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Degradation of chlorophenols (CPs) in an ultrasound-irradiated Fenton-like system at ambient circumstance: The QSPR (quantitative structure–property relationship) study

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ABSTRACT

In this study, firstly the degradation of different chlorophenols (CPs) in a novel ultrasound-irradiated Fenton-like system was investigated. Then, based on the selected quantum chemical and physicochemical descriptors, by the use of partial least squares analysis, a good prediction quantitative structure–property relationship for the obtained degradation rate constants of CPs in the anaerobic culture was obtained. It was found that the energy of the highest occupied molecular orbital, characterizing the ability of a molecule to lose electrons or to be oxidized, played an important role in the CPs disappearance process. The greater the Dipole moment value, the higher the CPs degradation rate constant. And CPs with large absolute hardness values tended to have slow degradation rate. The model can be also used to explain the degradation mechanism and enhancement role of ultrasound. It can be concluded that the degradation of CPs in the US/Fenton-like system can be ascribed to homogeneous Fenton oxidation in the bulk solution. The synergistic role of US irradiation is expected to enhance Fenton reaction instead of directly decompose CPs in the system.

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1. Introduction

Chlorophenols (CPs) are a series of priority toxic pollutants listed in the US EPA Clean Water Act [1]. They are widely used for the production of dyes, drugs, pesticides and fungicides. CPs are hardly biodegradable and difficult to remove from the environment by conventional treatment technologies. Therefore, the pollution of CPs is of great environmental concern because of its great toxicity and suspected carcinogenicity.

Over the past decades, Advanced Oxidation Technologies (AOTs) have been accepted as efficient ways for the degradation of toxic and recalcitrant organic pollutants. However, generally high requirement of reaction conditions and cost limits the application of these AOTs. In our previous study, a novel Fenton-like system (Fe/EDTA) utilized low cost iron powder (Zero-Valent Iron, ZVI) and Ethylenediaminetetraacetic acid (EDTA) was successfully developed to degrade 2,4-dichlorophenol (2,4-DCP) and 4-chlorophenol (4-CP) [2,3]. In the ambient reaction circumstance, H_2O_2 can be auto-transformed from air through a series of ligand reactions (Eqs. (1)–(5)) [2] instead of direct addition, which are depicted as follows:

$$Fe^{2+} + EDTA + H_2O \xrightarrow{k_1} [Fe^{II}(EDTA)(H_2O)]^{2-} \tag{1}$$

$$[Fe^{II}(EDTA)(H_2O)]^{2-} + O_2 \overset{k_2,k_{-2}}{\rightleftharpoons} [Fe^{II}(EDTA)(O_2)]^{2-} + H_2O \tag{2}$$

$$[Fe^{II}(EDTA)(O_2)]^{2-} \xrightarrow{k_3} [Fe^{III}(EDTA)(O_2^-)]^{2-} \tag{3}$$

$$[Fe^{II}(EDTA)(H_2O)]^{2-} + [Fe^{III}(EDTA)(O_2^-)]^{2-} \xrightarrow{k_4} [(EDTA)Fe^{III}(O_2^{2-})Fe^{III}(EDTA)]^{4-} + H_2O \tag{4}$$

$$[(EDTA)Fe^{III}(O_2^{2-})Fe^{III}(EDTA)]^{4-} \xrightarrow{k_5,H^+} 2[Fe^{III}(EDTA)H_2O]^{-} + H_2O_2 \tag{5}$$

In the presence of ZVI and generated H_2O_2, Fenton-like oxidation reactions occur and the CPs could be oxidative degraded completely. It was interesting to note that ultrasound (US) plays a significant synergistic role in the degradation of 2,4-DCP and 4-CP within the Fenton-like system. And we speculated that enhancement of the Fenton-like oxidation reactions by US is predominant [3].

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Quantitative structure–property relationships (QSPR), which correlate molecular structural descriptors with their environmental property parameters, could be used to study degradation mechanism of CPs in the US/Fenton-like system efficiently. Empirical molecular descriptors such as Hammett sigma constants are usually difficult to obtain for some compounds with complex structures. Whereas quantum chemical descriptors can be easily obtained by computation, can clearly describe defined molecular properties, and are not restricted to closely related compounds. So the development of QSPR models in which quantum chemical descriptors are used is very important. According to the present chemometric theory, relevant data should be considered in QSPR studies as much as possible because this increases the probability of a good characterization of compounds [4]. As a consequence of the increase of the number of descriptors, the inter-correlation of independent variables (multicollinearity) will become more important. Under these circumstances, regression analysis (a method frequently used in QSPR studies) will not be useful, especially when the number of observations in the training set is less than four or five times the number of independent variables in a model. To solve this problem, the partial least squares (PLS) method, a widely used chemometric method first developed by [5], will be used in this study. PLS finds the correlation between matrix Y (containing dependent variables-usually only one for QSPR studies) and a matrix X (predictor variables) by reducing the dimension of the independent and dependent variables, and at the same time, maximizing the correlation between the independent and dependent matrices. This method has already been successfully adopted in the prediction of dechlorination of CPs through utilization of zero-valent iron [6].

In the present study, five kind of CPs were chosen to be degraded in the US/Fenton-like system, respectively. The obtained degradation rate constants' logarithmic value ($\log k$) of CPs is recognized as a key descriptor, which can reflect the tendency of degradation process. Then the QSPR study of $\log k$ and molecular structural descriptors of CPs was carried out. A better understanding of the molecular structures that determine the degradation process is therefore obtained for predicting the degradation rate of CPs. The results will also help to understand the degradation mechanism of CPs in the US/Fenton-like system well.

2. Materials and methods

2.1. Experimental

Purified *o*-chlorophenol (2-CP), *m*-chlorophenol (3-CP), *p*-monochlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) were obtained from Fisher Company (Singapore). 2,4,6-trichlorophenol (2,4,6-TCP) was purchased from Sigma–Aldrich (Singapore). Iron powder (325 mesh, purified) and Na_2EDTA (dihydrate salt, >99%) were also obtained from Fisher Company and ultra pure water was used to prepare all solutions. The detailed experimental apparatus, procedure and analysis method have been already indicated in our pervious study [2]. In this study, as for the degradation of different CPs in the US/Fenton-like system, the experiments were all conducted at an optimized initial parameters that are depicted as follows: CPs 0.8 mM, EDTA 0.32 mM, US input power 385 W, air flowrate 1.0 mL/min and temperature 20 °C.

2.2. QSPR method

The PM3 Hamiltonian contained in the quantum chemical computation software WinMOPAC 2.0(Fujitsu) was used to compute the quantum chemical descriptors of different chlorophenols. MOPAC was run with the following keywords PM3, ESP, POLAR, DIPOLE, BONDS, ENPART, PRECISE, NOINTER.

It has been suggested that an adequate model should include as many descriptors as possible to increase the probability of a good characterization of compounds [4]. Therefore, a total of 19 MOPAC derived descriptors were selected in the study. Among the 19 descriptors, 12 descriptors reflected the overall characters of the CPs molecules. They are molecular weight (Mw), heat of formation (HOF), total energy (TE), electronic energy (EE), core–core repulsion energy (CCR, CCR = TE − EE), average molecular polarizability (α), Dipole moment (μ), energy of the highest occupied molecular orbital (E_{homo}), energy of the lowest unoccupied molecular orbital (E_{lumo}), the net atomic charge of carbon atom (qC), the net atomic charge of hydrogen atom (qH), and the net atomic charge on chlorine atom (qCl).

In addition, three combination descriptors and four physicochemical parameters were also considered as independent

Table 1

Physico-chemistry and quantum chemistry descriptors of chlorophenols.

Descriptors[a]	2-CP	3-CP	4-CP	2,4-DCP	2,4,6-TCP
V_{p}	2.530	1.420	0.087	0.116	0.008
$\log K_{\text{ow}}$	2.150	2.490	2.400	3.030	3.830
$\text{p}K_{\text{a}}$	8.450	8.950	9.250	7.800	6.700
$^1X^{\text{V}}$	2.653	2.611	2.647	3.165	3.684
HOF	−118.158	−119.340	−119.129	−145.000	−165.347
TE	−1398.107	−1398.120	1398.118	−1699.505	−2000.835
EE	−5553.354	−5489.758	−5476.585	−6775.868	−8166.252
CCR	4155.246	4091.639	4078.468	5076.363	6165.417
Dipole, μ	1.918	0.445	1.394	1.841	1.002
E_{homo}	−9.041	−9.009	−8.951	−9.055	−9.125
E_{lumo}	0.029	0.049	0.048	−0.217	−0.442
Mw	128.558	128.558	128.558	163.003	197.448
Polar, α	59.621	60.544	60.846	70.280	81.178
qC	−0.084	−0.085	−0.084	−0.085	−0.089
qH	0.131	0.134	0.133	0.144	0.156
qCl	0.069	0.064	0.063	0.075	0.092
$E_{\text{lumo}} - E_{\text{homo}}$	9.070	9.058	8.999	8.838	8.683
$E_{\text{lumo}} + E_{\text{homo}}$	−9.012	−8.960	−8.903	−9.272	−9.567
$(E_{\text{lumo}} - E_{\text{homo}})^2$	82.265	82.047	80.982	78.110	75.394

[a] 12 descriptors reflected the overall characters of the CPs molecules: molecular weight (Mw), heat of formation (HOF), total energy (TE), electronic energy(EE), core–core repulsion energy (CCR, CCR = TE − EE), average molecular polarizability (α), Dipole moment (μ), energy of the highest occupied molecular orbital (E_{homo}), energy of the lowest unoccupied molecular orbital (E_{lumo}), the net atomic charge of carbon atom (qC), the net atomic charge of hydrogen atom (qH), and the net atomic charge on chlorine atom (qCl). Three combination descriptors: $E_{\text{lumo}} - E_{\text{homo}}$, $(E_{\text{lumo}} - E_{\text{homo}})^2$, $E_{\text{lumo}} + E_{\text{homo}}$; and four physicochemical parameters: vapour pressure (V_{p}), the logarithm of the partition coefficient for *n*-octanol/water ($\log K_{\text{ow}}$), acid dissociation constant ($\text{p}K_{\text{a}}$), and the first-order valence molecular connectivity index ($^1X^{\text{V}}$).

variables. They are $E_{\text{lumo}} - E_{\text{homo}}$, $(E_{\text{lumo}} - E_{\text{homo}})^2$, $E_{\text{lumo}} + E_{\text{homo}}$, vapour pressure ($V_p$), the logarithm of the partition coefficient for *n*-octanol/water ($\log K_{\text{ow}}$), acid dissociation constant (pK_a), and the first-order valence molecular connectivity index ($^1X^V$). The $E_{\text{lumo}} - E_{\text{homo}}$ and $E_{\text{lumo}} + E_{\text{homo}}$ can be related to absolute hardness and electronegativity [7–8], respectively. Log K_{ow}, pK_a and $^1X^V$ were already proven to be significant in the QSPR studies of chlorophenols [9–11]. V_p is an important parameter for the CPs degradation in ultrasound-irradiated systems [12]. The value of the four physicochemical parameters (V_p, $\log K_{\text{ow}}$, pK_a and $^1X^V$) were obtained from other references [13–15]. The unit of HOF is kJ, and the units of energy, charge, polarizability, dipole moment, V_p are electron volts (eV), atomic charge units (a.c.u), atomic units (a.u.), debye, mmHg, respectively. The values of all the 19 descriptors are listed in Table 1.

SIMCA software (Simca-P, Version11.0, Umetrics AB) was used to perform the PLS analysis. The conditions for the computation were based on the default values of the software. The criterion used to determine the model dimensionality-the number of significant PLS components-is cross validation (CV). With CV, when the fraction of the total variation of the dependent variables that can be predicted by a component, Q^2, for the whole data set is larger than a significance limit (0.097), the tested PLS component is considered significant. When the cumulative Q^2 for the extracted components, Q^2_{cum}, is larger than 0.5, the model is considered to have a good prediction ability. Model adequacy was mainly measured as the number of PLS principal components (*A*), the correlation coefficient between observed values and fitted values (*R*), and the significance level (*P*). Besides the standard error of predicted values (SE-Pred.) given by PLS analysis, another standard error (SE) was adopted to compare the prediction precision of different models. SE was defined as in multiple regression analysis, i.e. $\text{SE} = \dfrac{\sqrt{\sum_{i-1}^{n} [\log k(\text{observed})_i - \log k(\text{predicted})_i]^2}}{n-A-1}$, where *n* stands for the number of compounds in the training set.

3. Results and discussion

3.1. Degradation of CPs in the US/Fenton-like system

As shown in Fig. 1(a), pseudo first-order degradation kinetic of five CPs could be well applied in the US/Fenton-like system, respectively (R^2 at least > 0.98 for five CPs). Obviously, the five CPs could be rapidly degraded in the US/Fenton-like system. It can be also concluded that the sequence of CPs degradation rate constants is 2,4,6-TCP < 2,4-DCP < 4-CP < 2-CP < 3-CP. The values of observed degradation kinetic constant (k_{obs}) of five CPs are listed in Table 2.

In the previous studies, we have investigated the effect of different experimental conditions, such as ultrasound power, initial CPs concentration, pH and temperature, on the degradation of 2,4-DCP and 4-CP in the US/Fenton-like system, respectively [2–3]. Similar effects of environmental conditions on the degradation rate of both CPs were observed. As a result, optimized initial parameters were confirmed and applied in this study for the degradation of five CPs in the US/Fenton-like system. Furthermore, it can be concluded that the main oxidant generated in the US/Fenton-like system is due to the reactions between ZVI, EDTA and dissolved oxygen [3]. The types of CPs and different initial concentrations have insignificant effect on the oxidant generation rate but just affected the oxidant consumption rate. As a result, the degradation circumstances are assumed to be same when conducting the different CPs degradation at the optimal conditions in the US/Fenton-like system, respectively.

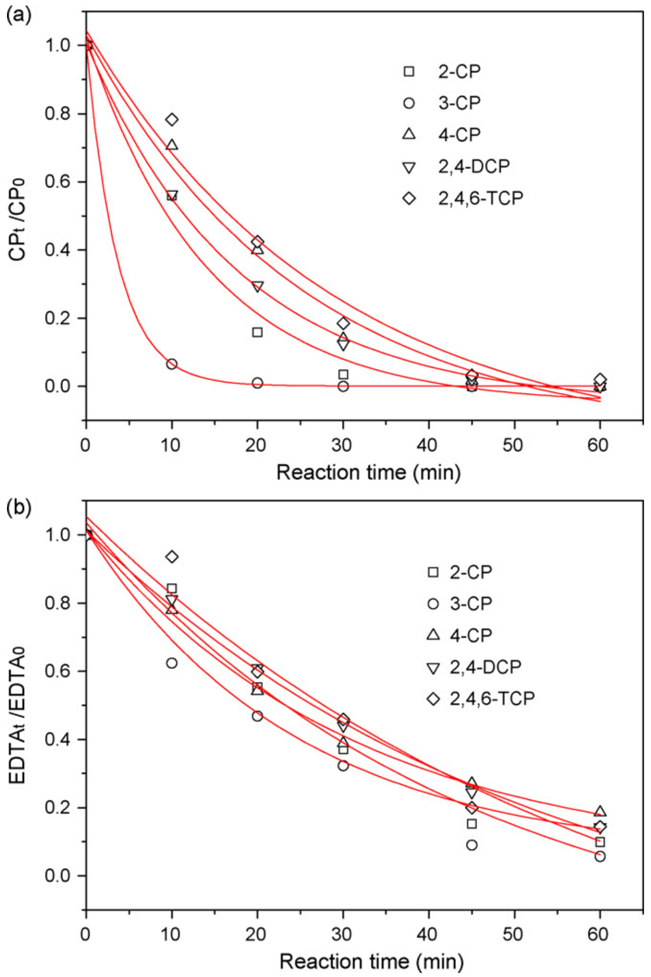

Fig. 1. Degradation of five CPs in the Ultrasound-irradiated Fenton-like system (US/Fe/EDTA) (a) degradation of CPs versus reaction time; (b) degradation of EDTA versus reaction time. The initial parameters were: CPs 0.8 mM, EDTA 0.32 mM, US input power 385 W, air flowrate 1.0 mL/min and temperature 20 °C.

Table 2
The CPs under study and their disappearance rate constants (log *k*).

No.	Compound	Observed		Predicted		Diff[a]	SE-Pred[b]
		k_{obs} (min^{-1})	log *k* (Obs)	k_{pred} (min^{-1})	log *k* (Pred)		
1	2-CP	0.113	−0.946	0.118	−0.927	−0.019	±0.034
2	3-CP	0.232	−0.645	0.226	−0.645	−0.011	±0.037
3	4-CP	0.091	−1.031	0.093	−1.031	−0.007	±0.038
4	2,4-DCP	0.076	−1.115	0.069	−1.160	0.031	±0.026
5	2,4,6-TCP	0.072	−1.141	0.075	−1.125	−0.015	±0.036

k_{obs} and log *k* (Obs): observed degradation constants of CPs, values were obtained in Section 3.1; log *k* (Pred): predicted values by optimized model (model 10) of this QSPR study.

[a] Diff = log *k* (Obs) − log *k* (Pred).

[b] SE-Pred: standard errors of the predicted values.

The simultaneous degradation of EDTA with the five CPs was also investigated, respectively. As shown in Fig. 1(b), the difference of EDTA degradation in the five systems was insignificant, though the degradation rates of different CPs in the US/Fenton-like system were very different. The degradation of EDTA could be also well applied by pseudo-first-order kinetic and the k_{obs} values confined in a narrow range ($0.036\,\mathrm{min}^{-1} < 5\ k_{obs}\ (\mathrm{EDTA}) < 0.045\,\mathrm{min}^{-1}$). It indicated that different types of CPs did not influence the EDTA degradation rate in the US/Fenton-like system and the competitive degradation relationship between CPs and EDTA could be ignored [3]. Therefore, the k_{obs} (EDTA) values obtained from the five CPs degradation in the US/Fenton-like system, can be excluded from the following QSPR study.

3.2. The QSPR study of CPs degradation in the US/Fenton-like system

At first, PLS analysis with $\log k_{obs}$ as dependent variable and the total 19 quantum chemical descriptors as independent variables was conducted and it resulted in an QSPR model (1) with parameters of $A = 1$, $Q^2_{cum} = 0.862$, $R = 0.982$, $P = 5.878 \times 10^{-6}$, as listed in Table 3. $R^2_{X(\mathrm{adj})(\mathrm{cum})}$ and $R^2_{Y(\mathrm{adj})(\mathrm{cum})}$ stand for the cumulative variance of all the X's and Y's explained by all extracted components, respectively. So it can be seen from Table 3 that the two PLS principal components explained 95.0% of the variance of the independent variables, and 95.9% of the variance of the dependent variable.

Although the PLS method offers the advantage of handling data sets which include large number of independent variables, considerably worse predictions would be obtained if many irrelevant descriptors are included in the PLS model [16]. To obtain an optimal model, it is necessary to perform a PLS analysis that excludes the least significant descriptors. Variable importance in the projection (VIP) is a parameter that shows the importance of a variable in a model. Terms with a large value of VIP, generally larger than 1, are the most relevant for explaining the dependent variable. In a model, the smaller VIP value of the descriptor, the less significant the descriptor is in explaining the log *k*. As a result, such a PLS analysis could be conducted and resulted in model (2) by excluding the least significant descriptor from model (1). Following the same PLS analysis procedure, the least significant descriptor was removed from the former model step by step until only two descriptors were left in the model, thus models (2)–(18) could be obtained successively, as shown in Table 3. The optimal PLS model could be selected with respect to the statistics Q^2_{cum}, R, and P. Since Q^2_{cum} value was determined by the CV method, the greater the Q^2_{cum} value, the more robust or stable the model. The SE in this study was a measure of prediction precision, the lower the SE, the better the prediction precision. Comparing with these statistical indices of models (1)–(18), it is found that the Q^2_{cum} of model (10) was the largest and the SE of model (15) was the smallest, indicating that model (10) was the most robust and best prediction precision QSPR model within all the 18 PLS models. In model (10), nine descriptors, i.e. V_p, $\log K_{ow}$, qH, qC, E_{lumo}, pK_a, μ, qCl, $E_{lumo}+E_{homo}$ and α have been kept out, indicating that the nine descriptors are of less importance to predict the log *k* of CPs. If the nine descriptors are included in PLS models, they can increase the "background noise" of the models, resulting in less robustness and poor significance of PLS models as indicated by models (1)–(9). On the contrary, the other 10 descriptors are essential to model log *k* of CPs. If they are excluded from PLS models, the molecular structure character relevant to log *k* cannot be well described, leading to PLS models with bad prediction precision as indicated by models (11)–(18).

Table 3
QSPR Model fitting results.

Model	*A*	$R^2_{X(\mathrm{adj})(\mathrm{cum})}$	$R^2_{Y(\mathrm{adj})(\mathrm{cum})}$	Q^2_{cum}	*R*	*P*	SE
1	2	0.950	0.959	0.862	0.982	5.878*E*−06	0.059
2	2	0.983	0.938	0.844	0.972	7.226*E*−06	0.072
3	2	0.984	0.937	0.840	0.971	7.260*E*−06	0.073
4	2	0.984	0.937	0.837	0.971	7.271*E*−06	0.073
5	2	0.985	0.940	0.840	0.973	7.106*E*−06	0.071
6	2	0.984	0.940	0.836	0.973	7.092*E*−06	0.071
7	2	0.987	0.944	0.845	0.974	6.882*E*−06	0.069
8	2	0.990	0.945	0.844	0.975	6.805*E*−06	0.068
9	2	0.990	0.940	0.830	0.973	7.103*E*−06	0.071
10	3	0.999	0.990	0.955	0.993	4.178*E*−06	0.042
11	3	0.999	0.990	0.952	0.995	4.179*E*−06	0.042
12	3	1.000	0.989	0.947	0.995	4.214*E*−06	0.042
13	3	0.999	0.989	0.938	0.995	4.222*E*−06	0.042
14	3	0.999	0.989	0.920	0.995	4.236*E*−06	0.042
15	1	0.622	0.930	0.662	0.970	3.256*E*−06	0.063
16	3	1.000	0.993	0.953	0.994	3.434*E*−06	0.043
17	2	1.000	0.977	0.842	0.990	4.358*E*−06	0.044
18	1	1.000	0.750	0.537	0.868	1.184*E*−05	0.118

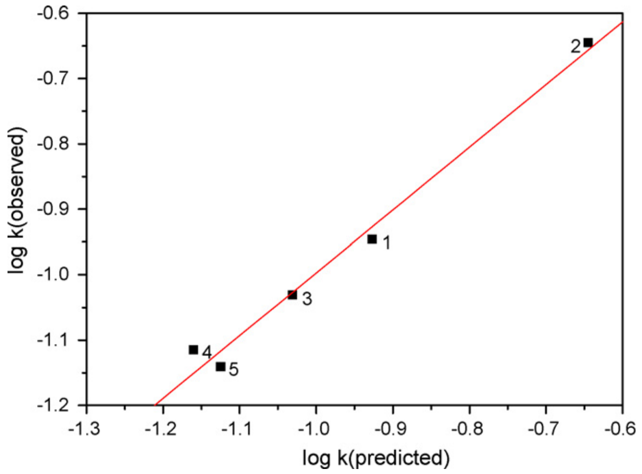

Fig. 2. Fitting plot of the observed and the predicted log *k* (the numbers correspond to those in Table 2).

As the cross-validated Q^2_{cum} value of model (10) is 0.955 that is remarkably above 0.50, model (10) is surely stable and has good prediction ability. Using this model, the values of log *k* of five CPs can be predicted, as listed in Table 2. Furthermore, the relationship between the observed and predicted log *k* values obtained by the model (10) is plotted and shown in Fig. 2. The compound numbers in Fig. 2 correspond to those in Table 2. It was found that the correlation between observed and fitted $\log k_{obs}$ values of model (10) is significant ($R = 0.993$, $P = 4.178 \times 10^{-6}$).

From the PLS weights (W^* [1] and W^* [2]) of variables listed in Table 4, it can be seen how much a single variable contributes in each PLS component to the modeling of log *k*. The first PLS component is mainly related to the descriptors CCR, EE, TE, Mw, ${}^1X^V$, $E_{lumo}-E_{homo}$, $(E_{lumo}-E_{homo})^2$ and HOF. It implies that these descriptors are highly inter-correlated, as shown in Table 5. Since Mw, ${}^1X^V$, TE, EE, HOF and CCR are relevant to molecular size, the first PLS component may condense information on the size of CPs molecules. It can be concluded that the larger size of CPs, the higher the degradation rate constants. According to [7], absolute hardness can be defined as $-1/2(E_{lumo}-E_{homo})$, therefore, it can be concluded that the first PLS component also condenses information about CPs absolute hardness. The second PLS component is mainly related to the descriptors E_{homo} and μ that are inter-correlated (Table 5). The absolute values of W^* [2] for both descriptors are larger than 0.613 and much larger than the absolute values of W^* [2] for the other descriptors. Therefore, the second PLS component is mainly related to the ability of CPs molecule to lose electrons and

Table 4
The PLS weights, VIPs and pseudo-regression coefficients of the optimal model.

Variables	W^* [1]	W^* [2]	VIP	Coefficients (a)	Coefficients (b)
E_{homo}	−0.333	−0.768	1.386	0.796	1.670
μ	−0.274	−0.613	1.215	0.261	8.730×10^{-2}
$(E_{\text{lumo}} - E_{\text{homo}})^2$	0.391	0.151	1.062	−0.275	-1.448×10^{-2}
$E_{\text{lumo}} - E_{\text{homo}}$	0.389	0.144	1.057	−0.269	−0.254
${}^1X^V$	−0.300	0.103	0.865	0.058	2.544×10^{-2}
HOF	0.292	−0.124	0.855	0.018	1.704×10^{-4}
MW	0.290	−0.128	0.849	0.032	2.104×10^{-4}
TE	−0.290	0.128	0.849	−0.032	-2.401×10^{-5}
EE	0.288	−0.132	0.848	−0.018	-3.073×10^{-6}
CCR	−0.288	0.132	0.847	0.014	3.063×10^{-6}
Constants				4.752	19.555

Coefficients (a), scaled and centered; coefficients (b), unscaled.

the CPs molecule polarity. It can be concluded that increasing the μ values leads increase of log *k* values, and the greater the E_{homo} values, the higher the CPs degradation rate constants.

The VIP values for the independent variables in the optimal model (model (10)) are also listed in Table 4. The table also presents the pseudo-regression coefficients of the independent variables and constants transformed from PLS results. From the positive and negative symbols of the coefficients of the independent variables, one can evaluate the effects of each independent variable on log *k*. Based on the unscaled coefficients of the predictor variables and a constant from PLS results of the model (10), a QSPR equations like those obtained from multiple regression analysis can be obtained as follows:

$$\begin{aligned}\log\ k = {} & 19.555 + 1.670\,E_{\text{homo}} + 8.730 \times 10^{-2}\mu \\ & -1.448 \times 10^{-2}(E_{\text{lumo}} - E_{\text{homo}})2 - 0.254\,(E_{\text{lumo}} - E_{\text{homo}}) \\ & +2.544 \times 10^{-21}X^V + 1.704 \times 10^{-4}\text{HOF} \\ & +2.104 \times 10^{-4}\text{MW} - 2.401 \times 10^{-5}\text{TE} - 3.073 \times 10^{-6}\text{EE} \\ & +3.063 \times 10^{-6}\text{CCR} \qquad (6)\end{aligned}$$

Observing Table 4, some discussions can be made:

1. The descriptors E_{homo}, μ, $E_{\text{lumo}} - E_{\text{homo}}$ and $(E_{\text{lumo}} - E_{\text{homo}})^2$ are more significant than the other descriptors in governing the log *k* values of the CPs.
2. The greater the E_{homo} values, the higher the CPs degradation rate constants. The descriptor E_{homo} characterizes the ability of a molecule to lose electrons or to be oxidized. The higher the E_{homo} values, the greater tendency of a compound to loose electrons or to be oxidized. Thus, it can be concluded that CPs tend to be oxidized in the US/Fenton-like system. Furthermore, it is interesting to note that E_{lumo} was excluded from the QSPR model. E_{lumo} characterizes the tendency of a compound to accept electrons or to be reduced. The greater the E_{lumo} values, the lesser the tendency for a compound to accept electrons. Therefore, it can be concluded that reductive dechlorination of CPs on ZVI surface in the US/Fenton-like system is insignificant. Since E_{homo} instead of E_{lumo} was included in the QSPR model, it can be concluded that oxidative degradation of CPs is predominant. From our previous study [2], it can be seen that reductive degradation of 2,4-DCP by ZVI was very weak. The direct dechlorination of CPs by zero-valent iron in the system could thus be neglected.

   Increasing $E_{\text{lumo}} - E_{\text{homo}}$, and $(E_{\text{lumo}} - E_{\text{homo}})^2$ values of the CPs leads to decreasing log *k* values. Since $-1/2(E_{\text{lumo}} - E_{\text{homo}})$ was defined as absolute hardness by [7], it can be concluded that CPs with large absolute hardness values, tend to have slow degradation rate.
3. The greater the Dipole moment (μ) values, the higher the CPs degradation rate constants. The descriptor μ characterizes the size of a molecule polarity. The higher value of μ, the higher the size of molecule polarity. Therefore, it can be concluded that higher polarity of CPs molecules make it easier to be degraded in the US/Fenton-like system.
4. The higher the values of the TE, EE and HOF, the higher the degradation rate constants, and the higher the CCR values, the lower the degradation rate constants. TE = EE + CCR, EE included the repulsion energy between electrons, the attraction energy between electron and atomic nucleus and the energy of electron spin. According to the molecular orbital theory, TE in a molecule was directly associated with total energy of occupied molecular orbital, which included the information of total bonds energy in a molecule. A molecule with lower TE (higher values) indicated that it had lower CCR (lower values) and EE (higher values), so the total bond energy of this molecule was lower. In this situation, the molecule was in stable state. Therefore, when a chlorophenol molecule had higher TE values, corresponding with higher EE values and lower CCR values, it was more difficult to be degraded in the US/Fenton-like system. Similarly, theoretically a compound with more negative HOF or lower HOF is more stable [17]. Therefore it is reasonable that the coefficient of HOF is positive in Eq. (1), which implies that the higher the HOF, the more unstable or reactive the CPs, and thus the greater the log *k* values.

Table 5
Correlation coefficients of the selected descriptors ($P < 0.05$).

	E_{homo}	$(E_{\text{lumo}} - E_{\text{homo}})^2$	$E_{\text{lumo}} - E_{\text{homo}}$	μ	${}^1X^V$	MW	HOF	TE	EE	CCR
E_{homo}	1.000									
$(\text{E}_{\text{lumo}} - \text{E}_{\text{homo}})^2$	−0.341	1.000								
$\text{E}_{\text{lumo}} - \text{E}_{\text{homo}}$	−0.332	1.000	1.000							
μ	0.908	−0.284	−0.276	1.000						
${}^1X^V$	0.014	−0.945	−0.948	−0.022	1.000					
MW	−0.017	−0.934	−0.937	−0.053	1.000	1.000				
HOF	−0.084	0.937	0.940	0.039	0.997	−0.998	1.000			
TE	0.017	0.934	0.942	0.053	−1.000	−1.000	0.998	1.000		
EE	0.022	0.932	0.935	0.050	−0.999	−0.999	0.996	0.999	1.000	
CCR	−0.024	−0.931	−0.935	−0.049	0.999	0.999	−0.995	−0.999	−1.000	1.000

5. The higher values of the Mw, ${}^{1}X^{\mathrm{V}}$, the higher the values of degradation rate constants. This is because both descriptors are highly inter-correlated (Table 5). It can be concluded that the larger the size of CPs, the higher degradation rate constants. The result was not consistent with observed $\log k$ values that descended with higher Mw and ${}^{1}X^{\mathrm{V}}$ values. However, as shown in Table 4, the both descriptors had low VIP values indicating that they are not important in predicting $\log k$ in the US/Fenton-like system.
6. In addition, it was found that two descriptors, V_p and $\log k_{\mathrm{ow}}$, were firstly excluded from the optimization models (V_{p} and $\log k_{\mathrm{ow}}$ was excluded from model (2) and model (3), respectively). V_{p} can be used to characterize the gas–liquid partition ability of volatile compounds. In an Ultrasound-irradiation system, compounds with higher V_{p} make it more easy to enter cavitation bubbles and thus improve associated rate [12]. The exclusion of V_{p} from the optimized QSPR model indicated that direct ultrasonic decomposition of CPs in the US/Fenton-like system was insignificant. Therefore, the synergistic effect of Ultrasound on CPs degradation in the system can be mainly ascribed to the enhancement of Fenton oxidation reactions, as proposed in our previous study [3]. The descriptor $\log k_{\mathrm{ow}}$ can be used to stand for the absorption degree of CPs on the ZVI surface. CPs molecule with higher $\log k_{\mathrm{ow}}$ makes it easier to adsorb on the ZVI surface. From Table 2, it can be seen that the value of $\log k_{\mathrm{ow}}$ rises with increase in the number of substitute chlorine in CPs molecule. It can be concluded that degradation of CPs do not occur on the surface of ZVI in the US/Fenton-like system. As a result, the degradation of CPs can be ascribed to Fenton oxidation reactions. US irradiation is expected to enhance the Fenton reaction instead of direct degradation of CPs. The degradation reaction of CPs is expected to occur in the bulk solution.

4. Conclusion

With the usage of PLS method and 19 quantum chemical descriptors computed by PM3 Hamilitonian, an optimized QSPR model was developed for degradation of five CPs in a US irradiated Fenton-like system. As a result of the obtained model, CPs with greater, $E_{\mathrm{lumo}} - E_{\mathrm{homo}}$, $(E_{\mathrm{lumo}} - E_{\mathrm{homo}})^2$, Mw, ${}^{1}X^{\mathrm{V}}$ and CCR values tend to be degraded slower, whereas CPs with higher values of E_{homo}, μ, TE, EE and HOF values tend to be degraded faster. The degradation of CPs in the US/Fenton-like system can be ascribed to homogeneous Fenton oxidation in the bulk solution. Ultrasound irradiation is expected to enhance Fenton reaction instead of directly decomposing CPs in the system.

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References

[1] USEPA, http://www.epa.gov/OGWDW/ccl/ccl2.html, 2005.
[2] T. Zhou, Y.Z. Li, F.S. Wong, et al., Enhanced degradation of 2,4-dichlorophenol by ultrasound in a new Fenton like system (Fe/EDTA) at ambient circumstance, Ultrason. Sonochem. 15 (2008) 782–790.
[3] T. Zhou, T.T. Lim, X. Lu, et al., Simultaneous degradation of 4CP and EDTA in a heterogeneous Ultrasound/Fenton like system at ambient circumstance, Sep. Purif. Technol. 68 (2009) 367–374.
[4] R. Kaliszan, Quantitative structure retention relationships applied to reversed-phase high-performance liquid chromatography, J. Chromatogr. A 656 (1993) 417–435.
[5] S. Wold, H. Wold, W.J. Dunn III. Report UMINF-83, Department of Chemistry, University of Umeå, Sweden, 1984.
[6] Y.H. Liu, F.L. Yang, J.W. Chen, et al., Linear free energy relationships for dechlorination of aromatic chlorides by Pd/Fe, Chemosphere 50 (2003) 1275–1279.
[7] P.G. Pearson, Absolute electronegativity and hardness correlated with molecular orbital theory, Proc. Natl. Acad. Sci. U.S.A. 83 (1986) 8440–8441.
[8] J.C. Faucon, R. Bureau, J. Faisant, et al., Prediction of the fish acute toxicity from heterogeneous data coming from notification files, Chemosphere 38 (1999) 3261–3276.
[9] E. Argese, C. Bettiol, G. Giurin, et al., Quantitative structure–activity relationships for the toxicity of chlorophenols to mammalian submitochondrial particles, Chemosphere 38 (1999) 2281–2292.
[10] F. He, X. Yuan, X. Cheng, et al., The QSBR (quantitative–structure biodegradation relationship) study about the aerobic biodegradation of phenols, Chin. Environ. Sci. 21 (2001) 152–155.
[11] H. Yang, Z. Jiang, S. Shi, Aromatic compounds biodegradation under anaerobic conditions and their QSBR models, Sci. Total Environ. 358 (2006) 265–276.
[12] Y. Nagata, M. Nakagawa, H. Okuno, Sonochemical degradation of chlorophenols in water, Ultrason. Sonochem. 7 (2000) 115–120.
[13] M. Czaplicka, Sources and transformations of chlorophenols in the natural environment, Sci. Total Environ. 322 (2004) 21–39.
[14] A. Ribeiro, M.H. Neves, M.F. Almeida, et al., Direct determination of chlorophenols in landfill leachates by solid phase micro-extraction-gas chromatography–mass spectrometry, J. Chromatogr. A 975 (2002) 267–274.
[15] L. Feng, L.S. Wang, Y.H. Zhao, et al., Effects of substituted alilines and phenols on root elongation of cabbage seed, Chemosphere 32 (1996) 1575–1583.
[16] M. Luco, Prediction of the brain–blood distribution of a large set of drugs from structurally derived descriptors using partial least-squares (PLS) modeling, J. Chem. Inf. Comput. Sci. 39 (1999) 396–404.
[17] V. Fried, H.F. Hameka, U. Blukis, Physical Chemistry, Macmillan Publishing Co. Inc., New York, 1977.