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Degradation mechanism study of amine collectors in Fenton process by quantitative structure-activity relationship analysis

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Abstract: In this study, advanced oxidation processes (AOPs), Fenton process, was applied to degrade ten amine collectors. The experimental results indicated that most of the tested amines could be removed rapidly and effectively at pH=4, while the degradation of quaternary ammonium compounds was less than others. To research the Fenton oxidation process, the degradation-rate constants of amine collectors were calculated by the pseudo-second order kinetic model, then which was used as the dependent variable to establish a quantitative structure activity relationship (QSAR) model. Meanwhile, 16 molecular structure descriptors and quantum mechanical parameters for amine collectors were simulated and analyzed by using Materials Studio software. The optimum QSAR model was established based on the partial least squares regression (PLS) method and confirmed by the statistics analysis. The model revealed that hydrogen bond acceptor (HBA) and the maximum values of electrophilic attack in C atom sites ($f(-)_c$) were the major effect factors for the degradation-rate constants of amine collector.

Keywords: amine collectors, Fenton process, QSAR, degradation mechanism, quantum chemistry

1. Introduction

Amines, as one of the most important cationic collectors, are widely applied to concentrate iron ores by reverse flotation of the gangue particles (mainly silicates and quartz) (Calgaroto et al., 2016). With the rising demand for iron concentrates around the world, the consumption of amine collectors increased constantly. Some part of amines was deposited in sediments and soil with massive amine applied for industrial flotation processes (Araujo et al., 2010). Ultimately, they leaked into wastewater and groundwater, which resulted in the accumulation of collectors and their degradation products in the environment. These compounds and their derivatives caused synergistic effects with ions and other dissolved pollutants, and they would be harmful for aquatic organisms and ecosystem (Schultz et al., 1991; Fernandez et al., 2014; Wang et al., 2016). Consequently, the degradation or elimination of amine collectors has drawn more and more attention hitherto.

Conventional wastewater treatments like adsorption, chemical precipitation, coagulation-flocculation, ion exchange, activated sludge processes, and bioremediation techniques have been widely used to separate the residual cationic collectors from aqueous environment (Hao et al., 2000; Wiesmann et al., 2007; Giacco et al., 2017). However, these treatments could only remove cationic collectors partially. For instance, Van Ginkel et al. (1995) reported a bacterial degradation for dodecylamine and the biodegradation rate was 80% in one week. Deo and Natarajan (1998) used bacterial metabolites alone to degrade two primary amines and the results showed that only 30% of amines could be removed from the solution. In recent decades, advanced oxidation processes (AOPs)-Fenton process have attracted more and more attention to disposal of industrial wastewater because they can degrade the non-biodegradable chemicals into less toxic products by oxidation reactions (Li et al, 2017). The Fenton process, as the representative of AOPs, has a remarkable efficiency to oxidize wide diversity pollutants with short reaction time (Huang et al., 2017). Elhalil et al. (2016) investigated

the degradation of malachite green dye in aqueous solution by the Fenton process and the maximum degradation efficiency of 93.83% could be obtained. Sohrabi et al. (2017) studied the removal of Carmoisine edible dye from aqueous solutions by the Fenton and photo Fenton systems.

The molecular structure has significant effect on its chemical reactivity and physicochemical properties, and the corresponding mechanisms are widely studied by Quantitative Structure Activity Relationship (QSAR) methods (Hopfinger, 1980). Recently, several QSAR models were established to reveal the relationship between the chemical structures and the degradation capabilities in wastewater treatment processing (Li et al., 2013). Zhu et al. (2014) investigated the degradation rates of organic pollutants by an ozonation process, and a QSAR model was developed to illustrate the degradation mechanism. It has provided a deeper insight into the rules of universal and propagable ozonation. In the work of Jia et al. (2015), the QSAR models of oxidative degradation for organic pollutants in the Fenton process were established to explain how the structures of pollutants influence their degradation efficiencies.

To the best of our knowledge, the fact was that several works of the application of QSAR in the activities of amine have been done. Börnick et al. (2001) found a linear relationship between available pK_a values of protonated amines (used to estimate the biodegradability of aromatic amines) and the logarithm of the experimental degradation rates. Belanger et al. (2016) vastly improved the knowledge of amine oxides toxicity by developing acute QSARs for an alga (*Desmodesmus subspicatus*), an invertebrate (*Daphnia magna*) and a fish (*Danio rerio*) using the appropriate array of OECD (Organization for Economic Cooperation and Development) Test Guidelines. However, there are few investigations about the Fenton degradation of amine collectors by the QSAR method. Thus, the purpose of this study is to determine the degradation capabilities of amine collectors with the Fenton oxidation process and develop QSAR models to interpret the relationship between amine collector structures and their degradation characteristics.

2. Materials and methods

2.1 Materials

The tested amine collectors, such as dodecylamine (DDA), hexadecylamine (HDA), octadecylamine (ODA), N-methyldodecylamine (MDA), dodecyl tertiary amine (DTA), N,N-dimethyloctadecylamine (DOA), dodecyl trimethyl ammonium chloride (DTACl), dodecyl trimethyl ammonium bromide (DTABr), hexadecyl trimethyl ammonium bromide (HTABr), and dodecyl propyl ether amine (DPEA) were provided from Sinopharm Chemical Reagent Co., Ltd and used without further purification (purity $\geq 99\%$). The corresponding molecular structures were optimized by using density functional theory (DFT) methods in Materials studio 6.0.

2.2 Catalyst preparations

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, sulfuric acid, hydrochloric acid, 30% of hydrogen peroxide (H_2O_2), and sodium hydroxide were of analytical grade and purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Deionized water was applied throughout all experiments. A 0.25 mol/dm^3 of H_2O_2 and 0.25 mol/dm^3 of Fe (II) stock solution was prepared to compound the Fenton reagent. In order to avoid iron precipitation, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved at pH 4 of deoxygenized water. Sulfuric acid and sodium hydroxide of analytical grade reagents were used to adjust the initial pH before degradation process.

2.3 Fenton degradation experiments

First of all, the initial chemical oxygen demand (COD) values of ten amine collectors were determined based on the standard method 5220D for the examination of water and wastewater (Rice et al., 2012). COD values were used to characterize the concentration of the organics in this study. H_2O_2 and Fe(II) solutions were mixed by 1:2 of the molar $[\text{Fe(II)}]:[\text{H}_2\text{O}_2]$ ratio to prepare the Fenton reagent (Santos et al., 2011; Liu et al., 2013). The pH value of amine solutions was adjusted to 4.0 with 1 mol/dm^3 H_2SO_4 solution, which was the optimal pH for the Fenton degradation (Rodrigues et al., 2009). Subsequently, the predetermined amount of the Fenton reagent solution was added to 150 cm^3 of 500 mg/dm^3 of amine collector solutions and the intermixtures were stirred using magnetic stirrers. Meanwhile,

Fenton degradation experiments were conducted at 25 °C. The samples of amine collectors were taken out in different times to determine COD values change during the degradation process. Besides, pH of the samples was adjusted to 9.0 in order to transform the residual Fe(II) into Fe(III) and terminate the oxidation reaction.

2.4 Molecular descriptors and statistical analysis

In this paper, quantum chemical and physicochemical parameters such as dipole (μ), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy of the highest occupied molecular orbital (E_{HOMO}), molecular volume (V), electronic energy (EE), total energy (TE) were analyzed as molecular descriptors. Furthermore, Fukui indices were calculated by Dmol³ (LDA-PWC/DND (3.5) basis) in Materials Studio 6.0 program. The smearing of electronic occupations and density mixing were set at 0.005 Ha, 0.2 charge and 0.5 spin. The molecular connectivity index of order 2 for the degree of linearity (${}^2\chi_p$) and the Shape index of order 3 for the degree of branching toward the center (${}^3\chi_c$) were calculated as topological indices. AlogP, a hydrophobic parameter, was selected as a molecular description for QSAR study.

In order to select the major molecular descriptions to establish the QSAR, a correlation matrix about all parameters were made. Then, the partial least squares (PLS) regression method, as one of statistical methods in the Materials Studio, was used to establish QSAR model in this paper. The model quality was characterized by the determination coefficient (R^2), the number of observations (n), the standard error of estimate (SE) and the significance level (P) (Huang et al., 2015). Besides, the cross validation (Q_{cum}^2) was calculated to evaluate the developed QSAR models (Eriksson et al., 2003).

3. Results and discussions

3.1 Degradation of amine collectors

The initial COD_{cr} values of ten amine collectors were measured to determine whether they were suitable for the Fenton degradation process, and the results showed that amine collectors had enough high COD_{cr} values to adopt the Fenton oxidation. The results of the degradation are displayed in Table 1. Subsequently the degradation rates of amines by the Fenton reagent were established, and the COD_{cr} values of amine collectors as a function of time are shown in Fig. 1. It can be observed that the degradation of primary amine, secondary amines, tertiary amine and ether amine were more efficient than quaternary ammonium compounds (DTACl and DTABr). Furthermore, ten amines, during the Fenton process, had the similar tendency that COD_{cr} values of amine collectors decreased rapidly in a very short time, and then remained stable with the growth of reaction time.

According to previous test results in the study of Guedes et al. (2003), degradation characteristic of amine could be calculated by the pseudo-second order kinetic model, which was shown as Eq. (1):

$$\frac{1}{c} = \frac{1}{c_0} + k_{ow}t \quad (1)$$

where C is the concentration of amine (mg/dm^3), C_0 is the initial concentration of amine collector (mg/dm^3) and k_{ow} is the degradation-rate constant ($(mg \cdot (dm^3)^{-1})^{-1} \cdot s^{-1}$). In this paper, degradation rate constants of the tested amines were calculated according to Eq. (1) and the calculation results are shown in Table 1. It was worth mentioning that Fenton degradation effects on the shorter alkyl chain of quaternary ammonium salts were ignored because their COD values were too poor to establish exact pseudo-second order kinetic models. Based on the experimental data listed in Fig. 1, kinetic equations of amine collectors were constructed. The results indicated that degradation efficiency of DPEA, owned the k_{ow} of 8.08×10^{-4} , was highest value among ten amines, whereas HTABr exhibited the lowest degradation efficiency with k_{ow} value of 1.73×10^{-4} . The degradation efficiency of the tested amines was listed in order as follows: DPEA > ODA > HDA > DOA > DDA > MDA > DTA > HTABr. It can be seen that the substituent groups played a major contributor in the Fenton degradation process for tested amines. The ether group has an obvious promotion for the oxidation of hydroxyl radicals, whereas the ionization of amine collectors hindered this reaction. In addition, the branch degrees and alkyl chain length of molecules have some impacts on degradation efficiency of amines as well.

Table 1. The values of COD_{cr} before and after the degradation by Fenton

Tested amines	The initial COD _{cr} (mg·dm ⁻³)	The COD _{cr} after degradation (mg·dm ⁻³)	Degradation rate (%)
DDA	288.0	33.1	88.50
HDA	285.6	23.7	91.70
ODA	287.4	18.06	93.72
MDA	26736	29.39	89.02
DTA	242.3	51.17	78.88
DOA	266.4	10.53	96.05
DPEA	314.5	18.06	94.26
DTACl	183.6	153.5	16.39
DTABr	198.6	162.8	18.03
HTABr	207.7	81.27	60.87

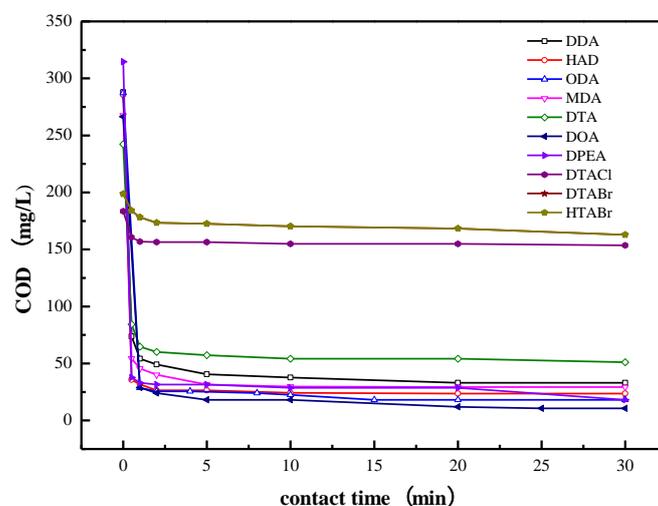
Fig. 1. The degradation COD_{cr} of the amines by Fenton in various times

Table 2. The kinetics parameters of typical amine collectors

Tested amines	Kinetic equations	R ²	k _{ow}
DDA	$y = 3.49 \times 10^{-4} t + 2.638$	0.992	3.49×10^{-4}
HDA	$y = 4.83 \times 10^{-4} t + 2.453$	0.997	4.83×10^{-4}
ODA	$y = 5.12 \times 10^{-4} t + 1.148$	0.970	5.12×10^{-4}
MDA	$y = 3.41 \times 10^{-4} t + 3.610$	0.986	3.41×10^{-4}
DTA	$y = 2.49 \times 10^{-4} t + 4.010$	0.998	2.49×10^{-4}
DOA	$y = 3.59 \times 10^{-4} t - 1.475$	0.974	3.59×10^{-4}
HTABr	$y = 1.73 \times 10^{-4} t + 5.036$	0.989	1.73×10^{-4}
DPEA	$y = 8.08 \times 10^{-4} t + 1.338$	0.984	8.08×10^{-4}

3.2 Calculation of molecular structure descriptors and establishment of QSAR model

The essence of Fenton process was an oxidation reaction. In the Fenton oxidation process, Fe²⁺ and hydrogen peroxide were used as the catalyst and the oxidant, respectively. Based on the classical free radical mechanism, the Fenton reaction process was described by the following equations (Wang et al., 2017):





Therefore, it could be considered that the chemical stability of amine collector played an important role in their degradation process. From the above displayed oxidation mechanism of the Fenton process (Eq. (2)-Eq. (5)), it could be concluded that the oxidization degree was related with the concentration of OH radical, the ability of molecules to gain or loss electron and the molecular stability. To further reveal the relationship between molecular structures of amine collectors and the degradation of Fenton oxidation, the QSAR model with a good predictive ability was established by transforming the properties of chemical structures into effective numerical quantities such as quantum mechanical parameters, physic-chemical parameters and topological indices (Karelson et al., 1996). The rate constants in Fenton oxidation process (k_{ow}) and 16 descriptors selected from molecular structures parameters and quantum mechanical parameters were calculated to be variables, listed in Table 3. Besides, the accurate and predictable QSAR model is:

$$\log k_{ow} = -3.9173 + 0.2020\text{HBA} + 6.5879f(-)_c \quad (6)$$

where $n = 8$ is the number of amines in the training set, the determination coefficient ($R^2 = 0.89$) and cross validation ($Q^2_{(cum)} = 0.76$) are the most frequently used to evaluate the fitness and predictive ability of a developed QSAR model (Carroll and Ruppert, 1988; Song et al., 2006).

Table 3. Calculation results of Quantum-chemical descriptors

amines	$\log k_{ow}$	TE (Ha)	EE (Ha)	E_{HOMO} (ev)	E_{LUMO} (ev)	dipole moment (debye)	HBD	HBA
DDA	-3.4572	-523.5480	-6.4166	-4.829	1.335	1.445	2	1
HDA	-3.3162	-679.3676	-8.3772	-4.874	1.388	1.3910	2	1
ODA	-3.2907	-757.2794	-9.2863	-4.911	1.338	1.2477	2	1
MDA	-3.4674	-562.4948	-6.86113	-4.453	1.401	1.3990	1	1
DTA	-3.6038	-601.4453	-7.1009	-4.517	1.362	0.4392	0	1
DOA	-3.4449	-835.1774	-9.7994	-4.563	1.319	0.4354	0	1
HTABr	-3.7622	-3367.501	-12.7443	-3.916	0.028	10.3717	0	0
DPEA	-3.0926	-715.1330	-7.8860	-4.953	1.289	1.9222	2	2

(HBD: Hydrogen bond donor; HBA: Hydrogen bond acceptor)

amines	$f(+)_c$	$f(0)_c$	$f(-)_c$	$A \log P$	$2\chi_P$	$3\chi_c$	Molecular area (vdW area)
DDA	0.034	0.041	0.052	3.7650	3.9706	0	302.5605
HDA	0.027	0.045	0.063	5.3502	5.3849	0	383.8516
ODA	0.020	0.042	0.063	6.1428	6.0920	0	434.7823
MDA	0.022	0.042	0.060	4.1733	4.2855	0	320.3938
DTA	0.024	0.029	0.034	4.5347	4.9853	0.3162	340.4118
DOA	0.019	0.026	0.034	6.9125	7.1066	0.3162	472.19668
HTABr	0.020	0.018	0.015	5.6450	7.6101	1.3959	475.9646
DPEA	0.027	0.039	0.051	3.6523	4.9366	0	380.8138

3.3 Model validations

According to the developed QSAR model as shown in Eq. (6), R^2 and $Q^2_{(cum)}$ of the derived model were 0.89 and 0.76, respectively, what demonstrated that the QSAR model had the 89% prediction accuracy and no danger of over-estimating. To further verify the statistical capability of the model, the linear correlation equation between the experimental and predicted values was presented in Fig. 2, where x and y represent experimental value and values, respectively; R is the liner relativity index; SE is the standard error and P is the p -value test. As shown in Fig. 2, the standard error was close to zero and the value of R was above 0.90, what indicated that the correlation had certain significance. Besides, $p < 0.05$ was widely applied as the threshold for error probability. Consequently, the developed model could be further used to interpret the degradation mechanism of amines in the

Fenton process, and it has well predictive ability for the degradation efficiency of amine collectors in the oxidative degradation process.

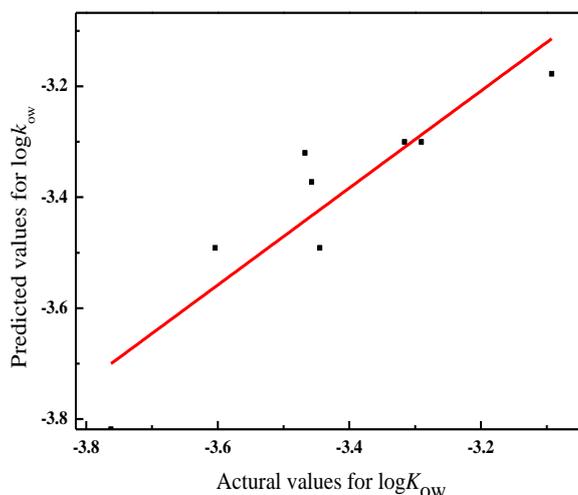


Fig. 2. Linear correlation equation between actual values and predicted values
($y = 0.8749x - 0.4087$, $R = 0.90904$, $SE = 0.1637$, $P = 0.009$)

3.4 Model explanation

The positive relationship between $\log k_{ow}$ and Hydrogen bond acceptor (HBA) could be seen from Eq. (6). HBA indicated the susceptibility to be attacked by hydroxyl radical and the potential of forming hydrogen bond. The formation of hydrogen bond was not conducive to the stability of the molecular structure in the aqueous solution and benefit of the reaction of Fenton degradation. As shown Table 3, aliphatic amine, with almost the same number of HBA, were likely to induce the formation of N-H...O bond between -NH₂ and -OH, while other amines might form different kinds of hydrogen bond. Take DPEA for example: except for one -N atom, dodecyl propyl ether amine also has one O atom to promote the formation of O-H...O bond. Hence, the HBA number of DPEA was higher than other aliphatic amines, and k_{ow} of DPEA was also larger than aliphatic amines. Conversely, quaternary ammonium salts, with no HBA, have obvious advantages of structural stability in solution containing hydroxyl radical and the values of k_{ow} are quite lower.

The positive relationship between k_{ow} values with $f(-)_c$ could be also observed from Eq. (6). It was known that the Fukui function, a descriptor of local reactive, given the preferred region where density was easier to be changed by some chemical species when a mass of electrons was modified. Therefore, these descriptors indicated the deform tendency of the electronic density at a given position to accept or donate electrons (Ayers and Parr, 2000; Al-Wabli et al., 2016). In addition, the corresponding condensed or atomic Fukui function on a certain atom site was possibly defined as the following equations:

$$f_j^- = q_j(N) - q_j(N-1) \quad (7)$$

$$f_j^+ = q_j(N+1) - q_j(N) \quad (8)$$

$$f_j^0 = \frac{1}{2}q_j(N+1) - q_j(N-1) \quad (9)$$

where q_j is the atomic charge evaluated from the Mulliken population analysis or electrostatic derived charge at the j th atomic site. The neutral, anionic and cationic chemical species were represented as N , $N+1$ and $N-1$, respectively. An electrophilic f_j^- , nucleophilic f_j^+ and free radical attack f_j^0 on the reference molecule could be obtained from these equations. Fenton oxidative degradation was closely associated with the attack of OH radical to the main chain. Hence, the Fukui functions of the C atom were calculated and the maximum of them is listed in Table 3. The electrophilic Fukui functions (expressed as $f(-)$) were presented in Fig. 3. The zones of electrostatic reaction and nucleophilic reaction were indicated by red and blue color, respectively. It was obvious that quaternary

ammonium salt had less electrostatic reaction, and the reaction areas were mainly concentrated around halogen atoms. However, the halogen atoms are separated from the backbone chain with the dissolution of quaternary ammonium salts in the solution, which eventually leads to insignificant effect on oxidation. As shown in Eq. (6), there was a positive relationship between k_{ow} values and $f(-)_c$. The value of $f(-)_c$ was a measurement of the affinity for electrophilic attack. The higher $f(-)_c$ was, the easier it was for C-H bonds of amines to be ruptured.

Consequently, the different substituent groups influenced the formation of hydrogen bonds and the oxidation reaction, engender the different reaction sites, thus they caused the different degradation rates of amines eventually.

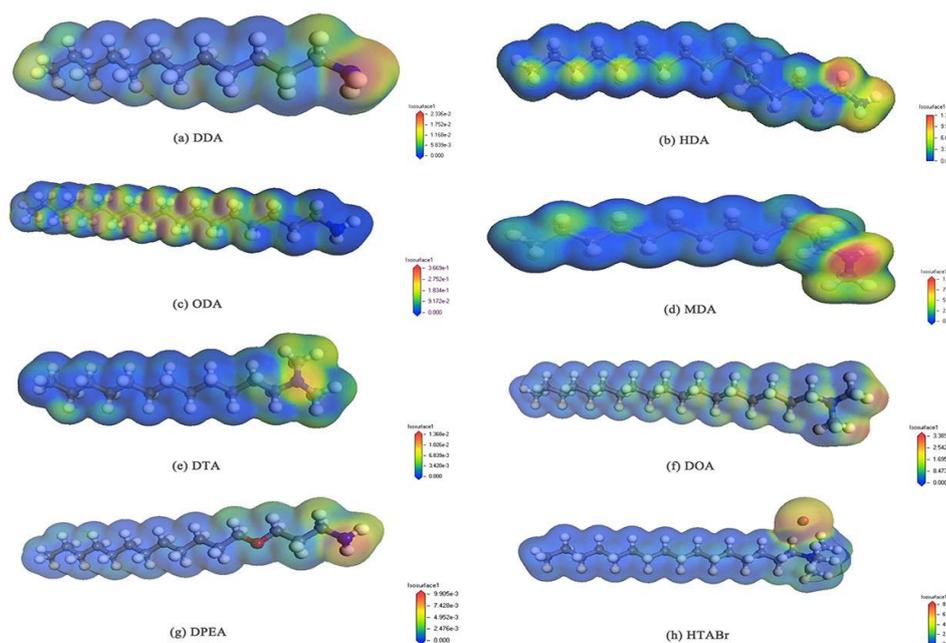


Fig.3. Optimized structures and electrophilic Fukui functions of tested amine

4. Conclusions

Tested amines were demonstrated to be effectively degraded in the Fenton oxidization process, and the substituent groups had a substantial impact on the degradation efficiency of amines. The QSAR models were established based on the Fenton degradation mechanism and the PLS method. The mechanistic models indicated that the degradation rule of amines in the Fenton process was strongly related to HBA and $f(-)_c$. Besides, there was significant positive correlation between HBA or $f(-)_c$ and $\log k_{ow}$.

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