Chiang Mai J. Sci. 2021; 48(4) : 1079-1088
http://epg.science.cmu.ac.th/ejournal/
Contributed Paper

Salen-Porphyrin Complex-Catalyzed Degradation of Chlorophene by Hydrogen Peroxide

Xujie Lu [a,c], Liang Wang*[b], Xiao-Jun Yang [d], Rui-Na Liu [a] and Xue-Fei Zhou*[c,d,e]

[a] College of Ecology and Environment, Hainan Tropical Ocean University, Sanya 572022, China.
[b] Shandong Provincial Key Laboratory of Water and Soil Conservation and Environmental Protection, College of Resources and Environment, Linyi University, Linyi 276000, China.
[c] Key Laboratory of Clean Dyeing and Finishing Technology of Zhejiang Province, Shaoxing University, Shaoxing 312000, China.
[d] Key Laboratory of Green Chemical Engineering Process of Ministry of Education, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430205, China.
[e] Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, China.

*Author for correspondence; e-mail: wangliang.cn@163.com, lgdx602@sina.com

Received: 6 October 2020
Revised: 14 November 2020
Accepted: 27 November 2020

ABSTRACT

The present study aimed to investigate degradation and detoxification of chlorophene (CP). The removal percent of CP of each parameter was investigated and compared in catalytic treatments in the presence of hydrogen peroxide using salen, porphyrin and salen-porphyrin complexes as the biomimetic catalysts. The CP concentration and degradation products of treated CP solutions were analysed by HPLC and LC-TOF-MS, respectively. Their toxicity were evaluated according to the growth inhibition of *Chlorella vulgaris* (*C. vulgaris*), and explained in terms of total carbon content (TCC). Comparing the removal percent of CP in three above-mentioned processes, it could be concluded that, in the process by the use of zinc salen-porphyrin complex ($ZnPSC_6$), CP degradation and detoxification were rather better than zinc salen complex (Zn(salen)) and zinc porphyrin complex (Zn(Phe-TPP))-treatments, and further improved when imidazole and pyridine were added. The results reported in this work indicate that $ZnPSC_6$ derived from the combination of salen and porphyrin complexes significantly improved the CP degradation in catalytic treatment.

Keywords: biomimetic catalysis, catalytic degradation, chlorophene, ecotoxicity, salen-porphyrin complex

1. INTRODUCTION

With the development of modern technology, pharmaceuticals and personal care products (PPCPs) have been widely applied in the world. Meanwhile, more and more people have focused concerns on the toxicity of PPCPs as new emerging pollutants [1, 2]. Although PPCPs have low level in environmental concentration with a short half-life, they endanger the health of humans by accumulating in the food chain in the process of releasing to the environment [3]. Among them, chlorophene (CP), as a fungicide, is also widely used in hospital, family, industry and agriculture because of its wide spectrum and high efficiency. CP is similar to chlorophenols in toxic properties.

CP is relatively hydrophobic with a *n*-octanol/water partition coefficient (LogKow) of 3.6-4.2. When released to the environment, it is easy to accumulate in sediments and organisms. CP is potential persistent organic pollutant and may remain in soil or water for prolonged period. It was documented that CP had carcinogenic and mutagenic activity in animals [4]. These properties cause low removal efficiency of CP by general technologies. It has been reported that CP was detected in a number of natural waters (up to 10 μg/L). Thus, the degradation process of CP needs to be further studied [5].

Generally, the physical and chemical processes are mainly used in the field of CP treatment. He *et al.* [6] investigated the UV irradiation for the destruction of CP in aqueous solution. Another study, carried out by Bolobajev and Goi [7], showed that the addition of Fe(II) substantially improved the CP treatment by H_2O_2. In addition, Perko *et al.* studied the reactivity of three different metallic alloys such as Raney Al-Ni, Devarda's Al-Cu-Zn alloy, and Arnd's Cu-Mg alloy for the hydrodechlorination of CP, in which CP could be completely dechlorinated using Al in the form of Raney Al-Ni alloy in alkaline aqueous solution at ambient temperature and pressure during 20 h of vigorous stirring [8]. Furthermore, biodegradation is the important process reported to be active in catalyzed removal of CP [5, 9, 10]. However, biocatalysis has disadvantages of low efficiency and chemocatalysis has disadvantages of low selectivity. Therefore, achieving a considerable extended degradation is more likely if the advantages of biocatalysis and chemocatalysis are combined. This may be expected to be a simple and feasible approach that allows the selectivity and efficiency of degradation to be considered simultaneously. Meanwhile, biomimetic catalysis is increasingly used for oxidation, such as the application of salen and porphyrin complexes [11, 12].

Salen complex as a member of biomimetic catalyst family has extensive catalytic activities for various organic substrates. Metalloporphyrins have active centers similar to those of lignin peroxidase (LiP) and manganese peroxidase (MnP) which catalyze the oxidation of C–C, C–O in the structure [13]. Furthermore, salen-porphyrin binuclear complexes can be used as an active site model of metalloenzymes. They had advantages as follows: combining performances of salen and porphyrin complexes; combining performances of chemo- and bio-catalysts [14]. In fact, it was observed by Li *et al.* [15] that the increase in the active sites in the binuclear complex resulted in the increasing conversion of substrates. They were thus used in this work for improving the chlorophene degradation in aqueous solution. The relevant results would provide a conceptual guide for utilization of salen-porphyrin complex to treat POPs.

2. MATERIALS AND METHODS

2.1 Chemicals

Chlorophene (chromatographic grade) and methanol (chromatographic grade) were purchased from Sigma-Aldrich and stored at 4 °C. Chloroform (Sinopharm Chemical Reagent Co., Ltd) was dried with $NaHCO_3$ and $CaCl_2$, and distilled prior to use. Other chemicals (Sinopharm Chemical Reagent Co., Ltd) used were analytical grade chemicals. A Milli-Q-Plus ultrapure water was used in all experiments.

2.2 Synthesis of Salen-porphyrin Complex

Salen-porphyrin complex was prepared following the procedure as published in the literature [16].

Firstly, HPTPP (5,10,15-triphenyl-20-*p*-hydroxyl phenyl porphyrin) was prepared. *p*-Hydroxyl benzaldehyde (22 g) and benzaldehyde (55 ml) were mixed in a flask at 140 °C for 20 min using propionic acid (1800 mL) as solvent. The reaction continued at 130 °C for 30 min after pyrrole (50 mL) was added, and the mixture was placed for 12 h at room temperature without agitation. Part of propionic acid (~50 %) was removed with vacuum evaporation, and ethanol was added equally.

The reaction was left standing for 24 h, and the precipitate was recovered by filtration, washed with ethanol, dried in vacuum and purified with chloroform in a neutral alumina column. HPTPP obtained in purification was vacuum-dried and eluted with a mixture of chloroform and petroleum ether (1:1) in a neutral alumina column.

Secondly, salen-OH was prepared. Salicylaldehyde (620 mg), *o*-phenylenediamine (560 mg) and *2*,5-dihydroxybenzaldehyde (680 mg) were stirred in chloroform (62 mL) at 25 °C for 20 h. The solution obtained after precipitation was vacuum-dried and eluted with column chromatography. The salen-OH obtained after elution was concentrated and purified by silica gel column.

Thirdly, salen$(CH_2)_6$Br was prepared. Salen-OH (0.20 mmol) and Br$(CH_2)_6$Br (2.0 mmol) were dissolved in acetone (20 mL), and was added with anhydrous K_2CO_3 (3.70 mmol). The mixture was refluxed in dark for 5 h, vacuum-dried and purified with chloroform using extraction. The organic layers containing salen$(CH_2)_6$Br were collected, dried with anhydrous Na_2CO_3 and purified with chloroform with column chromatography.

Fourthly, HPTPP-$(CH_2)_6$-salen ($HPSC_6$) was prepared. HPTPP (0.30 mmol) reacted with salen$(CH_2)_6$Br (3.0 mmol) in acetone (30 mL) in the presence of anhydrous K_2CO_3 (3.0 mmol). at 25 °*C* for 15 h in dark. After that, the mixture was vacuum-dried, extracted with chloroform and washed with ultrapure water. The organic phases were collected and dried with anhydrous Na_2SO_4 to obtain $HPSC_6$, and then purified using chloroform with silica gel column.

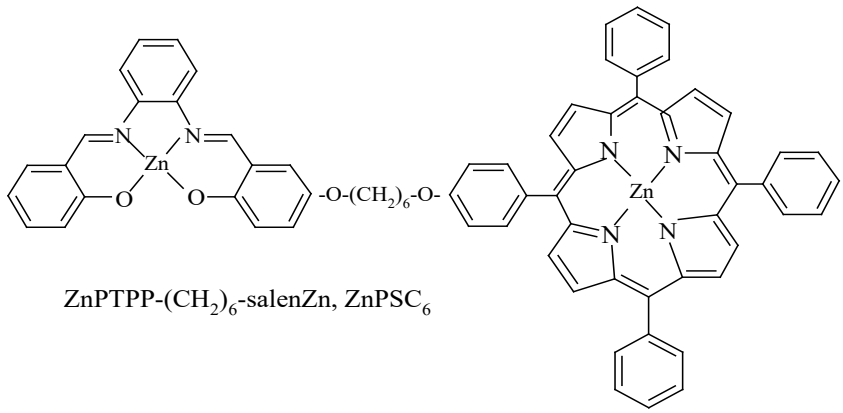
Fifthly, ZnPTPP-$(CH_2)_6$-salenZn ($ZnPSC_6$) was prepared. $HPSC_6$ (0.30 mmol) was refluxed in chloroform (20 mL) for 10 min, reacted with $Zn(CH_3COO)_2$ (in saturated methanol solution, 10 mL) for 5 h in refluxing. The mixture was dried with anhydrous Na_2SO_4 and purified using chloroform with silica gel column to obtain $ZnPSC_6$ (Figure 1).

The whole synthesis was carried out in a nitrogen atmosphere.

$ZnPSC_6$: $Zn_2C_{70}H_{52}N_6O_4$, 66.30 % C (66.07 %), 4.23 % H (4.11 %), 6.76 % N (6.51 %). ^{1}H-NMR ($CDCl_3$): $(CH_2)_n$, 1.243-1.652; -O-CH_2, 3.411; P-O-CH_2, 4.194; -phenyl, 7.261-7.296; -phenyl 3,5/-phenyl 3',5', 7.774-7.872; -phenyl 2,6/-phenyl 2',6', 8.112-8.203; -C=N, 8.596/8.603; -Pyrrole-H, 8.85-8.92.

2.3 Synthesis of Zn(salen) Complex

Salen was synthesized in methanol using ethylenediamine and salicylaldehyde, and Zn(salen) was obtained in refluxing from the reaction of salen with $Zn(CH_3COO)_2$ [17].



ZnPTPP-$(CH_2)_6$-salenZn, $ZnPSC_6$

Figure 1. $ZnPSC_6$.

2.4 Synthesis of Zinc Porphyrin (Zn(Phe-TPP))

N-Chloroacetyl phenylalanine (0.11 mol) and 5-(p-hydroxylphenyl)-10,15,20- tris(p-chlorophenyl) porphyrin (0.38 mol) were prepared following the procedure as described in the literature [18], and then they were subjected to the equimolar reaction in N,N-dimethylformamide (DMF, 50 mL) in the presence of pyridine (50 mL) and potassium carbonate (2 g) to obtain 5-p-(N-phenylalanine formyl methoxyl) phenyl-10,15,20-tris(p-chlorophenyl) porphyrin (Zn(Phe-TPP)) and purified with a neutral alumina column chromatography, followed by the reflux in DMF for 30 min in the presence of zinc acetate (0.2 mmol). The mixture was precipitated at room temperature. The sediment obtained by filtration was dried, eluted with alumina column chromatography, and finally was recrystallized in chloroform-ethanol to obtain Zn(Phe-TPP). Zn(Phe-TPP): $ZnC_{55}H_{36}O_4N_5Cl_3$; 65.33 % C (65.88 %), 3.47% H (3.62 %), 6.38 % N (6.98 %). FTIR: -COOH, 1722 cm^{-1}; porphyrin ring, 1004 cm^{-1}; C-N, 1483 cm^{-1}; benzene ring in tetraphenyl porphyrin, 1594/1022/1003/880 cm^{-1}; porphyrin skeleton, 1547/1475/1243/1055 cm^{-1}; zinc porphyrin, 1364 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 8H/Ph-NH_2, 5.62; 8H/m-ArH, 6.74-7.46; 8H/O-ArH, 7.61-8.43; 8H/β-pyrrole, 8.95.

2.5 Catalytic Degradation of CP

The reaction was carried out in a flask immersed in a water bath using $ZnPSC_6$, Zn(salen) and Zn(Phe-TPP) as catalysts. H_2O_2 was added to the solution, and the mixture containing 0.02 mol/L CP was stirred at 120 r/min, during which pH value was adjusted with buffer solution (pH 3, 5: citric acid + sodium citrate; pH 7: sodium dihydrogen phosphate + dibasic sodium phosphate; pH 9: Tris + hydrochloric acid; pH 11: sodium bicarbonate + sodiun hydroxide). Taking out 0.50 mL reaction liquid at a certain reaction time after adding methanol and catalase, and then the mixture was separated in a SPE column (LC-C18) using methanol as eluent for the next analysis. Control trials were carried out in the absence of catalyst.

To make it simple, the ratio of C_t/C_0 was used to characterize the catalytic rate. Replicates were performed and good reproducibility was obtained in this work, with a coefficient of variation less than 3%.

2.6 Determination of CP and TCC

The CP content was determined at 230 nm on HPLC equipped with Zorbax Eclipse Plus C18 column (250 mm×4.6 mm×5 μm). A mixture of methanol and water (4:1, v/v) was used as the mobile phase and the flow rate was set at 1 mL/min. The total carbon content (TCC) of the CP solutions obtained from the treatment was analyzed with an elemental analyzer (Vario EL).

2.7 LC-TOF-MS

Identification of the CP degradation products was performed with negative ion mode on an Agilent 5600 LC-TOF-MS, equipped with a Agilent Poroshell 120 SB-C18 (3.0 mm×100 mm×2.7 μm). This HPLC system was connected to a time-of-flight mass spectrometer (MSD-TOF, Agilent Technologies) equipped with an electrospray interface under the following operating parameters: capillary 4500 V, nebulizer 50 psig, drying gas 10 L/min, gas temperature 280 °C, fragmentor 195 V, skimmer 60 V. The mixture of methanol and water (4:1, v/v) was used as the mobile phase and the flow rate was set at 0.20 mL/min. Spectra were acquired over the m/z 50-1000 range at a scan rate of 1 s/spectrum.

2.8 Toxicity Evaluation

The toxicity was evaluated according to the growth inhibition of the unicellular green algae *Chlorella vulgaris* (*C. vulgaris*) following a previously reported procedure [19].

Replicates (at least 3 replicates) were carried out and better reproducibility was obtained, with a coefficient of variation less than 3% (significant power>90%).

3. RESULTS AND DISCUSSION

3.1 Optimization of Reaction Conditions

In the catalytic oxidation of CP, $ZnPSC_6$, Zn(Phe-TPP) and Zn(salen) were used in the presence of hydrogen peroxide. This is expected that the reactivity of the catalysts depended on their structure (Figure 2); after the catalytic oxidation of 40 min by $ZnPSC_6$, the conversion of CP was 100 % at 30 °C, 82 % by Zn(Phe-TPP), and was only 78 % by Zn(salen) (Figure 2a). $ZnPSC_6$ was an active catalyst due to the well-defined structure combining the salen and porphyrin complex. In $ZnPSC_6$, there are two active sites to enhance the catalytic activity of the complex [20], clearly increasing the conversion of CP.

The effect of $ZnPSC_6$ concentration on the degradation of CP was investigated, as shown in Figure 2b. In range of 0 ppm-3 ppm, the degradation rate of CP evidently increased with the increasing $ZnPSC_6$ concentration; when $ZnPSC_6$ concentration was set at 3 ppm-5 ppm, little effects of $ZnPSC_6$ concentration were observed. A low catalyst concentration (3 ppm) was sufficient to demonstrate the activity of $ZnPSC_6$ in the oxidations of CP. In the catalytic oxidation of CP, no improvement after reaction of 30 min was achieved despite a higher concentration (5 ppm) of $ZnPSC_6$ (Figure 2b). In this case, the degradation rate of CP in the $ZnPSC_6$ catalyzed reaction was about 12-fold higher than the uncatalyzed reaction. The effect of reaction temperature on the CP degradation is shown in Figure 2c. The degradation rate of CP increased with the increasing reaction temperature, however, little improvement was achieved in CP degradation when the reaction temperature was regulated in the range of 30 °C-50 °C. Similar results were found for hydrogen peroxide dosage that a superior degradation was obtained for CP under the dosage of 0.8 mmol/L hydrogen peroxide (Figure 2d). In addition, the $ZnPSC_6$-catalysed reaction rate of CP was positively dependent on pH when pH value was set in the range of 3-7 compared to 7-9 (Figure 2e). At pH = 7, the catalytic rate of 30 min was 2-fold higher than the rate at pH 3, but there was a decrease in the catalytic rate at pH 9. Therefore, the oxidation rate of CP reached the highest value at pH 7, and its conversion was maximal after 40 min at pH 7. Lin and co-workers studied the effect of pH on the intramolecular structure of porphyrin [21]. They found that in acidic solution the activity of porphyrin decreased due to the protonation. Yamada also reported that neutral or weak alkaline solution favored the equilibrium between mononuclear and binuclear complexes towards the catalytically more active species [22]. To summarize, neutral or weakly alkaline medium had positive effect on the formation of reactive hydroxyl and superoxide radicals, and thus driving the oxidation of CP by these active species [23]. The activity of salen and porphyrin complexes has been reported to be strongly dependent on the coordination state of the complex [24]. An attempt was hence made in this work to improve the performance of $ZnPSC_6$-catalysed reaction of CP through the addition of axial ligand, such as imidazole and pyridine. In studies with a UV-vis spectrometer, $ZnPSC_6$ was found to form a new complex with imidazole and/or pyridine. In this study, it was observed that the activity of $ZnPSC_6$ complex was found to increase with addition of imidazole and/or pyridine in terms of the C/C_0 value (Figure 2f), in which the catalytic rate of 20 min at pH 7 in the presence of imidazole and pyridine (imidazole + pyridine) was about 10 times that in the absence of ligand (C/C_0 value: 0.017 for the presence of imidazole and pyridine; 0.16 for the absence of ligand), and the reaction time required to achieve the optimal CP removal was also reduced from 40 min to 20 min, correspondingly.

3.2 Degradation Products

Catalytic oxidation of CP gave the three main compounds (product A, product B, product C), as presented in Scheme 1. This may be related to the mechanism involving a superoxo radical (Zn-O-O•, Scheme 1) [25, 26], which afforded

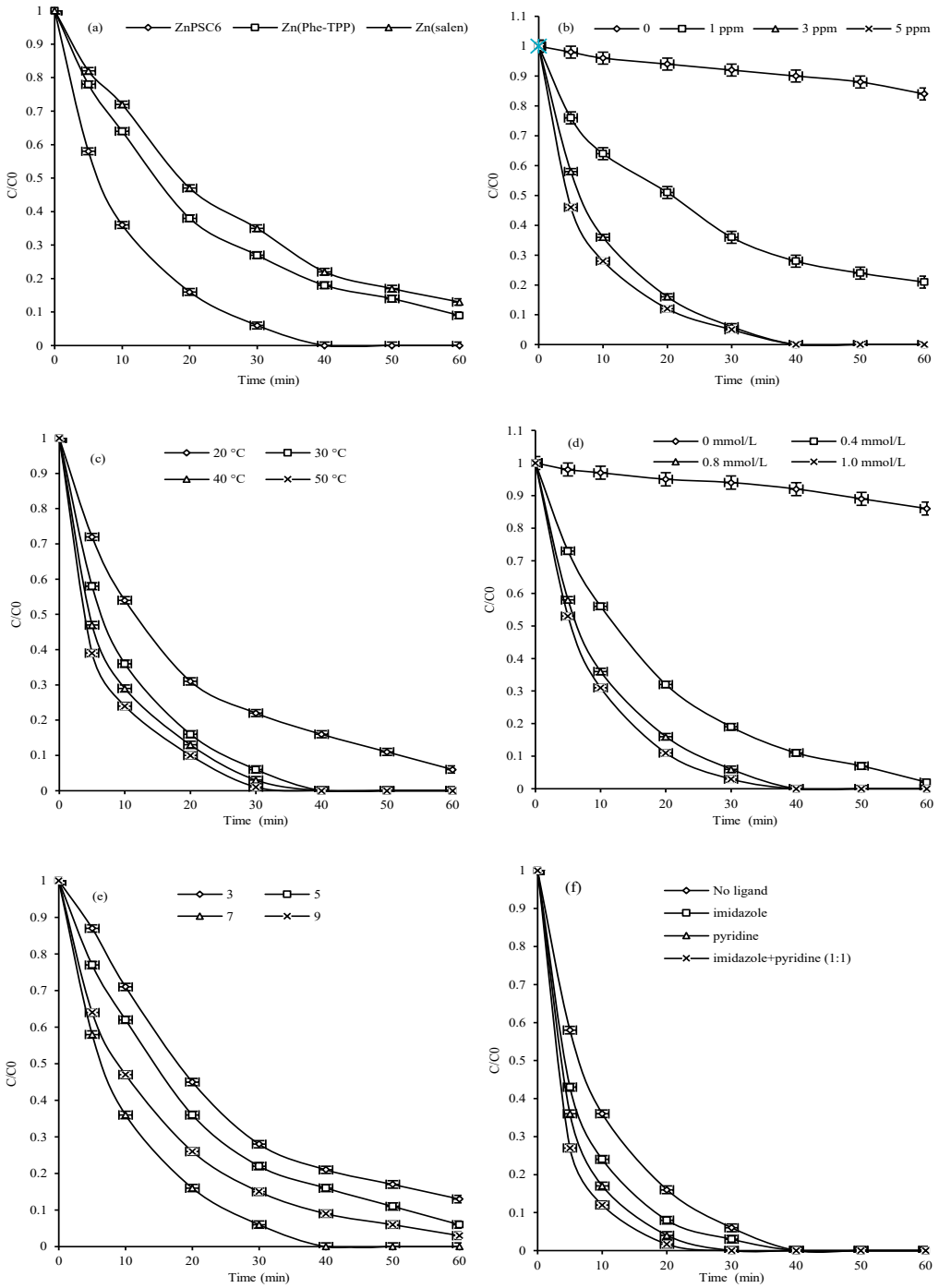
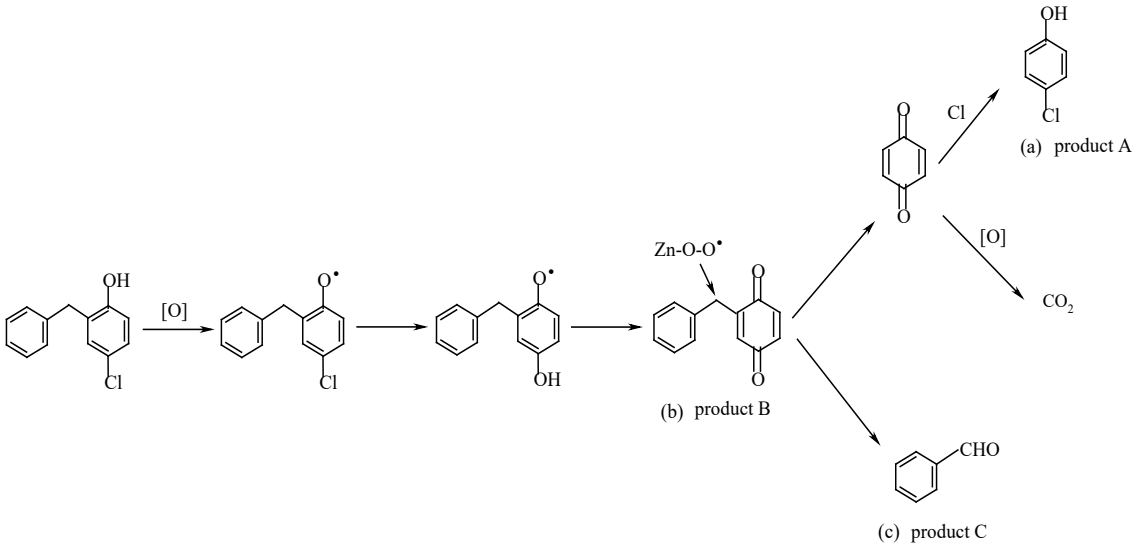


Figure 2. Effect of reaction conditions on CP degradation. Effect of different catalysts (a); effect of $ZnPSC_6$ concentration (b); effect of reaction temperature (c); hydrogen peroxide dosage (d); effect of pH value (e); effect of ligands (f). (a) and (b): [CP]=0.04 mmol/L, [$ZnPSC_6$]=3 ppm, pH=7.0, [H_2O_2]=0.80 mmol/L, temperature=30 °C; c, d, e and f: [CP]=0.04 mmol/L, [$ZnPSC_6$]=3 ppm, temperature=30 °C, [ligand]=0.1 ppm.



Scheme 1. Proposed reaction pathway for catalytic oxidation of chlorophene.

phenolic radicals by abstracting hydrogen atom, followed by the releasing of chlorine atoms and forming of quinone compound (product B) within chlorophene. The latter preferentially caused a reaction that broke the linkage between two aromatic rings due to the attack by the Zn-O-O•, further affording the product C and 1,4-benzoquinone. Product A was most likely obtained via an addition of Cl^- at C_4 of 1,4-benzoquinone. In addition, part of 1,4-benzoquinone may be further oxidized followed by oxidative ring-opening of quinone rings yielding carbon dioxide (CO_2) by a stepwise oxidative degradation, probably catalyzed by these complexes [27].

Otherwise, according to the relative abundance, $ZnPSC_6$ significantly favoured the formation of chlorine-free compounds such as product B (Figure 3b) and product C (Figure 3c) compared to chlorine-containing compound (product A, Figure 3a), especially in the presence of ligands, when compared to Zn(salen) and Zn(Phe-TPP), which was obviously superior to the findings reported in literatures [28-30]. Furthermore, benzaldehyde (product C) derived from CP accounted for a high relative abundance, which would provide favourable conditions for elimination of CP toxicity.

3.3 Ecotoxicity of Treated-solutions

The ecotoxicity of the CP solutions obtained in catalytic treatments were further evaluated in consideration of the aboved mentioned aromatic products and the results are contrastively presented in Table 1 in terms of growth inhibition of *C. vulgaris* in treated-solutions. The cell number in all of the treated solutions was greater than the control solution, and all samples were more toxic than the deionized water. The formation of benzaldehyde indicated the degradation and mineralization of CP (Scheme 1), thus causing a decrease in the toxicity of solutions [31]. However, it was observed that the $ZnPSC_6$-treated solution weakly inhibited the growth of *C. vulgaris* compared to the other solutions. Moreover, although the relative abundance of product C (benzaldehyde) was the highest in $ZnPSC_6$-treated (imidazole + pyridine) group, the solution toxicity did not significantly change. This may be associated with

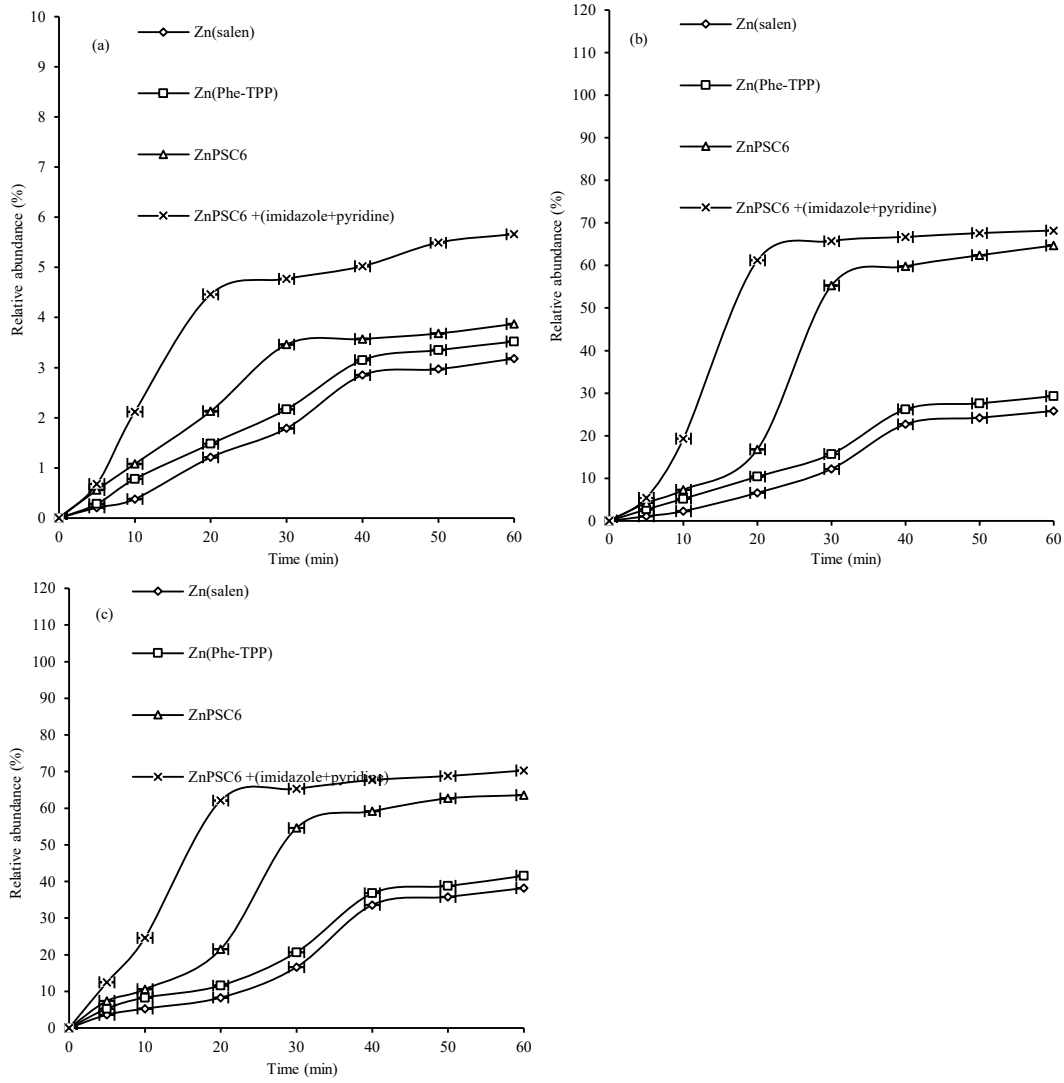


Figure 3. Effect of reaction time on degradation products. product A (a); product B (b); product C (c). Relative abundance (%) = peak abundance/base peak abundance. Base peak = strongest peak.

trace amounts of toxic ligands (imidazole + pyridine) present in the solution. The effect of catalysis on solution toxicity could be explained in terms of TCC [32, 33], as shown in Table 1. After CP solutions were treated with these catalysts, their TCCs significantly decreased when compared to the control, suggesting a considerable mineralization confirmed by the release of CO_2 (Scheme 1), especially for the $ZnPSC_6$-treatment. However, the addition of imidazole and pyridine into the solution slightly increased the TCC level.

4. CONCLUSIONS

Biomimetic catalysts had enzymatic and chemical catalytic properties and $ZnPSC_6$ as a salen-porphyrin complex showed the best

Table 1. Individual cell counts and TCC of solution.

Individual cell counts ±0.2						
Time (h)	**Control**	**Zn(salen)**	**Zn(Phe-TPP)**	**$ZnPSC_6$**	**$ZnPSC_6$ +(imidazole+pyridine)**	**Deionized water**
24	1.35	1.45	2.07	2.47	2.64	3.56
72	2.32	5.74	7.38	16.37	15.78	22.78
120	4.27	8.84	11.67	26.17	24.67	31.67
TCC (%) ±0.02						
	1.24	0.36	0.31	0.21	0.24	0.24

activity for degrading CP using H_2O_2 as oxidant. Chlorophene was sufficiently degraded by the $ZnPSC_6$-process compared to Zn(salen) and Zn(Phe-TPP)-treatments. The CP removal was evidently affected by reaction parameters, and the addition of imidazole and pyridine showed the best performance in improving $ZnPSC_6$-catalysis in terms of CP removal. Using growth inhibition of *C. vulgaris*, it was concluded that oxidation of CP by $ZnPSC_6$ catalysis reduced the solution toxicity. This was related to the fact that the level of degradation products containing chlorine atoms and TCC in $ZnPSC_6$-treated solution was particularly low.

Acknowledgments

This work was supported by Scientific Research and Trial-Production Project of Sanya (2017KS07), Open Research Foundation of Shandong Provincial Key Laboratory of Water and Soil Conservation and Environmental Protection of Linyi University (STKF201910), Open Research Foundation of Key Laboratory of Clean Dyeing and Finishing Technology of Zhejiang Province of Shaoxing University (QJRZ1906), and Open Research Foundation of Key Laboratory of Green Chemical Engineering Process of Ministry of Education of Wuhan Institute of Technology (GCP20190210).

References

[1] Tanoue R., Nozaki K., Nomiyama K., Kunisue T. and Tanabe S., *J. Chromatogr. A,* 2020; 1631. DOI: 10.1016/j.chroma.2020.461586.

[2] Baumer A., Bittermann K., Kluver N. and Escher B.I., *Environ. Sci.-Proc. Imp.,* 2017; **19**: 901-916. DOI 10.1039/c7em00099e.

[3] Wang Z., Zhang X.-H., Huang Y. and Wang H., *Environ. Pollut.,* 2015; **204**: 223-232. DOI 10.1016/j.envpol.2015.04.021.

[4] Kenda M., Karas K.N., Iida M., Kojima H. and Sollner D.M., *Environ. Health Persp.,* 2020; **128**: 107005. DOI:10.1289/EHP6596.

[5] Vidal-Limon A., Suarez P.C.G., Arellano-Garcia E., Contreras O.E. and Aguila S.A., *Bioconjugate Chem.,* 2018; **29**: 1073-1080. DOI 10.1021/acs.bioconjchem.7b00739.

[6] He Z., Zhang A., Li Y., Song S., Liu Z., Chen J. and Xu X., *J. Environ. Sci. Heal. A,* 2011; **46**: 1-8. DOI 10.1080/10934529.2011.526065.

[7] Bolobajev J. and Goi A., *Chem. Eng. J.,* 2017; **328**: 904-914. DOI 10.1016/j.cej.2017.07.043.

[8] Perko J., Kamenicka B. and Weidlich T., *Monatsh. Chem.,* 2018; **149**: 1777-1786. DOI 10.1007/s00706-018-2230-y.

[9] Shi H.H., Peng J.B., Li J.H., Mao L., Wang Z.Y. and Gao S.X., *J. Hazard. Mater.,* 2016; **317**: 81-89. DOI 10.1016/j.jhazmat.2016.05.064.

[10] Maqbool Z., Hussain S., Imran M., Mahmood F., Shahzad T., Ahmed Z., Azeem F. and Muzammil S., *Environ. Sci. Pollut. Res.,* 2016; **23**: 16904-16925. DOI 10.1007/s11356-016-7003-8.

[11] Ma R., Guo M. and Zhang X., *Catal. Today,* 2018; **302**: 50-60. DOI 10.1016/j.cattod.2017.05.101.

[12] Zhang P.C., Wang S., Ma S.Q., Xiao F.S. and Sun Q., *Chem. Commun.,* 2020; **56**: 10631-10641. DOI 10.1039/d0cc04351f.

[13] Wu C.-D., He W.-L. and Zhao M., *Angew. Chem. Int. Edit.,* 2018. DOI 10.1002/anie.201810294.

[14] Wang G.Y., Yan W.W., Zhang X.H., Ruan W.J. and Zhu Z.A., *Acta Phys.-Chim. Sin.,* 2012; **28**: 2774-2782. DOI 10.3866/PKU.WHXB201209261.

[15] Li J.W., Ren Y.W., Qi C.R. and Jiang H.F., *Chem. Commun.,* 2017; **53**: 8223-8226. DOI 10.1039/c7cc03499g.

[16] Zhao X.J., Ruan W.J., Zhu Z.A., Jin L.M. and Fan S.-D., *Chinese J. Org. Chem.,* 2006; **26**: 1087-1092.

[17] Liu Z.C., Liu F., Lu Y., Xie M.X. and Zhang Y.Q., *J. Leshan Teachers College,* 2002; **17**: 30-33 (in Chinese).

[18] Huang S., Sun L. and Ye C., *Chem. J. Chinese U. (Chinese Edition),* 1983; **4**: 381-384.

[19] Thongrom B., Amornpitoksuk P., Suwanboon S. and Baltrusaitis J., *Korean J. Chem. Eng.,* 2014; **31**: 587-592. DOI 10.1007/s11814-013-0262-x.

[20] Ju P., Wu S., Su Q., Li X., Liu Z., Li G. and Wu Q., *J. Mater. Chem. A,* 2019; **7**: 2660-2666. DOI 10.1039/C8TA11330K.

[21] Lin W., Hu Q., Jiang K., Yang Y., Cui Y. and Qian G., *J. Solid State Chem.,* 2016; **237**: 307-312. DOI 10.1016/j.jssc.2016.02.040.

[22] Yamada S., *Coordin. Chem. Rev.,* 1999; **190**: 537-555. DOI 10.1016/S0010-8545(99)00099-5.

[23] Bayat Z.E., Rahiminezhad H. and Zakavi S., *Appl. Organometal. Chem.,* 2019; **33**. DOI 10.1002/aoc.4678.

[24] Meininger D.J., Arman H.D. and Tonzetich Z.J., *J. Inorg. Biochem.,* 2017; **167**: 142-149. DOI 10.1016/j.jinorgbio.2016.08.014.

[25] Peng J., Zhang C., Zhang Y., Miao D. and Gao S., *Environ. Pollut.,* 2019; **252**: 1933-1941. DOI 10.1016/j.envpol.2019.05.148.

[26] Bach A., Shemer H. and Semiat R., *Desalination,* 2010; **264**: 188-192. DOI 10.1016/j.desal.2010.04.011.

[27] Shimazaki Y. and Yamauchi O., *Indian J. Chem.,* 2011; **50**: 383-394.

[28] Benitez F.J., Acero J.L., Garcia-Reyes J.F., Real F.J., Roldan G., Rodriguez E. and Molina-Díaz A., *Chem. Eng. J.,* 2013; **230**: 447-455. DOI 10.1016/j.cej.2013.06.120.

[29] Onesios-Barry K.M., Berry D., Proescher J.B., Sivakumar I.K.A. and Bouwer E.J., *Appl. Environ. Microbiol.,* 2014; **80**: 2440-2450. DOI 10.1128/AEM.03693-13.

[30] Bolobajev J., Öncü N.B., Viisimaa M., Trapido M., Balcıoğlu I. and Goi A., *Environ. Technol.,* 2015; **36**: 348-357. DOI 10.1080/09593330.2014.948493.

[31] Bao T., Damtie M.M., Hosseinzadeh A., Frost R.L., Yu Z.M., Jin J. and Wu K., *Appl. Clay Sci.,* 2020; **195**. DOI 10.1016/j.clay.2020.105735.

[32] Li L., Liu Y., Zhang S., Liang M., Li F.Y. and Yuan Y.M., *J. Hazard. Mater.,* 2020; **399**. DOI 10.1016/j.jhazmat.2020.122883.

[33] Gopinath A. and Krishna K., *Photochem. Photobiol.,* 2019; **95**: 1311-1319. DOI 10.1111/php.13130.