Research Article

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Cement-based composites with ZIF-8@TiO_2-coated activated carbon fiber for efficient removal of formaldehyde

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Abstract: Formaldehyde is one of the most common indoor air pollutants that seriously damage human health. It is of significant importance to effectively remove indoor formaldehyde. In this work, a novel cement-based composite with ZIF-8@TiO_2-coated activated carbon fibers (TiO_2-ACFs) was prepared and shown to remove the indoor formaldehyde effectively. TiO_2 was coated on ACFs via atomic layer deposition, and then ZIF-8 was grown on the surface of TiO_2-ACFs. The ZIF-8@TiO_2-ACFs were then mixed with cement slurry and thus formed a cement-based composite, which exhibited excellent formaldehyde removal performance. In particular, if assisted with UV light, the removal efficiency for formaldehyde by the cement-based composite showed an obvious increase.

Keywords: formaldehyde removal, cement, ZIF-8, TiO_2, carbon fiber

1 Introduction

Formaldehyde is a major indoor air pollutant and also a world-recognized potential carcinogen. It seriously damages human health. When the concentration of formaldehyde reaches 0.1 mg/m^3 indoors, it will have a peculiar smell and cause discomfort. When the concentration reaches 30 mg/m^3, it will immediately cause death [1–3]. During the past years, various removal technologies for formaldehyde have been developed, including plant purification, physical adsorption, photocatalytic oxidation, low-temperature plasma catalytic degradation, and metal oxide catalysis [4–8]. However, these methods still have some negative problems. Plant purification has a slow adsorption rate and low adsorption efficiency. There exist desorption problems in the physical adsorption methods. The photocatalytic oxidation methods rely on too much ultraviolet radiation, which will produce ozone and harm people's health. The cost of low-temperature plasma catalytic degradation methods is too high. It is easy to produce dust pollution in the recovery process of metal oxide catalysts. So, it is very important to develop a novel material for the efficient and stable removal of formaldehyde.

Zinc-based zeolitic imidazolium framework, ZIF-8, is a promising metal-organic framework material in the field of hazardous gas removal. There are abundant micropores in its framework structure and larger molecular cages in the mesoporous range. Micropores, less than 2 nm in size, can produce a very strong van der Waals force and effectively absorb various harmful small molecular gases. The mesopores also greatly promote adsorption. In addition, ZIF-8 has a large specific surface area and pore volume. It can be prepared easily, quickly, and economically [9–12]. However, ZIF-8 is usually a brittle crystalline material, which limits its application. Therefore, it is necessary that ZIF-8 is grown on suitable macroscopic substrate to form a crystalline film for practical application [13–15]. Activated carbon fiber (ACF) is a novel, efficient, and multifunctional adsorption material. The specific surface area of ACFs is as large as 1,000–3,000 m^2/g. There are also abundant micropores, and the micropore volume is more than 90%, rendering the ACFs with a higher adsorption capacity and faster adsorption rate than granular activated carbon,

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and has higher adsorption efficiency for harmful gas molecules [16,17]. However, the micropores of ACFs are radial, and the diffusion resistance is small, which makes it easy for desorption to occur [18]. Loading functional particles such as ZIF-8 nanocrystals on it can improve the adsorption efficiency and prevent desorption.

Cement mortar is widely used as a wall material in buildings. If the cement mortar has the function of removing formaldehyde indoors, it can greatly reduce the harm of indoor decoration pollution to human health [19,20]. It is of practical significance to design cement-based composites with ZIF-8@ACFs. In this study, ZIF-8 was first coated on the surface of ACFs, and then ZIF-8@ACFs were added to cement mortar to obtain cement-based composites. In order to avoid the falling off of ZIF-8 from the fiber, atomic layer deposition (ALD) technology is used in the process of preparation. Nanolayer TiO_2 film can be formed by an alternating gas precursor pulse in the reaction chamber and a chemical adsorption reaction on the surface of the deposition substrate. Even if the ACF substrate is inert, the TiO_2 thin film can be coated on it stably via ALD. The O atoms of TiO_2 provide reaction sites for ZIF-8 growth. The composite ZIF-8@TiO_2-ACFs was prepared. It is very stable and has excellent formaldehyde adsorption performance due to the advantages of ACFs and ZIF-8 [21,22]. Then, it is convenient for combining ZIF-8@TiO_2-ACFs with cement paste. The structure, interaction, and performance of the cement-based composites with ZIF-8@TiO_2-coated ACFs were studied in this work. It provides new ideas and experimental examples for the production of low-cost and safe indoor decoration materials.

2 Experimental

2.1 Materials

The ordinary Portland cement CEM I 42.5 produced by Huaxin Cement Co., Ltd, China, with a specific gravity of 3.13 and a surface area of 350 m^2/kg was used. The chemical composition of cementing materials is shown in Table 1. The foaming agent is produced by Qingdao Ecocare Co., Ltd, China. TiO_2-ACFs via ALD were prepared in our laboratory. 2-Methylimidazole (2-MeIM) (98% purity) was from Macklin. Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99% purity) and formaldehyde solution was purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai.

2.2 Preparation of ZIF-8@TiO_2-ACFs

ZIF-8 crystal materials were synthesized in an ultrapure water solution. About 1.18 g of $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in 10 ml deionized water, and 22.65 g of 2-MeIM was dissolved in 80 ml deionized water. Mix the two solutions under stirring conditions. Then, ZIF-8 nanocrystals were obtained by hydrothermal reaction at 80°C for 24 h, followed by centrifugal separation for 15 min. They were then cleaned with deionized water and dried at room temperature. TiO_2-ACFs were obtained via ALD in our laboratory. A Savannah S100 ALD reactor (Savannah System, Cambridge NanoTech., Inc., USA) equipped with a gas-flow system was used during the TiO_2 deposition process. The titanium and oxygen precursors were titanium(IV) isopropoxide and H_2O, respectively. The reactive temperature was 150°C. The purge gas and carrier gas for both precursors were high-purity nitrogen (N_2, 99.999%). The ACFs were placed in the ALD reactor and dried in vacuum at 150°C for 5 min prior to the ALD processing. Then, the deposition process began. Each complete ALD cycle lasted for 56.25 s. The TiO_2-ACFs used in this work were deposited for 1,000 cycles. The ZIF-8@ACFs or ZIF-8@TiO_2-ACFs were prepared using a similar method as ZIF-8. Just need to put 3 g ACFs or TiO_2-ACFs [22,23] into the 2-MeIM solution in advance. Finally, the sample was fully cleaned with deionized water and dried at room temperature.

2.3 Preparation of cement-based composites and test of formaldehyde adsorption

The preparation process of foamed cement is to pour the dry materials into the mixer, mix them evenly, and then add water according to the water–cement ratio of 0.4 and continue to stir. Then, a certain amount of foaming agent is mixed with water according to the scale of 1:30. Pour the mixture into a three-neck bottle and stir at high speed for

Table 1: Chemical composition of cementing materials/wt%

Chemical constitution	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	Ignition loss
In cement	21.99	5.92	3.26	58.64	1.98	0.74	0.27	0.4	2.6	3.5

5 min until the foaming is stable. 150 mL foam and 1 g ZIF-8@TiO_2-ACFs are poured into 1 kg cement, and then mixed for 3 min. The cement-based composite is obtained. The preparation process is shown in Figure 1.

The samples used for the formaldehyde adsorption test were molded by a size of 200 mm × 200 mm × 3 mm and remolded after 24 h. The desired amount of test specimen is then placed in a sealed formaldehyde environment. A formaldehyde concentration tester was used to test the formaldehyde adsorption performance.

2.4 Characterization

Scanning electron microscopy (SEM) used for morphology characterization of ACFs, TiO_2-ACFs, ZIF-8@TiO_2-ACFs, and cement-based composites is JSM-5610LV, JEOL Co. Ltd, Japan. Bruker Tensor 27 Fourier transform infrared spectroscopy (FT-IR) is used for the changes of groups in the samples. In the adsorption test, the formaldehyde standard solution was heated to become gas before placing it into the test chamber. The test is static at room temperature, and relative humidity was 40–60%. The initial concentration of formaldehyde is 35 ± 5 mg/m^3 as high concentration or 8 ± 2 mg/m^3 as low concentration in a test chamber (0.5 m^3). The mass of cement-based composites was 3 g in every test. Formaldehyde concentration was recorded at 1-min interval during the test.

3 Results and discussion

3.1 Structure and morphology of ZIF-8@TiO_2-ACFs and cement-based composites

The structure and morphology of the materials were characterized by SEM. The SEM images of ACFs (a), TiO_2-ACFs (b), ZIF-8@ACFs (c), ZIF-8@TiO_2-ACFs (d), foamed cement (e), and cement-based composites (f) are shown in Figure 2. The surface of ACFs is very smooth. In Figure 2b, the morphology of TiO_2-ACFs is similar to ACFs, and the surface is also smooth. TiO_2 nanolayer is thin and dense enough, and it cannot be observed from SEM. The ZIF-8 can grow on the surface of fibers hardly due to the chemical inertness of ACFs. As can be seen from Figure 2c, the loading amount is few. In contrast, the growth of ZIF-8 on the surface of TiO_2-ACFs is more easily (Figure 2d). The loading amount is much more than that on ACFs, and ZIF-8 grows into a continuous crystalline film on the fiber. The O atoms from TiO_2-ACFs provide many reaction sites during the growth process of ZIF-8, so the growth of crystal on the surface becomes fast and simple. The morphology of foamed cement is shown in Figure 2e. There exist many holes in the cement, and the diameter is about dozens of microns. The cement-based composites containing ZIF-8@TiO_2-ACFs and foamed cement were also prepared successfully. As can be seen from Figure 2f, the fibers are distributed roughly uniformly in the cement.

The FT-IR spectra of ACFs, TiO_2-ACFs, ZIF-8@TiO_2-ACFs, and cement-based composites are shown in Figure 3. Comparing the curves of ZIF-8@TiO_2-ACFs and ACFs (TiO_2-ACFs), the typical peaks of ZIF-8 are observed, and they are consistent with those reported in literature. The peaks at 680 and 745 cm^{-1} are attributed to the imidazole ring out-of-plane bending vibrations. While the peaks at 1,310 and 1,110 cm^{-1} are due to in-plane bending vibrations. The peaks at 1,432 and 1,590 cm^{-1} are due to the effects of imidazole ring stretching or bending and C=N stretching, respectively. Observing the curve of cement-based composites, the typical peaks of ZIF-8 are also shown obviously at 680, 1,110, 1,432, and 1,590 cm^{-1}. In addition, there are many –OH groups in foamed cement, and these can also be seen in the spectrum. Bands at 3,450–3,650 cm^{-1} can be attributed to the stretching vibration of free −OH groups and intermolecular and intramolecular hydrogen bondings.

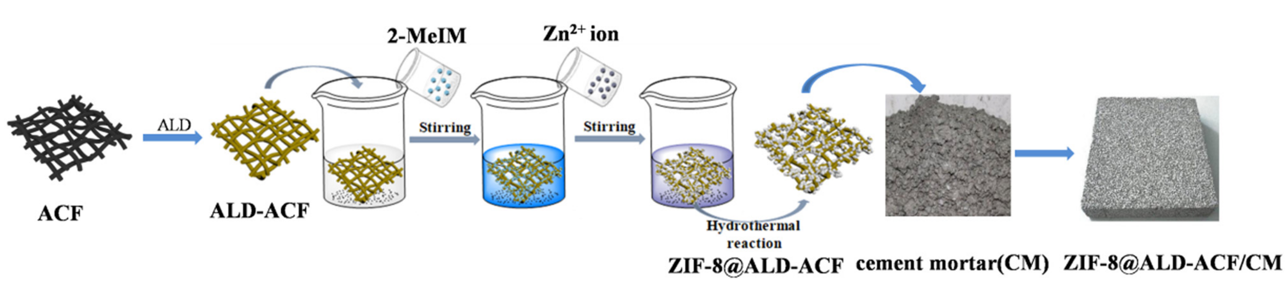

Figure 1: The preparation process of the cement-based composites.

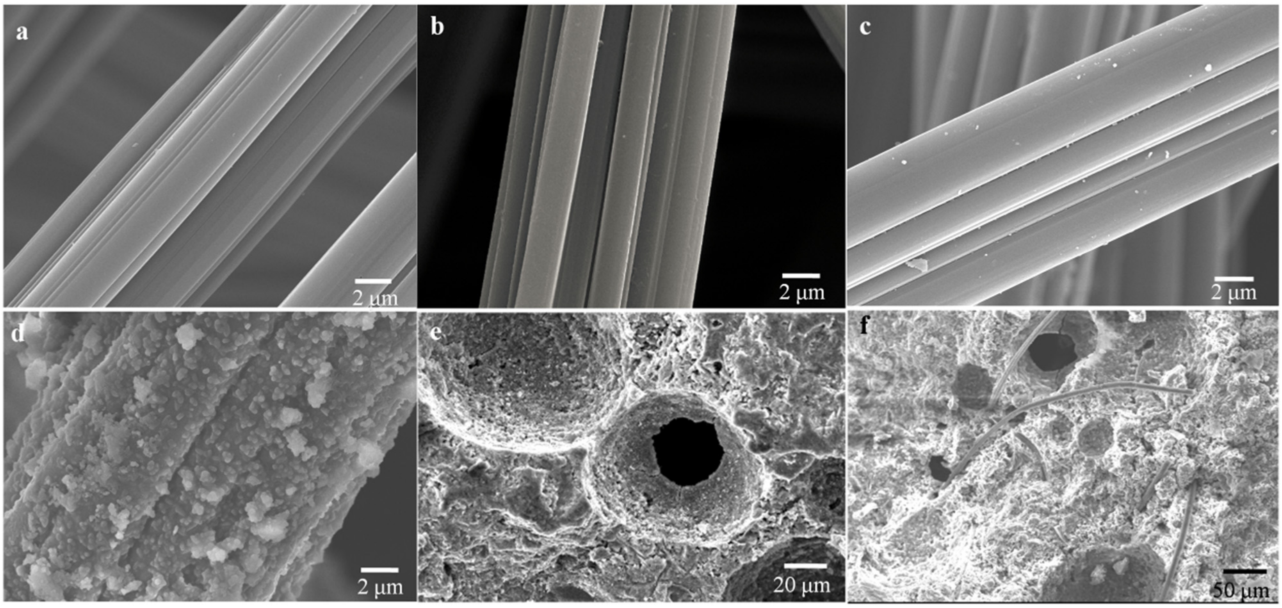

Figure 2: SEM images of ACFs (a), TiO_2-ACFs (b), ZIF-8@ACFs (c), ZIF-8@TiO_2-ACFs (d), foamed cement (e), and cement-based composites (f).

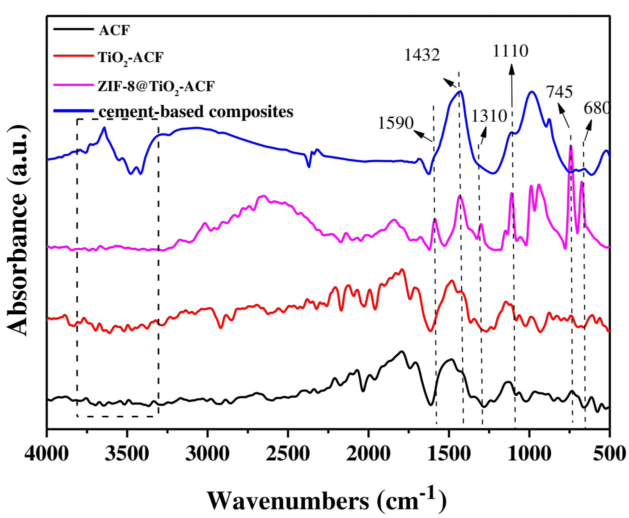

Figure 3: FT-IR spectra of ACFs, TiO_2-ACFs, ZIF-8@TiO_2-ACFs, and cement-based composites.

3.2 Formaldehyde adsorption properties of cement-based composites

3.2.1 Adsorption test of high-concentration formaldehyde

To study the formaldehyde adsorption performance of the cement-based composites, a test was designed. About 20 g of cement-based samples are taken and placed in a sealed 40 mg/m^3 formaldehyde environment to test its adsorption performance. The analysis results of the test for high-concentration formaldehyde removal can be seen in Figure 4. The formaldehyde removal efficiency was calculated using equation (1) and adsorption capacity q_t using equation (2).

$$\text{Removal efficiency(\%)} = \frac{C_0 - C_t}{C_0} \times 100\%, \tag{1}$$

$$q_t \left(\frac{\text{mg}}{\text{g}}\right) = \frac{C_0 - C_t}{M} \times V, \tag{2}$$

where C_0 and C_t represent the formaldehyde concentration when initial time = 0 and time = t (1, 2, and 3 until 212 min) in the test chamber (mg/m^3). q_t represents the formaldehyde adsorption capacity every 1 min until 212 min. M is the weight of the cement-based composites (g), and V is the volume of the test chamber (m^3).

In Figure 4a, the formaldehyde removal efficiency of foamed cement and cement-based composites is shown. The change trend of the two curves was similar within 15 min, and the removal rate was fast. After 15 min, the removal efficiency of foamed cement slowed down obviously. The speed was basically unchanged from 30 min, and the maximum value was 59.07% in 35 min. The removal efficiency of cement-based composites kept growing until 74.54% in 35 min. The whole curves of formaldehyde removal of cement-based composites under normal light and UV light can be seen in Figure 4(b). From 0 to 60 min, the adsorption rate gradually increased almost linearly with time. The two curves nearly coincided below 50 min. The curve under UV light was always higher than that under normal light after 50 min. The removal efficiency of cement-based composites

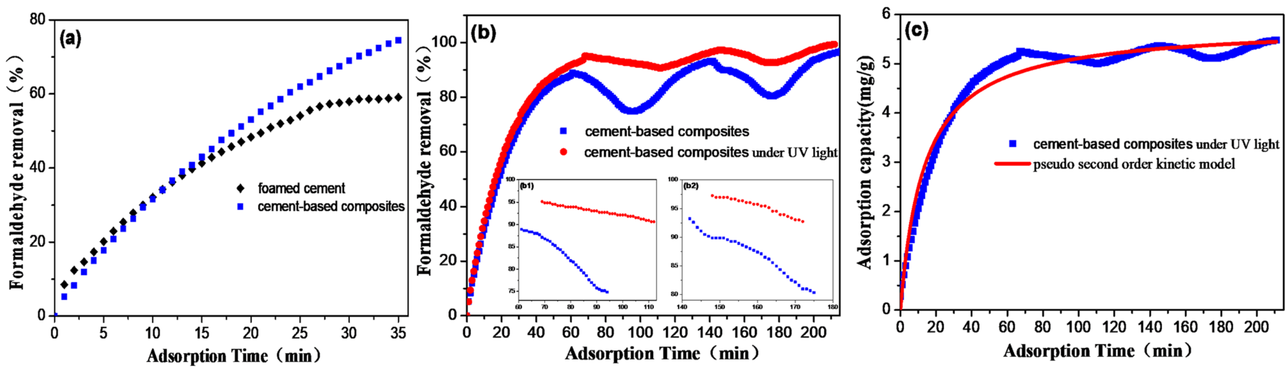

Figure 4: Formaldehyde removal of foamed cement and cement-based composites (a), formaldehyde removal of cement-based composites under normal light and UV light (b), and adsorption capacity and fitting curve under UV light (c).

under normal or UV light was up to about 90% at 60 min. After 60 min, the removal rate becomes slow until 212 min. The maximum value of the removal efficiency was 96.32 and 99.40% in 212 min for cement-based composites under normal light and UV light, respectively. But from 60 to 180 min, there were two highly visible desorption processes. The first time was 61–94 min (88.96–74.85%) and 69–112 min (94.86–90.63%) for cement-based composites under normal and UV light, respectively. The second was 142–175 min (93.25–80.37%) and 148–172 (97.28–92.75%) for the samples under normal and UV light, respectively. This was mainly due to the many holes in the cement, and the diameter is very big about dozens of microns. The detailed reasons will be analyzed in the following mechanism part. In Figure 4c, adsorption capacity and fitting curve under UV light are shown. In 212 min, the maximum formaldehyde adsorption capacity of cement-based composites under UV light was 5.48 mg/g. The change trend was the same as that in Figure 4b. It basically fits the pseudo-second-order kinetic model. Equation (3) is used for evaluating the pseudo-second-order kinetic model.

$$q_t(\text{mg/g}) = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, \tag{3}$$

where k_2 represents the pseudo-secondary adsorption rate constant. q_e is the equilibrium adsorption capacity. In this work, the fitting equation is shown below:

$$q_t = \frac{0.012 \times 5.794^2 \times t}{1 + 0.012 \times 5.794 \times t} (R^2 = 0.96).$$

3.2.2 Adsorption test of low-concentration formaldehyde

The adsorption test for low-concentration formaldehyde is similar to that for high concentration. About 20 g cement-based samples are taken and placed in a sealed 10 mg/m^3 formaldehyde environment to test its adsorption performance. Figure 5 shows the formaldehyde removal of foamed cement and cement-based composites under normal light and UV light. No matter under which kind of light, formaldehyde removal is fast and takes no more than 10 min. In Figure 5a and b, the formaldehyde adsorption times by foamed cement (9.27 s) and cement-based composites (9.21 s) under normal light are shown in the curve graph and bar chart, respectively. The change trend of both adsorption curves is similar due to the very low concentration of formaldehyde. Both samples can remove formaldehyde fast enough. In Figure 5c and d, the low-concentration formaldehyde removal by foamed cement and cement-based composites under UV light is shown. It takes 9.18 s for foamed cement and only 8.13 s for cement-based composites. Because of the photocatalytic degradation of formaldehyde by TiO_2 under UV light, the adsorption process by cement-based composites becomes more quickly.

3.3 Mechanism of formaldehyde removal

The removal mechanism is also studied. The mechanism diagram can be seen in Figure 6. The functional ACFs coated with TiO_2 nanolayer and crystalline ZIF-8 disperse in porous cement. Many holes with a diameter of dozens of microns exist in cement-based composites. Due to the macropore structure, the composites can capture formaldehyde (high and low concentrations) fast and efficiently. On the other hand, the formaldehyde molecules can also be desorbed from the macropores easily due to their extremely mismatched size. This is also the reason that two highly visible desorption processes exist in Figure 4b. There exist many micropores in ZIF-8, with a bore diameter of 0.34 nm and a cage diameter of 1.16 nm, which

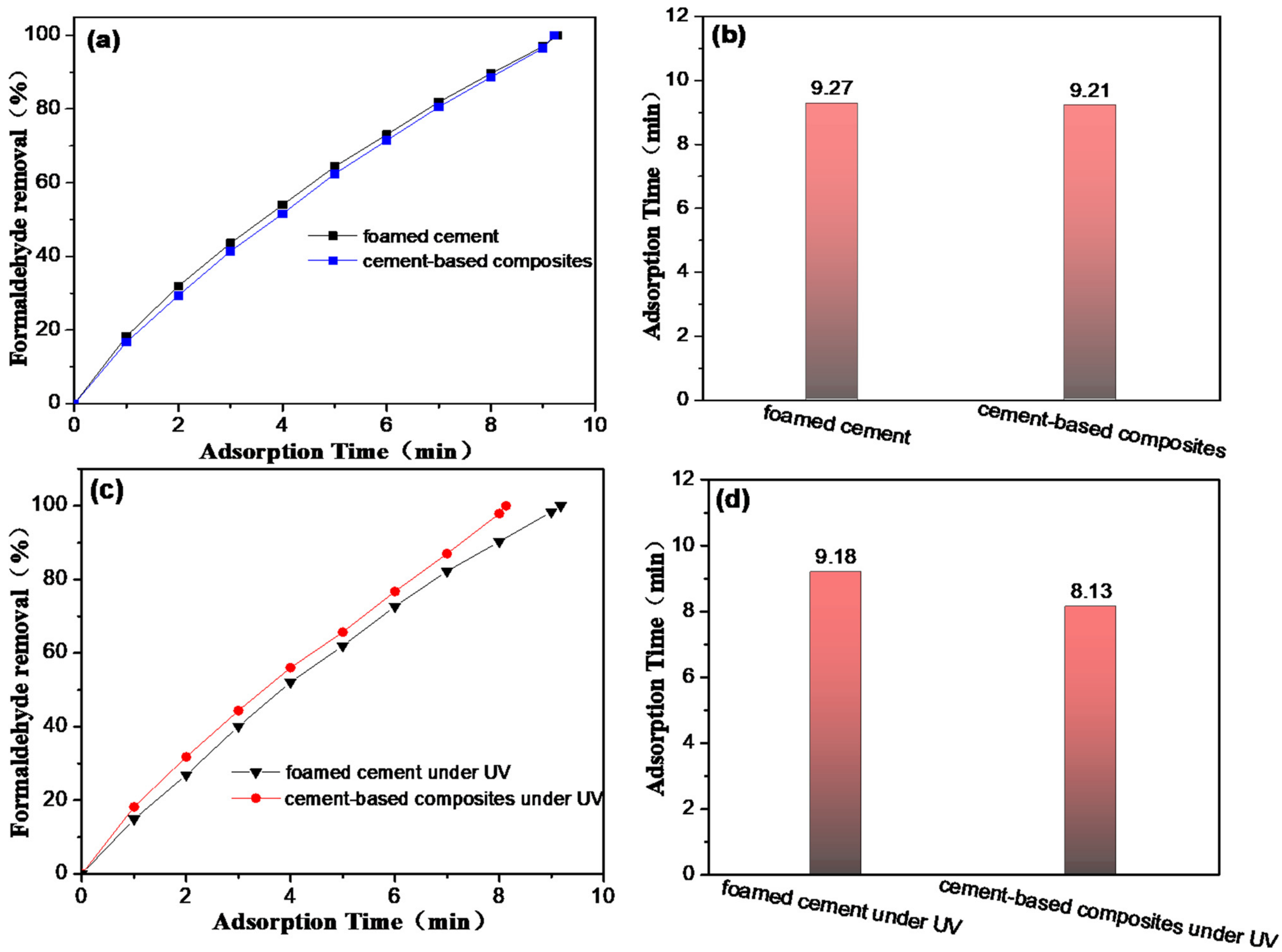

Figure 5: Formaldehyde removal of foamed cement and cement-based composites under normal light (a and b) and UV light (c and d).

is suitable for molecule adsorption. ZIF-8 is coated on TiO_2-ACFs, and the specific surface area of fibers and ZIF-8 is huge. The formaldehyde molecules can be further adsorbed by ZIF-8@TiO_2-ACFs after being captured by the micrometer-sized pores of cement-based composites. Most formaldehyde with high concentration can be adsorbed, but partial desorption is inevitable. Low-concentration formaldehyde can be adsorbed completely. When this process is carried out under UV light,

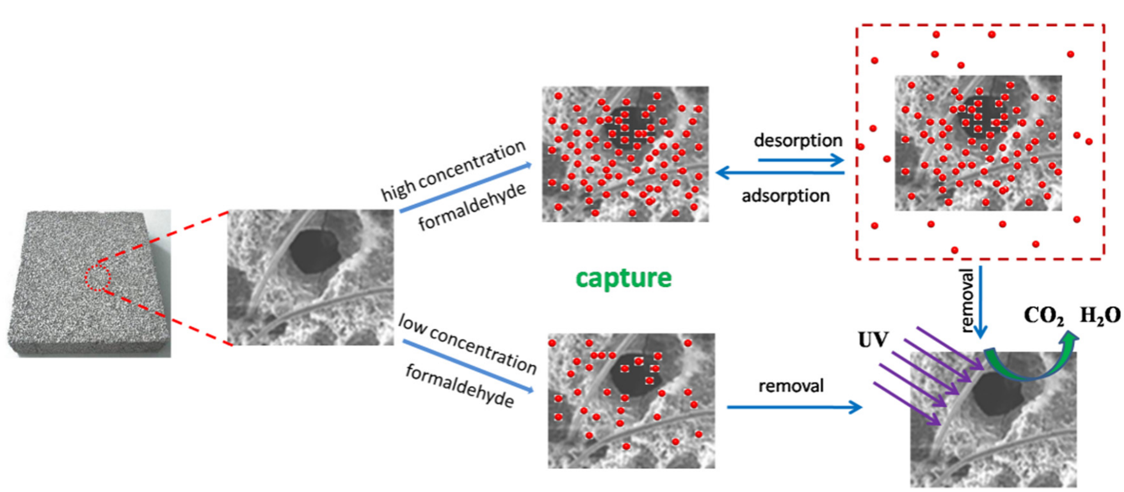

Figure 6: Formaldehyde removal mechanism by cement-based composites.

captured formaldehyde becomes H_2O and CO_2 due to the photocatalysis of TiO_2 nanolayer. The process contains multiple steps. The formaldehyde molecules were first captured fast by the big holes of cement and then adsorbed by ZIF-8 and ACFs. The desorption process becomes slow enough through micropores. Harmful molecules were broken down by photocatalytic decomposition to completely disappear. The photocatalytic process is accompanied by adsorption and desorption. Due to the continuous reduction of formaldehyde molecules, the equilibrium shifts toward a positive direction, and formaldehyde can be completely removed.

4 Conclusion

In summary, a kind of novel cement-based composite for removing indoor formaldehyde was successfully obtained. Regardless of whether it absorbs high- or low-concentration formaldehyde, the composite demonstrates very good performance. Due to the synergistic removal process, microns in cement-based composites, micropores in ZIF-8, and photocatalytic decomposition by TiO_2-ACFs, formaldehyde can be removed completely. The maximum formaldehyde adsorption capacity under UV light was 5.48 mg/g. Using 20 g cement-based composites for absorbing 10 mg/m^3 formaldehyde under UV light, it takes only 8.13 s for 100% removal. In this work, cement, a commonly used building material, is endowed with the functionality of formaldehyde removal, which is of great significance for protecting human health indoors.

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Data availability statement: The data are available from the corresponding author on reasonable request.

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