Interfacial $CoAl_2O_4$ from ZIF-67@γ-Al_2O_3 pellets toward catalytic activation of peroxymonosulfate for metronidazole removal

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HIGHLIGHTS

- ZIF-67 derived $CoAl_2O_4$@γ-Al_2O_3 pellet ($CoAl_2O_4$@AP) was synthesized.
- $SO_4{}^{\cdot-}$, $\cdot OH$, $^1O_2$ and $O_2{}^{\cdot-}$ were produced in the $CoAl_2O_4$@AP/PMS system.
- $SO_4{}^{\cdot-}$ and $^1O_2$ played the vital roles in oxidative removal of metronidazole.
- $CoAl_2O_4$@AP showed high activity, stability and reusability in catalytic reactions.

GRAPHICAL ABSTRACT
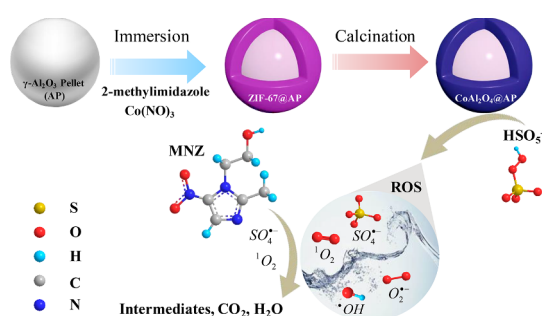
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ABSTRACT

Metal organic frameworks (MOFs)-based catalysts are rising stars in advanced oxidation processes (AOPs) to generate reactive oxygen species (ROS). Nevertheless, constructing an affordable and recyclable MOFs-derived catalyst with high reactivity and stability is highly desirable but still challenging. Herein, we unprecedentedly designed a novel $CoAl_2O_4$@γ-Al_2O_3 pellet ($CoAl_2O_4$@AP) as a heterogeneous catalyst to activate peroxymonosulfate (PMS) toward ROS generation for metronidazole (MNZ) removal. A $CoAl_2O_4$ shell was formed on the pellet surface by direct calcination of the surface-nucleated ZIF-67 on γ-Al_2O_3 pellets. The strong and unique interactions between the Co species of ZIF-67 and γ-Al_2O_3 resulted in the formation of interfacial $CoAl_2O_4$. The $CoAl_2O_4$@AP exhibited a remarkably higher efficacy for PMS activation than ZIF-67-derived Co_3O_4 and commercial Co_3O_4. The effects of several reaction parameters (i.e., PMS dosage, reaction temperature, initial pH, and background inorganic ions) on MNZ removal were comprehensively investigated and the degradation pathways of MNZ were elucidated. The Co^{2+}/Co^{3+} and oxygen vacancies of $CoAl_2O_4$@AP were the intrinsic active centers for PMS activation to simultaneously generate a diversity of ROS, among which $SO_4{}^{\cdot-}$ and $^1O_2$ played the decisive roles in MNZ decomposition. After the reaction, $CoAl_2O_4$@AP can be easily separated from the bulk solution and regenerated via a PMS-assisted cleaning process, making the composites highly appealing for practical applications. This pioneering work on constructing microscopic $CoAl_2O_4$-based composites expands the application of MOFs-based catalysts in novel AOPs systems for the treatment of persistent emerging pollutants.

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1. Introduction

Despite the tremendous benefits of various antibiotics for treating human and animal infections, the persistence of the antibiotics in the environment has intensified, in particular, in aquatic ecosystems [1,2] due to the discharge of wastewater. Significant correlations between the antibiotic resistance and risks of human health have been previously reported [3–5]. It is therefore urgent to minimize the spread of antibiotics via controlling their discharge and release from human activities. Toward this goal, emerging technologies of advanced oxidation processes (AOPs) have been developed based on a wide array of peroxides such as hydrogen peroxide, ozone, and persulfates [6–12]. Reactive oxygen species (ROS), such as sulfate radical ($SO_4^{\cdot-}$) and hydroxyl radical ($\cdot OH$), can be produced by activating peroxymonosulfate (PMS) or peroxydisulfate (PDS) via thermal, ultrasound and ultraviolet stimulations [13–15], whereas these approaches require a high energy input. Transition metals, especially Co^{2+}, can effectively activate PMS to generate $SO_4^{\cdot-}$ [16,17]. However, the AOPs systems relying on homogeneous catalysis are restricted by the inherent drawbacks of secondary pollution and the difficulty in recycling the metal ions. Therefore, heterogeneous catalysts stand out as the substitutes to activate PMS to generate ROS without excessive addition of metal ions and the associated secondary contamination [8,18–24].

Up to date, most efforts have been devoted to designing Co-based nanoscale catalysts (CNCs) [25]. Among them, CNCs derived from Co-based metal organic frameworks (Co-MOFs), such as ZIF-67 [26], are outstanding candidates due to the unique characteristics of MOFs, including high specific surface areas, hierarchically porous structure and tunable chemical compositions. Unfortunately, the performance of Co-MOFs-derived CNCs is still plagued by the inevitable aggregation during the operation in AOPs, due to their inherent high surface energy at the nanoscale [27–30]. Furthermore, the utilization of Co-MOFs derived CNCs in large-scale operations usually requires high investments of intensive energy and effort in the recycling and regenerating procedures, which limit their practical applications. In this regard, immobilizing Co-MOFs on macroscale supports, such as activated carbon pellets [31], zeolite beads [32], nickel foam [33], resin [34] or polypropylene membrane [35] to form highly dispersed and recyclable CNCs exalted as a feasible strategy to overcome the aforementioned engineering limitations. Moreover, Co-MOFs can be used as precursors to derive novel Co-based oxides and composites (e.g. Co_3O_4 [20,36], $CoFe_2O_4$ [29,30]) with higher activity and better stability. For example, commercial Al_2O_3 ceramic membrane has been explored as a support to immobilize ZIF-67 derived Co_3O_4 for PMS reactions [37]. The resultant Co_3O_4 within the Al_2O_3 ceramic membrane filter was responsible for PMS activation to generate $SO_4^{\cdot-}$ and $\cdot OH$ for sulfamethoxazole removal, and the composite membrane filter could be regenerated by a PMS-assisted cleaning process. However, the relatively higher cost of Al_2O_3 ceramic membrane may hinder the scale-up applications of Co_3O_4 nanoparticle functionalized membrane. Therefore, it is highly desirable to synthesize Co-MOFs-derived CNCs with low cost, high reactivity, reusability and stability for PMS-based AOPs. Meanwhile, it is also inspiring to explore the possibility of converting Co-MOFs into other novel structures of CNCs.

Encouraged by our previously successful works on the fabrication of separable composites in environmental remediation [38–40], in this work, we used the commercially affordable activated alumina pellets (γ-Al_2O_3, 3–5 mm in diameter) and the ZIF-67 as the precursors to synthesize CNCs to address the engineering bottlenecks. γ-Al_2O_3 pellets are selected as the support because of their high mechanical strength and thermodynamic stability under rigorous conditions. As expected, the evolved $CoAl_2O_4$ shells were successfully coated onto the surface of γ-Al_2O_3 pellets. The macroscopic $CoAl_2O_4@\gamma$-Al_2O_3 pellet (CoAl$_2$O$_4$@AP) was then used as a heterogeneous catalyst to activate PMS for degrading metronidazole (MNZ). MNZ was selected as a representative contaminant due to its ubiquitous occurrence in wastewater at a mg/L level and potential risks to induce antibiotic resistance in waterborne bacteria [1,41]. To the best of our knowledge, this is the first study using $CoAl_2O_4$-containing pellets as the catalysts for PMS activation. The advantages of using $CoAl_2O_4@AP$ in AOPs lie in their low cost, scalable production, high activity and satisfactory reusability, which are of vital significance to extend their service life especially in practical fixed-bed operations.

2. Materials and methods

2.1. Materials

Some chemicals, 2-methylimidazole (2-MIM), Oxone ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) (as a PMS precursor), commercial nano-Co_3O_4 and metronidazole (MNZ) were supplied by Aladdin, China. Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), methanol, ethanol (EtOH), *tert*-butanol (TBA), p-benzoquinone (BQ), L-histidine (HD), sodium hydroxide (NaOH), and nitric acid (HNO_3) were purchased from Sinopharm, Shanghai, China. All the chemicals, unless otherwise stated, were used without further purification. Commercial γ-Al_2O_3 pellets (APs, Sinopharm, Shanghai) with 3–5 mm in diameter were firstly washed using deionized (DI) water and then dried overnight at 105 °C prior to further usage.

2.2. Synthesis of CoAl$_2$O$_4$@AP

The precursor of $CoAl_2O_4@AP$, ZIF-67 modified AP (ZIF-67@AP), was synthesized by an *in-situ* growth method [37]. Firstly, APs were fully immersed into Solution A (480 mM of 2-MIM in methanol) for 30 min without stirring. This step was followed by methanol washing for three times. Subsequently, the resultant APs were placed into Solution B (60 mM of $Co(NO_3)_2 \cdot 6H_2O$ in methanol) for another 30 min without stirring. After washing with methanol, the samples were immediately transferred into the mixtures of Solution A and B without disturbance. After aging for 24 h, the purple products were separated and washed with methanol and DI water for several times, and dried at 105 °C overnight to obtain ZIF-67@AP. The as-obtained ZIF-67@AP was calcined under 450 °C for 3 h in static air with a heating rate of 5 °C/min. After cooling to room temperature naturally, the blue products were obtained, washed by DI water and dried at 105 °C overnight, denoted as $CoAl_2O_4@APs$. For comparison, ZIF-67 powders were prepared according to the reported methods [37], and the obtained ZIF-67 powders were subject to calcination at 450 °C for 3 h to synthesize ZIF-67 derived Co_3O_4 nanoparticles.

2.3. Characterizations

The surface morphologies as well as elemental distributions were acquired by a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan) coupling with energy dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) spectra of samples were recorded on an X'Pert PRO diffractometer (PANalytiical, Holland, Cu K$_\alpha$, $\lambda = 0.15406$ nm) with 40 KV accelerating voltage and 40 mA current. The wide-angle data were collected from 5° to 80° at a scan speed of 0.6°/min. UV–Vis absorption spectra were detected on a spectrophotometer (UV3600, Shimadzu, Japan) with an integrating sphere and BaSO$_4$ was used as the reference sample. Meanwhile, X-ray photoelectron spectroscopy (XPS) analysis was used to determine the surface elemental compositions and valence states of $CoAl_2O_4@AP$ related materials.

2.4. Evaluation of catalytic activity

Batch experiments were performed to assess the catalytic efficacy of $CoAl_2O_4@APs$ for PMS activation. In each degradation reaction, a certain amount of catalysts ($CoAl_2O_4@APs$) and 80 mL of MNZ (20 mg/

3. Results and discussion

3.1. Physicochemical characterizations

The morphologies of CoAl$_2$O$_4$@APs samples are shown in Fig. 1. The bare ZIF-67 exhibits uniform and rhombic dodecahedron structures within with particle sizes range of 150–500 nm (Fig. 1a). After calcination at 450 °C for 3 h, the pristine polyhedral structures completely collapsed into nanosized grain-like aggregates with irregular morphologies (Fig. 1 b and c). Meanwhile, the color has also changed from bright purple (ZIF-67) to black (Co$_3$O$_4$). The particle sizes of ZIF-67 derived Co$_3$O$_4$ are in the range of 40–100 nm (Fig. 1c). Large blocks with rough surface are found for CoAl$_2$O$_4$@AP-related samples (Fig. 1d-f). The in-situ formation of ZIF-67 and subsequent calcination did not change the pristine morphologies of AP samples despite that the color was changed from white to purple, and finally to blue. Noting that the color of CoAl$_2$O$_4$@AP surface is not black as an Al$_2$O$_3$ ceramic membrane immobilized Co$_3$O$_4$ catalyst derived from ZIF-67 [37], which is probably due to the different surface property of supports.

XRD measurements were conducted to study the crystallographic structures of ZIF-67@AP derived samples (Fig. 2). Three distinguishable peaks at around 37.6°, 45.8° and 67.0° were detected for all the samples, which are the typical diffraction peaks of the [3 1 1], [4 0 0] and [4 4 0] planes for γ-Al$_2$O$_3$ (JCPDS#: 10–0425), respectively. The additional peaks at 14.5°, 28.2°, and 72.0° were also observed for AP, indicating the existence of boehmite (AlO(OH) (JCPDS#: 83–2384). Interestingly, several new peaks at 18.8°, 20.5° and 40.7° emerged for ZIF-67@AP, ascribed to the formation of bayerite (Al(OH)$_3$) (JCPDS#: 74–1119). Therefore, in situ growth of ZIF-67 on AP surface would result in the hydration of γ-Al$_2$O$_3$ and change the surface structures of AP. When ZIF-67@APs were subject to pyrolysis, the characteristic peaks of Al(OH)$_3$ and AlO(OH) disappeared, due to the dehydration of Al(OH)$_3$ and AlO(OH) at high temperatures. After reacting with PMS, the characteristic peaks of Al(OH)$_3$ appeared again, which was probably resulted from the hydration of the support surface in the aqueous environment. Unfortunately, we failed to detect the signals of Co-based oxides for ZIF-67@AP and CoAl$_2$O$_4$@AP, despite that the characteristic peaks of Co$_3$O$_4$ were observed from the calcined ZIF-67 sample (Fig. S1). The energy dispersive X-ray (EDX) mapping implied the presence of cobalt in ZIF-67@AP and CoAl$_2$O$_4$@AP, verifying the successful immobilization of Co onto the surface of AP (Fig. S2). The Al, O and C elements in the spectra originated from the pristine substrate and precursors used for the sample preparation.

UV–Vis spectroscopy in the region of 200–800 nm was used to further verify the cobalt species and the coordination chemistry of cobalt elements on AP surface. As depicted in Fig. 3, there are no peaks in AP assigned to Co-related oxides. When APs were in situ modified with ZIF-67, four absorption bands located at 540, 564, 582 and 620 nm emerged for the ZIF-67@AP samples. The former three peaks can be assigned to $^4A_2$ (F) → $^4T_1$(P) transition of tetrahedral Co^{2+} coordination, which is consistent with the previously identified Co^{2+} in ZIF-67 [44]. Additionally, the last peak at 620 nm matches well with the absorption band of α-Co(OH)$_2$, which also features a tetrahedral Co^{2+} site [45]. The formation of α-Co(OH)$_2$ could be ascribed to the coordination of surface Co with H$_2$O during the synthesis [46]. These findings imply the formation of ZIF-67 on AP. After calcination, the spectra of CoAl$_2$O$_4$@AP show an intense triplet at 545, 580, and 630 nm, indicating the tetrahedrally coordinated Co^{2+} in the CoAl$_2$O$_4$ phase [47,48]. The blue color is owing to the absorption of light during the range of 545–630 nm. The Co species, i.e. CoAl$_2$O$_4$, is barely reduced and formed during the migration of Co^{2+} into tetrahedral sites of the γ-Al$_2$O$_3$ lattice [49], which is of great advantage to defend the shedding of Co-based catalysts. Furthermore, another intense band centered at around 250 nm is also discernible in CoAl$_2$O$_4$@AP sample, ascribed to electron transfer from O$_2^{2-}$ to Co^{3+} in the octahedral coordination, giving rise to a distinct greenish hue to the samples [50,51]. The partial

oxidation of Co^{2+} to Co^{3+} was probably due to the gradient of Co concentration and the excessive Co^{2+} over CoAl$_2$O$_4$@AP [49,52]. Interestingly, the UV–Vis absorption bands of the used CoAl$_2$O$_4$@AP samples are similar to those of fresh CoAl$_2$O$_4$@AP samples, suggesting the structural robustness of the CoAl$_2$O$_4$@AP. Noting that no peaks at 380 nm and 700 nm were observed, indicating the absence of Co$_3$O$_4$ phase in ZIF-67@AP and CoAl$_2$O$_4$@AP samples [47].

The chemical compositions and bonding configurations of ZIF-67@AP and CoAl$_2$O$_4$@AP were investigated via XPS characterization and the C 1s peak at 284.8 eV was used as the reference. Fig. S3 depicts the peaks of Co 2p, O 1s, C 1s, and Al 2p for ZIF-67@AP and CoAl$_2$O$_4$@AP, which are in good agreement with the observation of EDX characterization (Fig. S2). The Co 2p$_{3/2}$ spectra of ZIF-67@AP manifest three peaks at 780.5, 782.1 and 786.1 eV (Fig. 4a) as found in ZIF-67 [46]. The first two peaks are the characteristic Co^{2+} species while the last peak is assigned to the shake-up satellite (marked as "Sat.") of Co^{2+} species, which are consistent with the UV–Vis results of ZIF-67 derived composites. Meanwhile, ZIF-67@AP shows another peak at 779.7 eV, assigned to Co^{3+} species, which is probably originated from the unstable α-Co(OH)$_2$ as analyzed by UV–Vis that were partially converted into CoO(OH) species [46]. After calcination at 450 °C, the Co 2p$_{3/2}$ spectra of CoAl$_2$O$_4$@AP (Fig. 4b) also consist of two Co species. Specifically, the peak at 779.7 eV confirms the existence of Co^{3+}, whereas those at 780.9 and 782.3 eV belong to the high-spin Co^{2+} species [53,54]. The board peak at 786.4 eV is a typical shake-up satellite of high-spin Co^{2+} species [55,56], which stems from the distributions of Co^{2+} in tetrahedral and octahedral sites [57]. Clearly, the binding energy of Co^{2+} species in CoAl$_2$O$_4$@AP is slightly higher than that of ZIF-67@AP by 0.4, 0.2, and 0.3 eV, respectively. Such peak shifting, on the basis of UV–Vis results, might be attributed to the gradual phase transition from Co-OH of ZIF-67 to α-Co(OH)$_2$, and ultimately CoAl$_2$O$_4$. It should be noted that the area ratio of Co^{2+}/Co^{3+} for CoAl$_2$O$_4$@AP is 6.81, while the ratio for ZIF-67@AP is only 3.87, suggesting that the density of oxygen vacancy of CoAl$_2$O$_4$@AP is higher than that of ZIF-67@AP [58]. Meanwhile, the O 1s spectra of ZIF-67@AP and CoAl$_2$O$_4$@AP can be deconvoluted into three components [36], including lattice oxygen species (529.9 eV, marked as O$_{Lattice}$), oxygen defects (531.1 eV, marked as O$_{Defect}$), and hydroxyl groups or surface-adsorbed oxygen species (532.1 eV, marked as O$_{Surface}$). The higher O$_{Defect}$/O$_{Lattice}$ ratio of CoAl$_2$O$_4$@AP also indicates that the CoAl$_2$O$_4$@AP (6.89)
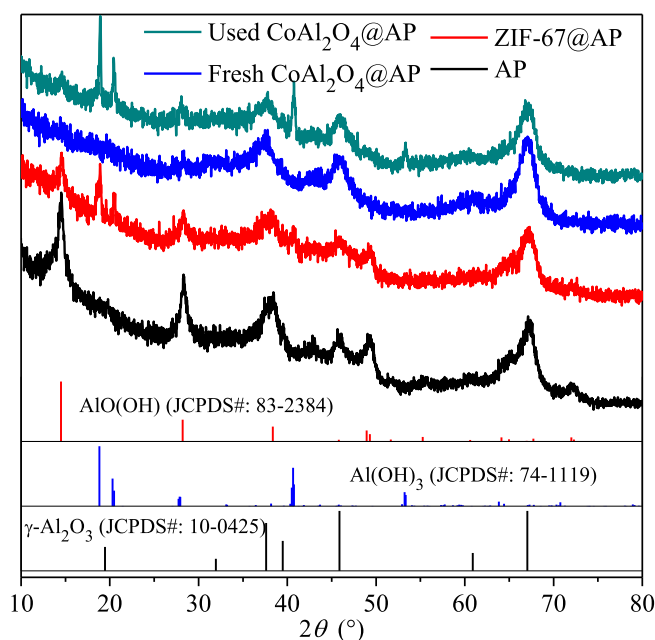
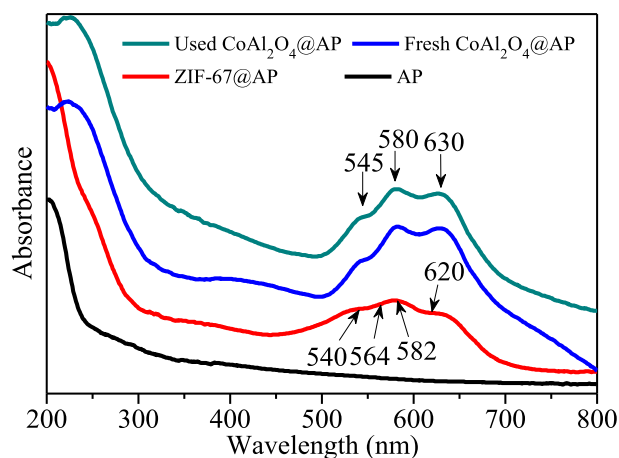**Fig. 2.** XRD spectra of AP, ZIF-67@AP and CoAl$_2$O$_4$@AP.

Fig. 3. UV–Vis spectra of AP, ZIF-67@AP and CoAl$_2$O$_4$@AP.

Fig. 5. MNZ removal by PMS activated with different materials ([PMS]$_0$ = 1.0 mM, [CoAl$_2$O$_4$@AP] = [ZIF-67@AP] = 20 g/L, [Co$_3$O$_4$] = 4 g/L, [MNZ]$_0$ = 20 mg/L, pH = 6.48, T = 25 ± 1 °C).

possessed more oxygen vacancies than ZIF-67@AP (0.85), which might be helpful to improving the catalytic activity of the CoAl$_2$O$_4$@AP towards PMS activation.

3.2. Catalytic performance

Fig. 5 shows the comparison of MNZ removal efficiencies over CoAl$_2$O$_4$@AP and other catalysts including ZIF-67@AP, commercial nano-Co$_3$O$_4$ powders and ZIF-67 derived Co$_3$O$_4$ powders. Four control experiments were conducted including MNZ alone, MNZ oxidation by sole PMS, adsorption removal by sole CoAl$_2$O$_4$@AP, and homogeneous Co^{2+}/PMS systems. Less than 4% of MNZ was removed by sole PMS, implying that self-decomposition of PMS could not generate sufficient ROS for MNZ removal. Meanwhile, an extremely low MNZ removal efficiency (1%) was obtained by CoAl$_2$O$_4$@AP alone, revealing that the CoAl$_2$O$_4$@AP had almost no adsorption capacity toward MNZ. Besides, the contribution of MNZ removal by natural volatilization was very limited and could be ignored.

In the catalytic systems, 33%, 67% and 5% of MNZ concentrations were reduced by PMS activated with ZIF-67@AP (20 g/L), ZIF-67 derived Co$_3$O$_4$ (4 g/L), and commercial nano-Co$_3$O$_4$ (4 g/L), respectively.
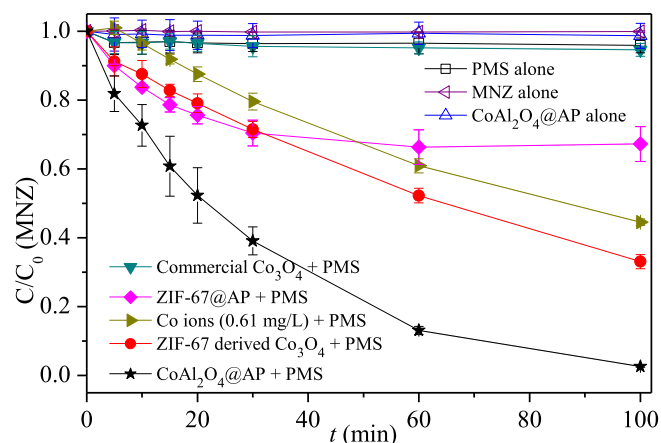
Encouragingly, MNZ removal was markedly enhanced and reached 97% within 100 min when CoAl$_2$O$_4$@AP (20 g/L) was used as an activator. In the current study, the Co loading amount on CoAl$_2$O$_4$@AP was around 0.30 wt% (detected by ICP-OES), implying that the maximal dosage of CoAl$_2$O$_4$ participated in PMS activation was 180 mg/L, which is much lower than Co$_3$O$_4$ powders (4 g/L). These results implied that CoAl$_2$O$_4$@AP is a highly effective catalyst to activate PMS for ROS generation and MNZ decomposition, due to the well-dispersed and highly reactive CoAl$_2$O$_4$ layer formed on the macro-sized AP supports. In addition, only trace Co ions (0.61 mg/L) were leached from the CoAl$_2$O$_4$@AP/PMS system, and the contrasted removal efficiency of MNZ by homogeneous Co/PMS system was 55% within 100 min. Obviously, PMS was heterogeneously activated by the CoAl$_2$O$_4$@AP composite rather than the leached Co ions.

3.3. Reaction parameters-regulated MNZ removal

3.3.1. Effect of PMS dosage

As revealed in Fig. 6a, MNZ removal was enhanced with the increased dosage of PMS. Specifically, when 0.5 mM of PMS was used,
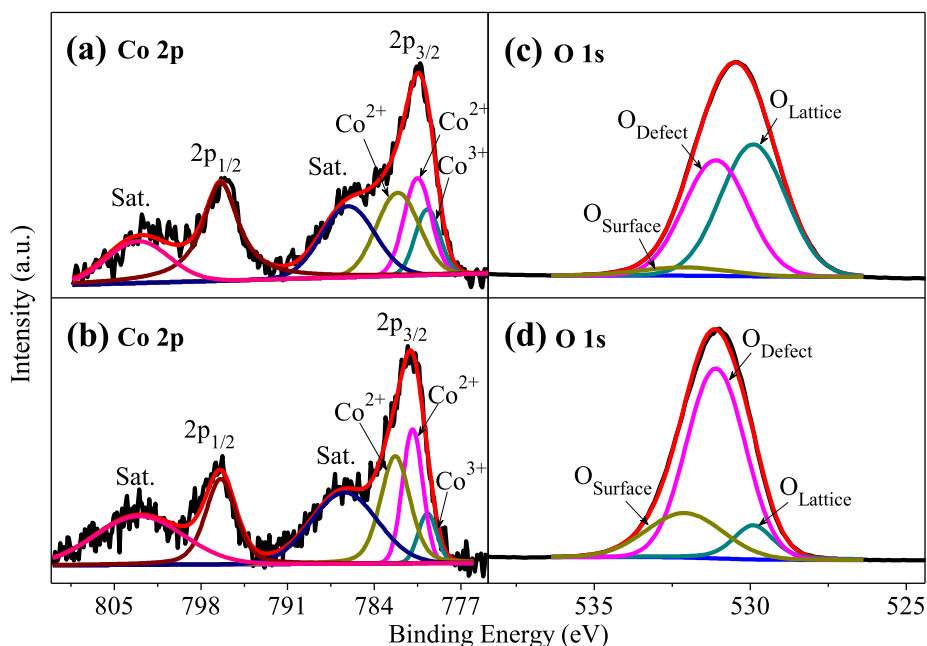

Fig. 4. XPS analysis for Co 2p and O 1s of ZIF-67@AP (a, c) and CoAl$_2$O$_4$@AP (b, d).

only ~40% of MNZ was removed in 60 min, suggesting that PMS was insufficient in this system. A dramatic enhancement in MNZ removal was obtained by increasing the PMS dosage to 1.0 mM. The removal efficiency at the PMS dosage of 1 mM was two times higher than that of 0.5 mM, and the first-order reaction rate constants (k_{obs}) for MNZ removal remarkably increased from 0.014 to 0.032 min^{-1}. Further increasing PMS dosage from 1 to 3 mM linearly augmented the k_{obs} values (Fig. 6b), ascribed to the fact that increasing PMS dosage would produce more ROS to speed up the MNZ oxidation.

3.3.2. Effect of solution temperature

Fig. 7 shows that the MNZ removal was boosted with the elevated solution temperature from 15 to 35 °C. For example, a complete MNZ removal was achieved within 30 min at 35 °C, while only 36% of MNZ was removed at 15 °C within the same period. By fitting the kinetic model, MNZ removal was found to follow the first-order reaction kinetics and their rate constants were 0.014, 0.032 and 0.18 min^{-1} at 15, 25 and 35 °C, respectively. As MNZ oxidation by CoAl$_2$O$_4$@AP/PMS is a surface catalytic process, the activation energy (E_a) could be calculated by the following Arrhenius-type equation:

$$\ln k_T = -E_a/RT + \ln A$$

where k_T is the first-order reaction rate constant (min^{-1}) at different temperatures (T, K); E_a is the activation energy for degradation (kJ/mol); A is a time pre-factor while R is the gas constant of 8.314 J/(K·mol). By fitting k_T versus $-1/T$, E_a was calculated to be 41.32 kJ/mol, suggesting that MNZ removal by CoAl$_2$O$_4$@AP/PMS was a chemical reaction-limited process.

3.3.3. Effect of initial solution pH

The effect of initial solution pH (3.23–10.86) on MNZ removal was investigated (Fig. 8). The pH induced PMS self-decomposition toward MNZ removal was very limited at the initial pH range from 3.23 to 9.08. At higher initial pH 10.86, only about 22% of MNZ was removed, which was due to the alkaline activation of PMS [59]. CoAl$_2$O$_4$@AP/PMS coupled system exhibited a higher MNZ removal efficiency than bare PMS oxidation system over initial pH 3.23–10.86, verifying the positive role of CoAl$_2$O$_4$@AP in PMS activation/catalysis. The pH-regulated performance of CoAl$_2$O$_4$@AP/PMS is probably ascribed to the electrostatic interactions of CoAl$_2$O$_4$@AP, MNZ and/or PMS for producing ROS [60]. In the current study, pH$_{PZC}$ of CoAl$_2$O$_4$@AP was determined to be 7.9. The pK$_{a2}$ value of PMS is 9.4 [61], while the pK$_a$ value of MNZ is 2.6 [62]. The solution pH after reaction generally increased with the increased initial pH (Table S1). In the case of initial pH < 9.08, CoAl$_2$O$_4$@AP was mainly positively charged, and the PMS molecules presented in the form of HSO$_5^-$. At this stage, the electrostatic attraction between CoAl$_2$O$_4$@AP and HSO$_5^-$ is favorable for activating HSO$_5^-$ into ROS. In this context, CoAl$_2$O$_4$@AP/PMS can maintain high MNZ removal. At initial pH 10.86, the transformation of HSO$_5^-$ to SO$_5^{2-}$ was expected, while CoAl$_2$O$_4$@AP was negatively charged. The

electrostatic repulsion of SO$_5^{2-}$ and CoAl$_2$O$_4$@AP gave rise to a deleterious effect on the decomposition of PMS and the formation of ROS.

3.3.4. Effect of co-existing inorganic anions

As shown in Fig. 9, the presence of different inorganic anions (i.e., NO$_3^-$, PO$_4^{3-}$, HCO$_3^-$, SO$_4^{2-}$, and Cl$^-$) caused varying effects on MNZ removals. With respect to the removal efficiency in 100 min, 10 mM HCO$_3^-$ and 10 mM Cl$^-$ showed remarkable inhibitions on MNZ removal, while 10 mM PO$_4^{3-}$, 10 mM SO$_4^{2-}$ and 10 mM NO$_3^-$ exerted slight inhibition effects. In detail, < 20% of MNZ removal can be attained in the presence of HCO$_3^-$ or Cl$^-$, while the removal efficiency can maintain at above 90% for PO$_4^{3-}$, SO$_4^{2-}$ and NO$_3^-$. However, with respect to k_{obs} for MNZ removal, PO$_4^{3-}$ exhibited a significant enhancement in MNZ removal and the k_{obs} value increased by 1.4 times compared with the control group, whereas for SO$_4^{2-}$ and NO$_3^-$, the k_{obs} values decreased by 1.5 and 1.6 times, respectively. Compared to CoAl$_2$O$_4$@AP/PMS system without ions, the k_{obs} values for the cases of HCO$_3^-$ and Cl$^-$ decreased by 6.1 and 8.7 times, respectively. The positive influence of 10 mM PO$_4^{3-}$ is probably ascribed to the fact that PMS could be pre-activated by the phosphate anions [63], which was favorable for the subsequent CoAl$_2$O$_4$@AP catalysis. This is also partially confirmed by the current work, in which over 22% of MNZ was removed by a PO$_4^{3-}$ (10 mM) /PMS system (without CoAl$_2$O$_4$@AP) in Fig. S4. The negative impact of SO$_4^{2-}$ is a result of the formation of less reactive S$_2$O$_8^{2-}$ via Reaction 1 [64]. The inhibition effect of NO$_3^-$ may be resulted from the scavenging reactions between NO$_3^-$ and SO$_4^{\cdot-}$, and the subsequent formation of NO$_3^{\cdot-}$ with a lower oxidation potential Reaction 2 [64]. With respect to either the removal efficiency or the k_{obs} values, the inhibitory effect of HCO$_3^-$ or Cl$^-$ was much stronger than that of NO$_3^-$ or SO$_4^{2-}$. Such a significant inhibition effect of Cl$^-$ might be caused by the formation of less reactive chlorine species like HOCl (Reactions 3–5) [64] while the inhibitory effect of HCO$_3^-$ was due to its reaction with SO$_4^{\cdot-}$ and $\cdot$OH, accompanying with the formation of much less reactive radical of CO$_3^{\cdot-}$ (Reactions 6 and 7) [65].

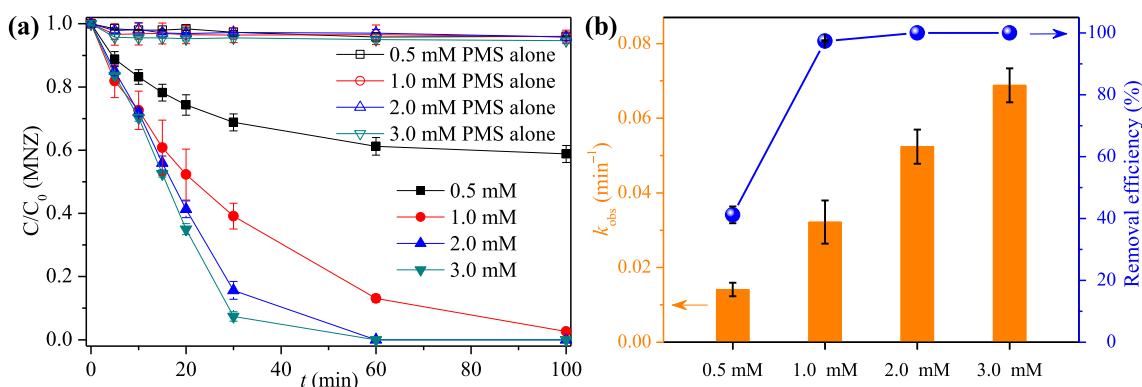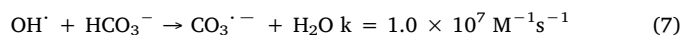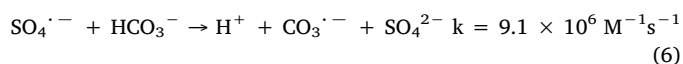$$SO_4^{\cdot-} + SO_4^{2-} \rightarrow S_2O_8^{2-} + e^- \quad k = 4.4 \times 10^8 \ M^{-1}s^{-1} \quad (1)$$

$$SO_4^{\cdot-} + NO_3^- \rightarrow SO_4^{2-} + NO_3^\cdot \quad k = 2.1 \times 10^6 \ M^{-1}s^{-1} \quad (2)$$

$$SO_4^{\cdot-} + Cl^- \rightarrow SO_4^{2-} + Cl^\cdot \quad k = 2.7 \times 10^8 \ M^{-1}s^{-1} \quad (3)$$

$$Cl^\cdot + Cl^- \rightarrow Cl_2^{\cdot-} \quad k = 8.0 \times 10^9 \ M^{-1}s^{-1} \quad (4)$$

$$Cl_2^{\cdot-} + OH^- \rightarrow HOCl^{\cdot-} + Cl- \quad k = 4.5 \times 10^7 \ M^{-1}s^{-1} \quad (5)$$

$$SO_4^{\cdot-} + HCO_3^- \rightarrow H^+ + CO_3^{\cdot-} + SO_4^{2-} \quad k = 9.1 \times 10^6 \ M^{-1}s^{-1} \quad (6)$$

$$OH^\cdot + HCO_3^- \rightarrow CO_3^{\cdot-} + H_2O \quad k = 1.0 \times 10^7 \ M^{-1}s^{-1} \quad (7)$$
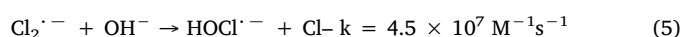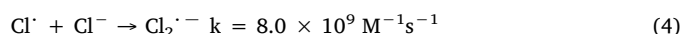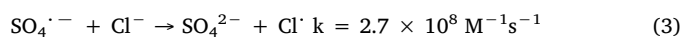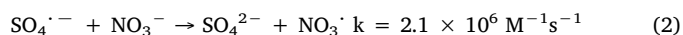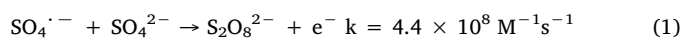
Fig. 6. Effect of PMS dosage on MNZ removal ([CoAl$_2$O$_4$@AP] = 20 g/L, [MNZ]$_0$ = 20 mg/L, pH = 6.48, T = 25 ± 1 °C).
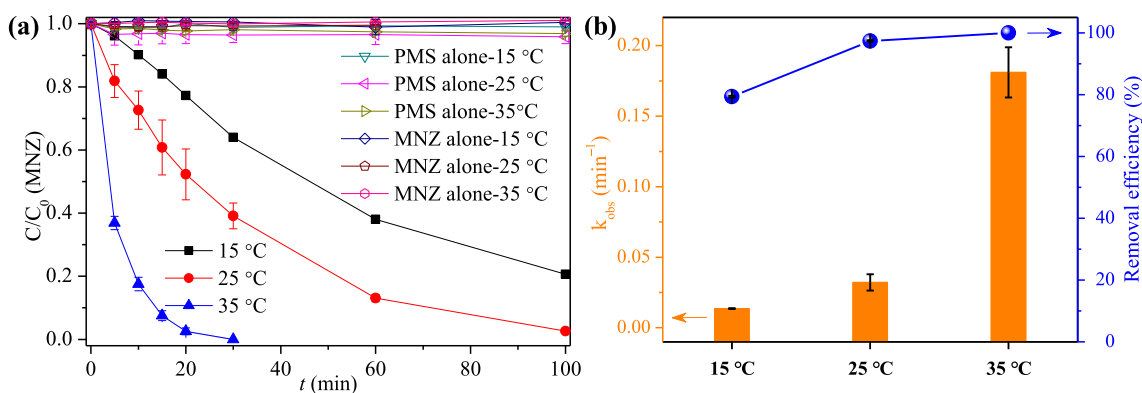
Fig. 7. Effect of solution temperature on MNZ removal ([CoAl$_2$O$_4$@AP] = 20 g/L, [MNZ]$_0$ = 20 mg/L, [PMS]$_0$ = 1.0 mM, pH = 6.48).

3.4. Stability and recyclability of CoAl$_2$O$_4$@AP

The reusability and stability of CoAl$_2$O$_4$@AP was assessed in multiple runs. The fresh CoAl$_2$O$_4$@AP was firstly subject to activating PMS for MNZ removal. The used monolithic CoAl$_2$O$_4$@AP was then harvested by a simple gauze-based filtration from bulk solution, followed by being washed with sufficient DI water and dried at 105 °C. The collected CoAl$_2$O$_4$@AP was employed for a second run. The identical procedures were repeated for a third run of CoAl$_2$O$_4$@AP toward PMS activation. The results in Fig. 10 indicated that a slight decrease (< 10%, from 97% to 92%) of MNZ removal efficiency was found for the second run. However, in the third run, the removal efficiency experienced a moderate decline (from 92% to 80%). The concentration of detected Co ions leached from CoAl$_2$O$_4$@AP was 0.22 mg/L after the third run, which was still lower than the environmental quality standards for surface water of China (GB 3838–2002) (1 mg/L). PMS solution (1 mM) without MNZ was employed to treat the used CoAl$_2$O$_4$@AP, followed by washed with sufficient DI water and dried at 105 °C. After the cleaning with PMS solution, the catalytic efficacy of CoAl$_2$O$_4$@AP was recovered with complete MNZ removal within 60 min in the fourth run. The decreased catalytic performance of CoAl$_2$O$_4$@AP might be due to the presence of intermediates from oxidized MNZ, which covered the surface reactive sites of CoAl$_2$O$_4$@AP and thus weakened their catalytic reactivity. Another reason might be the loss of active sites such as Co^{2+} species and defective O (refer to Reactions 8 and 9). The PMS-assisted cleaning process can not only eliminate the absorbed intermediates on CoAl$_2$O$_4$@AP surface but also recover the active sites through a redox process (refer to Reactions 10 and 11). Obviously, CoAl$_2$O$_4$@AP has an excellent catalytic activity and can be easily regenerated, which are attributed to the interfacial CoAl$_2$O$_4$ shell formed on micro-sized supports. These features indicate that CoAl$_2$O$_4$@AP could be an attractive candidate for potential wastewater treatments because of their high performance and feasibility in

dead-end filtration processes or fixed-bed reactors.

3.5. Possible degradation mechanism

3.5.1. Interactions of CoAl$_2$O$_4$@AP with PMS

In situ ATR-IR, confocal Raman and XPS characterizations were used to probe the PMS reaction with CoAl$_2$O$_4$@AP. The peaks found at 3272 ~ 3274 cm^{-1} in the ATR-IR spectra (Fig. 11a) are ascribed to the presence of hydrogen bonds between the surface adsorbed H$_2$O molecules on CoAl$_2$O$_4$@AP and PMS. Over the activation course, the hydrogen bonds centered reactions achieved equilibrium, suggesting that such reactions were not responsible for PMS activation. Based on previous work [38], the peaks at around 1060, 1092 ~ 1101 and 1243 ~ 1244 cm^{-1} are due to the symmetric and/or asymmetric stretching vibrations of S–O bonds in PMS. A slight red shift (by 9 cm^{-1}) for the S–O bond from about 1101 to 1092 cm^{-1} was found when CoAl$_2$O$_4$@AP were added into PMS solution for 30 min. The red shift implies that the electron density of S–O bond within HSO$_5^-$ generally decreased because of the redox processes between HSO$_5^-$ and active sites of CoAl$_2$O$_4$@AP. The surface catalytic centers of CoAl$_2$O$_4$@AP interacted with the terminal H–O bond of HSO$_5^-$ to withdraw electrons from the S–O bonds, thus elongating the S–O bond (neighboring H–O bond) and inducing a red shift. No shifts were detected when the reaction was prolonged to 80 min, indicating that the electron-donating/-withdrawing processes reached an equilibrium stage.

Three characteristic peaks from in situ confocal Raman spectra of PMS are shown in Fig. 11b. The peaks at around 882 cm^{-1} (marked as A), 981 cm^{-1} (marked as B) and 1062 cm^{-1} (marked as C) are due to the peroxide O-O bond, the stretching vibration modes of S-O bonds for SO$_4^{2-}$ and HSO$_5^-$, respectively. The progressive decreases in intensities of A and C suggest the activation of PMS on CoAl$_2$O$_4$@AP. Obviously, both I$_A$/I$_B$ and I$_C$/I$_B$ values decreased with the proceeded reaction. The variation profiles indicated that the cleavages of peroxide
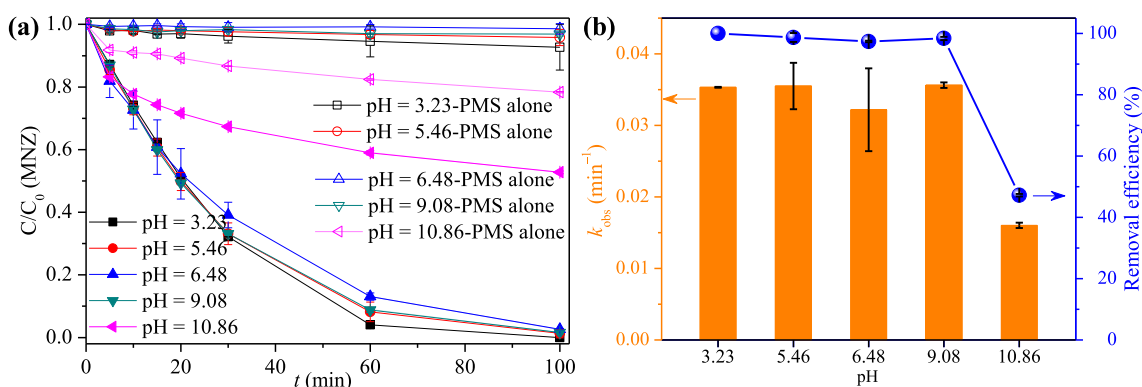

Fig. 8. Effect of initial pH values on MNZ removal ([CoAl$_2$O$_4$@AP] = 20 g/L, [MNZ]$_0$ = 20 mg/L, [PMS]$_0$ = 1.0 mM, T = 25 ± 1 °C).
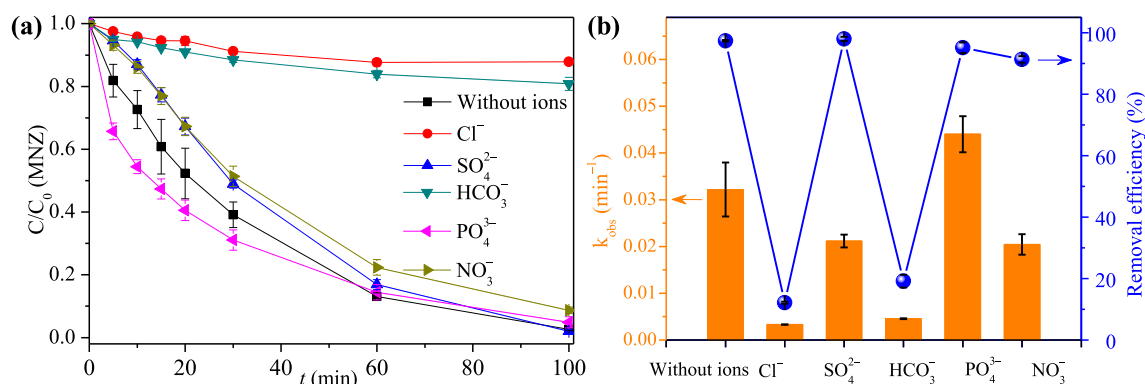
Fig. 9. Effect of co-existing inorganic ions on MNZ removal ([CoAl$_2$O$_4$@AP] = 20 g/L, [MNZ]$_0$ = 20 mg/L, [PMS]$_0$ = 1.0 mM, [Cl$^-$] = [SO$_4^{2-}$] = [HCO$_3^-$] = [PO$_4^{3-}$] = [NO$_3^-$] = 10 mM, pH = 6.48, T = 25 ± 1 °C).
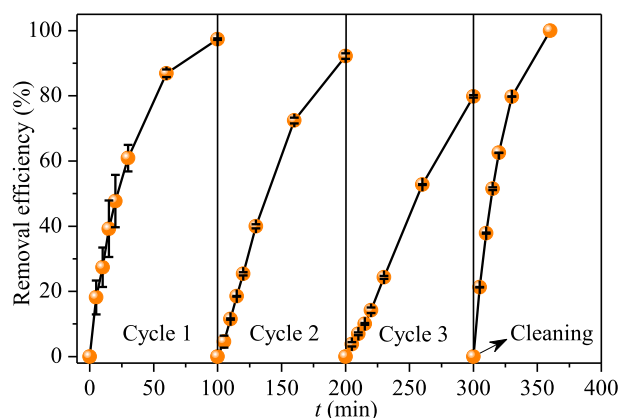

Fig. 10. Reusability of CoAl$_2$O$_4$@AP toward PMS activation for MNZ removal ([CoAl$_2$O$_4$@AP] = 20 g/L, [MNZ]$_0$ = 20 mg/L, [PMS]$_0$ = 1.0 mM, pH = 6.48, T = 25 ± 1 °C).

bond and/or S–O bond occurred, giving rise to the formation of ROS.

The Co 2p and O 1s spectra of the used CoAl$_2$O$_4$@AP are shown in Fig. 12. From the XPS fitting results (Figs. 4 and 12, Table 1), the oxidation states of surface Co and O elements had changed. For example, the contents of Co^{2+} and Co^{3+} changed from 52.88% and 7.77% for the fresh CoAl$_2$O$_4$@AP to 48.91% and 20.03% for the used CoAl$_2$O$_4$@AP, respectively. The decreased ratio of Co^{2+}/Co^{3+} from 6.81 to 2.44 suggested the electron transfer from CoAl$_2$O$_4$@AP to PMS, resulting in the formation of more Co^{3+} species because of the redox process of Co^{2+} species and PMS for ROS formation via Reactions 8 and 9 [15,53]. As show in Reactions 10 and 11 [17], more Co^{3+} species is favorable for the production of SO$_5^{\cdot-}$ (0.81 V$_{NHE}$) but detrimental to the formation of $\cdot$OH (1.9–2.7 V$_{NHE}$) and SO$_4^{\cdot-}$ (2.6–3.1 V$_{NHE}$) [66,67], which explains the gradual decline of MNZ removal in the second and third run. After PMS-assisted cleaning, the activation efficacy of CoAl$_2$O$_4$@AP was recovered in the fourth run, which probably resulted from the formation of Co^{2+} species mediated by the redox processes of Reactions 10 and 11. O 1s analysis (Figs. 4 and 12, Table 1) shows that, after the PMS reaction, the content of O$_{Defect}$ and the ratio of O$_{Defect}$/O$_{Lattice}$ decreased, implying that the defects (such as oxygen vacancies) within CoAl$_2$O$_4$@AP participated in PMS activation. The presence of oxygen vacancies is favorable for adsorbing PMS onto CoAl$_2$O$_4$@AP surface, which undoubtedly facilitated PMS activation [68]. XPS analysis confirmed that the defects and electron-transfer reactions are critical for PMS activation by CoAl$_2$O$_4$@AP.

$$\equiv Co^{II}O_x(OH)_y + HSO_5^- \rightarrow \equiv Co^{III}O_x(OH)_{y+1} + SO_4^{\cdot-} \quad (8)$$

$$\equiv Co^{II}O_x(OH)_y + HSO_5^- \rightarrow \equiv Co^{III}O_x(OH)_y^+ + \cdot OH + SO_4^{2-} \quad (9)$$
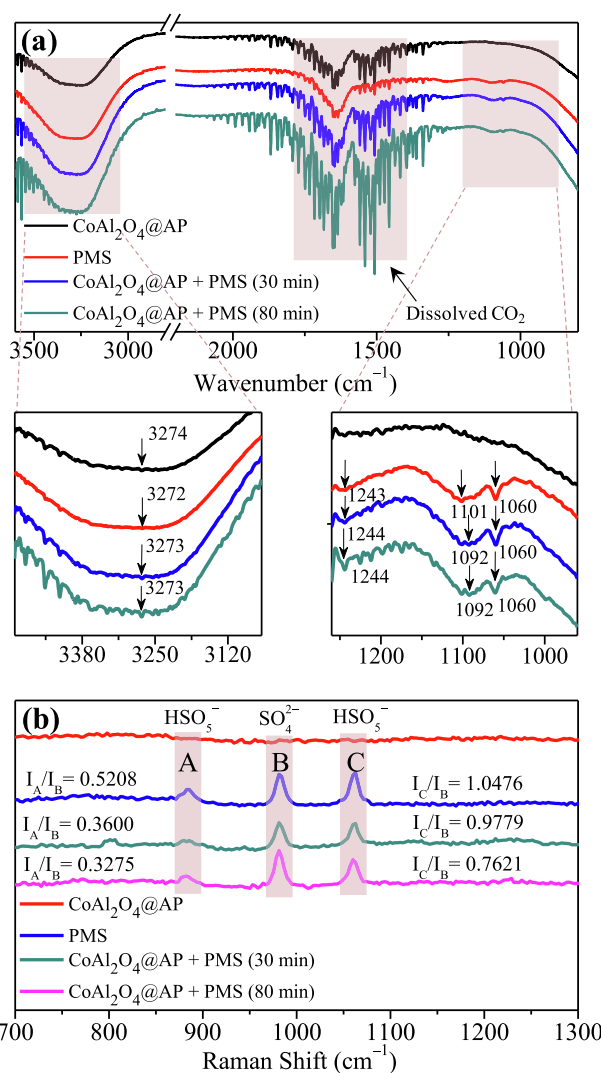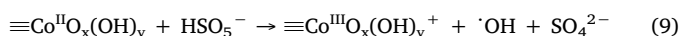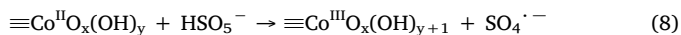
Fig. 11. *In situ* ATR-IR spectra (a) and Raman spectra (b) detected for CoAl$_2$O$_4$@AP/PMS related reaction systems.

$$\equiv Co^{III}O_x(OH)_{y+1} + HSO_5^- \rightarrow \equiv Co^{II}O_x(OH)_y + SO_5^{\cdot-} + H_2O \quad (10)$$

$$\equiv Co^{III}O_x(OH)_y^+ + HSO_5^- \rightarrow \equiv Co^{II}O_x(OH)_{y-1}^+ + SO_5^{\cdot-} + H_2O \quad (11)$$
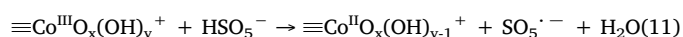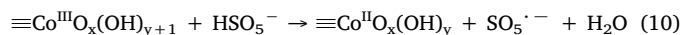
3.5.2. ROS in CoAl$_2$O$_4$@AP/PMS system

Quenching experiments were carried out to probe the types of ROS
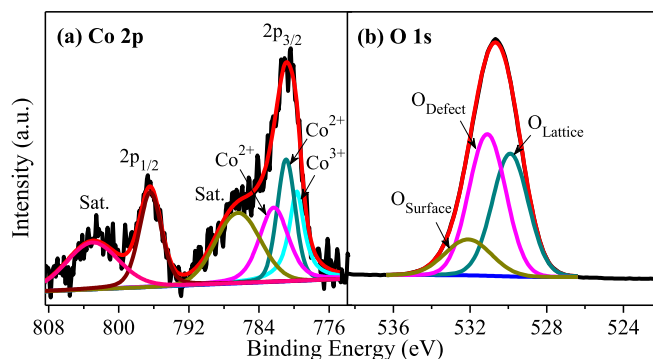
Fig. 12. XPS analysis for Co 2p (a) and O 1s (b) of used CoAl$_2$O$_4$@AP.

contributing to the MNZ oxidation in the CoAl$_2$O$_4$@AP/PMS system. Ethanol (EtOH) and *tert*-butanol (TBA) were first employed to determine the contributions of SO$_4$$^{\cdot-}$ and $^{\cdot}$OH. As shown in Fig. 13, 97% of MNZ was removed in 100 min without EtOH or TBA. When 5 mM EtOH was added into the reaction system, the removal efficiency of MNZ significantly decreased to ~39%. Further increasing the concentration of EtOH to 100 mM led to a complete inhibition to MNZ removal. However, TBA relatively weakly inhibited the MNZ removal. The removal efficiency can reach 80% with the addition of 100 mM TBA, much higher than that of the case with 5 mM EtOH. Even though the concentration of TBA increased to 500 mM, the removal efficiency was still higher than that of the system with 5 mM EtOH. Therefore, despite of the presence of $^{\cdot}$OH, SO$_4$$^{\cdot-}$ plays a decisive role in MNZ oxidation by the CoAl$_2$O$_4$@AP/PMS system. Other quenching agents, p-benzoquinone (BQ) and $_L$-histidine (HD), were also employed to verify the roles of O$_2$$^{\cdot-}$ and ^{1}O$_2$ accordingly [69,70].

Previous work indicates that HD and BQ can directly consume PMS [38,70]. To verify this, we measured the decomposition of 1 mM PMS by 1 mM BQ and 1 mM HD. The results show that (Fig. S5), in current work, < 20% and 10% of PMS was decomposed for HD and BQ, respectively; however, complete decomposition of PMS by CoAl$_2$O$_4$@AP occurred. The k_{obs} value for PMS consumption was determined to be 0.031 min^{-1}, which was comparable to that for MNZ removal (0.032 min^{-1}) by CoAl$_2$O$_4$@AP activated PMS. These findings imply that HD or BQ induced PMS consumption was very limited. Therefore, 1 mM BQ and 1 mM HD were further used to probe the role of O$_2$$^{\cdot-}$ and ^{1}O$_2$ in MNZ removal. Fig. 13 shows that HD caused higher inhibition to MNZ removal than BQ, implying that ^{1}O$_2$ played a more important role than O$_2$$^{\cdot-}$. This is because that, if the role of O$_2$$^{\cdot-}$ were stronger than ^{1}O$_2$, 1 mM BQ (1.2 × 10^6 s^{-1}, 1 × 10^5 s^{-1}, 3.8 × 10^4 s^{-1} and (0.9–1) × 10^6 s^{-1} for scavenging $^{\cdot}$OH, SO$_4$$^{\cdot-}$, ^{1}O$_2$ and O$_2$$^{\cdot-}$, respectively) would show much stronger inhibition to MNZ removal than 1 mM HD (5 × 10^6 s^{-1}, 2.5 × 10^6 s^{-1}, 6.6 × 10^4 s^{-1} and < 10^{-3} s^{-1} for scavenging $^{\cdot}$OH, SO$_4$$^{\cdot-}$, ^{1}O$_2$ and O$_2$$^{\cdot-}$, respectively) [38]; however, the result is reverse. The inhibition effect of 100 mM EtOH (1.9 × 10^8 s^{-1}, (1.6–7.8) × 10^6 s^{-1}, 3.8 × 10^2 s^{-1} and < 10^2 s^{-1} for scavenging $^{\cdot}$OH, SO$_4$$^{\cdot-}$, ^{1}O$_2$ and O$_2$$^{\cdot-}$, respectively) is comparable to that for 1 mM HD, further verifying that both SO$_4$$^{\cdot-}$ and ^{1}O$_2$ are dominant ROS for MNZ removal. By comprehensively analyzing the quenching results, it is reasonable to infer that

multiple ROS (^{1}O$_2$, O$_2$$^{\cdot-}$, SO$_4$$^{\cdot-}$ and $^{\cdot}$OH) were formed in CoAl$_2$O$_4$@AP/PMS system, and ^{1}O$_2$ and SO$_4$$^{\cdot-}$ were the decisive ROS in MNZ degradation [64].

3.5.3. MNZ mineralization and degradation products/pathways

TOC tests were employed to evaluate the MNZ mineralization by CoAl$_2$O$_4$@AP/PMS system. The result shows that the TOC removal efficiency increased with the increasing reaction time (Fig. S6). Typically, after 60 min reaction, the TOC removal efficiency reached 12.76%. When the reaction time increased to 100 min, the TOC removal efficiency increased to 18.83%. In theory, under a given volume, it will need 5.265 mM electrons from PMS to realize the complete degradation of 20 mg/L MNZ (refer to Reaction 12). Without interference, 1 mM PMS can provide 1 mM electrons. Following these rules, it can be concluded that about 18.99% of 20 mg/L MNZ can be mineralized, which is very close to the tested TOC removal efficiency (18.83%). The TOC removal efficiency after 100 min reaction is far lower than MNZ removal efficiency (97%), suggesting that most of MNZ molecules were probably transformed into other intermediates. Therefore, HPLC/MS/MS was used to probe the possible intermediates and oxidation pathways of MNZ by CoAl$_2$O$_4$@AP/PMS system.

$$C_6H_9N_3O_3 + 45/4O_2 \rightarrow 6CO_2 + 9/2H_2O + 3NO_3^- \quad (12)$$
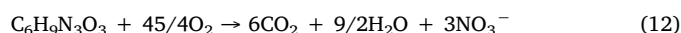
Five kinds of by-products with *m/z* of 143.08, 117.07, 104.07, 172.07 and 202.08 were detected in the MS spectra with a positive ionization mode (Fig. S7). The relative distribution ratios for the products with *m/z* of 143.08, 117.07, 104.07, 172.07 and 202.08 are 11.12%, 14.90%, 4.15%, 57.68% and 12.14%, respectively. The negative ionization mode of HPLC/MS/MC is also used for product detection. However, there is no signal in this mode. This is attributed to the fact that MNZ is a compound containing –NO$_2$ group, which can be easily detected by the positive ionization mode of HPLC/MS/MS [71,72]. According to the *m/z* spectra, the tentative degradation products were proposed. Their molecular structures and m/e information are summarized in Fig. 14 and Table 2. In general, MNZ could be degraded by ROS through various pathways. In detail, direct oxidation of MNZ resulted in the formation of P$_{201}$-1, P$_{201}$-2 and P$_{201}$-3 (1–4). The resultant P$_{201}$-3 was further degraded to P$_{171}$-1 via decarboxylation/dehydrogenation processes (5) and to P$_{103}$-1/P$_{103}$-2 through the combined processes of decarboxylation, denitrification, chain cleavage, rearrangement and dehydration reactions (6–11). The pathways of 6–11 caused the formation of P$_{142}$-1, P$_{142}$-2, P$_{142}$-3 and P$_{142}$-4 (12–16). The combination of oxidation and decarboxylation led to the formation of P$_{171}$-2 (15, 17), and the direct denitrification process of P$_{171}$-1 and P$_{171}$-2 led to the formation of P$_{142}$-2 and P$_{142}$-5 (18, 19). The decarboxylation and oxidation further transformed P$_{142}$-4 and P$_{142}$-5 to P$_{116}$ (20, 21). As the oxidation proceeded, some of these by-products might eventually be mineralized into CO$_2$ and H$_2$O.

At last, the antibacterial activity experiments were conducted to study the biotoxicity of the by-products. However, the results showed that there is little change in bacterial population of *E. coli* K12 treated with DI water, 20 mg/L MNZ solution before and after reaction by CoAl$_2$O$_4$@AP/PMS system. This result implies that there exsits no biotoxicity change for *E. coli* K12 (Fig. S8). We think this is probably due to the insensitivity of *E. coli* K12. The precise evaluation merits an

Table 1

XPS fitting results for the Co 2p and O 1s of ZIF-67@AP, fresh CoAl$_2$O$_4$@AP, and used CoAl$_2$O$_4$@AP.

Sample	Co 2p				O 1s			
	Co^{2+}	Co^{3+}	Satellite	Co^{2+}/Co^{3+}	O$_{Lattice}$	O$_{Defect}$	O$_{Surface}$	O$_{Defect}$/O$_{Lattice}$
ZIF-67@AP	53.60	13.86	32.54	3.87	51.83	43.86	4.31	0.85
Fresh CoAl$_2$O$_4$@AP	52.88	7.77	39.35	6.81	10.01	68.95	21.04	6.89
Used CoAl$_2$O$_4$@AP	48.91	20.03	31.06	2.44	39.77	45.78	14.44	1.15
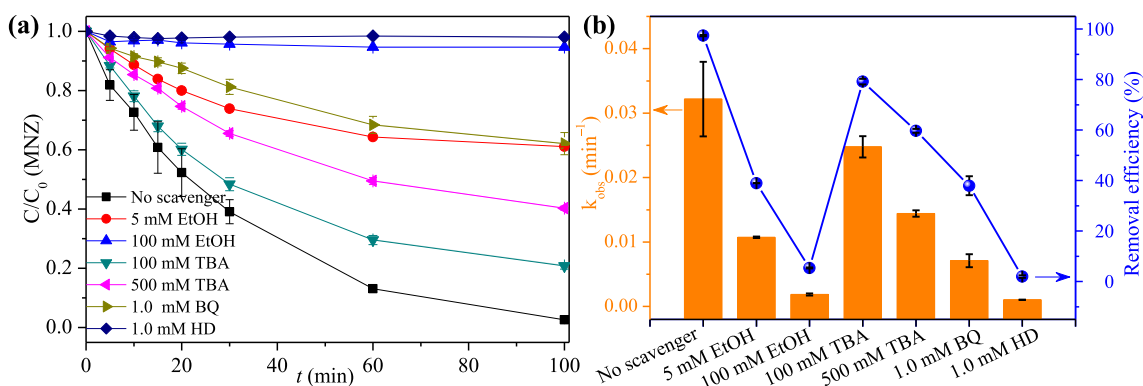
Fig. 13. Effect of various scavengers on MNZ removal ([CoAl$_2$O$_4$@AP] = 20 g/L, [MNZ]$_0$ = 20 mg/L, [PMS]$_0$ = 1.0 mM, pH = 6.48, T = 25 ± 1 °C).

in-depth study using sensitive bacterial, like *Vibrio fischeri*, as the testing organisms for the toxicity monitoring of by-products [73].

4. Conclusions

In this work, we successfully synthesized a interfacial CoAl$_2$O$_4$ shell/layer γ-Al$_2$O$_3$ pellet (CoAl$_2$O$_4$@AP) through a combined strategy of in situ growth of ZIF-67 onto the pellet surface and the subsequent calcination. The CoAl$_2$O$_4$@AP composites demonstrated unprecedentedly catalytic activity to activate PMS toward ROS generation for MNZ removal. Benefitted from the unique coordination reactions of Co, Al and O elements, CoAl$_2$O$_4$ as the heterogeneous catalytic species within CoAl$_2$O$_4$@AP exhibited a higher catalytic activity than ZIF-67 derived Co$_3$O$_4$ and commercial Co$_3$O$_4$ toward PMS activation. The

effects of PMS dosage, solution temperature, initial pH and co-existing ions on MNZ removal and the possible degradation pathways of MNZ were investigated. Co^{2+}/Co^{3+} and oxygen vacancies within CoAl$_2$O$_4$@AP facilitated the generation of SO$_4^{\cdot-}$, ·OH, O$_2^{\cdot-}$ and ^{1}O$_2$ from the activated PMS. SO$_4^{\cdot-}$ and ^{1}O$_2$ were identified as the decisive ROS in MNZ removal. The catalytic reactivity of aged CoAl$_2$O$_4$@AP can be recovered via a PMS-assisted cleaning procedure, which holds a great promise in practical applications. This work provides new insights into constructing monolithic CoAl$_2$O$_4$-containing catalysts toward ROS generation and expands the application of novel MOFs-based catalysts for environmental remediation.
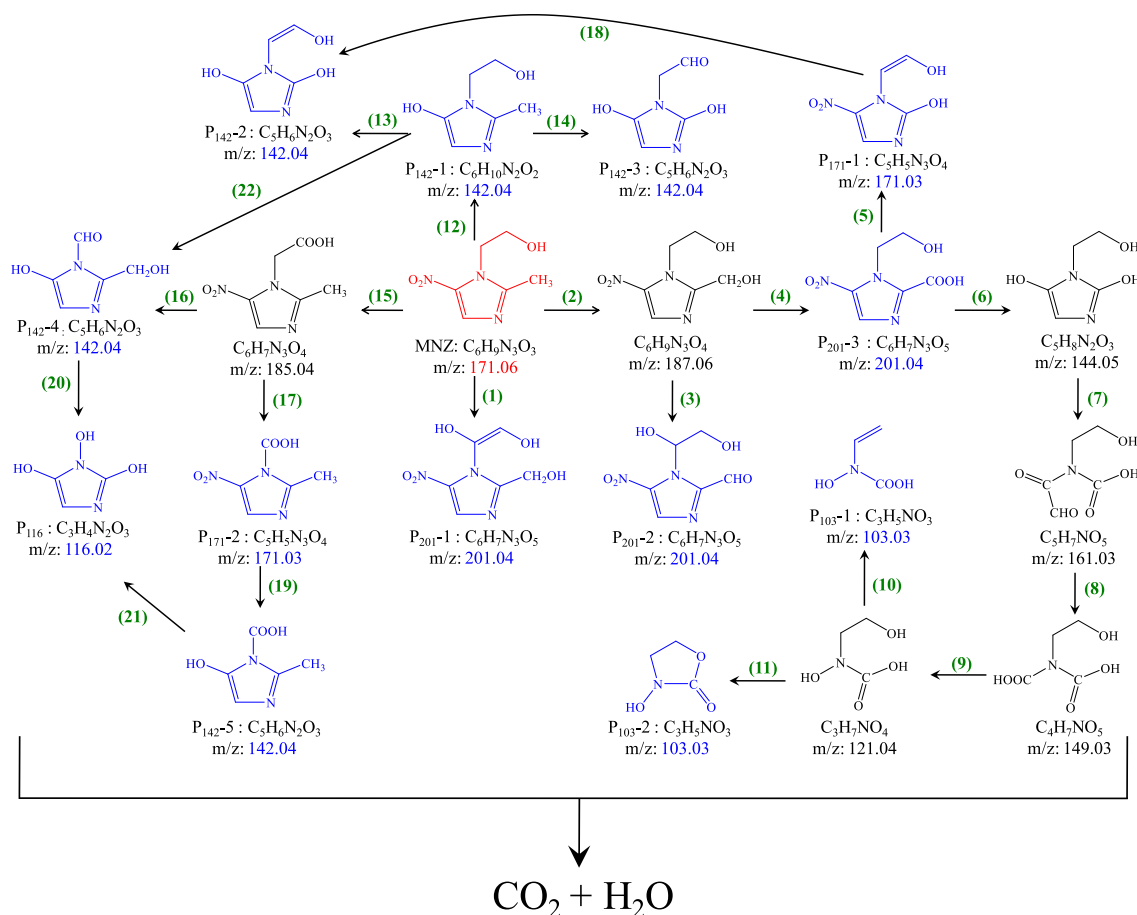

Fig. 14. Proposed oxidation products and pathways for MNZ degradation by CoAl$_2$O$_4$@AP/PMS system.

Table 2
Intermediate products of MNZ during the treatment process detected by HPLC/MS/MS.

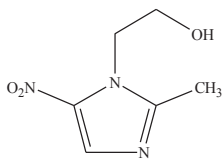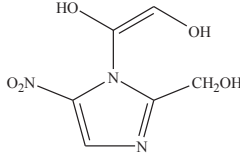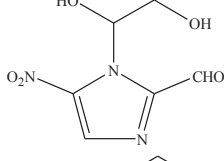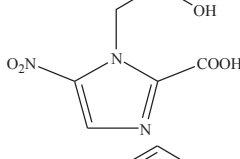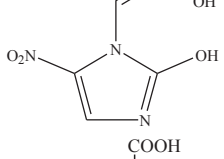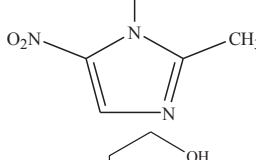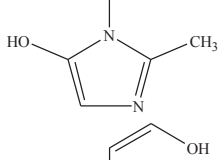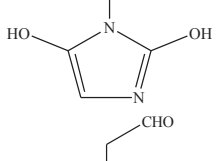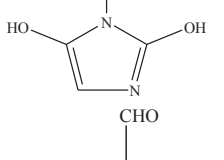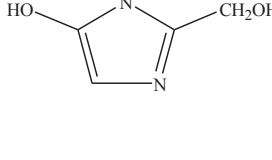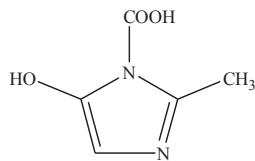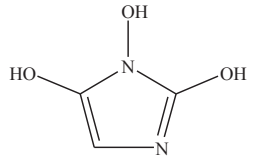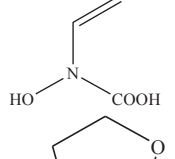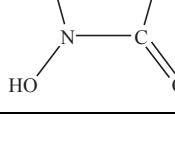| Item	Rt	MW	Molecular formula	Structural formula
MNZ	6.01	171.06	$C_6H_9N_3O_3$	
P_{201-1}	6.41	201.04	$C_6H_7N_3O_5$	
P_{201-2}	6.41	201.04	$C_6H_7N_3O_5$	
P_{201-3}	6.41	201.04	$C_6H_7N_3O_5$	
P_{171-1}	6.01	171.03	$C_5H_5N_3O_4$	
P_{171-2}	6.01	171.03	$C_5H_5N_3O_4$	
P_{142-1}	1.34	142.04	$C_6H_{10}N_2O_2$	
P_{142-2}	1.34	142.04	$C_5H_6N_2O_3$	
P_{142-3}	1.34	142.04	$C_5H_6N_2O_3$	
P_{142-4}	1.34	142.04	$C_5H_6N_2O_3$	

Table 2 (*continued*)

Item	Rt	MW	Molecular formula	Structural formula
P_{142-5}	1.34	142.04	$C_5H_6N_2O_3$	
P_{116}	1.69	116.02	$C_3H_4N_2O_3$	
P_{103-1}	1.99	103.03	$C_3H_5NO_3$	
P_{103-2}	1.99	103.03	$C_3H_5NO_3$	

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.125339.

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