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Experimental study on photocatalytic degradation efficiency of mixed crystal nano-TiO$_2$ concrete

Abstract: The photocatalytic mixed crystal nano-TiO$_2$ particles were incorporated with concrete by means of the internal doping method (IDM) and spraying method (SPM) in this paper. To evaluate the photocatalytic degradation efficiency of mixed crystal nano-TiO$_2$ concrete, the methyl orange (MO) was chosen to simulate pollutants. The physiochemical characteristics and photocatalytic performance of mixed crystal nano-TiO$_2$ concrete prepared by above two different methods were experimentally investigated under UV irradiation and solar irradiation. Furthermore, the effects of two key influential factors including pollutant concentration and irradiation condition were also analyzed and discussed. Experimental results indicate that the nano-TiO$_2$ concrete prepared by the spraying method (SPM) exhibits maximum photocatalytic degradation efficiency of 73.82% when the sprayed nano-TiO$_2$ slurry concentration is 10mg/L. The photocatalytic degradation efficiency of unpolished nano-TiO$_2$ concrete is much higher than that of polished nano-TiO$_2$ concrete under the same exposure time of UV irradiation. Moreover, the photocatalytic degradation efficiency of nano-TiO$_2$ concrete decreases with the increase of pollutant concentration. The irradiation condition has an obvious influence on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete. In the aspect of applications, the practical recommendations for the nano-TiO$_2$ concrete with self-cleaning capacity were presented according to the experimental results.

Keywords: mixed crystal; nano-TiO$_2$ concrete; X-ray diffraction; pollutant concentration; irradiation condition; photocatalytic degradation efficiency

1 Introduction

With the rapid development of industrialization and urbanization, environmental pollution has become an increasingly serious social problem that can’t be neglected indeed. As one of the most significant traditional construction materials (steel and cement), the cement is facing enormous concerns due to its activity has been considered as one of the primary causes of air pollution [1]. To mitigate the environment impact of cement production, varieties of physical, chemical and biological methods such as adsorption, precipitation, and bioremediation have been proposed by scientists [2]. Among the above methods, the photocatalysis technology has been considered as one of the most efficient solutions to address air pollutants owing to its superior photocatalytic activity, low cost, and complete degradation [3].

To seek a superior photocatalyst is one of the most significant problems in photocatalysis technology. Up to now, the nano-TiO$_2$ has been considered as one of the best choices as a good photocatalyst due to its chemical stability, non-toxicity and high photocatalytic activity. On the other hand, due to the high plasticity, good durability and easy material availability, the concrete has been widely utilized in the field of civil and building engineering. Therefore, it is an innovative idea that a new kind of nano-TiO$_2$ concrete with self-cleaning capacity is proposed by using the concrete as the carrier.

In recent years, the photocatalytic performance and innovative applications for kinds of novel nano materials have been in-depth investigated and discussed at home and abroad. He et al. [4] studied the mechanical and photocatalytic properties of two types of nano-TiO$_2$ concrete by using X-ray diffraction, scanning electron microscopy, and degradation efficiency tests. It was found that the photocatalytic performance of the modified nano-TiO$_2$ concrete was much better than that of the original nano-TiO$_2$ concrete. Elena et al. [5] systematically evaluated the photocatalytic activity of the Sol-Gel nano-TiO$_2$ particles for photocatalytic cement composites by comparing the degradation of Methylene Blue (MB) under UV irradiation. An experimental study on the photocatalytic performance of nano-TiO$_2$...
incorporated self-compacting glass mortar (SCGM) was performed by Guo et al. [6]. Experimental results showed that the photocatalytic performance of SCGM proved an obvious decrease of NO with the increase of NO2 under UVA irradiation. Ge et al. [7] comprehensively summarized several advances and potential applications of TiO2 nanotube arrays on the photoelectrocatalytic degradation efficiency of pollutants. Yi et al. [8] presented an experimental investigation on the adsorptive degradation performance of hydrophobic/hydrophilic nano-SiO2 under different organic pollutant solutions. The hydrophobic nano-SiO2 exhibited superior adsorption capacity on soluble organic compounds. Feng et al. [9] prepared photocatalytic TiO2 composite cement pastes by a smear method and systematically investigated the microstructure, photocatalytic properties and durability. Test results showed that the TiO2 composite cement pastes possessed better degradation properties after they were immersed in an acid or alkaline solution. A novel active catalyst called as diatom-FeOx composite was experimentally investigated by Krishna et al. [10] to study the photocatalytic degradation efficiency. Test results showed that the diatom-FeOx composite exhibited high activity in catalyzing the photodegradation of Rh-6G. Zhang et al. [11] evaluated and discussed the effects of nano-SiO2 on the photocatalytic behavior and durability of cementitious composite incorporated with nano-SiO2. The results indicated that the nano-SiO2 could dramatically improve the photocatalytic performance and durability of cementitious composites. Samim et al. [12] discussed and compared the visible light photocatalytic activity of the ZnO nanostructures prepared by different modification strategies. The photocatalytic activity of the ZnO nanostructures was significantly correlated with the charge dynamics across the nanostructured interface. The reduced graphene oxide-Bi2WO6 photocatalyst with different RM values were successfully compounded by using hydrothermal method [13]. Experimental results indicated that the photocatalytic activity of oxide-Bi2WO6 for the degradation of Rho-damine-B increased gradually when the RM values were enhanced from 0 to 2%. Huang et al. [14] proposed a new type of nano-TiO2 emulsified asphalt mixture, and investigated four influence factors (nano-TiO2 particle size, dosage, degradation time and light intensity) on the photocatalytic performance of nano-TiO2 emulsified asphalt mixture. Shen et al. [15] proposed a kind of photocatalytic concrete with ultra-smooth surface manufactured by using the photocatalysis properties of nano-TiO2 particles. This kind of photocatalytic concrete is considered as a promising self-cleaning finishing material for the urban buildings.

Although many researchers have studied the photocatalytic property of kinds of nano materials, there is still little investigation being performed on the physicochemical characteristics and photocatalytic performance of nano-TiO2 concrete with self-cleaning capacity. In this research, the mixed crystal nano-TiO2 particles were incorporated with the concrete by means of the internal doping method (IDM) and spraying method (SPM). The physicochemical characteristics of mixed crystal nano-TiO2 were identified by X-ray diffraction (XRD). The methyl orange (MO) was adopted to simulate pollutants for the investigation of photocatalytic degradation efficiency of mixed crystal nano-TiO2 concrete under UV irradiation and solar irradiation. Furthermore, the effects of two key influential factors including pollutant concentration and irradiation condition were also analyzed and discussed. Finally, the practical recommendations for the application of novel nano-TiO2 concrete with self-cleaning capacity were presented according to the experimental results.

2 Materials and experimental preparation

2.1 Test materials

There were three types of industrial materials used in this experiment, including the cement, nano-TiO2, and methyl orange. A commercially mixed crystal nano-TiO2 powder (type P25) was utilized as the photocatalyst for the preparation of nano-TiO2 concrete. The mixed crystal nano-TiO2 powder consists of 75 wt% anatase and 25 wt% rutile. The mixed crystal nano-TiO2 powder was purchased from Degussa, Germany, which has an average particle size of 21 nm, and a specific surface area of 50 m2/g. Table 1 shows the physical properties of the mixed crystal nano-TiO2 powder. The Chinese common Portland cement with a strength grade of 42.5 (type P-O 42.5) was utilized to prepare the nano-TiO2 concrete block samples. The natural medium sand with a maximum size of 4.75 mm is used as fine aggregate, and the crushed stone with the maximum

| Particle size (nm) | Specific surface area (m2/g) | Purity (%) | Bulk density (g/l) | pH |
|-------------------|-----------------------------|------------|-------------------|----|
| 21                | 50                          | 99:5       | 130               | 3:5-4:5 |
Experimental study on photocatalytic degradation efficiency of mixed crystal nano-TiO$_2$ concrete

Table 2: Mix proportions of nano-TiO$_2$ concrete

| Nano-TiO$_2$ concrete strength | Water (kg/m$^3$) | Cement (kg/m$^3$) | Sand (kg/m$^3$) | Gravel (kg/m$^3$) |
|------------------------------|-----------------|------------------|----------------|------------------|
| C30                          | 183             | 450              | 600            | 1192             |

size of 30 mm is used as coarse aggregate. The mix proportions of nano-TiO$_2$ concrete with nominal cube strength of 30 MPa in this study is presented in Table 2. The methyl orange (MO) was used as an organic pollutant to evaluate the photocatalytic degradation efficiency of nano-TiO$_2$ concrete by measuring its absorbance during the experiment. The methyl orange was purchased from China National Pharmaceutical Corporation.

2.2 Preparation of nano-TiO$_2$ concrete

The nano-TiO$_2$ powders are usually incorporated with concrete in two kinds of methods: (1) mix nano-TiO$_2$ powder with the concrete aggregates directly, which is called as the internal doping method; (2) spray nano-TiO$_2$ slurry on the surface of concrete blocks, which is called as the spraying method [16–19]. However, these methods generally exhibit a significant difference in the photocatalytic degradation performance of the mixed crystal nano-TiO$_2$ concrete. Therefore, two kinds of preparation methods including the internal doping method (IDM) and spraying method (SPM) were adopted and then a comparative research was conducted to investigate the photocatalytic degradation efficiency of mixed crystal nano-TiO$_2$ concrete with self-cleaning capacity.

In this experiment, for the internal doping method, the cement in concrete mix was equivalently substituted by the nano-TiO$_2$ powders with different contents (2%, 5%, 8%) to prepare the nano-TiO$_2$ concrete block samples. As for the spraying method, the concrete block samples were firstly prepared, and then the nano-TiO$_2$ slurry with different concentrations (5mg/L, 10mg/L, 15mg/L, 20mg/L) was sprayed on the surface of the concrete block samples. The sprayed nano-TiO$_2$ slurry on the surface of the concrete block samples was required to keep uniform and the thickness of spray coating was 1mm. All tested nano-TiO$_2$ concrete block samples are 8 cm in diameter, 1 cm in thickness and 100 g in weight. The nano-TiO$_2$ concrete block samples prepared by above methods are shown in Figure 1.

2.3 Nano-TiO$_2$ characterization

The XRD analysis was conducted by an X-ray diffractometer manufactured by Panalytical Corporation to obtain the physicochemical characteristics of mixed crystal nano-TiO$_2$ concrete. In this experiment, the tube voltage and current of the measuring instrument were fixed at 45 kV and 40 mA, respectively. Moreover, the UV-Vis spectrophotometer (type LAMBDA 650) was employed to test the material, and UV-Vis diffuse reflectance spectroscopy (DRS) was used to obtain the absorption spectrum, and further analyze the light absorption capacity.

2.4 Photocatalytic performance test

To evaluate the photocatalytic degradation efficiency of mixed crystal nano-TiO$_2$ concrete, the methyl orange (MO) was utilized to simulate pollutants in this experiment. Moreover, the mercury lamp and xenon lamp with the light power density of 80 W/cm$^2$ were also utilized to simulate the UV irradiation and solar irradiation condition, respectively, as shown in Figure 2. Especially, for the purpose of mitigating the effect of temperature variation, the temperature of MO solution was sustained at the controlled temper-
perature during the tests by placing a cooling jacket on the bottom of the beaker. The experimental process can be described as follows: (1) a volume of 300 ml methyl orange solution with a concentration of 10 mg/L was infused into a flat bottom beaker, and then the nano-TiO$_2$ concrete brick sample was also put into the beaker. Before illumination, the solution was placed in a photocatalytic reaction chamber and was stirred by a magnetic stirring apparatus for 30 minutes. (2) after the physical adsorption equilibrium of methyl orange solution was reached, a volume of 4 ml solution was extracted, and then centrifuged on a high-speed centrifuge with a speed of 12000 r/min for 1 minute. (3) the supernatant was extracted to measure the solution absorbance (recorded as $A_0$) by using a UV-Vis spectrophotometer. After the measurement, the initial solution was poured back to the beaker and continued to be degraded. (4) turn on the mercury lamp, and then placed the beaker under a 250W UV irradiation (or solar irradiation) with a distance of 20 cm. (5) after 15 minutes of UV irradiation (or solar irradiation), a volume of 4 ml MO solution was extracted and measured the solution absorbance (recorded as $A_{15}$) by using a UV-Vis spectrophotometer. After that, the second measured solution was poured back again to the beaker and continued to be degraded. (6) seven times continuous tests were carried out as the previous steps, and the solution absorbance in each time was recorded as $A_t$. In this experiment, the photocatalytic degradation efficiency ($D$) can be calculated by the solution absorbance, which is described by the following equation:

$$D = \frac{A_0 - A_t}{A_0} \times 100\%$$  \hspace{1cm} (1)

Where, $D$ is photocatalytic degradation efficiency. $A_0$ is the initial absorbance of the MO solution. $A_t$ is the final absorbance of the MO solution after $t$ minute photocatalytic degradation.

### 3 Results and discussions

#### 3.1 Photocatalysis mechanism

Figure 3 demonstrates the primary photocatalysis mechanism of nano-TiO$_2$ concrete. In this investigation, the nano-TiO$_2$ is a typical wide bandgap semiconductor material, which possesses a special energy band structure. This energy band structure of nano-TiO$_2$ consists of a low valence band (VB) filled with electrons and a high empty energy conduction band (CB). When the irradiation energy is larger than the bandgap width of nano-TiO$_2$, electrons ($e^-$) in the valence band (VB) can be excited to jump into the...
conduction band (CB), and the corresponding holes (h⁺) are generated in the valence band (VB), thus developing an “electron-hole” pair, as shown in equation (2). On the one hand, under the irradiation condition, electrons (e⁻) in the conduction band (CB) can further react with the absorbed oxygen (O₂) and produce the superoxide ions (O₂⁻)

\[e^- + O_2 \rightarrow O_2^-\]  

(3)

\[O_2^- + H^+ \rightarrow HO_2^-\]  

(4)

\[HO_2^- + e^- + H^+ \rightarrow H_2O_2\]  

(5)

\[H_2O_2 + e^- \rightarrow OH^- + OH^-\]  

(6)

\[h^+ + OH^- \rightarrow OH^+\]  

(7)

3.2 X-ray diffraction (XRD) studies

Figure 4 displays the X-ray diffraction (XRD) spectra of nano-TiO₂ particles. As demonstrated in Figure 4, the characteristic diffraction peaks of anatase and rutile forms of TiO₂ can be detected in the spectrum of nano-TiO₂, which indicates that the nano-TiO₂ samples adopted in this paper are comprised of anatase and rutile mixed phase, corresponding to the phase composition of P25.
Based on the experimental data, the average crystal size of nano-TiO$_2$ can be calculated by measuring the broadening of the most intense peak of the phase in a diffraction pattern according to the Debye-Scherrer equation \[23\]. The calculated crystal size of nano-TiO$_2$ was about 20.86 nm.

### 3.3 The effect of internal doping method (IDM)

The effect of the internal doping method on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete is plotted in Figure 5. In these figures, the horizontal coordinate represents the exposure time under UV irradiation (t) and the vertical coordinate represents the photocatalytic degradation efficiency of the nano-TiO$_2$ concrete (D). It can be obviously seen from Figure 5 that the photocatalytic degradation efficiency of the nano-TiO$_2$ concrete prepared by the internal doping method is enhanced with the increase of the exposure time of UV irradiation. Moreover, for these nano-TiO$_2$ concrete after being polished, the photocatalytic efficiency exhibits a linear relationship with the exposure time of UV irradiation. However, for these nano-TiO$_2$ concrete without being polished, the photocatalytic degradation efficiency versus irradiation time curves are almost nonlinear. As demonstrated in Figure 5(a), when the nano-TiO$_2$ content is 2%, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 38.78% and 21.81%, respectively, after 120 min of UV irradiation. As demonstrated in Figure 5(b), when the nano-TiO$_2$ content is 5%, the final
Experimental study on photocatalytic degradation efficiency of mixed crystal nano-TiO$_2$ concrete

Figure 6: Photocatalytic degradation efficiency of concrete sprayed with different nano-TiO$_2$ concentrations

photic degradation efficiency of unpolished concrete and polished concrete is 33.94% and 22.74%, respectively, after 120 min of UV irradiation. As demonstrated in Figure 5(c), when the nano-TiO$_2$ content is 8%, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 42.19% and 32.48%, respectively, after 120 min of UV irradiation. It can be found from the above analysis that the photocatalytic degradation efficiency of nano-TiO$_2$ concrete (whether polished or unpolished) increases roughly with the increase of nano-TiO$_2$ content. The photocatalytic degradation efficiency of unpolished nano-TiO$_2$ concrete is much higher than that of polished nano-TiO$_2$ concrete under the same exposure time of UV irradiation, which indicates that the polishing process has a negative influence on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete.

What’s more, the nano-TiO$_2$ concrete still exhibits better photocatalytic performance after being polished, indicating that the nano-TiO$_2$ concrete possesses excellent surface durability and abrasion resistance compared with the common concrete. Additionally, it can be also observed that the effect of polishing process on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete becomes smaller with the increase of nano-TiO$_2$ content.

3.4 The effect of spraying method (SPM)

The effect of the spraying method on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete is plotted in Figure 6. It can be found from Figure 6 that the photocatalytic degradation efficiency of the nano-TiO$_2$ concrete pre-
pared by the spraying method increases with the increase of the exposure time of UV irradiation. The photocatalytic degradation efficiency of nano-TiO$_2$ concrete prepared by spraying method (SPM) is much higher than that of nano-TiO$_2$ concrete prepared by the internal doping method (IDM). As shown in Figure 6(a), when the sprayed nano-TiO$_2$ slurry concentration is 5mg/L, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 72.98% and 30.91%, respectively, after 120 min of UV irradiation. As shown in Figure 6(b), when the sprayed nano-TiO$_2$ slurry concentration is 10mg/L, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 73.82% and 30.10%, respectively, after 120 min of UV irradiation. As shown in Figure 6(c), when the sprayed nano-TiO$_2$ slurry concentration is 15mg/L, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 70.55% and 56.36%, respectively, after 120 min of UV irradiation. As shown in Figure 6(d), when the sprayed nano-TiO$_2$ slurry concentration is 20mg/L, the final photocatalytic degradation efficiency of unpolished concrete and polished concrete is 70.72% and 40.63%, respectively, after 120 min of UV irradiation. It can be found from the above analysis that the photocatalytic degradation efficiency of nano-TiO$_2$ concrete (whether polished or unpolished) is roughly unchanged with the increase of nano-TiO$_2$ slurry concentration. This indicates that the increase of nano-TiO$_2$ slurry concentration can't significantly improve the photocatalytic degradation efficiency when the nano-TiO$_2$ concrete is prepared by the spraying method (SPM). Furthermore, it can be also concluded that the polishing process has a more obvious influence on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete prepared by the spraying method than that of nano-TiO$_2$ concrete prepared by the internal doping method. This is because the polishing process can significantly change the density distributions of nano-TiO$_2$ particles on the surface of concrete prepared by the spraying method.

3.5 The effect of pollutant concentration

Figure 7 shows the photocatalytic degradation efficiency of nano-TiO$_2$ concrete under different pollutant (MO solution) concentrations. As shown in Figure 7(a), for the concrete mixed with 2% nano-TiO$_2$, when the initial concentration of MO solution is 5, 10 and 20 mg/L, the final photocatalytic degradation efficiency of nano-TiO$_2$ concrete is 58.78%, 56.42%, and 40.60%, respectively. As shown in Figure 7(b), for the concrete mixed with 8% nano-TiO$_2$, when the initial concentration of MO solution is 5, 10 and 20 mg/L, the final photocatalytic degradation efficiency of nano-TiO$_2$ concrete is 43.78%, 42.19% and 31.26%, respectively. It can be obviously seen from the above analysis that the photocatalytic degradation efficiency of nano-TiO$_2$ concrete decreases with the increase of pollutant (MO solution) concentration, signifying that the increase of pollutant concentration has a negative influence on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete.
efficiency when the pollutant (MO solution) has a low concentration. Moreover, the photocatalytic degradation efficiency of concrete mixed with 2% nano-TiO$_2$ decreases significantly when the pollutant (MO solution) concentration increases from 5 mg/L to 20 mg/L. However, for the concrete mixed with 8% nano-TiO$_2$, the photocatalytic degradation efficiency under the pollutant concentration of 5 mg/L is basically the same as that under the pollutant concentration of 10 mg/L. Besides, the photocatalytic degradation efficiency of concrete mixed with 8% nano-TiO$_2$ only has a slight decrease when the pollutant (MO solution) concentration increases from 5 mg/L to 20 mg/L. It can be concluded from the above comparison that the effect of pollutant concentration on the photocatalytic degradation efficiency of concrete mixed with 2% nano-TiO$_2$ is more obvious than that of concrete mixed with 8% nano-TiO$_2$.

### 3.6 The effect of irradiation condition

Figure 8 shows the photocatalytic degradation efficiency of nano-TiO$_2$ concrete under different irradiation condition. As plotted in Figure 8(a), for the concrete mixed with 2% nano-TiO$_2$, the final photocatalytic degradation efficiency of nano-TiO$_2$ concrete is 38.78% and 27.24%, respectively, when the irradiation condition is UV irradiation and solar irradiation. As plotted in Figure 8(b), for the concrete mixed with 8% nano-TiO$_2$, the final photocatalytic degradation efficiency of nano-TiO$_2$ concrete is 42.19% and 31.63%, respectively, when the irradiation condition is UV irradiation and solar irradiation. As plotted in Figure 8(c), for the concrete sprayed with 10mg/L nano-TiO$_2$ slurry, the final photocatalytic degradation efficiency of nano-TiO$_2$ concrete is 73.82% and 40.15%, respectively,
when the irradiation condition is UV irradiation and solar irradiation. As plotted in Figure 8(d), for the concrete sprayed with 20mg/L nano-TiO$_2$ slurry, the final photocatalytic degradation efficiency of nano-TiO$_2$ concrete is 70.72% and 32.27%, respectively, when the irradiation condition is UV irradiation and solar irradiation. It can be found from the above analysis that the irradiation condition has an obvious effect on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete. The photocatalytic degradation efficiency of nano-TiO$_2$ concrete under UV irradiation is much higher than that of nano-TiO$_2$ concrete under solar irradiation. This can be explained by the fact that the photocatalytic activity of nano-TiO$_2$ concrete is primarily activated and taken effect under the UV irradiation. The polished nano-TiO$_2$ concrete exhibits low photocatalytic degradation efficiency under solar irradiation owing to the less ultraviolet light in sunlight. In addition, it can be also observed from Figure 8(a), 8(b) that the photocatalytic degradation efficiency of nano-TiO$_2$ concrete prepared by internal doping method (IDM) can be improved to some extent, when the nano-TiO$_2$ content increases from 2% to 8%. Nevertheless, the increase of nano-TiO$_2$ slurry concentration from 10mg/L to 20mg/L fails to enhance the photocatalytic degradation efficiency of nano-TiO$_2$ concrete prepared by spraying method (SPM), as shown in Figure 8(c), 8(d).

4 Application recommendations

Based on the experimental results and analysis, some practical recommendations about the mixed crystal nano-TiO$_2$ concrete are put forward. The nano-TiO$_2$ concrete prepared by the spraying method (SPM) exhibits maximum photocatalytic degradation efficiency of 73.8% when the sprayed nano-TiO$_2$ slurry concentration is 10mg/L. Therefore, it is highly recommended to incorporate the nano-TiO$_2$ with the concrete by the spraying method (SPM) in order to obtain superior photocatalytic performance of nano-TiO$_2$ concrete.

The polished nano-TiO$_2$ concrete still possesses better photocatalytic performance to some extent, but the photocatalytic degradation efficiency is much lower than that of unpolished nano-TiO$_2$ concrete. Considering the photocatalytic performance and abrasion resistance, it is recommended to incorporate the nano-TiO$_2$ with the concrete by the internal doping method (IDM) when the nano-TiO$_2$ concrete is utilized for pavement materials. However, when the nano-TiO$_2$ concrete is used for wall building materials, it is suggested to incorporate the nano-TiO$_2$ with the concrete by the spraying method (SPM) for good photocatalytic performance and convenient construction.

5 Conclusions

In this paper, a novel kind of photocatalytic nano-TiO$_2$ concrete with self-cleaning capacity was prepared by the internal doping method (IDM) and spraying method (SPM). The photocatalytic degradation efficiency of mixed crystal nano-TiO$_2$ concrete prepared by above two methods was experimentally investigated. According to the experimental results, the following conclusions can be drawn:

1. The photocatalytic degradation efficiency of nano-TiO$_2$ concrete (whether polished or unpolished) increases slightly with the increase of nano-TiO$_2$ content, which denotes that increasing nano-TiO$_2$ content can enhance the photocatalytic efficiency when the nano-TiO$_2$ concrete is prepared by internal doping method (IDM).

2. The photocatalytic degradation efficiency of unpolished nano-TiO$_2$ concrete is much higher than that of polished nano-TiO$_2$ concrete under the same exposure time of UV irradiation. The polishing process has a negative influence on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete.

3. The photocatalytic degradation efficiency of nano-TiO$_2$ concrete (whether polished or unpolished) is nearly unchanged with the increase of nano-TiO$_2$ slurry concentration. The increase of nano-TiO$_2$ slurry concentration can't significantly improve the photocatalytic efficiency when the nano-TiO$_2$ concrete is prepared by the spraying method (SPM).

4. The photocatalytic degradation efficiency of nano-TiO$_2$ concrete decreases with the increase of pollutant (MO solution) concentration, signifying that the pollutant concentration has a negative effect on the photocatalytic degradation efficiency of nano-TiO$_2$ concrete.

5. The irradiation condition significantly influences the photocatalytic degradation efficiency of nano-TiO$_2$ concrete. The photocatalytic degradation efficiency of nano-TiO$_2$ concrete under UV irradiation is much higher than that of nano-TiO$_2$ concrete under solar irradiation.

Acknowledgement: This project was financially supported by the National Natural Science Foundation of China (No.51778066).
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