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Removal of Formaldehyde from Overactivated-Carbon-Fiber-Loaded Biological Enzyme

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To remove formaldehyde effectively, we used activated carbon fiber as a carrier to prepare the composite materials (biological enzyme/activated carbon fiber) by loading biological enzyme on its surface. A one-factor-at-a-time design and orthogonal design were used in the experimental design methods to optimize the biological enzyme based on soya protein. The experimental results indicate that the pH value was the most significant condition for optimizing the biological enzyme. The optimum orthogonal design conditions were proposed to be a reaction temperature of 80°C, a pH of 4, a reaction time of 6 h, and an amino nitrogen content of up to 5.4%. In addition, the morphologies of the composite materials were characterized with scanning electron microscopy, and the removal efficiency of formaldehyde was investigated with the acetyl acetone method. The results show that the formaldehyde removal efficiency was the best and the removal rate was 80% when the loading time was 8 h. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2619–2623, 2013

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INTRODUCTION

Formaldehyde (HCHO) is one of the most important pollutants in the air, and it is considered a cancer-causing material.[1,2] It is reported that long-term exposure to indoor air containing even a few parts per million of formaldehyde may cause nasal tumors, irritation of the mucous membranes of the eyes, and skin irritation.[1,3] Therefore, the abatement of HCHO at moderate temperatures is a problem that should be solved quickly. To date, most studies for the elimination of HCHO have focused on four methods: physical absorption,[4,5] photocatalytic oxidation,[6] low-temperature plasma catalytic degradation,[7] and metal oxide catalyst oxidation.[8,9]

However, most of the methods mentioned for reducing and controlling indoor formaldehyde pollution have many shortcomings. The adsorption process is too slow, and its adsorption capacity is obviously low for physical adsorption.[10] The photocatalytic oxidation is overly dependent on ultraviolet irradiation, which can lead to the conversion of oxygen in air into ozone, which is harmful to the human body.[11] As a result, it is hard to extrapolate these methods to a greater scale. The necessary equipment for the plasma technology method is expensive. In addition, this method has the best removal effects at high concentration, but when at low concentrations, it has no obvious results. Metal oxide catalyst oxidation has its drawbacks in the recovery of catalysts, which leads easily to dust pollution.[12]

There is a growing tendency toward the use of biomass; these methods are becoming more and more competitive costwise with traditional methods. So, it is necessary to further study biological enzymes based on soya protein more reasonably and effectively.

The experimental design is of great importance to the high amino nitrogen (AN) content of biological enzymes because the process is very complex and influenced by many factors, such as the substrate concentration, temperature, pH, reaction time, and so on. The results so far indicate that the control of the temperature, pH, and reaction time is crucial to the AN content of biological enzymes.[13] Therefore, an appropriate experimental design can be used to study the effects of diverse kinds of factors on the process to make it better understood and even optimized to improve its performance.

Orthogonal design is one of the very important statistical methods that use the Taguchi parameter design methodology,[14,15] and it allows the effects of many factors with two or more levels on a response to be studied in a relatively small number of runs.[16] The orthogonal array makes it easier to analyze the design. When used properly, orthogonal design may provide an efficient and powerful method to determine the optimal combination of factor levels.[17] Thus, orthogonal arrays were used in this experiment to explore an optimum method for making biological enzyme, and a series of experiments were conducted.

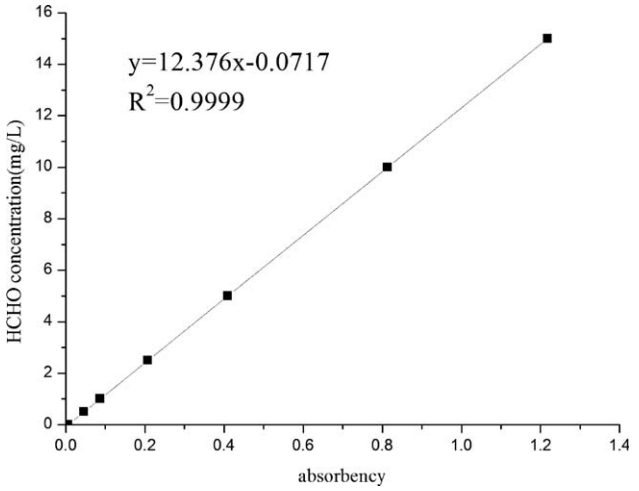

Figure 1. Standard curve of HCHO.

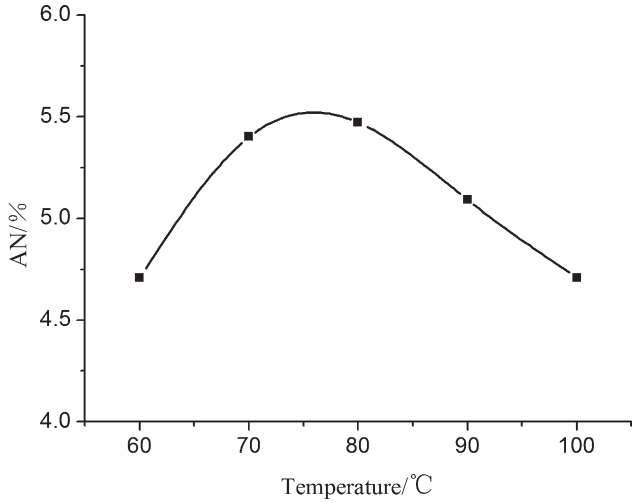

Figure 2. Effect of the temperature on the AN content.

The notation L_a (b^c) is used on behalf of the orthogonal array, where a represents the number of experimental runs, b represents the number of levels for each factor or variable, and c is the number of factors investigated.

One-factor-at-a-time design is a conventional method, which studies one factor at a time and keeps the levels of the other factors as constant. In this study, we attempted to investigate the effects of various factors on the AN content of a biological enzyme. The experimental design included one-factor-at-a-time design (temperature, pH, and reaction time) and orthogonal design.

In this study, on the basis of the situation of soy protein and the reaction between formaldehyde and amino groups, a biological enzyme was made, and the AN content was determined for the first time. In addition, the biological enzyme was loaded onto the activated carbon fiber.[18] Through the synergy process of adsorption and reaction, the composite materials reacted with the formaldehyde. As a result, the formaldehyde could be effectively removed.

EXPERIMENTAL

Materials

Formaldehyde was provided by Tianjin Yingda Rare Chemical Factory. Soya protein was obtained from AOBOX. Citric acid was purchased from Tianjin Guangfu Fine Chemical Research Institute. Activated carbon fiber, provided by Tianjin Municipal Key Laboratory of Fiber Modification and Functional Fiber, was used as the carrier of the biological enzyme.

Characterization

A spectrophotometer (VIS-7220, BRAIC) was used to investigate the absorbance of the composite materials to formaldehyde. The morphology of the activated carbon fiber loaded with biological enzyme was characterized by scanning electron microscopy (SEM; Philips, XL 30 ESEM).

Standard Curves of HCHO[19]

The acetyl acetone method was used to make the standard curves of HCHO, in which the concentration was between 0 and 15 mg/L.

As the curve shows, at $R = 0.9999$ (Figure 1), the absorbance value and formaldehyde concentration had a good linear relationship; therefore, the formaldehyde concentration determined in this way could replace its real value. The adsorption formula was as follows:

$$Y = 12.376X - 0.0717 \quad (1)$$

where Y is the concentration of HCHO (mg/L) and X is the absorption value of HCHO.

Determine of the AN Content

AN was tested in this way. We weighed 2.5 g of reaction liquid, added 50 mL of distilled water and two to three drops of phenolphthalein solution as an indicator, and titrated this with 0.05 mol/L NaOH solution until a faint pink color is obtained and its color did not fade within 30 s. We then added 6 mL of formaldehyde solution and five drops thymol blue indicator and titrated this with 0.05 mol/L NaOH solution until a blue-purple color was obtained and its color did not fade within 30 s; we put down this volume as V_1. At the same time, we conducted a blank experiment with distilled water and wrote this volume down as V_0. Its computation formula was as follows:[20]

$$\mathrm{AN}\,(\%) = (V_1 - V_0)m \times 14.01 \times 10^{-3}/25C \times 100\% \quad (2)$$

where V_1 is the NaOH volume consumption after the addition of HCHO (mL), V_0 is the NaOH volume consumption after the

Table I. Effect of the Temperature on the AN Content

Temperature (°C)	60	70	80	90	100
V_1 (mL)	20.0	22.9	23.2	21.6	20.0
AN (%)	4.71	5.40	5.47	5.09	4.71

Table II. Effects of the pH on the AN Content

pH	3.0	3.5	4.0	4.5	5.0
V_1 (mL)	19.4	19.5	20.8	20.0	19.7
AN (%)	4.57	4.59	4.90	4.71	4.64

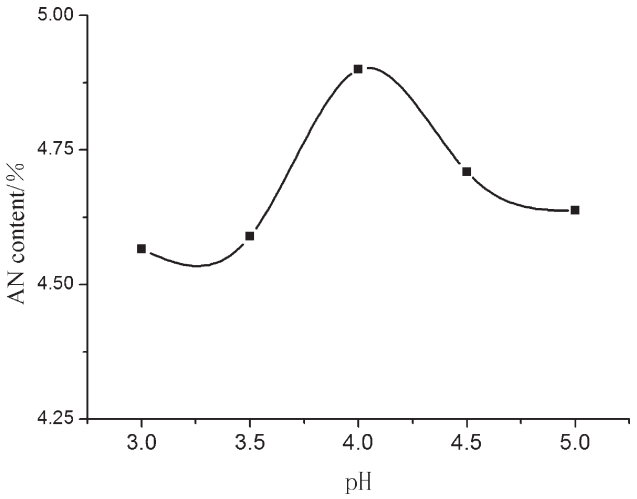

Figure 3. Effect of the pH on the AN content.

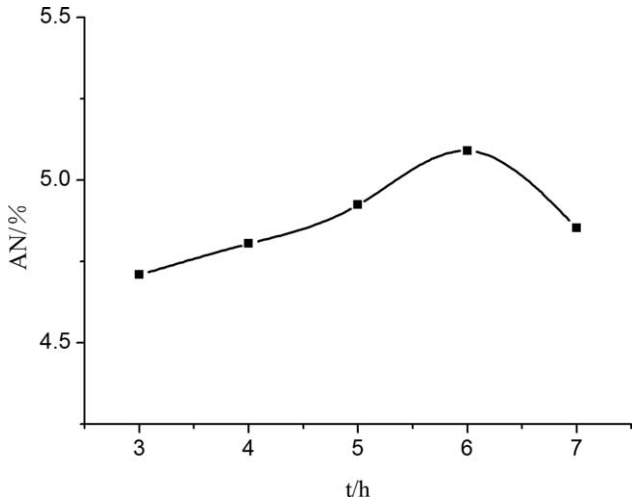

Figure 4. Effect of the reaction time (*t*) on the AN content.

addition of the blank solution (mL), *m* is the concentration of NaOH (moL/L), and *C* is the quality score of the specimens (g/g).

Batch Experiments

Four series of batch experiments were conducted in a 250-mL, round-bottom flask and were denoted as series I, II, III, and IV. Each round-bottom flask contained 100 mL of distilled water and 20 g of soya protein. Moreover, each experiment was replicated at least three times to obtain accurate results.

In these experiments, we examined the effects of the temperature (60–100°C) on biological enzymes in the series, respectively. We investigated the AN content of the biological enzyme at different initial pHs (3.0–5.0) in series II. In series III, we studied the effects of reaction times of 4, 5, 6, 7, and 8 h on the biological enzyme. The optimization experiments in series IV were conducted according to the orthogonal design method. An orthogonal design of L_9 (3^4) was used in the experiment with three important parameters (temperature, pH, and reaction time). The evaluation criterion of the best biological enzyme was based on the maximum AN content.

In all batches, 20 g of soya protein and 100 mL of distilled water were added to each round-bottom flask, respectively. When the soya protein dissolved, citric acid was added to adjust the pH value. Each round-bottom flask was incubated with continuous stirring.

Preparation of the ACF Loaded with Biological Enzyme

The activated carbon fiber (1 g) was impregnated into the biological enzyme (20 mL) with an optimal AN content. After the composite materials were ultrasounded for 30 min at 40°C, they were soaked for 4, 8, 12, or 24 h and then dried in an oven at a temperature of 40°C. As a result, they could be used to absorb formaldehyde.

Table III. Effects of the Reaction Time on the AN Content

Time (h)	3	4	5	6	7
V_1 (mL)	20.0	20.4	20.9	21.6	20.6
AN (%)	4.71	4.80	4.92	5.09	4.85

RESULTS AND DISCUSSION

Effect of the Temperature on the AN Content

Under the same reaction conditions, different temperatures (60–100°C) were set after the pH value was adjusted to 4 with citric acid. Then the AN content was measured with a 0.05 mol/L NaOH solution. The research results are shown in Table I and Figure 2.

Figure 2 shows the effect of the temperature on the AN content. When the temperature increased from 60 to 100°C, the AN content reached a maximum at 80°C. When the temperature continued to rise from 80 to 100°C, however, it decreased gradually. This might have been caused by the increase in the motion of the protein chain, so the subbond strengths of the advanced structure decreased with increasing temperature.[21] Meanwhile, with the appearance of the thermal denaturation, the hydrophobic part in the proteins was exposed to solvent, and accordingly, the AN content increased (60–80°C). However, the solution viscosity increased with increasing temperature between 80 and 100°C; thereby, the reactions were spatially confined, and the AN content declined. Hence, the reaction temperature should be 80°C.

Effect of the pH on the AN Content

Under the same reaction conditions, different pHs (3, 3.5, 4, 4.5, and 5) were set with citric acid when the temperature was 80°C. Then, the AN content was measured with 0.05 mol/L NaOH solution titration. The research results are shown in Table II and Figure 3.

The effects of the pH on the AN content are shown in Figure 3. The AN content gradually increased with increasing pH from 3 to 4 and reached a maximum at 4 at the beginning of the reaction; however, its content trended toward reduction when the pH value continued to rise (4–5) as the reaction progressed. This might have been because hydrolysis, caused by the low concentration of citric acid, was found to be incomplete, whereas an excessive concentration of citric acid could lead to the breakage of protein and amino acid and further produce some worthless byproduct. It turned out that the AN content was low.[22]

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Table IV. Combination of the Factors and Level on Soya Protein Hydrolysis

	Factor		
Level/factor	A: Temperature (°C)	B: Reaction time (h)	C: pH
1	70	5	3.0
2	80	6	4.0
3	90	7	5.0

Symbols A, B, and C represent factors of temperature, reaction time, and pH. Symbols 1, 2, and 3 represent the concentration levels of each factor.

Effect of the Reaction Time on the AN Content

Depending on the other fixed elements mentioned previously, with the temperature set at 80°C and the pH value set to 4 with citric acid, we selected times of 3, 4, 5, 6, and 7 h to continue the experiment. Then, the AN content was measured by titration with a 0.05 mol/L NaOH solution. The research results are shown in Table III and Figure 4.

The effect of the reaction time on the AN content is presented in Figure 4. The AN content increased gradually with the duration of acidic hydrolysis and decreased finally after 6 h. As the experimental session progressed, the AN content reached a summit value. When the hydrolysis reaction continued, secondary reactions of amino acid occurred easily, and a series of reactions of other substances in protein also occurred under the conditions of acid and high temperature. So the yields of amino acid were affected, and this led to a general decrease in the AN content. For this reason, a longer reaction time was not better. However, when the hydrolysis time was too short, the hydrolysis was not complete and was affected the efficiency of hydrolysis. From the results of these tests, the most suitable reaction time was found to be 6 h.

Optimization Results by the Orthogonal Design Method

Several factors affected the completeness of the hydrolysis process of the proteins; these included the temperature, time, and pH. To maximize the AN content and minimize the amino acid damage, a single-factor analysis and orthogonal experimental design were used to explore optimal conditions for hydrolysis. The factors included temperature (A), time (B), and pH (C). The AN content was used as a criterion. Three factors were selected with three levels of each factor, and the orthogonal experimental design L_9 (3^4) was applied (shown in Tables IV and V).

Table V. L_9 (3^4) Orthogonal Array and Experimental Results

Number L_9 (3^4)	A	B	C	AN content (%)
1	70	5	3	0.41
2	70	6	4	0.44
3	70	7	5	0.45
4	80	5	4	0.48
5	80	6	5	0.48
6	80	7	3	0.43
7	90	5	5	0.45
8	90	6	3	0.44
9	90	7	4	0.54
k_1	0.433	0.447	0.427	
k_2	0.463	0.453	0.487	
k_3	0.477	0.473	0.460	
R	0.044	0.026	0.060	
Optimum	A_3	B_2	C_2	

The arrangements of columns A, B, and C were decided by orthogonal design for 3 (factor) × 9 (run number). Every row of each run number represents one experimental replicate, and every run was carried out twice.

As Table V shows, the results showed that the most influential factor was the pH value; this was sequentially followed by the temperature and reaction time. The best reaction conditions were as follows: a pH value of 4, a reaction temperature of 80°C, and a reaction time of 6 h.

Morphology of the Fibers

The SEM micrographs of the control and ACF loaded for 8 h are shown in Figure 5. The surface morphology of the activated carbon fiber treated with biological enzyme was similar to that of the unprocessed sample. This was attributed to the preservation of the primary porosity of the fiber and the loading of the biological enzyme. With loading, the composite materials had a synergistic promotion effect on the adsorption and degradation of formaldehyde.

Removal of Formaldehyde

A certain amount of activated carbon fiber was impregnated with the biological enzyme for 4, 8, 12, or 24 h and was baked for later use.

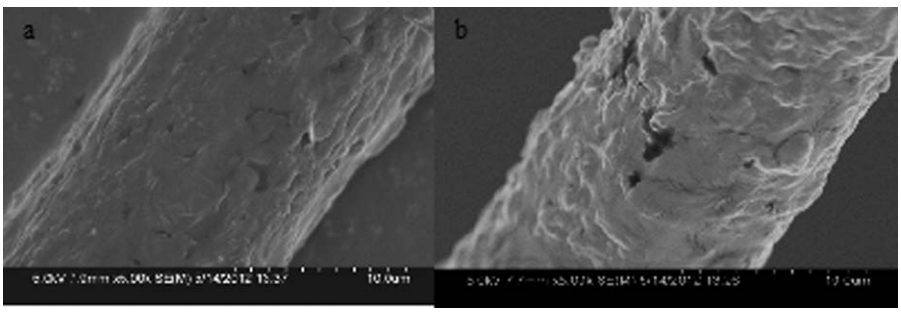

Figure 5. SEM micrograph of the (a) control and (b) ACF loaded for 8 h.

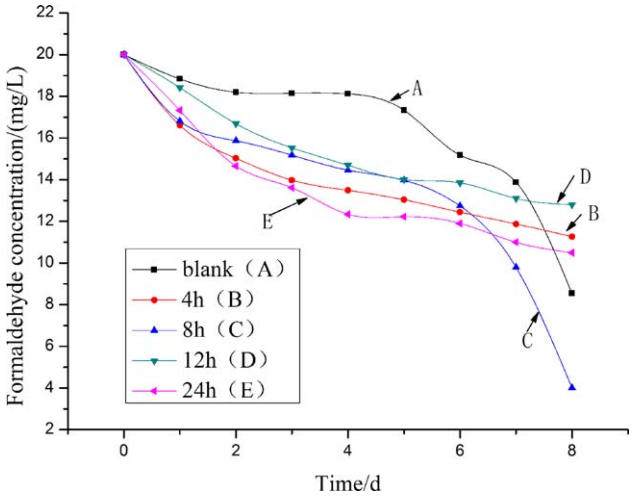

Figure 6. Adsorption curve of formaldehyde: (A) the blank sample of activated carbon fiber without biological enzyme loaded and the activated carbon fiber loaded with a biological for (B) 4, (C) 8, (D) 12, and (E) 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The same amount of composite materials was weighed, and 20 mL (20 mg/L) of a standard formaldehyde solution prepared in advance was placed in the borosilicate glass. The prepared composite materials were impregnated in the formaldehyde solution and placed in the dark. Then, the absorbency was measured through spectrophotometry for 24 h to study the formaldehyde adsorption and removal effects. The result is shown in Figure 6.

The adsorption curve of formaldehyde is shown in Figure 6. The results show that the formaldehyde concentration decreased with time, and it demonstrates that the activated carbon fiber loaded with biological enzyme was effective in the removal of formaldehyde. The effects of removing formaldehyde were not ideal in curves B, D, and E. The conditions in curve C achieved the best result. When the enzyme was loaded for 8 h, the removal rate reached up to 80%. This may have been because the dipping time was too short and the biological enzyme was not fully loaded on the activated carbon fiber of curve B. In curves D and E, the amount of biological enzyme loaded on the activated carbon fiber was too much, and the pores were blocked. As a result, the porosities of the activated carbon fiber decreased, and the removal rate was ineffective.

CONCLUSIONS

The factors influencing the preparation of the biological enzyme were studied. According to the method for measuring the AN content, the optimum reaction conditions were as follows: 80°C, pH 4, and a reaction time of 6 h. The biological enzyme was loaded onto the activated carbon fiber through an impregnation method. The optimized technology of the preparation of the composite materials included first the dispersion the biological enzyme into the activated carbon fiber under ultrasonic action for 40 min and then impregnation for 8 h. Compared with the biodegradation of formaldehyde in the literature, the composite materials had a good adsorption and degradation effect on the formaldehyde, and its removal rate could reach 80%.

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