Analysis of phenol degradation in pulsed discharge plasma system based on Back-Propagation artificial neural network model

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Abstract. Due to the advantages of Artificial Neural Network (ANN) for analyzing complex reaction system, the oxidation process of phenol in a pulsed discharge plasma system is simulated using an ANN model. Reaction factors including solution with pH values of 3.6, 5.4 and 9.8, and hydroxyl radicals (·OH) scavengers (Na₂CO₃ and n-butyl alcohol) are considered, and the changing trends of phenol degradation under various experimental conditions are simulated and predicted by the Back-Propagation (BP) neural network model. The obtained results show that the BP neural network model can effectively predict the degradation efficiency of phenol in the reaction system. According to the results, acidic solution is favourable for phenol oxidation and increase in the Na₂CO₃ and n-butyl alcohol addition will greatly restrain the phenol degradation. The restraining effect of scavengers on phenol degradation indicates that ·OH is one of most important active species for phenol oxidation in the pulsed discharge plasma system.

1. Introduction
As one of advanced oxidation technologies (AOTs), pulsed discharge process in aqueous solution can produce several oxidation processes, such as UV oxidation, electrical oxidation and chemical oxidation etc. Thus pulsed discharge plasma technology has been paid increasing attention for organic wastewater treatment since Sato et al. reported the decolorization effect of pulsed discharge plasma on dye wastewater [1]. Many conclusions have also been obtained, including factors analysis of the oxidation process [2-4], such as electrical parameters (pulse voltage, pulse frequency), reactor parameters (electrode geometry and electrode distance), gas-liquid conditions (initial solution pH, initial solution conductivity, gas bubbling varieties and gas bubbling rates etc.), and mechanism analysis of pollutants degradation in the pulsed discharge system [5].

For the mechanism of organic compounds degradation in the pulsed discharge plasma system, researchers have done many works. In their researches, hydroxyl radicals (·OH) is considered as one of most important species for organic pollutants degradation in the pulsed discharge plasma system, so it is very important to measure the change of ·OH generation amount in the pulsed discharge plasma system for illustrating the important effect of ·OH on pollutants degradation. However, ·OH has the...
characteristics of short existence time ($10^{-6}$ s), higher reaction activity and lower concentration. Therefore, there is no an effective method to determine •OH concentration in a reaction system. However, the effect of •OH for organic compounds oxidation in the pulsed discharge system could be indicated in other ways, such as investigating the change of solution pH or •OH scavengers addition on the change of organic compounds degradation efficiency. On the other hand, pulsed discharge plasma for wastewater treatment is a complicated process and a variety of factors could control the oxidation process. So it is difficult to clarify the effect of various factors on organic compounds degradation in the pulsed discharge system.

Back-Propagation (BP) artificial neural network is a kind of multilayer feed forward neural network, including an input layer, several hidden layer(s) and an output layer [6]. The basic principle of BP is the input signals transmit forward. Errors of the hidden layers are estimated according to the results obtained from the hidden layers and then the error of the input layer is estimated. The process circulates constantly until the precision of the output layer is achieved. BP has functions of non-linear mapping, high degree fault-tolerance, self-organization and self-learning. So it has been applied in many fields, such as function approximation, pattern recognition, category message, and data compression etc. [7-8].

According to the advantages of BP and the characteristics of pulsed discharge plasma system, the BP artificial neural network was used to simulate the oxidation process of the pulsed discharge plasma to show the crucial effect of •OH in the oxidation process. In this paper, phenol was chosen as a target pollutant and then models of phenol degradation under different conditions of initial solution pH values, Na$_2$CO$_3$ addition and n-butyl alcohol addition were simulated. The research would provide some theory basis for explaining the mechanism of pulsed discharge plasma in wastewater treatment.

2. Experimental

2.1. Experimental system

The experimental apparatus consists of a pulsed high voltage power supply and a multi-needle-to-plate electrode geometry reactor, which is same as those of our previous work [9]. The reactor vessel is made from a Plexiglas TM cylinder (75 mm diameter and 100 mm length). The separation distance (d) between the needle anodes and the plate cathode is 15 mm. The seven-needle stainless-steel anode, comprised of one needle in the centre and the other six distributed uniformly around a circle of 7.5 mm radius, is secured within a resin disc. The ground plate electrode is a stainless-steel disc (40 mm diameter, 1.5 mm thickness) with eight 0.5 mm diameter finestras on it. In the investigation, the corona discharge voltage was 21 kV and pulse frequency was adjusted to 50 Hz. Gas was bubbled into the reactor through the finestras by pump and the air bubbling rate was controlled at 5 L min$^{-1}$ in all experiments of the study.

2.2. Experimental method and analytical procedure

Phenol is selected as a target pollutant in the study. 250 mL phenol solution with 100 mg L$^{-1}$ concentration is used in all experiments. The phenol solution was circulated through the reactor by a peristaltic pump. Solutions of 0.01mol/L KCl was employed to adjust solution conductivity. In the paper, the initial electrical conductivity of phenol solutions were adjusted to 100 $\mu$S cm$^{-1}$ when n-butyl alcohol was used as radical scavenger and 200 $\mu$S cm$^{-1}$ when sodium carbonate was used as radical scavenger. The initial pH value of 100 mg L$^{-1}$ phenol solution, with 100 $\mu$S cm$^{-1}$ solution conductivity was about 7.0. Solution pH was hardly affected by the addition of n-butyl alcohol with different concentration into experimental solutions. PH values of solutions were about 10.5 by adding Na$_2$CO$_3$ within 0.1–1.0 mmol L$^{-1}$ concentration. In the study, the initial pH of phenol was controlled at 3.6, 5.4, and 9.8, respectively. The addition amount of Na$_2$CO$_3$ was 0.1, 0.5 and 1.0 mmol L$^{-1}$, respectively, while the n-butyl alcohol amount was 0.1, 0.5, 1.0 and 5.0 mmol L$^{-1}$, respectively. Concentration of phenol was analyzed by means of high performance liquid chromatography.
3. Theory and model analysis

3.1. BP artificial neural network

BP has a structure of three layers or more, including one input layer, several hidden layers, and an output layer. As a kind of multilayer feed forward neural network, the main characteristics of BP are the signals transmit forward and the errors transfer reversely. Through studying and training, the input signals transmit from the input layer to the hidden layers and then to the output layer. The output values are gotten from the functions of every layer. Figure 1 illustrates a structural drawing of a three layers structure of the BP. In the figure, \( X_1, X_2, \ldots, X_n \) are the input values, \( Y_1, Y_2, \ldots, Y_m \) are the predictive values, and \( w_{ij}, w_{jk} \) are the weights. Through training, the projective relation between \( X^* = (X_1, \ldots, X_n) \) and \( Y^* = (Y_1, \ldots, Y_m) \) could be set up. The network set up through training has capacities of associative memory and prediction.

![BP Neural Network Diagram](image)

**Figure 1.** Topology of BP neural network.

3.2. Model and simulation

In the study, initial solution pH, Na\(_2\)CO\(_3\) concentration and n-butyl alcohol concentration were taken as influencing factors and the degradation rates of phenol under different experimental conditions were reviewed. Then the optimization toolbox of Matlab was firstly used to determine the reviewing target in the study. The transfer function of the hidden layers nodes was selected as tansig, the transfer function of the output layer nodes was selected as purelin. After normalization, the samples should be training in the network and the initial weights matrix would be generated at random. During the training process, weights and threshold values of every layer could be adjusted and the iteration finished until achieving the given studying target. Precision of the model could be evaluated by comparing the actual values and predicted values, and then the changing trend of phenol degradation under different initial solution pH, Na\(_2\)CO\(_3\) addition and n-butyl alcohol addition was simulated.

4. Results and Discussion

4.1. Effect of pH

According to the established BP neural network model, the effect of initial solution pH values for phenol degradation was first considered in the paper. The initial solution pH values were controlled at 3.6, 5.4 and 9.8, respectively. The simulated model of phenol degradation under different initial solution concentrations and discharge time are shown in figure 2.

From the figure 2, it can be seen that the degradation rates of phenol increase with the increase of pulse discharge time within the investigated time and solution pH. On the other hand, it also can be indicated from the figure that the acidic solution condition is favourable for phenol degradation. The
degradation rates of phenol are lower in neutral and basic solution and change of the degradation rate is gently under both conditions of neutral and basic solution. Therefore, the solution pH should be controlled at the acidity for achieving higher degradation rates of phenol. The reason for the results is that •OH has higher oxidation effect under the condition of acidic solution.

Figure 2. Degradation rate of phenol with different initial solution pH values and time.

4.2. Effect of Na₂CO₃ addition
The simulation results of phenol degradation under different concentration Na₂CO₃ addition and reaction time according the BP model are shown in figure 3.

Figure 3. Degradation rate of phenol with different Na₂CO₃ concentration and time.

From the results of figure 3, it can be seen that the degradation rates of phenol decrease with the increase of Na₂CO₃ addition within the concentration scope of Na₂CO₃ addition. The prediction results indicate the collection of Na₂CO₃ for •OH, and also show the effect of •OH on phenol degradation in the pulsed discharge plasma system.

4.3. Effect of n-butyl alcohol addition
Using the BP model, the simulation results of phenol degradation under different concentrations of n-butyl alcohol addition are shown in figure 4.
Figure 4. Degradation rate of phenol with different n-butyl alcohol concentration and time.

It can also be seen from figure 4 that with the increase of n-butyl alcohol concentration, the degradation rate of phenol decreases. When the addition concentration of n-butyl alcohol exceeds 2 mmol L⁻¹, the reduction of phenol degradation is little. The results indicate the collection effect of n-butyl alcohol for •OH and all the •OH produced during pulsed discharge process might react with the n-butyl alcohol under the condition of certain amount of n-butyl alcohol addition, phenol degradation under such a condition might due to other physical and chemical effect produced in the reaction system. The results confirm the effect of •OH for phenol degradation and also indicate the change of •OH amount under different n-butyl alcohol addition during pulsed discharge process.

5. Conclusion
In the paper, the BP artificial neural network model of phenol degradation in a pulsed discharge plasma system is set up to review the effect of pH values, Na₂CO₃ addition and n-butyl alcohol addition on phenol degradation. Phenol degradation by changing solution pH values and adding •OH scavengers can be predicted well by the established BP model in the research. From the research, •OH is confirmed to be one of most important species for phenol degradation in the pulsed discharge system.

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