Synergistic effect of adsorption and photocatalysis for the degradation of toluene by TiO$_2$ loaded on ACF modified by Zn(CH$_3$COO)$_2$

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Received: 25 March 2021 / Accepted: 18 May 2021 / Published online: 5 June 2021

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Abstract
Activated carbon fiber (ACF) was modified by Zn(NO$_3$)$_2$, ZnCl$_2$, and Zn(CH$_3$COO)$_2$, respectively, and then, TiO$_2$ was loaded on the modified ACFs. The adsorption and photocatalysis performance were explored through the removal of toluene, and TiO$_2$/ACF-Ac modified by Zn(CH$_3$COO)$_2$ with the best toluene degradation performance was selected. The characterization results of a scanning electron microscope (SEM), X-ray diffraction spectra (XRD), and Fourier transform infrared spectrometer (FTIR) indicated that the samples were rough, and TiO$_2$ was mainly loaded on the surface containing large amount of oxygen-containing functional groups in anatase phase. An ultraviolet-visible diffuse reflectance spectrophotometer (UV-vis DRS) revealed that the catalyst enhanced the light response range. The photoelectric chemical experiment results demonstrated that the modified ACFs remarkably improved the charge transmission and the separation efficiency of electrons and holes. The adsorption saturation time reached 40 h and toluene photodegradation rate was 70%. Four toluene degradation intermediate products were determined by GC-MS, and the removal mechanism of toluene by TiO$_2$/ACF-Ac was discussed.

Keywords Modified ACF · TiO$_2$ · Photocatalysis · Adsorption · Toluene · Mechanism

Introduction
Volatile organic compounds (VOCs) can be divided into alkanes, aromatics, olefins, esters, etc., mainly from petrochemical industry, automobile exhaust, coating manufacturing, and so on. Most VOCs are toxic and carcinogenic, and some VOCs are also inflammable and explosive (Liu et al. 2019; Tong et al. 2019). When the concentration of VOCs in the environment reaches a certain level, it will cause serious damage to the human liver, kidney, brain, and nervous system. VOCs are important precursor to form ozone (O$_3$) and fine particles, and may also cause environmental pollution problems, such as haze and photochemical smog (Fan et al. 2020; Qun et al. 2019). Therefore, an effective VOC treatment method is urgently needed for human health and ecological environment safety.

At present, the treatment technologies of VOCs mainly include adsorption, low-temperature condensation, membrane separation, and catalytic oxidation (Hendry et al. 2019; Lelicińska-Serafin et al. 2019; Mok et al. 2020). Compared with other methods, photocatalysis oxidation technology has a great deal of merits, for instance simple operation, high efficiency, energy saving, safety, low cost, and mild reaction conditions (Weon et al. 2017). The conventional catalysts for VOC treatment mainly include TiO$_2$, g-C$_3$N$_4$, bismuth-based materials, graphene, and its composite materials. TiO$_2$ has become an ideal photocatalyst owing to its high photocatalytic activity, stable chemical properties, strong corrosion resistance, low cost, and no secondary pollution, so it has been extensively used in effluent disposal, air purge, and antibacterial fields (Assadi et al. 2018; Behnam et al. 2018; Elfalleh et al. 2017; Li et al. 2020a). For example, Assadi et al.
explored the performance of photocatalysis combined with surface discharge plasma in the removal of VOCs from animal quartering centers from pilot scale to industrial scale. The results showed that compared with single surface discharge plasma technology, the selectivity of CO2 was significantly improved, and the removal rate and energy yield of VOCs by combined technology were improved (Assadi et al. 2017; Assadi et al. 2015). However, the defects of TiO2, such as wide band gap, low utilization rate of sunlight, aggregation, and photogenerated electron (e−) and hole (h+) recombination, seriously restrict its practical application (Feizpour et al. 2019).

In addition, adsorption method is an important way for the purification of VOCs owing to its mature process, low cost, high removal rate, and so on (Cheng et al. 2020). Girma et al. (2018) studied the performance of Moringa stenopetala bark for adsorbing heavy metal ions from industrial wastewater. The results showed that the adsorption of metal ions on adsorbent was a spontaneous endothermic process and the interaction was mainly chemical adsorption. The removal rates of Cd (II), Pb (II), and Cu (II) were 94.80, 95.50, and 94.23%, respectively. Zhang et al. (2016e) introduced the first application of ET-5-type adsorbent in the removal of iodomethane from tail gas of acetic acid industry. The industrial application data showed that when the inlet content of iodomethane was greater than 1000×10−9, the outlet content was always less than 30×10−9, which fully met the operation of the process index.

Activated carbon fiber (ACF) is an advanced type of porous fibrous material with many advantages, such as high-efficiency adsorption, large surface area, excellent adsorption properties, standout porous structure, and bountiful surface functional groups. It is an environment-friendly adsorption, photocatalytic, and carrier material, and can be used for heavy metal wastewater, organic pollutants, and waste gas treatment (Liu et al. 2018; Miranda Zoppas et al. 2020). In order to improve the adsorption effect and selectivity, it is often necessary to adjust the pore structure of ACF or modify its surface characteristics. At present, the common modification methods mainly include surface oxidation and reduction, loading metals and metal oxides, and microwave modification (Qiu et al. 2018; Zhang et al. 2019). Studies have shown that due to the multi-functionality of metal oxides, after loading onto ACF, a great deal of binding sites can be provided, thereby greatly improving the adsorption performance of ACF (Chen et al. 2017; Zhang et al. 2016a).

The strong adsorption properties of ACF can not only enrich the target pollutants, capture intermediate toxic products, and promote the photocatalytic performance of nano-TiO2 but also provide support for the renewable performance of TiO2 photocatalytic materials. Therefore, the preparation of bifunctional catalysts with adsorption and photocatalytic oxidation function has become a research hotspot in recent years (Popova et al. 2020). Nguyen et al. (2020) fabricated magnesium-ammonia-clay-based TiO2 supported on ACF (MgAC-TiO2) which is used to eliminate methylene blue (MB). The results revealed that the sintering of TiO2 was impeded due to the supplement of MgAC, while ACF could further improved the photocatalytic activity by preventing electron-hole recombination. Liu et al. (2010) explored the degradation performance of FeO/TiO2/ACF composites for the degradation of 2,4-dichlorophenol (2,4-DCP). The experimental data indicated that the removal efficiency of 2,4-DCP was promoted attributing to the adsorption of ACF; at the same time, the recombination of electron-hole pairs was prevented effectively by Fe loaded on TiO2. TiO2 irradiated by UV provided electrons to reduce Fe3+ and Fe2+ back to FeO, which prevented the active loss of FeO. Jain et al. (2019) loaded nano-TiO2 on ACF by an impregnation-hydrothermal method, and prepared TiO2/ACF composites, which were used to remove methylene blue (MB) from wastewater under continuous flow conditions. The results showed that ACF played a dual role of adsorption and fixation of nano-TiO2. However, the study of TiO2 loading on ACF modified by zinc salt for VOCs removal is rarely reported.

Hence, in this study, activated carbon fibers (ACFs) were firstly modified with Zn(NO3)2, ZnCl2, and Zn(CH3COO)2 respectively, by an ultrasonic-vacuum impregnation method; subsequently, TiO2 was loaded on the modified ACF by an ultrasonic-vacuum-assisted sol-gel method (Fig. 1). After that, toluene was selected, which is representative of VOCs, as the target pollutant, and the composites were applied to eliminate toluene. The adsorption and photocatalytic performance of each composite was investigated in the self-designed reactor. Combined with the results of characterization and analysis, the TiO2/ACF-Ac catalyst with the best removal performance was selected. Subsequently, the removal efficiency of toluene by TiO2/ACF-Ac under different factors was investigated to determine the optimal reaction conditions. Various intermediate products and main reaction pathways were analyzed based on the results of GC-MS, and the synergistic mechanism of adsorption and photocatalysis removal for toluene removal on TiO2/ACF-Ac was also explored.

Materials and methods

Materials

Activated carbon fiber (ACF) was purchased from Nantong Senyou Carbon Fiber Co., Ltd. Concentrated nitric acid (HNO3, 68%), zinc nitrate (Zn(NO3)2, AR), zinc acetate (Zn(CH3COO)2, AR), zinc chloride (ZnCl2, AR), anhydrous ethanol (C2H5OH, AR), acetic acid (CH3COOH), tetraethyl titanate (C8H16O4Ti, TBOT, AR), and carbon disulfide (CS2, AR) were supplied by Sinopharm Chemical Reagent Co., Ltd.
Preparation of modified ACF materials

Firstly, Zn(NO₃)₂, ZnCl₂, and Zn(CH₃COO)₂ solutions with the same mass concentration were prepared according to the standard of Zn concentration. Then, 10 pieces of ACFs were put into the prepared solution. The ACFs were immersed in a vacuum chamber for 10 min after ultrasonic treatment. The ultrasonic-vacuum impregnation process was repeated twice to realize the full impregnation of the ACF solution. Then, the impregnated ACF was placed in an oven at 105°C for drying, and the products were sealed and preserved. ACFs modified by zinc nitrate, zinc acetate, and zinc chloride are denoted as ACF-ₙc, ACF-ₐc, and ACF-₁c, respectively.

Preparation of TiO₂ composites supported on modified ACF

With tetrabutyl titanate as the presoma of titanium dioxide, ACF-based photocatalytic composites were prepared by the ultrasonic-vacuum-assisted sol-gel method. Anhydrous ethanol and acetic acid were mixed in a volume ratio of 2:1; then, 10 mL of tetrabutyl titanate (TBOT) was added to the mixture, and after that, the magnetic stirring lasted 30 min to obtain solution A. Solution B containing mixing solution of 10 mL ethanol, 2 mL acetic acid, and 30 mL deionized water was prepared under the condition of magnetic stirring. The B solution was slowly added to the A solution with intensive stirring. Subsequently, the stirring process lasted for 2 h, and then aged for 24 h at room condition. The modified ACFs with the shape of 20 mm × 20 mm squares were put into the aged sol. Then, the mixture was immersed in a vacuum drying oven for 10 min after ultrasonicication for 10 min, and the operation was repeated several times to achieve the compounding of materials. The impregnated composites were put into a kiln at 105°C for 2 h, and then cooled slowly to ordinary temperature. The composites were prepared after calcining the cooled productions at 450°C for 2 h in a tube furnace, with N₂ as protective gas and the heating rate was 50°C/min. TiO₂/ACF-ₙc, TiO₂/ACF-ₐc, and TiO₂/ACF-₁c composites were prepared and reserved.

Characterization of the catalyst

The crystalline phase and grain size of the composites were determined by X-ray diffraction spectra (XRD, PANalytical B.V., AXIOS-Petro) with power 2200 W, Cu-Kα radiation (λ=1.5406 Å). The components and chemical bound information of the samples were characterized by a Fourier transform infrared spectrometer (FTIR, Nicolet, Nexus). A scanning electron microscope (SEM, Hitachi, S4800) was used to investigate the morphologies of the composites. An X-ray photoelectron spectrometer (XPS, Thermo Scientific, K-Alpha) was employed to analyze the ultimate composition and valence state of the composites. The specific surface area and pore size of the samples were measured by the analysis of Brunauer-Emmett-Teller (BET, ASAP3020, Mike Instruments Co.). Adsorption was carried out at 77.4 K with N₂ as adsorbate, and desorption occurred at 300 K. An ultraviolet-visible diffuse reflectance spectrophotometer (UV-vis DRS, TU-1901, Beijing General Instrument Co.) was used to test the optical absorption properties of the composites. I-T photocurrent analysis can be used to determine the light response of materials. The working electrode is samples/conductive glass, the counter electrode is platinum wire, and the reference electrode is saturated calomel electrode. Under the bias voltage of 0.0V, the samples were irradiated by visible light with a 300-W xenon lamp purchased from Beijing Perfect Light Source Research Institute, and the photocurrent test was investigated.

Adsorption and photocatalysis property measurement

The composites were cut into squares of 20 mm×20 mm and fixed in the quartz tube reactor, and then, the self-assembly experimental device was operated without any pollutions to
the stable airflow at room temperature and atmospheric pressure, and subsequently, the dark reaction was carried out to make the composites fully absorb toluene with the initial concentration of 1000 mg/m³ and the flow rate of 120 mL/min. After reaching the adsorption equilibrium, the low-pressure mercury lamp was turned on for photocatalytic reaction. During the experiment, activated carbon was used to sample the inlet and exit toluene at regular intervals. The samples were resolved with carbon disulfide and injected into a gas chromatograph (GC, SP-3420A) to determine the strength of toluene. The degradation efficiency of gaseous toluene was calculated as follows:

\[ R = \frac{C_0 - C}{C_0} \times 100\% \]

where \( R \) is the removal efficiency, and \( C_0 \) (mg/m³) and \( C \) (mg/m³) mean the concentration of toluene at the initial time and \( t \) time, respectively.

In order to further investigate the photocatalytic performance of different catalysts, the classic Langmuir-Hinshelwood (L-H) kinetic model was employed. The L-H kinetic model used to fit the apparent rate constants of toluene degradation was given as follows:

\[ -\ln\left(\frac{C}{C_0}\right) = Kt \]

where \( K \) is the apparent reaction rate constant (min⁻¹), \( t \) is the reaction time (min), \( C_0 \) and \( C \) represent initial toluene concentration and the toluene concentration at time \( t \) (mg/m³), respectively.

**Results and discussion**

**Composition and structure characterization**

XRD is used to analyze the microstructure of the materials. The XRD patterns of samples are shown in Fig. 2(a). According to PDF card (JCPDS no 21-1272) (Hou et al. 2012), the anatase phase characteristic diffraction peaks of TiO₂ composites supported on modified ACFs with different zinc salts are observed at \( 2\theta = 25.32^\circ, 37.84^\circ, 48.07^\circ, 53.95^\circ, 55.10^\circ, \) and \( 62.75^\circ \) corresponding to 101, 004, 200, 105, 211, and 204 crystal planes, respectively. The XRD patterns of ACF-Nc and ACF-Ac composites show the characteristic diffraction peaks of ZnO at \( 2\theta = 31.73^\circ \) (100), \( 34.36^\circ \) (002), \( 36.20^\circ \) (101), \( 47.47^\circ \) (102), \( 56.53^\circ \) (110), and \( 66.29^\circ \) (200), indicating that ACF-Nc decomposed into ZnO under N₂ atmosphere calcination in the tube furnace. However, the characteristic diffraction peak of ZnO disappears after loading TiO₂, indicating that Zn ions do not exist in the form of ZnO alone during the preparation of TiO₂.

As shown in Fig. 2(b), which can fairly indicate nitrogen adsorption and desorption isotherms of TiO₂/ACF-Ac composites, the same curves could be found of all materials belonging to the type IV isotherm in the IUPAC adsorption isotherm (Zhang et al. 2016b). In the medium- to high-pressure region, due to the difference between the desorption vapor pressure and the saturation pressure in the adsorption process, the adsorption-desorption curves are inconsistent, and all the materials have H4 hysteresis loops (0.5~1.0), manifesting that there may exist irregular pore structure of the composites; furthermore, there is a mixture of micropores and mesopores (Zhao et al. 2012).

The appearance of mesopores may be due to the use of the vacuum ultrasonic impregnation method to make TiO₂ load to the pore interior, thus forming a variety of microporous and mesoporous channels, which lead to a big difference of specific surface area than before. The Barrett-Emmett-Teller (BET) method was applied to calculate the specific surface area, and Barrett-Joyner-Halenda (BJH) methods were performed to test the size and volume of the pore. From Table 1, a negative correlation can be discovered between the specific area of TiO₂/ACF-Ac and Zn(CH₃COO)₂ concentration. This may be due to that the introduction of Zn(CH₃COO)₂ into TiO₂ is more likely to agglomerate in the calcination process, resulting in the increase of the grain size of the composites. On the contrary, the volume of pores and surface area decreased, thereby reducing the photocatalytic degradation efficiency (Anonymous 2014).

From infrared spectra of the samples (Fig. 2(c)), a peak of -OH stretching vibration appears at 3440 cm⁻¹ in all materials. The narrow absorption peak at 1635 cm⁻¹ presents the
bending stretching vibration band of O-H adsorbed on the sample surface in water. The characteristic stretching vibration peak at 700–500 cm$^{-1}$ is observed, thanks to the fluctuation of Ti-O-Ti bond (Wang et al. 2011). The peak of ACF at 1084 cm$^{-1}$ is C-O stretching vibration peak, and there is a characteristic absorption peak in each composites, which can be put down to the combination of TiO$_2$ and C-O bond to form Ti-O-C stretching vibration peak (Eleutério et al. 2020). In TiO$_2$/ACF-Ac composites, the characteristic peaks of 1687–1512 cm$^{-1}$ and 1468–1410 cm$^{-1}$ are the results of dissymmetrical stretching oscillation and balanced stretching oscillation of -COO-, respectively, indicating that there is a double tooth coordination structure (B et al. 2019). The absorption peaks at 672 cm$^{-1}$ ions were Zn-O vibration absorption peaks, indicating that Zn was successfully loaded on ACF.

**Morphology and surface properties**

From the SEM images of samples (Fig. 3), it can be seen that, for all materials, there are many irregularly arranged fiber bands in the activated carbon; for each fiber band, there exists a linear groove and ridge in wire direction. The macropores in fibers facilitate the adsorption capacity of oxygen and toluene gas, and they are also beneficial to the reduction of pressure drop, so that more small molecule gases are rapidly aggregated on the surface of TiO$_2$ (Xiang et al. 2010). SEM images reveal that TiO$_2$ has been successfully loaded on modified ACF, but the morphology of TiO$_2$ on different modified ACFs is different. TiO$_2$ on TiO$_2$/ACF-Hc composites is the most smooth and uniform. TiO$_2$ on TiO$_2$/ACF-Nc is relatively smooth and uniform, but TiO$_2$ on ACF-Ac surface is relatively rough. The number of micropores and mesopores and the specific area of the composites increase owing to this rough structure which improves the adsorption capacity of toluene. The rough structure also increases the contact area between TiO$_2$ and toluene, which is conducive to promoting the photocatalytic reaction.

As shown in the SEM images of ACF-Ac composites with different impregnation times (Fig. 3(d–f)), TiO$_2$ agglomerates gradually with the increase of impregnation times, resulting in TiO$_2$ loading on the surface of ACF in the form of particles. However, in the process of one impregnation, only local TiO$_2$ is loaded on the ACF surface, and the loading of TiO$_2$ is low, which is not conducive to the late photocatalytic reaction. Therefore, in this experiment, the material was impregnated twice.

**XPS analysis**

To precisely analyze the character of TiO$_2$/ACF-Ac composites about its surface composition and valence state, all samples were tested by X-ray photoelectron spectroscopy. TiO$_2$/ACF-Ac composites contain four elements: Zn, Ti, O, and C, indicating that the composites have been successfully prepared. The characteristic peaks in the XPS spectrum of Zn

| Sample | Pore size (nm) | Pore volume (cm$^3$/g) | $S_{BET}$ (m$^2$/g) |
|--------|---------------|-------------------------|---------------------|
| 0.00 mol/L | 2.97 | 0.68 | 1674.65 |
| 0.01 mol/L | 1.81 | 0.53 | 1163.61 |
| 0.05 mol/L | 1.80 | 0.50 | 1117.59 |
| 0.10 mol/L | 1.78 | 0.45 | 1008.74 |

Fig. 3 SEM images of (a) TiO$_2$/ACF-Nc, (b) TiO$_2$/ACF-Hc, and (c) TiO$_2$/ACF-Ac and Zn(CH$_3$COO)$_2$-ACF, impregnated (d) one time, (e) two times, and (f) three times.
(Fig. 4(a)) with a binding energy of 1023.1 eV and 1046.4 eV are assigned to Zn2p\(_{3/2}\) and Zn2p\(_{1/2}\) respectively, indicating that Zn in TiO\(_2/\)ACF-Ac composites exists in the form of +2 valence, which also indicates that the valence state of Zn in the composites does not change during the preparation process (Lirong et al. 2009).

In the analysis of existing research, the O\(_2\) ions in the oxygen vacancy of Zn matrix have some relation to the characteristic peak with a binding energy of 531.6 eV according to the O1s spectra (Wang et al. 2018), and the characteristic peak with a binding energy of 530.5 eV corresponds to the lattice oxygen of TiO\(_2\), which further indicates the composites are successfully prepared (Li et al. 2019). In high-resolution Ti2p spectra (Fig. 4(c)), two main complex peaks were observed at 459.3 and 464.9 eV, corresponding to Ti2p\(_{3/2}\) and Ti2p\(_{1/2}\) spin-orbit splitting photoelectrons of Ti\(^{4+}\), respectively (Zhang et al. 2016d). In the XPS spectra of C1s (Fig. 4(d)), the C peak centered at 284.5 eV represents the C-C=C bond. The presence of C-O-R such as oxygenated carbon species is the genesis of 285.7 eV peak. The peak at 289.0 eV corresponds to the C=O bond (Su-Il et al. 2016). It indicates that the composites contain carbon element and the modified ACFs are successfully synthesized. In summary, the XPS analysis results clearly confirm the formation of TiO\(_2/\)ACF-Ac composites, which supports the analysis results of XRD.

**Electrochemical and optical properties**

The UV-vis diffuse reflectance spectra and transient photocurrent response of samples were investigated to explore the optical properties. As shown in Fig. 5(a), around the UV region with wavelength less than 380 nm, TiO\(_2/\)ACF-Hc showed obvious band gap absorption peak, while in the non-UV region with wavelength greater than 400 nm, there was almost no response. The reason for this phenomenon may be that the decomposition temperature of zinc salt during calcination is different, resulting in different crystallization times of Zn and TiO\(_2\) (Smirniotis et al. 2018). Both TiO\(_2/\)ACF-Ac and TiO\(_2/\)ACF-Nc composites have visible light feedback with wavelength greater than 400 nm. This may be due to the fact that Zn ions enter the lattice of TiO\(_2\) to replace O atoms and form a new doped energy level, thereby reducing the band gap and widening the optical absorption range of TiO\(_2\) that accords with the test results of XPS. By comparison with TiO\(_2/\)ACF-Nc, TiO\(_2/\)ACF-Ac has a wider range of visible light response wavelength, showing more excellent photocatalytic performance. Figure 5 (b) shows the photocurrent curve within 20 s under the bias voltage of 0.0 V and 0.1 M NaSO\(_4\) solution as the electrolyte. After three cycles, the photocurrents still had good reproducibility, indicating that the samples had good stability. Compared with other samples, the TiO\(_2/\)-

![Fig. 4](image.png)

(a) Zn 2p core level spectra. (b) O 1s core level spectra. (c) Ti 2p core level spectra. (d) C 1s core level spectra
ACF-Ac sample has a higher photocurrent intensity, suggesting that its photogenerated electrons and hole separation efficiency is more efficient, which make some works to the enhancement of photocatalytic performance.

**Optimum selection of composites**

In order to select the composites with the best performance among TiO\(_2\) supported on modified ACFs with different zinc salts, the toluene removal performances with the same conditions are tested. When the toluene inlet concentration, relative humidity, gas flow, and light intensity were 1000 mg/m\(^3\), 40%, 120 mL/min, and 24 W, respectively, the effect of concentration of Zn(CH\(_3\)COO)\(_2\) on TiO\(_2\)/ACF-Ac for toluene removal is shown in Fig. 7 (a) and (a'). Compared with bare TiO\(_2\)/ACF, Fig. 7 (a) shows that the adsorption saturation time of Zn(CH\(_3\)COO)\(_2\)-modified materials is longer, and the adsorption equilibrium time of TiO\(_2\)/ACF-Ac composites is up to 40 h. Moreover, with the increase of Zn(CH\(_3\)COO)\(_2\) concentration, the adsorption capacity and photocatalytic properties of TiO\(_2\)/ACF-Ac gradually decrease due to the destructions of the microporous structure and adsorption sites of the composites caused by too much modified solution ions, indicating that a small amount of Zn(CH\(_3\)COO)\(_2\) doping is more conducive to the adsorption and photocatalysis of TiO\(_2\)/ACF-Ac for toluene.

Calcination temperature affects the adsorption and photocatalytic properties of composites by affecting the texture properties and crystallinity (Aristanti et al. 2019). As shown in Fig. 7(b), under different calcination temperatures, the adsorption saturation time of toluene on TiO\(_2\)/ACF-Ac composites is different. When the toluene inlet concentration, relative humidity, gas flow, and light intensity were 1000 mg/m\(^3\), 40%, 120 mL/min, and 24 W, respectively, the adsorption saturation time at 400°C, 450°C, 500°C, and 550°C is 17, 40, 9, and 8 h, individually. As shown in Fig. 7(b'), when the temperature of calcination is lower than 450°C, the photocatalytic efficiency of TiO\(_2\)/ACF-Ac increases with the rise of temperature; In contrast, the photocatalytic efficiency will go down with the continuing rise of temperature. 450°C is the position of the highest removal efficiency. When the calcination temperature exceeds 450°C, the increase of temperature will change the type and amount of oxygen-containing functional groups on the surface of the composites, and reduce the adsorption sites, thereby reduce the adsorption performance of TiO\(_2\)/ACF-Ac composites for toluene (Sun et al. 2015). At the
same time, TiO$_2$ gradually transforms from anatase phase to rutile phase with the increase of calcination temperature, and the anatase content produced at 450°C is the maximal. The dislocation of defects in anatase lattice can produce oxygen vacancies that promote electron-hole separation, and increase the photocatalytic performance of TiO$_2$/ACF-Ac (Horti et al. 2019). As the temperature of calcination rises without interruption, the grain of TiO$_2$ gradually grows, and the phenomenon of sintering or even channel collapse or blockage occurs that eventually change the character of composite specific surface area and catalytic activity, making these performances reduce (Zhang et al. 2016c).

When the toluene inlet concentration, relative humidity, gas flow, and light intensity were 1000 mg/m$^3$, 40%, 120 mL/min, and 24 W, respectively, the performance of toluene removal by TiO$_2$/ACF-Ac with change of impregnation times is shown in Fig. 7 (c) and (c$'$). With the increase of impregnation times, the adsorption capacity and photocatalytic activity of TiO$_2$/ACF-Ac for toluene first increase and then decrease. The saturation adsorption time of TiO$_2$/ACF-Ac composites with one, two, and three impregnation times is 31, 40, and 12 h, respectively. Combined with the analysis of SEM results, it is obvious that the morphologies of the samples are modified by zinc ion doping, which can make the TiO$_2$ loaded on ACF present a rough and porous morphology, thereby improving the adsorption capacity. The loading amount of TiO$_2$ increases as coating times rise, which promotes the improvement of photocatalytic performance. However, when the loading amount is too high, TiO$_2$ would agglomerate and could not be uniformly loaded on the surface of ACF, which reduces the contact area between TiO$_2$ and toluene and the number of active sites, thereby reducing the removal efficiency of toluene.

When the toluene inlet concentration, gas flow, and light intensity were 1000 mg/m$^3$, 120 mL/min, and 24 W, respectively, the content of water vapor was adjusted to evaluate the effect of relative humidity (40%, 60%, 80%) on toluene removal by TiO$_2$/ACF-Ac composites. The results are shown in Fig. 7 (d) and (d$'$). As the index of relative humidity was increased, the TiO$_2$/ACF-Ac character of adsorption capacity for toluene decreases, while the photocatalytic performance increases instead. This is because exorbitant relative humidity will bring excessive vapor molecules which will occupy the adsorption sites of the composites, reducing the contact area between toluene and TiO$_2$/ACF-Ac. In addition, toluene is hydrophobic; when the adsorption sites are occupied by water vapor, toluene can only flow with air, thus reducing the adsorption effect of composites on toluene (Lin et al. 2013).
However, increasing water vapor can accelerate the production of hydroxyl radicals (·OH) that is of vital importance for photocatalytic reaction, and the oxidation of toluene can be decomposed into non-toxic and harmless substances to achieve harmless treatment. Therefore, relative humidity plays a dual role in toluene removal (Ho et al. 2019).

When the toluene inlet concentration, relative humidity, gas flow, and light intensity were 1000 mg/m$^3$, 40%, 120 mL/min, and 24 W, respectively, the effect of different stacking layers for toluene removal is shown in Fig. 7 (e) and (e'). The stacking method of the materials is as follows: one layer of material is placed in the center of the reactor; when the second layer is placed, the distance between the two composites is 2 cm, and the distance between each two pieces of the three layers is 2 cm. The adsorption saturation time of toluene was 15, 33, and 50 h with the layers of the composites being one layer, two layers, and three layers, respectively; moreover, the adsorption and the photocatalytic...
efficiency are improved. With the increase of the stacking layers, the cavities between the layers of the composites and the resistance of toluene molecules increase when passing through the composites, prolonging the residence time of toluene, which can not only improve the adsorption efficiency but also enable the intermediate products to react further, and realize the complete catalytic oxidation of toluene. In addition, the cavities between layers increase the retention time of toluene and prolonged the adsorption saturation time and also make the composites to more fully use light and improve the photocatalytic removal efficiency of toluene.

Ultraviolet light intensity can directly affect the generation of photogenerated electrons, thereby affecting the photocatalytic activity of composites. When the toluene inlet concentration, relative humidity, and gas flow were 1000 mg/m$^3$, 40%, and 120 mL/min, respectively, the effect of different UV light intensities (8W, 16W, 24W) for toluene removal on TiO$_2$/ACF-Ac composites is studied and shown in Fig. 7(f'). With
the increase of light intensity, the absorbability and photocatalytic performance of TiO$_2$/ACF-$\text{Ac}$ for toluene increase. The stronger the light intensity, the more photogenerated electrons and holes excited, and the more strong oxidizing free radicals generated, the higher the toluene removal rate (He et al. 2019). However, the light intensity is not proportional to the toluene removal rate; it is mainly because the stronger intensity of UV light can result in the more obvious thermal effect which is not unfavorable to the adsorption of toluene. However, the desorption rate of toluene from TiO$_2$/ACF-$\text{Ac}$ caused by the thermal effect is lower than the synergistic rate of adsorption–photodegradation. The overall performance is that the toluene removal rate increases with the increase of light intensity (Dilla et al. 2017).

The reacted composites are calcined in a tubular oven at 450°C to explore its cycle performance. When the toluene inlet concentration, relative humidity, gas flow, and light intensity were 1000 mg/m$^3$, 40%, 120 mL/min, and 24 W, respectively, the relationship between the number of cycles and removal efficiency is shown in Fig. 7(g). After three cycles of test, the removal efficiency of toluene still maintains at about 70%, indicating that TiO$_2$/ACF-$\text{Ac}$ composites have good cycle stability, and the slight decrease may be due to that the regeneration process does not completely release the adsorption sites and photocatalytic activity sites of the materials.

**Mechanism analysis of toluene removal by TiO$_2$/ACF-$\text{Ac}$ composites**

Combined with the research content, the synergistic mechanism of adsorption and photodegradation for toluene removal by TiO$_2$/ACF-$\text{Ac}$ composites is shown in Fig. 8 and Eqs. (1)–(7). The doping of Zn(CH$_3$COO)$_2$ makes TiO$_2$ load on the surface of ACF in a rough form, increases the contact area with toluene, and modifies the adsorption character of TiO$_2$/ACF-$\text{Ac}$ to toluene. Toluene is converted into CO$_2$, H$_2$O, and other intermediates via chemical reaction, which promotes the toluene captured by TiO$_2$/ACF-$\text{Ac}$ to transfer to the supericies of TiO$_2$ for the next reaction (Balbayaeva et al. 2018). ACF has good electronic conductivity and can transfer photogenerated $e^-$ and $h^+$ to the electron acceptor through the interface charge transfer, and the large pores between ACF fibers can reduce the mass transfer limitation and accelerate the flow of toluene among them.

TiO$_2$ produces photogenerated $e^-$ and $h^+$ under the excitation of ultraviolet light, and reacts with O$_2$, $\cdot$OH, and H$_2$O on the surface to generate hydroxyl radicals and superoxide radicals (Li et al. 2020b). The toluene molecules which were adsorbed will react with hydroxyl radicals and superoxide radicals and be transformed to CO$_2$, H$_2$O, and other intermediates (Reddy et al. 2015). Moreover, the direct desorption of the generated small molecule substances such as H$_2$O and CO$_2$ from the surface of the composites can achieve the in situ regeneration of the adsorbent.

Previous studies have shown that for the TiO$_2$ catalyst supported on ACF, the high specific surface area and three-dimensional structure of ACF can make the active components of the catalyst well dispersed, which can enhance the absorption of light energy and improve the mass transfer performance inside the catalyst. The strong adsorption properties of ACF can not only promote the photocatalytic performance of nano-TiO$_2$ but also provide support for the renewable performance of TiO$_2$ photocatalytic materials (Chen et al. 2017). In addition, the introduction of TiO$_2$ reduced the blockage of ACF micropore structure, promoted in situ regeneration, and reduced the risk of adsorption material failure caused by the increase of adsorption concentration. Therefore, the synergistic effect of adsorption and photocatalysis increased the removal performance of toluene.

\[
\begin{align*}
\text{TiO}_2 + h\nu &\rightarrow e^- + h^+ \quad (1) \\
O_2 + e^- &\rightarrow \cdot O_2^- \quad (2) \\
H_2O + h^+ &\rightarrow \cdot OH + H^+ \quad (3) \\
\text{OH}^- (\text{surface}) + h^+ &\rightarrow \cdot OH \quad (4) \\
\text{Toluene} + \cdot O_2^- &\rightarrow \text{products} \quad (5) \\
\text{Toluene} + \cdot OH &\rightarrow \text{products} \quad (6) \\
\text{Toluene} + H^+ &\rightarrow \text{products} \quad (7)
\end{align*}
\]

**Analysis of intermediate products**

To further study the reaction process of photocatalytic degradation of toluene, a certain volume of export gas samples was collected and analyzed by SCION SQ GC-MS. The test results indicate that the main intermediate products of toluene photodegradation were benzene (C$_6$H$_6$), phenol (C$_6$H$_5$O), benzaldehyde (C$_7$H$_6$O), and hexane (C$_6$H$_{14}$). The main reaction pathways of toluene photodegradation are proposed in Fig. 9. Under the irradiation of ultraviolet lamp, the photogenerated electrons and hydroxyl radicals are generated, which act on the methyl of toluene to dehydrogenate and generate hydrogen radicals (H·) and benzyl radicals (PhCH$_2$·) that further react with O$_2$ in the system to generate benzyl peroxy radicals (PhCH$_2$O$^\cdot$). The coupling product of PhCH$_2$O$_2$ is unstable and decomposes to benzyl alcohol that contains to be oxidized to form benzaldehyde (Feng et al. 2019). Phenol is produced when methyl groups on toluene are continuously to be oxidized to form benzaldehyde (Feng et al. 2019). Phenol is produced when methyl groups on toluene are further oxidized to form phenylacetic acid under the synergistic effect of ultraviolet light and O$_2$. After absorbing certain photons, toluene will
undergo splitting and isomerization reactions to produce long-chain products, such as hexane.

**Conclusion**

1. TiO$_2$/ACF-Nc, TiO$_2$/ACF-Hc, and TiO$_2$/ACF-Ac were successfully prepared by ultrasonic-assisted sol-gel method. Through the analysis of the crystal structure, morphology, and optical properties of the composites and the removal performance of toluene under the same conditions, the TiO$_2$/ACF-Ac composites with the highest toluene adsorption and photocatalytic performance were selected for subsequent experimental studies.

2. The characterization results of TiO$_2$/ACF-Ac indicated that TiO$_2$ with anatase phase was successfully loaded on ACF modified by Zn(CH$_3$COO)$_2$, and composites with rough surface were prepared. TiO$_2$/ACF-Ac composites contain large amount of oxygen-containing functional groups which are beneficial to the adsorption and photocatalytic oxidation of toluene. The results of optical properties showed that the modified ACF significantly improves the utilization efficiency of sunlight increasing the efficiency of charge transfer and separation of electron-hole pairs.

3. When TiO$_2$/ACF-Ac was calcined at 450°C and impregnated twice, the toluene inlet concentration, relative humidity, gas flow, and light intensity of this system were 1000 mg/m$^3$, 40%, 120 mL/min, and 24 W, respectively, the adsorption saturation time reached 40 h, and photodegradation rate was...
70%. As the index of relative humidity rises, the adsorption performance of TiO_2/ACF-Ac decreases significantly, while the photocatalytic performance increases remarkably.

(4) The toluene removal rate of TiO_2/ACF-Ac composites is positively correlated with the light intensity and the stacking layers of catalysts. After three cycle performance tests, TiO_2/ACF-Ac still had high toluene removal efficiency, indicating that the composites had good cycle performance.

**Acknowledgements** My deepest gratitude goes first and foremost to professor Fang Liu, for her constant encouragement and guidance. I am indebted to professor Chaocheng Zhao owing to his guidance in this manuscript. And I also thank other authors for their contributions to the manuscript.

**Availability of data and materials** The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Author contribution** All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Yuxi Bi and Encheng Sun. The first draft of the manuscript was written by Yuxi Bi and was checked by Encheng Sun and Shuai Zhang. The logic and grammar of the manuscript were examined by Fang Liu and Chaocheng Zhao. The spelling and reference information of the manuscript were checked by Feiran Du and Haidi Wei. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

**Funding** This work was supported by Sinopec-funded Science and Technology Project (320039/YG2010).

**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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