Evaluation on the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas

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Abstract. In order to evaluate the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas, the test samples were prepared by the spraying and mixing methods separately. The concentration variation of nitrogen oxide (mainly NO), hydrocarbons (HC) and CO was measured by using vehicle exhaust gas degradation test in the mixed input mode to simulate road working conditions, and the evolution law of each pollutant instantaneous degradation rate with time was analyzed. The results show that the concentration of each pollutant in vehicle exhaust gas will decrease by itself under ultraviolet (UV) radiation, but the speed is very slow, and photocatalytic pavement containing nano-TiO₂ can play a significant role in improving degradation efficiency. The efficiency of photocatalytic pavement material to degrade different pollutants is unbalanced, so its comprehensive degradation effect on vehicle exhaust gas can not be reflected by the degradation evaluation index to a single pollutant. In this study, a new evaluation index suitable for vehicle exhaust gas degradation test in the mixed input mode is put forward, which called comprehensive degradation rate (CDR). Its value is the instantaneous comprehensive degradation rate (ICDR) when any pollutant appears degradation failure. This index can not only reflect the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas, but also show its maximum degradation capacity to each pollutant.

1. Introduction

In recent years, with the increasing number of automobiles, vehicle exhaust gas has gradually become an important source of air pollution in Chinese cities. Vehicle exhaust pollution not only brings physical and mental harm to residents, but also seriously damages the ecological environment of the city. Some researchers have found in their exploration that the use of photocatalytic pavement to degrade vehicle exhaust gas is an effective way to solve this kind of problem [1-2]. How to evaluate the degradation effect of photocatalytic pavement material on vehicle exhaust gas has been paid more and more attention. Road engineers have studied this issue and put forward different evaluation indexes, such as degradation efficiency, degradation reaction time, average degradation rate, and the cumulative degradation rate considering the effect of the self-degradation of pollutants [3-4]. These indexes are aimed at evaluating the degradation efficiency of a single pollutant, but vehicle exhaust gas is a mixture of nitrogen oxide (mainly NO), hydrocarbons (HC), CO and other pollutants. In order to better simulate the road working conditions, some researchers adopt vehicle exhaust gas degradation test in the mixed input mode [5]. However, it is obvious that the indexes suitable for evaluating the degradation efficiency of a single pollutant can not fully reflect the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas.
In this study, the test samples were prepared by the spraying and mixing methods respectively, and the concentration variation of NO, HC and CO was measured and analyzed by using vehicle exhaust gas degradation test in the mixed input mode. On this basis, a new index is proposed to evaluate the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas.

2. Materials and testing program

2.1. Materials

Limestone coarse aggregates, fine aggregates and mineral powders were produced by Zhenjiang Maodi Industrial Co., Ltd. The 70A grade asphalt was produced by Jiangsu Baoli Asphalt Products Co., Ltd. The technical indexes of mineral materials and asphalt meet the requirements of the Chinese Technical Specifications for Construction of Highway Asphalt Pavements [6]. Nano-TiO₂ is from Nanjing Tianxing New Material Co., Ltd. It is a kind of white powder, the largest particle size is 50 nm, the specific surface area is 80 m²/g, and the content of active components is more than 99.7 M%.

2.2. Test sample preparation

Sample A was prepared by spraying a photocatalytic coating layer onto the surface of a common asphalt mixture rutting test sample with the standard dimensions of 30 cm×30 cm×5 cm. The preparation process of the photocatalytic coating layer is as follows: Nano-TiO₂ and polyester paint were mixed at the mass ratio of 1.5:20, then the mixture was sprayed onto the the surface of a rutting test sample as mentioned earlier at the content of 80 g/m², curing for 30 min until a thin photocatalytic film formed.

The preparation process of Sample B is as follows: Nano-TiO₂ was used to replace 50 M% mineral powder in the composition of AC-13 asphalt mixture whose synthetic gradation meets the requirements of the Chinese Technical Specifications for Construction of Highway Asphalt Pavements [6], as shown in table 1. The optimum asphalt content was determined by Marshall Test and road performance verification, and then the wheel-rolling method was adopted to prepare the rutting test sample with the same dimension as Sample A.

| Square mesh sieve size (mm) | 16 | 13.2 | 9.5 | 4.75 | 2.36 | 1.18 | 0.6 | 0.3 | 0.15 | 0.075 |
|----------------------------|----|------|-----|------|------|------|-----|-----|------|-------|
| Quality passing percentage (%) | 100.0 | 93.2 | 66.2 | 42.7 | 31.9 | 23.7 | 17.8 | 12.0 | 8.0 | 5.1 |

2.3. Instrumentation

The instrument is composed of three parts: the exhaust gas generator, the photocatalytic reactor and the exhaust gas concentration measuring device. A diesel generator 5GF-ME was used as the exhaust gas generator to provide the mixed input pollutant gas simulating the road working conditions for degradation test by considering the composition of its exhaust gas similar to that of vehicle exhaust gas. The photocatalytic reactor was a rectangular closed container, with fixed plexiglass plates on the four walls and the bottom, and PVC movable plates on the top. Three 8W ultraviolet (UV) lamps of 245 nm wavelength were installed under the top plate, which can simulate the natural light source in fine weather [7]. The concentrations of NO, HC and CO in the photocatalytic reactor were determined by a vehicle exhaust gas analyzer FLA-501.

2.4. Testing program

The process of degradation test is as follows:

- The test sample was placed in the center of the photocatalytic reaction container, then the diesel generator 5GF-ME was started; the exhaust gas was input until its initial concentration reached the required level of NO: 90~110 ppm, HC: 130~150 ppm, and CO: 0.9%~1.1%.
- The UV lamps were turned on to begin the test; the concentration of each pollutant was measured and recorded every 10 min from the beginning, then the test was finished after 180 min.
For the purpose of comparison, a non-sample degradation test was designed. Its process is the same as a common degradation test, but there is no sample in the photocatalytic reaction container.

3. Result analysis and discussion

3.1. The degradation effect of a single pollutant

The variation of pollutant concentration in vehicle exhaust gas with time can reflect visually the degradation ability of photocatalysis pavement material. The concentration-time curves of NO, HC and CO were obtained as shown in figure 1 by using degradation test on Sample A, B and Non-sample.

![Figure 1. Variation of pollutant concentration with time.](image)

From figure 1, it can be seen that the concentration of three pollutants show a decreasing trend. Compared with the Non-sample, the decrease range of pollutant concentration is much larger when Sample A and B were tested. This shows that the concentration of each pollutant in vehicle exhaust gas will decrease by itself under UV radiation, but the speed is very slow, and photocatalytic pavement containing nano-TiO₂ can play a significant role in improving degradation efficiency.

The instantaneous degradation rate is an index to evaluate the degradation efficiency of photocatalytic pavement material to a single pollutant at a certain time point. Taking into account the self-degradation effect of pollutants, the instantaneous degradation rate ($\eta_i$) at time point ($i$) is calculated according to the following equation.

$$\eta_i = \frac{Q_{W,i} - Q_{T,i}}{Q_{W,i}}$$

Where $Q_{W,i}$ or $Q_{T,i}$ are the concentration of a single pollutant in the closed container at time point ($i$) in the degradation test process of non-sample or photocatalytic pavement material sample, respectively.

The curves of instantaneous degradation rate of Sample A and B over time were obtained as shown in figure 2. From figure 2, it can be seen that

- The instantaneous degradation rates of NO, HC and CO show similar trends, that is, they increase rapidly in the initial stage, and gradually decrease as time goes on, and finally approach 0. This can be defined as the degradation failure stage of a single pollutant.
The instantaneous degradation rate of NO is much higher than that of the other pollutant. For example, the instantaneous degradation rate of NO has reached 100% at 40 min, but that of the other pollutant is less than 20%. The result shows that the efficiency of photocatalytic pavement material to degrade different pollutants is unbalanced, so its comprehensive degradation effect on vehicle exhaust gas can not be reflected by the degradation evaluation index to a single pollutant.

![Figure 2. Variation of instantaneous degradation rate with time.](image)

It can also be seen from figure 2 that the instantaneous degradation rate of Sample A is higher than that of Sample B. The reason may be that there are few effective Nano-TiO₂ distributed onto the surface of the test sample and the utilization ratio is low, and Nano-TiO₂ located in the interior of the test sample are difficult to play a useful role because of the poor light permeability of asphalt mixture.

### 3.2. The Comprehensive degradation effect of vehicle exhaust gas

In order to evaluate the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas, it is necessary to put forward an index that can include the degradation efficiency of various pollutants. Taking the concentration percentage of various pollutants as the weight, it is a good choice to calculate the comprehensive degradation efficiency by weighted superposition of the degradation efficiency of each pollutant. However, the concentrations of some pollutants are not of the same order of magnitude. For example, the concentration of CO in vehicle exhaust gas is usually tens to 100 times that of NO or HC. Therefore, if the concentration share of each pollutant is taken as a weight, the magnitude of the comprehensive degradation efficiency of vehicle exhaust gas will be mainly determined by the degradation efficiency of CO.

In this study, the weight of calculation will be determined by considering the concentration percentage of each pollutant in vehicle exhaust gas, the degree of harm to ecological environment, and the degradation effect of photocatalytic pavement material. The instantaneous comprehensive degradation rate (ICDR, \(S_i\)) of vehicle exhaust gas at time point \((i)\) is calculated by weighted superposition of the instantaneous degradation rates of these pollutants based on the following equation.

\[
S_i = \eta_{NO,i} \delta_{NO} + \eta_{HC,i} \delta_{HC} + \eta_{CO,i} \delta_{CO}
\]  

(2)

where \(\eta_{NO,i}\), \(\eta_{HC,i}\) or \(\eta_{CO,i}\) is the instantaneous degradation rate of NO, HC or CO at time point \((i)\), \(\delta_{NO}\), \(\delta_{HC}\) or \(\delta_{CO}\) is the calculation weight of NO, HC or CO, and \(\delta_{NO} + \delta_{HC} + \delta_{CO} = 1\).
The ICDR curves of Sample A and B over time were obtained as shown in figure 3. As can be seen from figure 3, the ICDR value of Sample A is much higher than that of Sample B at all time points, and this sort is consistent with the instantaneous degradation rate order of a single pollutant in figure 2. The ICDR value of Sample A increases rapidly at the initial stage, and then its growth rate begins to drop sharply until it approaches to 0. The ICDR change process of Sample B is similar, but its growth rate can’t decrease until 120 min. Therefore, the difference of the ICDR values between two test samples reaches the maximum value at 30 min, and then decreases gradually.

Figure 3. Variation of the ICDR value with time.

Since the maximum degradation efficiency of Sample A or B to NO is much greater than that to HC or CO, the moment when the ICDR growth rate begins to decline rapidly should correspond to that of NO degradation failure. Of course, this is caused by the initial concentration limit of the test, so that the ability of the test sample to degrade NO is not fully realized. The ICDR growth rate tends to be 0 at the moment when HC and CO degradation failures are reached.

The degradation ability of sample A is not fully reflected due to its degradation failure to NO. The ICDR difference of two samples decreases gradually from the maximum value, which is caused by the ICDR value of Sample A no longer includes the degradation efficiency to NO. Therefore, the subsequent test data can not accurately reflect the degradation efficiency difference of different photocatalytic pavement materials.

In this study, a new evaluation index called comprehensive degradation rate (CDR) is put forward. Its value is the ICDR when any pollutant appears degradation failure. This index can not only reflect the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas, but also show its maximum degradation capacity to each pollutant. The CDR values for Sample A and B were shown in table 2 respectively.

Table 2. The CDR values of two test samples

| Test sample type | CDR (%) |
|------------------|---------|
| Sample A         | 53.7    |
| Sample B         | 18.1    |

From table 2, it can be seen that the CDR value of Sample A is about 3 times that of Sample B, and the former is much higher than the latter. This shows that spraying nano-TiO2 directly onto the road surface has higher utilization efficiency and better degradation effect on vehicle exhaust gas compared with mixing method.
4. Conclusions
In this paper, photocatalytic road material test samples were prepared by the spraying and mixing methods respectively. The concentrations of NO, HC and CO were measured by using vehicle exhaust gas degradation test in the mixed input mode to simulate road working conditions. So, the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas was analyzed according to the test results.

(1) The concentration of each pollutant in vehicle exhaust gas will decrease by itself under UV radiation, but the speed is very slow, and photocatalytic pavement containing nano-TiO$_2$ can play a significant role in improving degradation efficiency.

(2) The efficiency of photocatalytic pavement material to degrade different pollutants is unbalanced, so its comprehensive degradation effect on vehicle exhaust gas can not be reflected by the degradation evaluation index of a single pollutant.

(3) A new evaluation index suitable for vehicle exhaust gas degradation test in the mixed input mode is put forward, which called comprehensive degradation rate (CDR). Its value is the instantaneous comprehensive degradation rate (ICDR) when any pollutant appears degradation failure. This index can not only reflect the comprehensive degradation effect of photocatalytic pavement material on vehicle exhaust gas, but also show its maximum degradation capacity to each pollutant.

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