Hydrothermal deposition of CoFe$_2$O$_4$ nanoparticles on activated carbon fibers promotes atrazine removal via physical adsorption and photo-Fenton degradation

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A B S T R A C T

Magnetic CoFe$_2$O$_4$ serves as a promising photo-Fenton reagent, but its low adsorption ability and catalytic activity inhibit the effective removal of atrazine (ATZ). Herein, activated carbon fiber/cobalt ferrite (ACF/CoFe$_2$O$_4$) composites were fabricated by hydrothermal deposition of CoFe$_2$O$_4$ nanoparticles around ACFs. As compared with CoFe$_2$O$_4$ nanoparticles, the ACF/CoFe$_2$O$_4$ composites showed better adsorption ability due to the synergistic effect between CoFe$_2$O$_4$ nanoparticles and ACF felts. The ATZ adsorption trend over the ACF/CoFe$_2$O$_4$ composites matched well with pseudo-first-order and pseudo-second-order kinetics model, suggesting that the diffusion and adsorption reaction played equal contribution to the ATZ adsorption. Notably, the ACFs in the ACF/CoFe$_2$O$_4$ composites decreased the band gap of CoFe$_2$O$_4$ nanoparticles from 1.82 eV to 1.62 eV, facilitating the enhanced photocatalytic activity. In the reaction system of ATZ, H$_2$O$_2$ and ACF/CoFe$_2$O$_4$ composites, the remarkable changes of Co and Fe valence states demonstrated that both Co$^{3+}$/Co$^{2+}$ and Fe$^{3+}$/Fe$^{2+}$ circulations took part in the Fenton-like reaction. The hydroxyl radicals that were generated in the photo-Fenton system effectively induced the oxidative degradation of ATZ. Moreover, the photo-Fenton degradation pathway of ATZ was proposed according to LC-MS analyses. Hence, the ACF/CoFe$_2$O$_4$ composite was a promising photo-Fenton catalyst to remove pesticide pollutants via physical adsorption and photo-Fenton degradation.

1. Introduction

Atrazine (ATZ, 1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) is widely used as a triazine herbicide in agriculture, whose widespread application does serious harm to aqueous environment and human health [1,2]. Considering its hazardous impacts on learning and memory systems, central nervous systems and endocrine, the complete elimination of ATZ from wastewater becomes an urgent challenge [3,4]. Conventional technologies including coagulation, biodegradation, ultrasonic degradation and chemical precipitation are ineffective, because ATZ is a refractory organic compound that exhibited resistant characteristics to chemical reaction and microbial degradation [5-8]. Fortunately, photo-Fenton degradation technology is developed as one of effective advanced oxidation process (AOP) strategies for the purification of resistant wastewater [9-11].

In Fenton systems, Co($^{II}$), Co($^{III}$), Fe($^{II}$) and Fe($^{III}$) ions are activated by electron scavenger agents (H$_2$O$_2$, O$_3$ and Cl$_2$), leading to forming ·OH radicals for the oxidative degradation of organic pollutants into H$_2$O and CO$_2$ [1,12]. In order to overcome the drawback that the soluble metal ions are difficultly separated from the wastewater, spinel-type cobalt ferrite (CoFe$_2$O$_4$) is an alternative Fenton-like reagent because of its magnetic property, stable phase structure and good catalytic activity [13]. Magnetic CoFe$_2$O$_4$ exhibit a high coercivity of approximately 4.3 kOe, which facilitates the rapid separation from a liquid-solid system under an external magnetic field [14,15]. CoFe$_2$O$_4$ semiconductors exhibit light response characteristics, showing excellent photocatalytic activity similar to TiO$_2$, Ag$_2$O, ZnO, g-C$_3$N$_4$ and SnO$_2$ [16-18]. Notably, the bandgap of CoFe$_2$O$_4$ is approximately 1.8 eV, remarkably narrower than TiO$_2$ of 3.0–3.2 eV, which make it match with solar spectrum and possess photocatalytic activity even under visible-light irradiations [19,20]. It is reasonably inferred that the CoFe$_2$O$_4$ can be used as an admired photo-Fenton catalyst for organic wastewater treatment under the
support of sunlight irradiations and electron scavenger agents.

The catalytic degradation process over photo-Fenton catalysts includes adsorption of organic pollutants, heterogeneously catalytic reaction and desorption of degradation products [21]. Despite CoFe₂O₄ is employed for a photocatalyst, its rapid electron-hole recombination may lead low quantum efficiency [22]. The electron acceptors such as Ag, Cu, PPy, carbon nanotube, carbon dot and graphene are generally used to modify CoFe₂O₄ photocatalysts, avoiding the recombination of photo-generated electron-hole pairs [22-25]. Among various carbon materials, activated carbon fibers (ACFs) exhibit the remarkable advantages including great electron storage capacity and high surface areas [21]. On the one hand, ACFs can effectively capture the photo-generated electrons from photocatalysts, and thus contribute to the electron-hole separation [21,26]. On the other hand, the microporous structure and great surface areas of ACFs facilitate the adsorption of organic pollutants, followed by the photodegradation reaction [21,26]. To our best knowledge, ACF/CoFe₂O₄ composites as promising photo-Fenton catalysts are rarely reported for wastewater treatment.

To effectively remove ATZ in wastewater, we firstly constructed ACF/CoFe₂O₄ composites by the hydrothermal deposition of CoFe₂O₄ nanoparticles around the fiber surfaces within ACF felts (Fig. 1). As compared with the other photo-Fenton catalysts, the ACF/CoFe₂O₄ composites exhibited the following advantages: (i) the ACF/CoFe₂O₄ composites were easily separated from the wastewater; (ii) the great surface areas and three-dimensional macropores of ACF/CoFe₂O₄ composites contributed to the adsorption of organic pollutants, facilitating their heterogeneously catalytic degradation; and (iii) the synergistic effect of CoFe₂O₄ and ACFs increased the catalytic activity of photo-Fenton regents. The main aims of this work were to hydrothermally fabricate ACF/CoFe₂O₄ composite, and to investigate its adsorption/catalysis mechanisms for ATZ removal.

2. Experimental

2.1. Materials

ATZ were purchased from Sigma Aldrich. Ethylene glycol (EG, 99 wt %), anhydrous ferric chloride (FeCl₃·5H₂O, 99 wt%), cobalt chloride hexahydrate (CoCl₂·6H₂O, 99 wt%) and anhydrous sodium acetate, tert-Butanol (t-BuOH) (99.5%) and methyl alcohol (MeOH) (99.9%) were purchased from Shanghai Titan Scientific Co., Ltd. The ACF felts by using polyacrylonitrile as precursors were purchased from Jiangsu Sutong Carbon Fiber CO., LTD.

2.2. Preparation of ACF/CoFe₂O₄ composites

ACF felts were treated by aqua regia at room temperature for 24 h. The pre-treated ACF felts were rinsed repeatedly with deionized water and dried at 60 °C. CoCl₂·6H₂O (0.59 g) and FeCl₃·5H₂O (1.35 g) were dissolved in 60 mL EG with a Co:Fe molar ratio of 1:2. Anhydrous sodium acetate (3.60 g) was added to the metal salt solution, followed by ultrasonic stirring for 30 min. The above mixed solution and 0.10 g ACF felts (2.0 cm × 2.0 cm × 0.2 cm) were placed in 100 mL Teflon-lined hydrothermal kettle (Shanghai Qiuini Instrument Technology CO., LTD.). The hydrothermal reaction was performed in an electric thermostatic drying oven (DHG-9140B, Shanghai Qiuini Instrument Technology CO., LTD.) at 180 °C for 24 h. The pressure inside the hydrothermal reactor was kept at approximately 3 MPa. Finally, the products (ACF/CoFe₂O₄ composites) were washed with deionized water for 5 times and then dried at 60 °C for 48 h. The CoFe₂O₄ nanoparticles were prepared by the same method without adding ACF felts.

2.3. Adsorption and photo-Fenton degradation tests

For the adsorption kinetics experiments, 0.15 g ACF felts, CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were added into 500 mL ATZ solution (15 mg/L), respectively. The pH value of the ATZ solution was adjusted to 4.0 by 5.0 wt% HNO₃ solution, and it did not change remarkably during the whole adsorption procedure. The ATZ adsorption procedure was carried out at room temperature (25 ± 2 °C) with the magnetic stirring of 170 r/min under a dark condition. At the as-given time intervals, 3.00 mL ATZ solution was transferred to a colorimetric dish, and its concentration was characterized by UV–vis spectrophotometer (UV-5500 PC, Shanghai Metash Instruments CO., LTD., Shanghai, China) at a wavelength of 223 nm.

For the photo-Fenton degradation tests, 0.15 g ACF felts, CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were placed in 500 mL ATZ solution (15 mg/L), respectively. A H₂O₂ solution (0, 2, 3, 4 or 8 mmol/L) was added to the ATZ solution. The pH value was adjusted to 4.0 by 5.0 wt% HNO₃ solution. The photo-Fenton catalytic tests were performed under the illumination of xenon lamp (300W, PLSSXE300, Beijing Felrai Technology Co., Ltd., China) with a wavelength range of 320–780 nm at room temperature. At the as-given time intervals, 3.00 mL ATZ solution was transferred to a colorimetric dish. The absorbance of the ATZ solution was characterized by UV–vis spectrophotometer (UV-5500 PC, Shanghai Metash Instruments CO., LTD.) at a wavelength of 223 nm, and the corresponding concentration was
calculated according to the Beer-Lambert’s law [27]. The photo-Fenton catalytic activities were evaluated according to the removal amounts of ATZ. For the concentration of H₂O₂ tests, the 5.0 mL test solution was added to a mixture of 100.0 mL deionized water and 10.0 mL H₂SO₄ solution (20.0 wt%). The mixed solution was titrated with KMnO₄ solution (0.02 mol/L) until the solution was reddish. The concentration of H₂O₂ was calculated according to the titer of KMnO₄ solution. The recycle tests of the ACF/CoFe₂O₄ composites were performed for four times in the ATZ solutions with 3.0 mmol H₂O₂ under light irradiation. For the second, third and fourth recycle tests, the ACF/CoFe₂O₄ composites were remained in the solution without any treatment. The appropriate amounts of ATZ were added into the previous solutions to keep the ATZ concentrations at 15 mg/L.

2.4. Characterisation

The phases of ACF felts, CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were analyzed by X-ray diffraction (XRD, Bruker D8) with a scanning angle range of 2θ = 10–80°. The morphology of ACF/CoFe₂O₄ composites were observed by field emission scanning electron microscopy (FESEM, MX2600, CamScan). The ACF/CoFe₂O₄ composites were calcined in a muffle furnace (SX2-5-120, Shanghai Yifeng Electric Furnace CO., LTD) at 900 °C for 2 h. According to the mass change before and after the calcination, the weight percentages of ACFs and CoFe₂O₄ nanoparticles in the ACF/CoFe₂O₄ composites were calculated. The elements in the ACF/CoFe₂O₄ composites were recorded by energy-dispersive spectrometry (EDS). The hydrophilic experiment over ACF felts was performed on contact angle instrument (JC2000D3, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd, China) using a drop of deionized water. An X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) was employed to characterized the element valence states of ACF/CoFe₂O₄ composites. The binding energies of the atoms were calibrated against a C1s of 284.6 eV. The light responses of the ACF felts, CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were tested by UV–vis diffuse spectrophotometer (UV-3600, Shimadzu) under the wavelength range of 250–800 nm. The band gap energies (Eₜ) of CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were calculated according to the Tauc plots [28]. The Bruauer–Emmett Teller (BET) surface areas of ACF felts, CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were analyzed by surface area and pore size analyzer (Nova 4000e, Quantachrome). The photoluminescence (PL) spectra were characterized by a fluorescence spectrophotometer (F-4600, Hitachi) with the excitation source of λ = 408 nm. The transient photocurrents of ACF felts, CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were measured by electrochemical workstation (CHI660E, Shanghai Chenhua Instruments, China) using a 50 s on/off cycle at a bias voltage of 0.5 V vs. SCE. The sample served as a working electrode, Ag/AgCl electrolyte served as a reference electrode, and the platinum plate served as a counter electrode. The 0.5 M Na₂SO₄ solution was used as electrolyte and xenon lamp (3000W, PLSSXE300, Beijing Feilai Technology Co., Ltd., China) served as excited light source. For the radical inhibition tests, 0.15 g ACF/CoFe₂O₄ composites were placed in 500 mL ATZ solution (15 mg/L). The H₂O₂ solution (3.0 mmol/L) was added to the ATZ solution. The pH value was adjusted to 4.0 by 5.0 wt% HNO₃ solution. 3 mol t-BuOH or MeOH solutions were added to the ATZ solution. The radical inhibition tests were performed under the illumination of xenon lamp (300 W, PLSSXE300, Beijing Feilai Technology Co., Ltd., China) with a wavelength range of 320–780 nm at room temperature. Thermogravimetric and differential scanning calorimetry analysis (TG-DSC, STA449F3 Jupiter, Netzsch) was performed in air atmosphere from 25 to 800 °C at a heating rate of 10 °C/min. Liquid chromatography-mass spectrometry (LC-MS, Agilent 1290 Infinity II-UltiVap) was used to analyze the photo-Fenton degradation intermediates of ATZ over ACF/CoFe₂O₄ composites.

3. Results and discussion

3.1. Phases of ACF/CoFe₂O₄ composites

The phase structures of the ACF felts, CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were characterized by XRD patterns (Fig. 2). ACFs exhibited a typical amorphous characteristic, as confirmed by the steamed bun peak at around 2θ = 22° (Fig. 2a). For the CoFe₂O₄ nanoparticles, the diffraction peaks 2θ = 35.5°, 43.5°, 57.2° and 62.7° corresponded to (311), (400), (511) and (440) planes of the spinel structure, respectively (Fig. 2b). The ACF/CoFe₂O₄ composites exhibited the characteristic peaks of both ACFs and CoFe₂O₄ (Fig. 2c). The weight percentages of ACFs and CoFe₂O₄ nanoparticles in the composites were 86.1% and 13.9%, respectively. The crystal size of CoFe₂O₄ was calculated according to the (311) crystal plane by the Scherrer equation. The crystal size of CoFe₂O₄ in the ACF/CoFe₂O₄ composites was approximately 11.7 nm.

3.2. Morphology of ACF/CoFe₂O₄ composites

The ACF felts were constructed by many microfilaments with the diameter of ~15 μm (Fig. 3a–c). The interlaced aggregation of the microfilaments contributed to forming the macropores, which facilitated the mass transport of organic pollutants from wastewater to adsorbent interior (Fig. 3a). The high-resolution FESEM images indicated that the ACFs exhibited smooth surfaces (Fig. 3b and c). After treatment with aqua regia, the ACF felts exhibited hydrophilicity, as confirmed by the contact angle of 0° (Fig. S1). The hydrothermal process supported in situ deposition of CoFe₂O₄ nanoparticles around the ACFs, leading to the formation of ACF/CoFe₂O₄ composites (Fig. 3d–f). The element distribution images of Co and Fe further demonstrated the uniform distribution of CoFe₂O₄ nanoparticles on the ACFs (Fig. 3g and h). The chemical elements of ACF/CoFe₂O₄ composites were composed of C, Fe, Co and O, as determined by EDS pattern (Fig. 3i). The C element was mainly derived from the ACFs, while the Fe, Co and O elements were derived from the CoFe₂O₄ nanoparticles. The particle sizes of CoFe₂O₄ particles on the ACFs was distributed around 87 nm (Fig. 3i), as confirmed by the particle size distribution histogram (Fig. S2). In the absence of ACF felts, the sizes of the pure CoFe₂O₄ particles were mainly distributed around 27 nm, which were lower than those in the ACF/CoFe₂O₄ composites (Figs. S2 and S3). The above results demonstrated that the ACFs could remarkably affect the particle size CoFe₂O₄ particles. During the hydrothermal reaction procedure, the —OH and —COOH functional groups on the ACFs that were generated due to the treatment of aqua regia...
served as the nucleation sites for CoFe$_2$O$_4$ nanoparticles. The crystal size of CoFe$_2$O$_4$ in the ACF/CoFe$_2$O$_4$ composites was only approximately 11.7 nm, as calculated according to the XRD pattern (Fig. 2). The ACFs supported the aggregation of these CoFe$_2$O$_4$ nanocrystals into the agglomeration with the greater particle sizes. The pore volumes, pore sizes and surface areas of ACFs, ACF/CoFe$_2$O$_4$ composites and CoFe$_2$O$_4$ nanoparticles were calculated according to the N$_2$ adsorption–desorption isotherms (Fig. S4 and Table S1). The pure ACF felts possessed great pore volume of 0.64 cm$^3$/g and BET surface area of 1248 m$^2$/g (Table S1). The pure CoFe$_2$O$_4$ nanoparticles did not have

Fig. 3. (a, b, c) FESEM images of ACFs, (d, e, f) FESEM image of ACF/CoFe$_2$O$_4$ composites, (g) Co element distribution map, (h) Fe element distribution map, and (i) EDS pattern of ACF/CoFe$_2$O$_4$ composites.

Fig. 4. XPS spectra of ACF/CoFe$_2$O$_4$ composites before the photo-Fenton reaction: (a) wide-scan spectrum, (b) C1s, (c) Co2p and (d) Fe2p.
porous structure, leading to the low BET surface area of 44 m²/g. After the combination of ACF felts and CoFe₂O₄ nanoparticles, the pore volume and surface area of the ACF/CoFe₂O₄ composites arrived at 0.55 cm³/g and 964 m²/g, respectively (Table S1). The ACF/CoFe₂O₄ composites possessed the micropores with pore sizes of 1.54/1.85 nm and mesopores with pore size of 3.95 nm. The micropores were mainly derived from the ACFs (Table S1), while the mesopores were ascribed to the aggregates of CoFe₂O₄ nanoparticles (Fig. 3). The great surface areas of catalysts made it easy to capture the organic pollutants on their surfaces [29].

3.3. Valence states of ACF/CoFe₂O₄ composites

The valence states of the ACF/CoFe₂O₄ composites and CoFe₂O₄ nanoparticles before the photo-Fenton reaction were characterized by XPS spectra (Figs. 4 and S5). The wide-scan XPS spectrum indicated that the ACF/CoFe₂O₄ composites consisted of C, Fe, Co and O elements (Fig. 4a), which was in good agreement with the EDS results (Fig. 3). The surface atomic contents of ACF/CoFe₂O₄ composites were calculated from the following equation:

\[
N_A = \frac{I_A}{S_F}
\]

(1)

\[
C_A = \frac{N_A}{\sum N_i} \times 100
\]

(2)

where \(I_A\) was peak area, \(S_F\) was sensitivity factor, \(N_A\) was normalized area, \(C_A\) was atomic percent. The atomic percentages of C, O, Fe, and Co were approximately 50.15%, 34.12%, 10.45% and 5.28%, respectively. The atomic ratio of Co:Fe was 1.19, much similar to the stoichiometric ratio of CoFe₂O₄. The C1s spectrum of the ACF/CoFe₂O₄ composites were split into several peaks at 284.6, 285.7 and 288.0 eV (Fig. 4b), which corresponded to the \(\text{C} = \text{C} - \text{C} - \text{C}, \text{C} - \text{O} \) and \(\text{O} - \text{C} = \text{O}\) bonds, respectively [30,31]. The C–OH and –COOH groups in the ACFs that were created by aqua regia treatment provided active sites for the uniform deposition of CoFe₂O₄ nanoparticles on their surfaces (Fig. 3). Interestingly, the characteristic peaks in the Co2p and Fe2p XPS spectra of the ACF/CoFe₂O₄ composites were much similar to those of the CoFe₂O₄ nanoparticles, suggesting that the ACFs had no obvious effect on the valence states of both Co and Fe ions (Fig. 4 and S5). The Co2p XPS spectrum was deconvoluted into five peaks at 780.2, 781.4, 786.2, 796.2 and 802.5 eV (Fig. 4c). The spin-orbital peaks due to Co2p₁/₂ and Co2p₃/₂ located respectively at 796.2 and 780.2 eV as well as the corresponding satellite peaks at 802.5 and 786.2 eV [32–34]. The characteristic peaks of Co³⁺ ions were not detected in the Co2p XPS spectrum (Fig. 4c and S5b). For the Fe2p XPS spectrum, the characteristic peaks of Fe2p₁/₂ and Fe2p₃/₂ located at 710.9 eV (octahedral site) and 713.3 eV (tetrahedral site), while those of Fe2p₁/₂ located at 724.5 eV [35,36]. The satellite peak located at 718.3 and 733.2 eV [35]. The binding energy peak at 709.8 eV due to Fe²⁺ was not detected in Figs. 4d and S5c, demonstrating that only Fe³⁺ ions existed in the CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites [37,38].

3.4. Optical response of ACF/CoFe₂O₄ composites

The optical properties of the ACF/CoFe₂O₄ composites were investigated by UV-Vis diffuse reflectance spectroscopy using the pure ACF felts and CoFe₂O₄ nanoparticles as control groups (Fig. 5). In the wavelength range of 250–800 nm, the ACF felts exhibited better optical absorption property than the pure CoFe₂O₄ nanoparticles (Fig. 5a). As compared with the CoFe₂O₄ nanoparticles, the incorporation of ACFs significantly improved the optical absorption capacity of the ACF/CoFe₂O₄ composites (Fig. 5a). The CoFe₂O₄ was a semiconductor, and its absorption peak located at around 450 nm. After the hydrothermal deposition of CoFe₂O₄ nanoparticles on the ACF felts, the corresponding absorption peak became broad and shifted to 475 nm (Fig. 5a). According to the Tauc plots (Fig. 5b), the band gap energies (\(E_g\)) of CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were calculated by the following formula [28]:

\[
(\alpha h\nu)^2 = A(h\nu - E_g)
\]

(3)

where \(\alpha\), \(h\nu\) and \(A\) are absorption coefficient, photon energy and a constant, respectively. Based on the linear region of \((\alpha h\nu)^2\) versus \(h\nu\) (Fig. 5b), the \(E_g\) values of CoFe₂O₄ nanoparticles and ACF/CoFe₂O₄ composites were calculated as 1.82 and 1.62 eV, respectively. Although
the ACF felts were not a semiconductor, they remarkably decreased the band gap energy of the CoFe$_2$O$_4$ nanoparticles in the composites.

Fig. 5c showed the PL spectra of ACF/CoFe$_2$O$_4$ composites, CoFe$_2$O$_4$ nanoparticles and ACF felts by using a xenon lamp as excitation source ($\lambda$ = 408 nm). The ACF felts had no obvious PL characteristic peak in the range of 420–580 nm. A strong peak at around 450 nm was detect in the PL spectrum of CoFe$_2$O$_4$ nanoparticles. Notably, the incorporation of ACFs remarkably decreased the peak intensity of ACF/CoFe$_2$O$_4$ composites as compared with CoFe$_2$O$_4$ nanoparticles (Fig. 5c). The reduced peak intensity for ACF/CoFe$_2$O$_4$ composites suggested that the ACFs contributed to hinder the electron-hole recombination [39]. Under the light irradiation, the as-generated electrons from CoFe$_2$O$_4$ nanoparticles could transfer to ACF felts [26,40]. Moreover, the photocurrent responses of the samples were used to characterize the separation efficiencies of photogenerated electrons (Fig. 5d). ACF felts had no obvious response, while CoFe$_2$O$_4$ nanoparticles and ACF/CoFe$_2$O$_4$ composites had obvious response characteristics between light on and light off (Fig. 5d). The ACF/CoFe$_2$O$_4$ composites showed the strongest photocurrent intensity among three samples, demonstrating that the ACF/CoFe$_2$O$_4$ composites had the best photogenerated electron-hole separation efficiency [41,42].

3.5. Adsorption properties of ACF/CoFe$_2$O$_4$ composites for ATZ removal

Under the conditions without both H$_2$O$_2$ and light irradiation, the ATZ removal over ACF felts, CoFe$_2$O$_4$ nanoparticles and ACF/CoFe$_2$O$_4$ composites was related to physical adsorption rather than catalytic degradation. The adsorption abilities of ACF felts, CoFe$_2$O$_4$ nanoparticles and ACF/CoFe$_2$O$_4$ composites were tested by the immersion of these adsorbents into an ATZ solution under dark conditions without adding H$_2$O$_2$ (Fig. 6). For all the adsorbents, the ATZ concentrations gradually decreased with time from 0 to 15 h (Fig. 6a). After 15 h, the ATZ removal efficiencies for the ACF felts, CoFe$_2$O$_4$ nanoparticles and ACF/CoFe$_2$O$_4$ composites arrived at 77.7%, 15.2% and 86.7%, respectively (Fig. 6b). Among three samples even under the same adsorbent weights, the ACF/CoFe$_2$O$_4$ composites possessed the best adsorption activity. The ATZ adsorption mechanism over these adsorbents was investigated according to the pseudo-first-order and pseudo-second-order kinetics models [43]:

\[
\frac{dq}{dt} = k_1(q_e - q_t)
\]

or

\[
q_t = q_e \left(1 - e^{-kt}ight)
\]

\[
\frac{dq}{dt} = k_2(q_t - q_e)^2
\]

or

\[
t = \frac{1}{kw^2} \cdot \frac{1}{q_t}
\]

where $q_t$ (mg/g) and $q_e$ (mg/g) were ATZ adsorption amounts at time points ($t$) and adsorption equilibrium state, respectively. $k_1$ (h$^{-1}$) and $k_2$ (mg g$^{-1}$ h$^{-1}$) were kinetics constants. The ATZ adsorption curves over the CoFe$_2$O$_4$ nanoparticles, ACF felts and ACF/CoFe$_2$O$_4$ composites were fit with the pseudo-first-order kinetics model ($R^2 > 0.99$), and the adsorption kinetics equations were as followed:

\[
q_t = 7.621(1-e^{-2.004t}); \quad R^2 = 0.987
\]

\[
q_t = 37.885(1-e^{-1.017t}); \quad R^2 = 0.993
\]

\[
q_t = 42.441(1-e^{-0.809t}); \quad R^2 = 0.997
\]

Moreover, the ATZ adsorption curves over the CoFe$_2$O$_4$ nanoparticles, ACF felts and ACF/CoFe$_2$O$_4$ composites were fit with the pseudo-second-order kinetics model ($R^2 > 0.99$), and the adsorption kinetics equations were as followed:

<table>
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<th>Catalyst</th>
<th>$q_{exp}$ (mg g$^{-1}$)</th>
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<th>Pseudo second-order kinetic model</th>
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The pseudo-first-order kinetics model was fit to describe a diffusion-controlled process, while the pseudo-second-order kinetics model was employed to demonstrate the adsorption reaction-controlled process at the interfaces of the liquids and adsorbents \[44\]. The ATZ adsorption performances over the \( \text{CoFe}_2\text{O}_4 \) nanoparticles, ACF felts and ACF/CoFe\(_2\text{O}_4\) composites were fit with both the pseudo-first-order and pseudo-second-order kinetics models, suggesting that the diffusion and adsorption reaction played equal contribution to the ATZ adsorption. The pseudo-first-order and pseudo-second-order kinetics parameters for the \( \text{CoFe}_2\text{O}_4 \) nanoparticles, ACF felts and ACF/CoFe\(_2\text{O}_4\) composites were listed in Table 1. The ATZ diffusion rates and adsorption reaction rates over the adsorbents depended on kinetics rate constants \( k_1 \) and \( k_2 \) values, respectively. The sequences of both the \( k_1 \) and \( k_2 \) values were as followed: CoFe\(_2\text{O}_4 \) nanoparticles \( > \) ACF felts \( > \) ACF/CoFe\(_2\text{O}_4\) composites. The CoFe\(_2\text{O}_4 \) nanoparticles with a powder structure contributed to the increase of the ATZ diffusion and adsorption reaction rates. However, the ACF felts or ACF/CoFe\(_2\text{O}_4\) composites with a bulk structure might inhibit the ATZ adsorption process. Fortunately, the ACF/CoFe\(_2\text{O}_4\) composites had the experimental and theoretical equilibrium adsorption amounts among all groups (Table 1), which was attributed to the synergistic effect between ACFs and CoFe\(_2\text{O}_4\). On the one hand, the ACF felts possessed the great pore volume of 0.64 cm\(^3\)/g and BET surface area of 1248 m\(^2\)/g, facilitating the physical adsorption of ATZ (Table S1). After ATZ adsorption for 15 h, the corresponding pore volume and BET surface area of ACF felts decreased to 0.45 cm\(^3\)/g and BET surface area of 807 m\(^2\)/g, respectively. At the same time, the pore sizes of ACF felts decreased from 1.30, 1.62, 1.94 nm to 1.20, 1.48 and 1.76 nm, respectively (Fig. S4d and Table S1). The above results demonstrated that the ATZ could enter in the pore interior of the ACFs during the adsorption procedure. The incorporation of the ACFs remarkably increased the surface areas of the ACF/CoFe\(_2\text{O}_4\) composites, and thus improved their ATZ adsorption ability (Fig. 6 and Table S1). On the other hand, the CoFe\(_2\text{O}_4\) nanoparticles contributed to the ATZ adsorption on the ACF/CoFe\(_2\text{O}_4\) composites. The SEM images indicated that the CoFe\(_2\text{O}_4\) nanoparticles uniformly deposited around ACFs in the ACF/CoFe\(_2\text{O}_4\) composites (Fig. 3). These CoFe\(_2\text{O}_4\) nanoparticles would hold back the ATZ pollutants transfer from the solution to the ACFs, leading to the lower adsorption rates of the ACF/CoFe\(_2\text{O}_4\) composites than those of the pure ACF felts within 2 h (Fig. 6). At the same time, the CoFe\(_2\text{O}_4\) nanoparticles that served as a shield layer hindered the ATZ...
Comparison of different catalysts for ATZ removal.

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>ATZ (mg/L)</th>
<th>pH</th>
<th>Catalyst (g/L)</th>
<th>Time (min)</th>
<th>Degradation efficiency (%)</th>
<th>References</th>
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<tr>
<td>Cds/RGO/g-C3N4</td>
<td>10</td>
<td>–</td>
<td>0.20</td>
<td>300</td>
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<tr>
<td>ZnO-g-C3N4/MoS2</td>
<td>10</td>
<td>–</td>
<td>0.3</td>
<td>300</td>
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<td>[46]</td>
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<tr>
<td>TiO2/BEW</td>
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<td>1.5</td>
<td>70</td>
<td>94.0</td>
<td>[47]</td>
</tr>
<tr>
<td>W-TiO2/clay</td>
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<td>6.2</td>
<td>0.25</td>
<td>240</td>
<td>&gt;90.0</td>
<td>[48]</td>
</tr>
<tr>
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<td>–</td>
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<td>18</td>
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<td>60</td>
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<td>[50]</td>
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<td>0.03</td>
<td>20</td>
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<td>[51]</td>
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<td>15</td>
<td>4.0</td>
<td>0.3</td>
<td>240</td>
<td>96.0</td>
<td>This work</td>
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</table>

Fig. 8. ATZ removal efficiencies over the ACF/CoFe2O4 composites after four consecutive cycles in the ATZ solutions with 3.0 mmol H2O2 under light irradiation.

3.6. Photo-Fenton degradation of ATZ over ACF/CoFe2O4 composites

In order to confirm whether Fenton-like reaction occurred during the ATZ removal procedure, the ACF felts, CoFe2O4 nanoparticles and ACF/CoFe2O4 composites were added in the mixed solution of ATZ and H2O2 under dark conditions, respectively (Fig. 7a and b). The ATZ removal performance over the ACF felts in the presence of H2O2 was much similar to that without adding H2O2 (Figs. 6b and 7b), suggesting that no Fenton-like reaction took place over the pure ACF felts. After the ATZ removal for 15 h, the removal efficiencies over the CoFe2O4 nanoparticles and ACF/CoFe2O4 composites in the presence of H2O2 arrived at 25.5% and 93.0%, respectively (Fig. 7b), which were significantly greater than those without H2O2 (Fig. 6b). The improved ATZ removal rates over the CoFe2O4 nanoparticles and ACF/CoFe2O4 composites were ascribed to the Fenton-like reaction occurred in the presence of H2O2.

The photo-Fenton degradation tests were carried out by soaking the ACF felts, CoFe2O4 nanoparticles and ACF/CoFe2O4 composites in ATZ solution with 3.0 mmol/L H2O2 under light irradiation (Fig. 7c and d). The ACF felts are not a semiconductor material, so they exhibit none photocatalytic activity. Both the H2O2 and light irradiation did not affect the ATZ removal performances of the ACF felts (Figs. 6 and 7). Interestingly, the CoFe2O4 nanoparticles and ACF/CoFe2O4 composites possessed better ATZ removal activity in the presence of H2O2 and light irradiation than that without H2O2 and/or light irradiation (Figs. 6 and 7). In the presence of H2O2 and light irradiation, the ATZ removal efficiencies over the CoFe2O4 nanoparticles and ACF/CoFe2O4 composites reached 39.0% and 97.6%, respectively, suggesting that the photocatalytic degradation of ATZ took place for the above two samples. The H2O2 concentrations greatly affected the catalytic activity of the ACF/CoFe2O4 composites (Fig. 7e and f). The ATZ removal efficiencies over the ACF/CoFe2O4 composites rose with increasing H2O2 concentrations from 0 to 3 mmol/L, and then descended as its concentrations increased further from 3 to 8 mmol/L (Fig. 7f).

The reusability of the catalysts was one of essential requirements in the industrial applications. The recycle tests of the ACF/CoFe2O4 composites were performed for four times under the same conditions. For the second, third and fourth recycle tests, the appropriate amounts of ATZ were added into the previous solutions to keep the ATZ concentrations at 15 mg/L. The ATZ removal performances over the ACF/CoFe2O4 composites showed the similar trends among four cycles (Fig. 8). Within 15 h of treatment time, the ATZ removal efficiencies for the first, second, third and fourth cycles arrived at 97.6%, 97.2%, 96.0% and 95.4%, respectively (Fig. 8). With the increase of cycle index, the ATZ removal efficiencies decreased slightly because of the following possibilities: (i) the as-adsorbed ATZ pollutants or intermediate products remained in the pores of the ACFs, and (ii) part of CoFe2O4 nanoparticles came off from the ACF/CoFe2O4 composite.

3.7. Synergistic mechanism between adsorption and photo-Fenton degradation for ATZ removal

Upon to now, various catalysts such as Cds/RGO/g-C3N4, ZnO-g-C3N4/MoS2, TiO2 nanoparticles involved boron enrichment waste (TiO2-BEW), W-TiO2/clay, Ag-WO3/SBA-15 and Nb2O5/CoFe2O4 have developed to remove ATZ [45–50]. Li et al. used drinking water treatment residuals (WTRs) as iron source and catalyst support [51]. The as-fabricated CoFe2O4@WTRs composites exhibited the ATZ degradation efficiency of 98.2%, but they were only fit for low concentration pollutants [51]. Notably, the above catalysts lacked enough adsorption capacity, and thus decreased the low ATZ removal efficiency (Table 2). Although chemically activated carbon could serve as a highly efficient adsorbent, it became ineffective as it reached adsorption saturation [53]. Interestingly, the ACF/CoFe2O4 composites exhibited the high ATZ removal efficiency of 96.0% because of the synergistic effect between desorption from the composites. The ACF/CoFe2O4 composites showed better ATZ adsorption capacity than the pure ACF felts and CoFe2O4 nanoparticles because of the synergistic effect rather than the simple linear combination. The similar experiment results were detected in our previous work [26]. The TiO2/ACF porous composites possessed better toluene adsorption ability than the single component although the adsorption capacity of TiO2 nanoparticles was much lower than that of ACF felts [26].
adsorption and photo-Fenton degradation (Figs. 6 and 7). The combination of ACF felts and CoFe$_2$O$_4$ nanoparticles made the ATZ removal efficiency of ACF/CoFe$_2$O$_4$ composites arrive at 86.7% even under a dark condition without adding H$_2$O$_2$ (Fig. 6). In order to further evaluate the adsorption of the ACF/CoFe$_2$O$_4$ composites on ATZ removal, the samples before and after the photo-Fenton degradation procedure were characterized by TG-DSC analyses (Fig. S6). For the raw ACF/CoFe$_2$O$_4$ composites, the weight loss of 2% in the range of 20–100 °C corresponded to the volatilization of adsorbed water, and the weight loss of 21% in the range of 150–800 °C corresponded to the part decomposition of ACFs (Fig. S6a). Notably, the weight loss in the range of 150–800 °C increased to 52% for the ACF/CoFe$_2$O$_4$ composites after the photo-Fenton degradation procedure (Fig. S6b). The obvious differences of weight loss in the range of 150–800 °C between before and after the degradation reaction suggested that the ACF/CoFe$_2$O$_4$ composites could effectively adsorb ATZ pollutants or intermediate products. The as-adsorbed ATZ on the ACF/CoFe$_2$O$_4$ composites led to the close contact between organic pollutants and catalysts, subsequently supporting the heterogeneously catalytic degradation via photo-Fenton reaction. In turn, the photo-Fenton degradation of ATZ on the ACF/CoFe$_2$O$_4$ composites continuously kept their physical adsorption unsaturation. The adsorption rates of adsorbents were positively correlated with the concentration gradients between the bulk wastewater and adsorbents [52, 53]. The ATZ removal over the pure ACF felts was mainly attributed to physical adsorption. The ATZ removal efficiencies over the ACF felts for the first, second, third and fourth cycles were 78.2%, 60.3%, 45.1% and 35.0%, respectively (Fig. S7). With increasing cycle times, the ACF felts began to reach an adsorption saturation, leading to the remarkably decrease of ATZ removal efficiencies. Fortunately, the catalytic degradation of ATZ on the ACF/CoFe$_2$O$_4$ composites increased the concentration gradients, and thus facilitated the ATZ adsorption by the adsorbents again. Even if the ATZ pollutants were continuously added in the recycle tests, the ATZ removal performances over the ACF/CoFe$_2$O$_4$ composites possessed the similar trends among four cycles (Fig. 8). The above results further demonstrated that part of ATZ pollutants were catalytically degraded in the previous cycle. Hence, the synergistic effects between physical adsorption and photo-Fenton degradation contributed to the effective ATZ removal. On the contrary, the ATZ removal efficiency over the CoFe$_2$O$_4$ nanoparticles was only 39.0% even after 15 h of treatment time (Fig. 7d). Firstly, the dispersion of the pure CoFe$_2$O$_4$ nanoparticles was significantly worse than that on the ACFs. The aggregates of the CoFe$_2$O$_4$ nanoparticles decreased the surface area to only 44.1 m$^2$/g, which could not effectively capture enough ATZ pollutants for the subsequently photo-Fenton degradation. Secondly, the amount of H$_2$O$_2$ (3.0 mmol/L) was much short for the ATZ mineralization. The H$_2$O$_2$ concentrations over the CoFe$_2$O$_4$ nanoparticles decreased rapidly from 3.0 mmol/L to 0.2 mmol/L in the initial stage of 4 h (Fig. S8). The ATZ removal efficiency descended with the decrease of H$_2$O$_2$, and then it was kept nearly constant after 4 h because of the H$_2$O$_2$ consumption (Fig. 7d and S8).

In order to investigate photo-Fenton degradation mechanism of ATZ, the valence state characteristics of the ACF/CoFe$_2$O$_4$ composites after the photo-Fenton reaction were characterized by XPS spectra (Fig. 9). There was no obvious difference of C1s spectra between before and after the photo-Fenton reaction, suggesting that the valence states of ACFs did not change remarkably during the ATZ degradation (Figs. 4b and 9b). For the fresh ACF/CoFe$_2$O$_4$ composites, only Co$^{2+}$ and Fe$^{3+}$ ions were observed by XPS spectra (Fig. 4c and d). Besides the Co$^{2+}$ and Fe$^{3+}$ ions, the Co$^{3+}$ and Fe$^{2+}$ ions were detected in the ACF/CoFe$_2$O$_4$ composites after the photo-Fenton reaction (Fig. 9). The peak at 782.3 eV in Fig. 9c was assigned to the Co$^{3+}$ ions at octahedral sites [54], while that at 709.8 eV in Fig. 9d was ascribed to the Fe$^{2+}$ ions at octahedral sites [37]. For the ACF/CoFe$_2$O$_4$ composites after the photo-Fenton reaction time of 15 h, the molar ratios of Co$^{2+}$/Co$^{3+}$ and Fe$^{2+}$/Fe$^{3+}$ arrived at 1.95 and 0.04, respectively. Therefore, it could be inferred that the photo-Fenton reaction supported the transfer of Co$^{2+}$ and Fe$^{3+}$ ions into Co$^{3+}$ and Fe$^{2+}$ ions, respectively.

The presence of H$_2$O$_2$ in the reaction system facilitated the occurrence of Fenton-like reaction over the CoFe$_2$O$_4$ nanoparticles or ACF/CoFe$_2$O$_4$ composites. As the Fenton-like reaction took place, the Co$^{2+}$ ions in the CoFe$_2$O$_4$ were oxidized into Co$^{3+}$ as well as the generation of hydroxyl radicals (·OH) [55]. At the same time, the as-produced Co$^{3+}$ ions in the CoFe$_2$O$_4$ nanoparticles.
ions and the Fe$^{3+}$ ions in the CoFe$_2$O$_4$ could react further with H$_2$O$_2$ to respectively form Co$^{2+}$ and Fe$^{2+}$ ions (Fig. 9). The as-formed Fe$^{3+}$ ions took part in the Fenton-like reaction, too [56]. The circulation reactions of Co$^{2+}$/Co$^{3+}$ and Fe$^{2+}$/Fe$^{3+}$ were expressed as followed:

$$\text{Co}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Co}^{2+} + \text{OH}^- + \cdot\text{OH}$$  \hspace{1cm} (14)
$$\text{Co}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Co}^{2+} + \cdot\text{OOH} + \text{H}^+$$  \hspace{1cm} (15)
$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \cdot\text{OOH} + \text{H}^+$$  \hspace{1cm} (16)
$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OH}^- + \cdot\text{OH}$$  \hspace{1cm} (17)

$$\text{ATZ} + \cdot\text{OH} \rightarrow \ldots \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (18)

Notably, the standard electrode potentials for $E^\circ$ (Co$^{3+}$/Co$^{2+}$) and $E^\circ$ (Fe$^{3+}$/Fe$^{2+}$) at a room temperature were 1.81 V and 0.77 V, respectively [55]. The Fe$^{3+}$ ions could be oxidized into Fe$^{3+}$ ions by the Co$^{3+}$ ions according to the oxidation-reduction reaction:

$$\text{Co}^{3+} + \text{Fe}^{3+} \rightarrow \text{Co}^{2+} + \text{Fe}^{2+}$$  \hspace{1cm} (19)

The -OH radicals possessed strong oxidizing property, which promoted the oxidative degradation of ATZ pollutants (Eq. 18). To evaluate the role of -OH radicals in advanced oxidation process, t-BuOH and MeOH were used as radical inhibitors. The t-BuOH or MeOH solution was 1000 times the concentration of H$_2$O$_2$ solution, which could completely inhibit -OH radicals [57]. In the presence of t-BuOH and MeOH, the ATZ degradation rates were 87.9% and 88.6%, respectively (Fig. 9). The ATZ degradation rate arrived at 97.5% in UV/H$_2$O$_2$ process without radical inhibitor, indicating that -OH radicals played an important role in the degradation of ATZ.

Besides the circulation reactions of Co$^{2+}$/Co$^{3+}$ and Fe$^{2+}$/Fe$^{3+}$, the concentrations of H$_2$O$_2$ played an important role in ATZ degradation. In the presence of Co$^{3+}$, Co$^{2+}$, Fe$^{3+}$ and Fe$^{2+}$ ions, the H$_2$O$_2$ contributed to the formation of -OH radicals (Eqs. 14–17). The ATZ removal abilities of ACF/CoFe$_2$O$_4$ composites were enhanced as the H$_2$O$_2$ concentrations increased from 0 to 3 mmol/L (Fig. 7e and f). However, the excessive H$_2$O$_2$ would capture -OH radicals, followed by the generation of the -OOH radicals with weak oxidization. Moreover, these -OOH radicals reacted further with -OH to produce H$_2$O and O$_2$. The corresponding chemical reactions were expressed as followed [58]:

$$\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \cdot\text{OOH}$$  \hspace{1cm} (20)
$$\cdot\text{OOH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$$  \hspace{1cm} (21)

Because the excessive H$_2$O$_2$ consumed part of -OH radicals (Eqs. 20 and 21), the ATZ removal efficiencies over the ACF/CoFe$_2$O$_4$ composites decreased gradually as the H$_2$O$_2$ concentrations were further increased over 3 mmol/L (Fig. 7e and f).

In the presence of H$_2$O$_2$ and light irradiation, photocatalytic reaction as well as Fenton-like reaction took part in the degradation of ATZ (Fig. 7). In this work, the xenon lamp was employed as a simulated solar light. The illumination of xenon lamp induced the generation of electron (e$^-$) and hole (h$^+$) pairs on the CoFe$_2$O$_4$ photocatalysts [59]. These electrons and holes were reacted with O$_2$ and H$_2$O to respectively create -O$_2$ and -OH radicals, as followed [21,59]:

$$\text{CoFe}_2\text{O}_4 + h\nu \rightarrow \text{CoFe}_2\text{O}_4(h^+_\text{vB} + e^-_{\text{CB}})$$  \hspace{1cm} (22)
$$\text{H}_2\text{O} + h^+_\text{vB} \rightarrow \text{OH} + \text{H}^+$$  \hspace{1cm} (23)
$$\text{O}_2 + e^-_{\text{CB}} \rightarrow \cdot\text{O}_2$$  \hspace{1cm} (24)

As compared with the CoFe$_2$O$_4$ nanoparticles, the ACFs significantly promoted the ATZ degradation ability of the ACF/CoFe$_2$O$_4$ composites (Fig. 7c and d). Firstly, the ACFs in the ACF/CoFe$_2$O$_4$ composites provide great surface areas for ATZ physical adsorption, and thus facilitated the subsequently catalytic degradation [21]. Secondly, the ACF/CoFe$_2$O$_4$ composites showed the better light absorption capacity than the pure CoFe$_2$O$_4$ nanoparticles in the wavelength range of 250–800 nm (Fig. 5a). The ACFs decreased the band gap of CoFe$_2$O$_4$ nanoparticles from 1.82 eV to 1.62 eV, and induced the redshift of absorption peak from 450 nm to 475 nm (Fig. 5). Thirdly, the presence of ACFs in the ACF/CoFe$_2$O$_4$ composites effectively inhibited the electron-hole recombination (Fig. 5c and d). The positive light response characteristics due to the presence of ACFs made the ACF/CoFe$_2$O$_4$ composites have excellent photocatalytic activity in a wide wavenumber range (Fig. 7c and d).
3.8. Catalytic degradation pathway of ATZ over ACF/CoFe$_2$O$_4$ composites

In the photo-Fenton reaction, the ATZ pollutants were oxidized by -OH radicals into CO$_2$ and H$_2$O via various intermediate products. In order to reveal the catalytic degradation pathway of ATZ over ACF/CoFe$_2$O$_4$ composites, the degradation products were detected by LC-MS (Fig. 10). Before the photo-Fenton reaction, only ATZ without any other organic matter was observed in the LC-MS spectrum (Fig. 10a and b). After the photo-Fenton reaction was performed for 7 h, both ATZ and intermediates were detected by LC pattern (Fig. 10a). The intermediates were composed of 2-chloro-4-ethylamino-6-propanolamine-1,3,5-triazine and 2-chloro-4-ethylamino-6-amino-1,3,5-triazine (Fig. 10c). When the catalytic degradation time was prolonged up to 15 h, no ATZ was remained in the wastewater. Only intermediate products including 2-chloro-4,6-diamino-1,3,5-triazine, 2-hydroxy-4,6-diamino-1,3,5-triazine and 2-hydroxy-4,6-dinitro-1,3,5-triazine were generated (Fig. 10d). Based on the LC-MS analyses, the catalytic degradation mechanisms of ATZ over ACF/CoFe$_2$O$_4$ composites could be demonstrated by the following chemical equations:

\[
\begin{align*}
\text{(25)} & \quad \text{ATZ} + 2\cdot \text{OH} \rightarrow \text{intermediate products} + \text{CO}_2 + \text{H}_2\text{O} \\
\text{(26)} & \quad \text{ATZ} + 16\cdot \text{OH} \rightarrow \text{intermediate products} + 3\text{CO}_2 + \text{H}_2\text{O} \\
\text{(27)} & \quad \text{ATZ} + 10\cdot \text{OH} \rightarrow \text{intermediate products} + 2\text{H}_2\text{O} + 6\text{CO}_2 \\
\text{(28)} & \quad \text{ATZ} + \cdot \text{OH} + e^- \rightarrow \text{intermediate products} + \text{Cl}^- \\
\text{(29)} & \quad \text{ATZ} + 12\cdot \text{OH} \rightarrow \text{intermediate products} + 8\text{H}_2\text{O} \\
\text{(30)} & \quad \text{ATZ} + 33\cdot \text{OH} + 5e^- \rightarrow 17\text{H}_2\text{O} + 3\text{CO}_2 + 5\text{NO}_3
\end{align*}
\]
The photo-Fenton degradation of ATZ was possibly carried out by the following steps: (i) the -OH radicals attacked the central carbon atom of atrazine side chain, and substituted for the hydrogen atom to produce 2-hydroxy-4,6-diamino-1,3,5-triazine was further mineralized into CO2, H2O and NO3 ions via the photo-Fenton degradation reaction (Eq. 30).

4. Conclusions

In summary, the ACF/CoFe2O4 composites were firstly fabricated by hydrothermal method. The spinel-type CoFe2O4 nanoparticles with particle sizes of ~87 nm deposited uniformly across ACFs. The ACF/CoFe2O4 composites could effectively remove ATZ via the adsorption and photo-Fenton degradation. The combination of ACF felts and bond in another side chain was also broken by C atrazine side chain, and substituted for the hydrogen atom to produce 2-

References

[25] M. Kaya, M. Zakhmakanir, S. Ozkar, M.R. Volkman, M. r. Volkman, Copper(0) nanoparticles supported on silica-coated cobalt ferrite magnetic particles: cost


