Fenton's reagent, *Environ. Sci. Technol.* 39 (2005) 9295–9302.
- [2] K. Ntampeliotis, A. Riga, V. Karayannis, V. Bontozoglou, G. Papapolymerou, Decolorization kinetics of Procion H-exl dyes from textile dyeing using Fenton-like reactions, *J. Hazard. Mater.* 136 (2006) 75–84.
- [3] I.S.X. Pinto, P.H.V.V. Pacheco, J.V. Coelho, E. Lorençon, J.D. Ardisson, J.D. Fabris, P.P. Souza, K.W.H. Krambrock, L.C.A. Oliveira, M.C. Pereira, Nanostructured $\delta\text{-FeOOH}$: an efficient Fenton-like catalyst for the oxidation of organics in water, *Appl. Catal. B: Environ.* 119–120 (2012) 175–182.
- [4] V. Cleveland, J.P. Bingham, E. Kan, Heterogeneous Fenton degradation of bisphenol A by carbon nanotube-supported Fe_3O_4 , *Sep. Purif. Technol.* 133 (2014) 388–395.
- [5] X. Yang, X. Xu, J. Xu, Y. Han, Iron oxychloride (FeOCl): an efficient Fenton-like catalyst for producing hydroxyl radicals in degradation of organic contaminants, *J. Am. Chem. Soc.* 135 (2013) 16058–16061.
- [6] A. Gajović, A.M.T. Silva, R.A. Segundo, S. Šturm, B. Jančar, M. Čeh, Tailoring the phase composition and morphology of Bi-doped goethite-hematite nanostructures and their catalytic activity in the degradation of an actual pesticide using a photo-Fenton-like process, *Appl. Catal. B: Environ.* 103 (2011) 351–361.
- [7] H. Hassan, B.H. Hameed, Oxidative decolorization of Acid Red 1 solutions by Fe-zeolite Y type catalyst, *Desalination* 276 (2011) 45–52.
- [8] L. Chen, J. Ma, X. Li, J. Zhang, J. Fang, Y. Guan, P. Xie, Strong enhancement on Fenton oxidation by addition of hydroxylamine to accelerate the Ferric and Ferrous iron cycles, *Environ. Sci. Technol.* 45 (2011) 3925–3930.
- [9] S. Navalon, M. de Miguel, R. Martin, M. Alvaro, H. Garcia, Enhancement of the catalytic activity of supported gold nanoparticles for the Fenton reaction by light, *J. Am. Chem. Soc.* 133 (2011) 2218–2226.
- [10] M. Soria-Sánchez, E. Castillejos-López, A. Maroto-Valiente, M.F.R. Pereira, J.J.M. Órfão, A. Guerrero-Ruiz, High efficiency of the cylindrical mesopores of MWCNTs for the catalytic wet peroxide oxidation of C.I. Reactive Red 241 dissolved in water, *Appl. Catal. B: Environ.* 121–122 (2012) 182–189.
- [11] F. Chen, X. Shen, Y. Wang, J. Zhang, $\text{CeO}_2/\text{H}_2\text{O}_2$ system catalytic oxidation mechanism study via a kinetics investigation to the degradation of acid orange 7, *Appl. Catal. B: Environ.* 121–122 (2012) 223–229.
- [12] T. Rhaefi, J.Y. Piquemal, L. Sicard, F. Herbst, E. Briot, M. Benedetti, A. Atlamsani, Polyol-made Mn_3O_4 nanocrystals as efficient Fenton-like catalysts, *Appl. Catal. A: Gen.* 386 (2010) 132–139.
- [13] F.L.Y. Lam, A.C.K. Yip, X. Hu, Copper/MCM-41 as a highly stable and pH-insensitive heterogeneous photo-Fenton-like catalytic material for the abatement of organic wastewater, *Ind. Eng. Chem. Res.* 46 (2007) 3328–3333.
- [14] X. Zhang, Y. Ding, H. Tang, X. Han, L. Zhu, N. Wang, Degradation of bisphenol A by hydrogen peroxide activated with CuFeO_2 microparticles as a heterogeneous Fenton-like catalyst: Efficiency, stability and mechanism, *Chem. Eng. J.* 236 (2014) 251–262.
- [15] X. Zhong, J. Barbier Jr., D. Duprez, H. Zhang, S. Royer, Modulating the copper oxide morphology and accessibility by using micro-/mesoporous SBA-15 structures as host support: Effect on the activity for the CWPO of phenol reaction, *Appl. Catal. B: Environ.* 121–122 (2012) 123–134.
- [16] O.P. Taran, S.A. Yashnik, A.B. Ayusheev, A.S. Piskun, R.V. Prihod'ko, Z.R. Ismagilov, V.V. Goncharuk, V.N. Parmon, Cu-containing MFI zeolites as catalysts for wet peroxide oxidation of formic acid as model organic contaminant, *Appl. Catal. B: Environ.* 140–141 (2013) 506–515.
- [17] M. Masarwa, H. Cohen, D. Meyerstein, D.L. Hickman, A. Bakac, J.H. Espenson, Reactions of low-valent transition-metal complexes with hydrogen peroxide. Are they "Fenton-like" or not? 1. The case of Cu^{+aq} and Cr^{2+aq} , *J. Am. Chem. Soc.* 110 (1988) 4293–4297.
- [18] L. Khachatryan, E. Vejerano, S. Lomnicki, B. Dellinger, Environmentally persistent free radicals (EPRs). 1. Generation of reactive oxygen species in aqueous solutions, *Environ. Sci. Technol.* 45 (2011) 8559–8566.
- [19] L. Liu, D. Jiang, A. McDonald, Y. Hao, G.L. Millhauser, F. Zhou, Copper redox cycling in the prion protein depends critically on binding mode, *J. Am. Chem. Soc.* 133 (2011) 12229–12237.
- [20] Y. Wang, W. Ma, C. Chen, X. Hu, J. Zhao, J.C. Yu, $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycling promoted by Ta3N5 under visible irradiation in Fenton degradation of organic pollutants, *Appl. Catal. B: Environ.* 75 (2007) 256–263.
- [21] A.N. Pham, A.L. Rose, T.D. Waite, Kinetics of Cu(II) reduction by natural organic matter, *J. Phys. Chem. A* 116 (2012) 6590–6599.
- [22] A.D. Bokare, W. Choi, Review of iron-free Fenton-like systems for activating H_2O_2 in advanced oxidation processes, *J. Hazard. Mater.* 275 (2014) 121–135.
- [23] A. Hameed, T. Montini, V. Gombac, P. Fornasiero, Surface phases and photocatalytic activity correlation of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_{4-x}$ nanocomposite, *J. Am. Chem. Soc.* 130 (2008) 9658–9659.

- [24] N. Pugazhenthiran, P. Sathishkumar, S. Murugesan, S. Anandan, Effective degradation of acid orange 10 by catalytic ozonation in the presence of Au-Bi₂O₃ nanoparticles, *Chem. Eng. J.* 168 (2011) 1227–1233.
- [25] S. Antonioti, E. Duñach, Studies on the catalytic oxidation of epoxides to α -diketones by Bi(0)/O₂ in DMSO, *J. Mol. Catal. A: Chem.* 208 (2004) 135–145.
- [26] G.B.O. Plata, O.M. Alfano, A.E. Cassano, 2-Chlorophenol degradation via photo Fenton reaction employing zero valent iron nanoparticles, *J. Photochem. Photobiol. A: Chem.* 233 (2012) 53–59.
- [27] W. Huang, L.M. Lyu, Y. Yang, M. Huang, Synthesis of Cu₂O nanocrystals from cubic to rhombic dodecahedral structures and their comparative photocatalytic activity, *J. Am. Chem. Soc.* 134 (2012) 1261–1267.
- [28] A.C. Silva, D.Q.L. Oliveira, L.C.A. Oliveira, A.S. Anastácio, T.C. Ramalho, J.H. Lopes, H.W.P. Carvalho, C.E.R. Torres, Nb-containing hematites Fe_{2-x}Nb_xO₃: The role of Nb⁵⁺ on the reactivity in presence of the H₂O₂ or ultraviolet light, *Appl. Catal. A: Gen.* 357 (2009) 79–84.
- [29] R. Li, W. Chen, H. Kobayashi, C. Ma, Platinum-nanoparticle-loaded bismuth oxide: an efficient plasmonic photocatalyst active under visible light, *Green Chem.* 12 (2010) 212–215.
- [30] F.E. Lopez-Suarez, S. Parres-Esclapez, A. Bueno-Lopez, M.J. Illan-Gomez, B. Ura, J. Trawczynski, Role of surface and lattice copper species in copper-containing (Mg/Sr)/TiO₃ perovskite catalysts for soot combustion, *Appl. Catal. B: Environ.* 93 (2009) 82–89.
- [31] F.E. Lopez-Suarez, A. Bueno-Lopez, M.J. Illan-Gomez, A. Adamski, B. Ura, J. Trawczynski, Copper catalysts for soot oxidation: alumina versus perovskite supports, *Environ. Sci. Technol.* 42 (2008) 7670–7675.
- [32] W. Ma, Y. Huang, J. Li, M. Cheng, W. Song, J. Zhao, An efficient approach for the photodegradation of organic pollutants by immobilized iron ions at neutral pHs, *Chem. Commun.* (2003) 1582–1583.
- [33] S. Antonioti, E. Duñach, Mechanistic aspects of the bismuth-catalysed oxidation of epoxides to α -diketones, *Eur. J. Org. Chem.* (2004) 3459–3464.