Predictive Model of Nonequilibrium Plasma Decontamination Efficiency for Gaseous Pollutant

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Abstract: The conception of energy conversion factor (E_f) and the predictive model of decontamination efficiency are put forward, respectively, by analyzing the quantitative relation of discharge power, molecular structure of pollutant (dissociation energy of chemical bond) and decontamination efficiency. The E_f of chemical bonds, such as S-H, C-S, C-Cl and C-H, are obtained by experimental data of H_2S and 2-chloroethyl ethyl sulfide (2-CEES) with the same pulsed corona plasma equipment. And then, the predictive model is used to estimate the decontamination efficiency of ethanethiol and 2-CEES by scale-up pulsed corona plasma equipment. As a result, the predictive values are close to experimental data. The model can be used to estimate whether the decontamination efficiency of redesigned plasma equipment attains the expectant target in the engineering design of nonequilibrium plasma equipment, therefore, it has an important application value in engineering design.

Keywords: nonequilibrium plasma, decontamination efficiency, gaseous pollutant; predictive model

1 INTRODUCTION

Nonequilibrium plasma (NEP) technology has been paid more and more attention in the treatment of various hazardous gaseous pollutants. But it is difficult to estimate whether the redesigned equipment can attain the expectant target in the engineering design of NEP decontamination equipment, especially when it is unfit for much hazardous gas to be tested. Under this situation, it has not been studied that which kind of parameter can be used to estimate the chemical reactivity of equipment till now. This paper will present the quantitative relation of decontamination efficiency, discharge power and molecular structure of pollutant based on experimental data, and a predictive model of plasma decontamination efficiency is put forward to provide an estimating method for NEP decontamination equipment.

2 PREDICTIVE MODEL OF NEP DECONTAMINATION EFFICIENCY

Energy yield (E_Y, absolute mass of pollutant decontaminated by unit energy consumption) is an important parameter on estimating a plasma equipment to decontaminate pollutant. It is calculated by the following equation:

$$E_Y = \frac{C_0 \eta Q}{P_T} \tag{1}$$

where, E_Y—energy yield, g/(kW·h);

C_0—initial concentration of pollutant, mg/m^3;

η—decontamination efficiency, %;

Q—gas flow rate, m^3/h;

P_T—average power of inputting plasma reactor, W.

It is well known that NEP chemical reactivity is in an energy conversion processing when active particles collide with pollutant molecules. It is also found that higher the decontamination efficiency is, lower dissociation energy chemical bond of the pollutant is in the same plasma system [1-4], which shows that decontamination efficiency of the pollutant has a close relation with its molecular structure (i.e. dissociation energy of chemical bond). Therefore, to some extent, the decontamination efficiency may be determined by the energy input and dissociation energy of chemical bond. Here, the energy conversion factor (E_f) is introduced to quantitatively associate E_Y with dissociation energy of chemical bond (E_b), and then we can obtain:

$$E_{f,i} = 0.0268 \frac{E_Y}{M} \times E_{b,i} = 0.0268 \frac{\frac{C_0 \eta Q}{M} \times E_{b,i}}{P_T} \tag{2}$$

where, $E_{f,i}$—energy conversion factor for chemical bond i, dimensionless;

M—molecular mass, g/mol;

$E_{b,i}$—dissociation energy of chemical bond, eV;

0.0268—coefficient generated by units transforming.

It can be seen that $E_{f,i}$ is equal to the total dissociation energy of chemical bond destroyed by plasma, so it is a dimensionless value. Formula (2) can be transformed to the following form:

$$C_0 \cdot \eta = \frac{M \cdot E_{f,i}}{0.0268 E_{b,i}} \times \frac{P_T}{Q} \tag{3}$$

So, $C_0 \cdot \eta$ and P_T/Q are variables for a pollutant in different experimental condition. If the experimental data (such as H_2S and 2-CEES) are substituted in formula (3), taking P_T/Q as x-axis and $C_0 \cdot \eta$ as y-axis, a line can be fit in a plotting figure. Then the values of $E_{f,\text{H-S}}$, $E_{f,\text{C-S}}$, $E_{f,\text{C-Cl}}$, $E_{f,\text{C-C}}$ and $E_{f,\text{C-H}}$ can be calculated from the slope of the line. According to E_f of these chemical bonds, the decontamination efficiency of other pollutants composing the above chemical bonds can be predicted in some condition. The predictive formula is as follows:

$$\eta = \begin{cases} 100\%, \text{ If } \dfrac{\sum (n_i \cdot E_{f,i}) \cdot M \cdot P_T}{0.0268 C_0 \cdot Q \cdot \sum (n_i \cdot E_{b,i})} > 1 \\ \dfrac{\sum (n_i \cdot E_{f,i}) \cdot M \cdot P_T}{0.0268 C_0 \cdot Q \cdot \sum (n_i \cdot E_{b,i})} \times 100\% \\ \text{If } \dfrac{\sum (n_i \cdot E_{f,i}) \cdot M \cdot P_T}{0.0268 C_0 \cdot Q \cdot \sum (n_i \cdot E_{b,i})} \le 1 \end{cases} \tag{4}$$

where, n_i□chemical bond number with the same dissociation energy in pollutant molecule.

Formula (4) is the decontamination efficiency predictive model, which presents the relation between decontamination efficiency, discharge power and molecular structure. The parameters involved in formula (4) are discharge power, initial pollutant concentration, molecular mass and dissociation energy of chemical bond and so on. The model has no relation with discharge mode or plasma reactor structure, so it should be universal. But its precision and applicability need to be validated and improved by lots of experimental data. This paper will give an elementary validation and bring forward improvement methods.

3 VALIDATION AND IMPROVEMENT FOR PREDICTIVE MODEL OF DECONTAMINATION EFFICIENCY

3.1 E_f of Chemical Bond

E_f values of chemical bonds must be obtained firstly for predicting by the model. Here, the former decontamination experimental data [5-6] of H_2S and 2-CEES ($C_2H_6SC_2H_5Cl$) are used to calculate E_f values of chemical bonds in these two chemicals, as show in Fig.1. The calculated E_f values can be used to predict the decontamination efficiency of ethanethiol and 2-CEES in scale-up experiment. Then the precision and applicability of the model can be validated by comparing predictive values with experimental data.

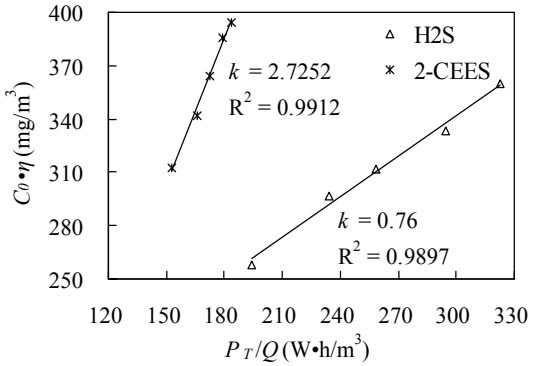

Fig. 1 Fitting calculation of E_f values for H_2S and 2-CEES

The dissociation energy of chemical bond will vary with its position for being influenced by atoms or radicals around. The dissociation energy of chemical bonds of H_2S, 2-CEES and ethanethiol are listed in Table 1.

According to the slope of the line in Fig. 1, we can obtain E_f value of chemical bond S-H:

$$\frac{M_{H_2S} \cdot E_{f,H-S}}{0.0268 E_{b,H-S}} = \frac{34 \cdot E_{f,H-S}}{0.0268 \times 3.95} = 0.76 \quad (5)$$

$$E_{f,\text{H-S}}=2.37\times10^{-3} \quad (6)$$

Similarly, we can obtain $E_{f,\text{C-S}}$, $E_{f,\text{C-Cl}}$, $E_{f,\text{C-C}}$ and $E_{f,\text{C-H}}$, by substituting the dissociation energy of chemical bonds in 2-CEES molecule in formula (7):

$$\frac{M_{2-CEES} \cdot E_{f,i}}{0.0268 E_{b,i}} = 2.7252 \quad (7)$$

Table 1 Dissociation energy of chemical bonds [7]

Pollutant	Chemicalbond	n_i	$E_{b,I}$, eV
H_2S	S□H	2	3.95
2-CEES	C□S	2	3.14
	CH_2□CH_3	1	3.56
	□SCH□H	4	4.04
	CH_2CH_2□H	3	4.36
	□C□Cl	1	3.65
	CH_2□CH_2Cl	1	3.85
	CHCl□H	2	4.21
Ethanethiol	C□S	1	3.19
	C□C	1	3.58
	S□H	1	3.79
	SC□H	2	4.07
	CH_2□H	3	4.36

We can take the obtained E_f values as the standard values, symbolized as $E^0_{f,\text{i}}$, shown as Table 2.

Table 2 E_f values of chemical bonds

chemical bond	$E^0_{b,I}$, eV	$E^0_{f,i}$
S□H	3.95	2.37×10^{-3}
C□S	3.14	1.84×10^{-3}
C□Cl	3.65	2.14×10^{-3}
C□C	3.56	2.10×10^{-3}
C□H	4.36	2.56×10^{-3}

3.2 Validation for Predictive Model of Decontamination Efficiency

Here, the precision of the model is validated by comparing predictive value with experimental data in the scale-up decontamination experiment of ethanethiol and 2-CEES by pulsed corona discharge.

The dissociation energy of chemical bonds in ethanethiol and 2-CEES molecule is shown in Table 1. Since the dissociation energy of chemical bond will vary with its position, a dissociation energy coefficient (σ) is defined as follows:

$$\sigma = \frac{E_b}{E^0{}_b} \quad (8)$$

For example, the dissociation energy of H-S is 3.79 eV in ethanethiol, but E^0_b is 3.95 eV from Table 2, so the dissociation energy coefficient $\sigma_{\text{H-S}}$= 3.79/3.95 = 0.9595.

According to E_f values in Table 2 and E_b of chemical bonds in ethanethiol molecule presented in Table 1, we can obtain E_f values of chemical bonds in ethanethiol molecule calculated by

$$E_{f,i} = \sigma_i \cdot E^0{}_{f,i} \quad (9)$$

The calculated results are listed in Table 3. Substituting the data of Table 3 and Table 2 in formula (4) respectively, we can obtain the predictive decontamination efficiency of ethanethiol and 2-CEES in some certain discharge conditions. The predictive results and experimental results are shown in Table 4.

Table 3 E_f values of chemical bonds in ethanethiol molecule

Chemical bond	n_i	$E_{b,i}$, eV	σ_i	$E_{f,i}$
S□H	1	3.79	0.9595	2.27×10^{-3}
C□S	1	3.19	1.016	1.87×10^{-3}
C□C	1	3.58	1.006	2.11×10^{-3}
SC□H	2	4.07	0.9335	2.39×10^{-3}
CH_2□H	3	4.36	1.000	2.56×10^{-3}
C_2H_5SH	$\sum(n_i\cdot E_{bi}) = 31.78$		$\sum(n_i\cdot E_{f,i}) = 1.87\times10^{-2}$	

Table 4 Predictive decontamination efficiency of ethanethiol and 2-CEES

Pollutant	C_0, mg/m^3	Q, m^3/h	P_T, W	η(Test), %	η(Predict), %	Predictive error, %
Ethanethiol	35	4.0	96	98.2	93.3	5.0
	126	1.2	96	97.3	86.4	11.2
2-CEES	253	1.2	112	98.9	100	1.1
	291	1.2	112	96.8	87.5	9.6

From Table 4, it can be found that the predictive results are close to experimental data under the experimental condition of low initial concentration (C_0) of pollutant or gas flow rate (Q), which indicates that the model is reasonable and feasible. But the predictive error will increase when C_0 or Q increases, which may be caused for two reasons:

1) Since the E_f values in Table 2 are obtained from experimental data of 2-CEES composed of some different chemical bonds, which ignores the reactive difference among the chemical bonds. So the E_f values are calculated just by the proportion of dissociation energy of chemical bonds, and they are average values actually. Therefore, the E_f values need to be corrected.

2) The predictive model is supposed that pollutant is decontaminated completely and mineralized. But pollutant may be decomposed to other organic compounds for only a part of chemical bonds destroyed when increasing initial concentration or gas flow rate. Therefore, it will make the test decontamination efficiency is higher than the predictive result because it will give a contribution for decontamination efficiency even only one chemical bond is destroyed.

3.3 Improvement for Predictive Model of Decontamination Efficiency

According to the above analysis on predictive error, two approaches to improve the model are presented:

1) Correcting and perfecting the E_f values of chemical bonds

Precise E_f values of chemical bonds can not be obtained by formula (7), because the reactivity, between pollutant with some different chemical bonds and plasma, is complex. Therefore, the E_f values of chemical bonds should be calculated by experimental data of pollutant being composed of only one kind of chemical bond, for example, $E_{f,\text{H-S}}$, $E_{f,\text{C-S}}$, $E_{f,\text{C-Cl}}$ and $E_{f,\text{C-H}}$ can be calculated by decontamination experimental data of H_2S, CS_2, CCl_4 and CH_4 respectively. Then a standard database can be established after obtaining enough E_f values of chemical bonds. Formula (4) can be validated and improved to promote the precision in decontamination efficiency prediction.

2) Improvement for predictive model

In formula (4), summation of all chemical bonds data, $\sum(n_i\cdot E_{bi})$ and $\sum(n_i\cdot E_{f,i})$, are used, which is based on the complete decomposation and mineralization of pollutant. So the predictive result is less than the experimental result, but it can be regarded as the lower limit of decontamination efficiency, min(η). If substituting the minimal dissociation energy of chemical bond in formula (4), we can obtain a bigger value, which can be regarded as the upper limit of decontamination efficiency, max(η). Therefore, the model can be improved to the following formula:

$$\min(\eta)=\begin{cases}100\%, \text{ If } \dfrac{\sum(n_i\cdot E_{f,i})\cdot M\cdot P_T}{0.0268C_0\cdot Q\cdot\sum(n_i\cdot E_{b,i})}>1\\ \dfrac{\sum(n_i\cdot E_{f,i})\cdot M\cdot P_T}{0.0268C_0\cdot Q\cdot\sum(n_i\cdot E_{b,i})}\times100\% \quad ,\\ \text{If } \dfrac{\sum(n_i\cdot E_{f,i})\cdot M\cdot P_T}{0.0268C_0\cdot Q\cdot\sum(n_i\cdot E_{b,i})}\le1\end{cases} \tag{10}$$

$$\max(\eta)=\begin{cases}100\%, \text{ If } \dfrac{E_{f,i}\cdot M\cdot P_T}{0.0268C_0\cdot Q\cdot\min(E_{b,i})}>1\\ \dfrac{E_{f,i}\cdot M\cdot P_T}{0.0268C_0\cdot Q\cdot\min(E_{b,i})}\times100\% \quad ,\\ \text{If } \dfrac{E_{f,i}\cdot M\cdot P_T}{0.0268C_0\cdot Q\cdot\min(E_{b,i})}\le1\end{cases} \tag{11}$$

According to formula (10) and formula (11), we can calculate and predict the range of decontamination efficiency of a pollutant by a NEP equipment: min (η)≤η≤ max(η).

4 CONCLUSIONS

The predictive model of decontamination efficiency is put forward based on analyzing the relation of discharge power, molecular structure of pollutant and decontamination efficiency. And the energy conversion factor (E_f) of chemical bonds, S-H, C-S, C-Cl and C-H, are obtained by the decontamination experimental data. Then the E_f values are used to estimate the decontamination efficiency of ethanethiol and 2-CEES, and the results show that the predictive values are close to experimental data, which indicates that the model is reasonable and available. The improved methods for the model are also discussed by the analysis of predictive error. It will be ascertained that the model can play an important role in the engineering design of NEP decontamination equipment after the experimental data to be improved.

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