Activation of peroxymonosulfate by CuCo$_2$O$_4$ nano-particles towards long-lasting removal of atrazine

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ABSTRACT

The effect of peroxymonosulfate (PMS) activated by nanocrystalline CuCo$_2$O$_4$ (NPS) on removal of atrazine (ATZ) was studied. First, the main experimental parameters were studied, including CuCo$_2$O$_4$ dose, PMS dose, initial pH value, and co-existing ion. The removal of ATZ (~99%) was attained under the optimal conditions (i.e., 150 mg/L CuCo$_2$O$_4$, 0.2 mM PMS, 5 mg/L ATZ, initial pH value of 6.8, and reaction time of 30 min). However, the removal of ATZ only reached 20.9% in the PMS alone system and there was no significant ATZ removal when adding CuCo$_2$O$_4$ alone into the solution, proving the good performance of the CuCo$_2$O$_4$/PMS system. Furthermore, reusability of CuCo$_2$O$_4$ was tested through five consecutive runs. To confirm which main active radicals were responsible in the system, two radical quenching experiments were carried out and electron paramagnetic resonance (EPR) was tested. In addition, the characterization of fresh and reacted CuCo$_2$O$_4$ NPs was tested by SEM, TEM, EDS, XRD, and XPS. Subsequently, based on the characterization of CuCo$_2$O$_4$ NPs and identification of radicals, ≡Cu$^{2+}$/≡Cu$^+$ and ≡Co$^{3+}$/≡Co$^{2+}$ were considered to be the main catalytic species, while the synergistic effect of Cu and Co played a crucial role. Finally, the degradation pathway of ATZ was proposed.

Key words: atrazine, catalytic mechanism, CuCo$_2$O$_4$, peroxymonosulfate

HIGHLIGHTS

- Nanoparticles CuCo$_2$O$_4$ was fabricated as peroxymonosulfate activator.
- ATZ could be effectively degraded by CuCo$_2$O$_4$/PMS system.
- Five degradation pathways of ATZ were proposed.
- CuCo$_2$O$_4$ has excellent reusability.

INTRODUCTION

For the last decade, the use of herbicides has become increasingly important in agriculture for weed control. As the most common used s-triazine herbicide, atrazine (ATZ) is widely applied for its high efficiency. Furthermore, ATZ has been applied for more than 40 years in over 80 countries (Hayes et al. 2002). However, because ATZ is heavily used in huge quantities, it has long been exposed to the environment. In addition, due to its high water mobility and persistence, traces of ATZ have been detected in surface water, even in groundwater (Khan et al. 2014; Li et al. 2018; Wang et al. 2020a). It will cause serious health problems, including impaired sexual development, deformsities, and cancer (Hayes et al. 2002) when the concentration of ATZ exceeds 0.0001 mg/L (Pelizzetti et al. 1990). The application of ATZ has been prohibited by official order in many European countries (Ji et al. 2015), but its use still remains widespread in China (Chen et al. 2011). Therefore, it is necessary to continuously improve and develop efficient ATZ removal techniques.

In recent years, conventional advanced oxidation processes (AOPs), such as photocatalytic (Luo et al. 2015; Khaleel et al. 2019), Fenton (De Laat et al. 1999; Klamerth et al. 2009), Fenton-like (Zhang & Zhou 2019), and ozonation (Kuosa et al. 2009), have been developed to degrade organic pollutants in wastewater. All of the above methods can produce hydrogen
radicals (HO•), whose redox potential is relatively high ($E^\circ = 2.8$ V). However, the deficiencies of the above treatment were non-negligible, including short life span of HO•, rigorous pH condition, and high cost. It has been found that SO4$^{2-}$ based on AOPs has a good performance on ATZ removal with a second-order rate constant of $10^6-10^9$ M$^{-1}$s$^{-1}$ (Zhao et al. 2016a). As a radical of high redox potential ($E^\circ = 2.5-3.1$ V) (Zhang et al. 2019a; Nimai et al. 2020), SO4$^{2-}$ has a long-life span to contact with the targeted contaminant (Du et al. 2020). Moreover, because of its great selectivity (Li et al. 2018), SO4$^{2-}$ can react actively with compounds of unsaturated bonds and aromatic ring structures (Li et al. 2017). A common and efficient source of SO4$^{2-}$ is peroxymonosulfate (PMS), which has been successfully activated by many methods, such as transition metals (Anipsitakis & Dionysiou 2003; Zhou et al. 2016; Wang et al. 2020b), UV irradiation (Olmmez-Hanci et al. 2011; Zhang et al. 2015), ultrasound (Lifka et al. 2003; Mahamuni & Adewuyi 2010; Zou et al. 2014), carbon-based catalysts (Chen et al. 2019), semiconductors (Jo et al. 2018), and so on.

Among those activation methods, transition metals have been regarded as one kind of low-cost and effective method, which is widely used in wastewater treatment to activate PMS. Transition metal catalysis can be divided into homogeneous and heterogeneous catalysis. The homogeneous catalysis often has high removal efficiency. For example, polychlorinated biphenyls (PCB) can be degraded by Fe2+/PMS system with over 90% PCB removal within 24 h (Rastogi et al. 2009). However, the homogeneous catalysts for PMS activation have some shortcomings, including high metal ion dosage, production of metal oxide sludge, difficult to be separated and recovered from solution, and strict pH conditions (Li et al. 2017; Ding et al. 2019). Especially, for its high solubility and toxicity, Co2+ ion released into the solution after treatment will cause secondary pollution. Many countries have prohibited the application of Co2+ in wastewater treatment as a consequence.

In contrast to homogeneous catalysts, heterogeneous catalysts are easier to recycle from the solution. More importantly, heterogeneous catalysts usually produce little ion leaching, and, as a result, have been widely studied to activate PMS. CuCo2O4 spinel nanoparticles (NPs) have the characteristics of stable crystal structure, large specific surface area, low solubility, and are also highly efficient to activate PMS (Feng et al. 2015b). In fact, CuCo2O4 is widely used in supercapacitors, electrochemical sensors, and lithium batteries for its low cost, higher electronic conductivity, and excellent capacitance performance than either copper oxide or single Co (Liu et al. 2018; Xu et al. 2019). Notably, CuCo2O4 has excellent electrochemical properties, such as high electrical conductivity, which may contribute to electron transfer in AOPs to generate more radicals. Moreover, as a bimetallic oxide, CuCo2O4 has higher catalytic activity than monometallic oxide due to the synergistic catalytic effect of Cu and Co (Song et al. 2020). However, only a few studies have reported its application in the field of AOPs. Therefore, it is worth studying the removal of ATZ by CuCo2O4/PMS system.

In this work, the nanomaterial CuCo2O4, that can activate PMS efficiently, was studied. The main goals of the study are as follows: (i) to investigate the effects of main experimental parameters and inorganic anions on the removal of ATZ; (ii) to prove the performance of CuCo2O4/PMS system by two comparative experiments; (iii) to evaluate the stability and reusability of CuCo2O4 by five recycling experiments; (iv) to identify the free radicals which make a contribution to ATZ removal; (v) to deduce the catalytic mechanism from known results; (vi) to analyze the intermediate products of ATZ in the CuCo2O4/PMS system and infer the removal pathway of ATZ.

**MATERIALS AND METHODS**

**Chemicals and reagents**

Atrazine (≥97.0%), cobalt nitrate (Co(NO3)2·6H2O, ≥98.5%), copper nitrate (Cu(NO3)2·3H2O, ≥98.5%), copper oxide (CuO, ≥98.5%), cobalt sesquioxide (Co2O3, ≥98.5%), sodium bicarbonate (NaHCO3, ≥98.5%), sodium nitrate (NaNO3, ≥98.5%), sodium hydrogen phosphate (NaHPO4, ≥98.5%), humic acid (HA, ≥90.0%), sodium chloride (NaCl, ≥98.5%), ethanol (EtOH), tert-butyl alcohol (TBA), and sodium hydroxide (NaOH, ≥98.0%) were purchased from Chengdu Kelong reagent company. Potassium peroxymonosulfate (PMS, KHSO5·0.5KHSO4·0.5 K2SO4) was obtained from Sigma-Aldrich. The original solution of ATZ (5 mg/L) was obtained through dissolving ATZ with ultrapure water with stirring for 12 h. Ultrapure water (18.2 MΩ cm) used in the experiments was produced by a UPH purification system (Ulupure, China).

**Preparation of catalyst**

In this study, CuCo2O4 nanoparticles were synthesized by sol-gel method (Zhao et al. 2016b). First, 0.025 mol Co(NO3)2·6H2O and 0.05 mol Cu(NO3)2·3H2O were dissolved in 100 mL deionized water and mechanically stirred at 300 rpm for 10 min. Then, 0.09 mol citric acid was added to the solution and stirred at 80 °C for 2 h. Next, after the mixture had been evaporated in a water bath of 90 °C for 1 h, the obtained gel complex was transferred to the oven and baked to a powder at the
temperature of 90 °C. Lastly, the powder was transferred to a muffle furnace and heated to 550 °C at a heating rate of 5 °C/min, and eventually dried at the temperature of 550 °C for 5 h.

Experimental procedures
In general, all ATZ removal experiments were conducted with water bath heating, and a mechanical stirring speed of 300 rpm, reaction time of 30 min, and initial pH value of 6.8. At the beginning of the experiment, 150 mL of atrazine solution was transferred into a 400 mL beaker. Then, the beaker was placed in a water bath until the temperature of the water bath rose to 30 °C. Subsequently, the required amount of catalyst and oxidant were added at the same time. The samples were taken with syringes at predetermined intervals and filtered immediately with 0.45 μm PTFE syringe filter disks. Prior to sampling, as quenching agents of free radicals, 20 μL tert-butanol and ethanol were added to the sampling tube. Each data were the average of corresponding experiments repeated three times. Except for organic solvents, the medium of all other solutions is ultrapure water.

Analytical methods
FEI Tecnai G2 F20 S-TWIN (Hillsboro, Oregon, USA) scanning electron microscope (SEM) and transmission electron microscopy (TEM) were utilized to scan the surface morphology of the fresh CuCo2O4 NPs. The surface elementary compositions of CuCo2O4 NPs were obtained by energy dispersive spectrometer (EDS). The CuCo2O4 NPs were characterized by X-ray diffraction (XRD) EMPYREAN diffractometer (PANalytical B.V., The Netherlands). An X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD, Kratos Co., UK) was used to characterize the chemical oxidation states on the surface of fresh and reacted CuCo2O4 NPs.

Atrazine concentration was detected by reversed-phase high performance liquid chromatography (Agilent USA) (Lai et al. 2018). A Bruker EMX-E spectrometer (Germany) was applied to monitor electron paramagnetic resonance (EPR) for detection of radicals. The intermediates of ATZ were analyzed by ultra performance liquid chromatography-quadrupole time of flight-mass spectrometer/mass spectrometer (UPLC-QTOF-MS/MS) system (Exion LC™ AC, X500R QTOF, SCIEX) (Hong et al. 2019). In the experiment, the removal of ATZ can be described by the pseudo-first-order kinetic pattern, which can be expressed as follows:

\[
\ln \left( \frac{C}{C_0} \right) = -k_{\text{obs}} t
\]

where \( C \) is the concentration of ATZ of the sample taken at instant \( t \), and \( C_0 \) is the initial atrazine concentration, \( k_{\text{obs}} \) is the kinetic rate constant, and \( t \) is the time of reaction.

RESULTS AND DISCUSSION
Characterization of CuCo2O4 NPs
SEM, TEM, EDS, and XRD analysis of CuCo2O4
The morphology and microstructure of CuCo2O4 NPs was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). According to Figure 1(a) and 1(b), CuCo2O4 NPs showed an irregular layered structure with some nanoparticles on the surface. In addition, CuCo2O4 NPs were nanoparticles with diameters varying from 80 to 100 nm, measured by ‘Nano measurer’ software. Figure 1(c) shows the chemical atomic ratio of Co and Cu is 2.27:1. The percentage of O after usage increased for the increase of the absorbed H2O on the CuCo2O4 NPs. Furthermore, CuCo2O4 NPs were characterized by XRD as shown in Figure 1(d). Figure 1(d) shows that the eight characteristic diffraction peaks at \( 2\theta = 19.0^\circ, 31.4^\circ, 36.8^\circ, 39^\circ, 44.5^\circ, 55.5^\circ, 59.6^\circ, 65.2^\circ \) can be indexed to (111), (220), (311), (222), (400), (422), (511), and (440) of spinel CuCo2O4 (Panayotov & Mehandjiev 1987), indicating the high purity of CuCo2O4. Moreover, the peak at 35.5° could be indexed to (−111) of CuO (JPCDS 48-1548), similar to the study by Wang et al. (2020c). The results were consistent with the removal of sulfamethazine by CuCo2O4/PMS system reported by Feng et al. (2015b). In addition, CuCo2O4 NPs exhibit a good performance in the structural stability since there was little difference and no new diffraction peak in the reacted particles, compared with the fresh CuCo2O4.
XPS analysis of CuCo2O4 NPs
To further understand the composition and chemical states of the elements on the surface of CuCo2O4, the XPS spectra of fresh and reacted CuCo2O4 NPs were acquired. Figure 2(a) shows a survey scan of CuCo2O4 NPs and illustrates the existence of Cu 2p, Co 2p, and O 1 s. Moreover, the binding energy was corrected by the carbon 1 s peak (284.8 eV) to obtain accurate spectra. Figure 2(b)–2(d) show the core level spectra of Co 2p, Cu 2p, and O 1 s.

The core-level spectra of Co 2p are shown in Figure 2(b) and four peaks at the binding energy of 780.45, 782.03, 795.54, and 797.30 eV were obviously observed. Corresponding to Co 2p3/2 and Co 2p1/2, respectively, both fitting peaks at 780.45 and 795.54 eV, which had a spin-energy separation of around 15 eV, indicated the existence of Co(II) (Wang et al. 2020c). In addition, the fitting peaks at 782.03 eV and 797.30 eV were assigned to Co(III) (Kibsgaard et al. 2012; Xu et al. 2018). In contrast to fresh CuCo2O4, the reacted CuCo2O4 NPs showed little difference in characteristic peak position and no new fitting peak was observed. As well, the peak area of Co(II) decreased from 45.44% to 42.25%, inferring the transformation between Co(II) and Co(III).

The XPS spectra of Cu 2p are displayed in Figure 2(c) to better understand the role of Cu in PMS activation process by CuCo2O4. Cu 2p3/2 was deconvoluted into two peaks with the binding energy of 934.08 eV and 937.17 eV, which were indexed into Cu(I) and Cu(II), respectively (Chen et al. 2020). Compared with the fresh CuCo2O4, the atom ratio Cu(I)/Cu(II) of reacted CuCo2O4 decreased from 7.29 to 7.00, which was supposed to be the conversion between Cu(I) and Cu(II).
Figure 2(d) depicts the core level spectra of O 1 s. The peak located at the binding energy of 530.61 eV was indexed into the lattice oxygen O$_{\text{A}}$ (O$_{\text{A}}$) in CuCo$_{2}$O$_{4}$ NPs and the peak at around 532.01 eV belongs to the OH (O$_{\text{B}}$) adsorbed at the surface of CuCo$_{2}$O$_{4}$ (Xu et al. 2016). Compared with the fresh CuCo$_{2}$O$_{4}$, the area of the fitting peak at 532.01 eV decreased from 48.29% to 14.36% in the reacted CuCo$_{2}$O$_{4}$. Meanwhile, a new peak assigned to the O (O$_{\text{C}}$) of adsorbed H$_{2}$O appeared at the binding energy of 533.27 eV, suggesting that the hydroxyl groups on the surface of CuCo$_{2}$O$_{4}$ are converted into adsorbed water after the activation of PMS in the treatment process (Xu et al. 2016).

Analysis of BET and FT-IR
Analysis of BET and FT-IR is located in Text S1 in the Supplementary Material.

Effect of main experimental parameters
Effect of CuCo$_{2}$O$_{4}$ dose
The effect of CuCo$_{2}$O$_{4}$ NPs’ dosage (0–400 mg/L) on the removal of ATZ was studied systematically. As seen from Figure 3(a) and 3(b), the ATZ removal was 7% when only PMS was added because of the weak oxidation capacity of PMS. However, with another addition of 20 mg/L CuCo$_{2}$O$_{4}$, the ATZ removal was enhanced significantly from 7% to 60% within 30 min. This manifests that PMS alone had a feeble effect on the removal of ATZ, and CuCo$_{2}$O$_{4}$ is superior in activating PMS. Moreover, the ATZ removal was highly dependent on the amount of catalyst when its addition was less than 150 mg/L. When its
dosage increased to 150 mg/L, a removal efficiency of >99% was achieved. Meanwhile, the $k_{obs}$ at 150 mg/L CuCo$_2$O$_4$ (0.160 min$^{-1}$) was nearly six times of that obtained at 20 mg/L CuCo$_2$O$_4$ (0.028 min$^{-1}$) in Figure 3(b). As more CuCo$_2$O$_4$ (>150 mg/L) was added, the removal efficiency remained at >99%. Its $k_{obs}$ increased from 0.160 min$^{-1}$ to 0.211 min$^{-1}$, 0.235 min$^{-1}$, 0.257 min$^{-1}$ when the dosage of CuCo$_2$O$_4$ increased from 150 mg/L to 200 mg/L, 300 mg/L, and 400 mg/L. The reasons for this phenomenon were as follows: (1) the increased active site could promote the activation of PMS at the CuCo$_2$O$_4$ NPs dosage of 0–150 mg/L, leading to the enhancement of the removal of ATZ; (2) when the dose of CuCo$_2$O$_4$ exceeded 150 mg/L, CuCo$_2$O$_4$ was no longer the limiting factor for ATZ removal. However, the number of radicals produced per unit time increased with the dosage of CuCo$_2$O$_4$, increasing the $k_{obs}$ value for ATZ removal. Therefore, the optimum dosage of CuCo$_2$O$_4$ was selected as 150 mg/L in the following experiments.

**Effect of PMS dose**

Figure 3(c) and 3(d) show the effect of PMS dosage (0 mM–0.40 mM) on ATZ removal. Compared with the ATZ removal by 150 mg/L CuCo$_2$O$_4$ alone, the removal of ATZ with the addition of 0.10 mM PMS and 150 mg/L CuCo$_2$O$_4$ significantly increased to 67% within 30 min of treatment. The phenomenon could be interpreted as follows. The CuCo$_2$O$_4$ almost had no adsorption on ATZ; (2) CuCo$_2$O$_4$ had a satisfactory performance in activating PMS in the CuCo$_2$O$_4$/PMS system. Furthermore, with the dose of PMS increasing from 0.10 mM to 0.20 mM, the ATZ removal was enhanced from 67% to >99%. When the addition of PMS exceeded 0.20 mM in the solution, the ATZ removal remained at >99%. For $k_{obs}$ mentioned in Figure 3(d), when the dosage of PMS increased from 0.1 mM to 0.15, 0.20, 0.25, 0.30, and 0.40 mM, $k_{obs}$ for ATZ removal increased from 0.052 min$^{-1}$ to 0.088, 0.160, 0.283, 0.302, 0.368 min$^{-1}$, respectively. The following points could account
for the results: (1) due to the direct oxidation by PMS, the increase of PMS dosage led to the enhancement of the removal of ATZ; (2) the active sites of CuCo$_2$O$_4$ had not been completely occupied by PMS, thus, with the increase of PMS, the contact between CuCo$_2$O$_4$ and PMS could be enhanced, producing more radicals to accelerate the ATZ removal. However, when more PMS (>0.2 mM) was added, the self-quenching phenomenon by excessive PMS reported by Shahzad et al. (2019) and Jawad et al. (2020) did not occur in the study. At the maximum additive amount of PMS, the excessive PMS in Shahzad’s study exceeded 2 mM, which was ten times that in the study. This might be the reason why there was no self-quenching phenomenon in the CuCo$_2$O$_4$/PMS system. Therefore, the optimum dosage of PMS was selected as 0.2 mM in the following experiment.

**Effect of initial pH**

The effect of different initial pH (3, 5, 8, 9, and 11) on the removal of ATZ was studied (Figure 4(a) and 4(b)). Figure 4(a) shows that ATZ was barely removed at pH 11 and the highest ATZ removal (≥99%) was reached at pH 5. Compared with the initial pH 5, the removal of ATZ at the initial pH 8 and 9 slightly declined to 94 and 85% and the corresponding $k_{\text{obs}}$ for the removal of ATZ decreased from 0.205 to 0.100 and 0.061 min$^{-1}$, respectively. In addition, the ATZ removal significantly dropped to 9.8% when pH decreased to 3.0 and the $k_{\text{obs}}$ declined from 0.205 to 0.003 min$^{-1}$.

Figure 4(c) shows the pH variation of the reaction solution at different initial pH. At the initial pH values of 5, 8, and 9, the pH of the solution dropped rapidly in the first 5 min due to the hydrolysis of PMS. For the next 25 min, the pH of the solution was maintained at 4.3, 5.5, and 6.4, respectively. When the initial pH value was 11, the pH of the solution decreased slightly...
in the first 3 min and then barely changed. At the initial pH value of 3, the pH value remained almost constant during the process of ATZ removal.

According to the above results, weak acidic or neutral conditions are more favorable for the removal of atrazine, which was in line with the removal of diphenylamine in PS/Fe\(^{3+}\)/Ag\(^+\) system (Li et al. 2009) and fluomequine in PS/Fe\(_2\)O\(_4\)/MWCNTs/PHQ system (Feng et al. 2015a). The following factors can be used to interpret the phenomenon. (1) The zeta potential of CuCo\(_2\)O\(_4\) at different pH (2—12) was detected. As illustrated in Supplementary Material, Figure S2, the zeta potential of CuCo\(_2\)O\(_4\) showed a decreasing trend with the increase of pH. The results suggested that the higher the pH of the aqueous solution, the stronger the negative charge on the surface of CuCo\(_2\)O\(_4\). PMS (HSO\(_5\)\(^–\) or SO\(_4\)\(^2–\)) was also negatively charged in the aqueous solution. Therefore, the electrostatic repulsion between PMS and CuCo\(_2\)O\(_4\) was enhanced at a higher pH of the solution. Due to this factor, the ATZ removal underwent a drastic decline when pH increased from 5 to 8, 9, and 11. (2) SO\(_4\)\(^2–\) was identified as the dominant radical which was in favor of the removal of organic pollution under the acidic condition (Li et al. 2009). In alkaline condition, SO\(_4\)\(^2–\) would have an active reaction with OH\(^–\) (Equation (1)). This reaction could produce HO\(^–\) and SO\(_4\)\(^2–\). The HO\(^–\) had a lower redox potential than SO\(_4\)\(^2–\) and the simultaneous production of SO\(_4\)\(^2–\) would inhibit the activity of SO\(_4\)\(^2–\) and HO\(^–\) (Deng et al. 2013). Therefore, ATZ removal was significantly reduced when the pH of the solution was alkaline. (3) An overly acidic environment (pH = 3) might also inhibit the ATZ removal since a large amount of H\(^+\) could react with active species of SO\(_4\)\(^2–\) and HO\(^–\) to form HSO\(_4\) and H\(_2\)O (Equations (2) and (3)) (Zhang et al. 2019b). The pKa of ATZ was 1.6 (Chandra & Usha 2021). Therefore, more ATZ molecules present as neutral ones, which were relatively hard to be degraded by radicals than ATZ\(^–\) ions at pH 3. In addition, the leaching of Co and Cu was detected in Supplementary Material, Figure S3. When the pH decreased to 3, the obvious increase of the metal leaching was observed, suggesting that the synergistic effect of Cu and Co in CuCo\(_2\)O\(_4\) NPs could be inhibited by the metal leaching of Cu and Co, which might be the reason for the decline in ATZ removal at lower pH (Chen et al. 2020). These factors might be the reason why ATZ removal dropped dramatically when pH value changes from 5.0 to 5.0.

\[
\begin{align*}
\text{SO}_4^{2–} + \text{OH}^– & \rightarrow \text{SO}_4^{2–} + \text{HO}^\ast \\
\text{H}^+ + \text{SO}_4^{2–} + \text{e}^- & \rightarrow \text{HSO}_4^- \\
\text{H}^+ + \text{HO}^\ast + \text{e}^- & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

(1)\n(2)\n(3)

**Effect of inorganic anions**

The actual wastewater usually contains many kinds of anions and other compounds, including NO\(_3\)\(^–\), HCO\(_3\)\(^–\), HPO\(_4\)\(^2–\), Cl\(^–\), and humic acid. These inorganic anions and compounds might have a complex effect on the removal of ATZ. As a result, these five substances were added to ATZ solution, respectively, to investigate their effect on ATZ removal. The results are shown in Figure 5(a)—5(f).

The effect of HCO\(_3\)\(^–\) (0, 1, 10, and 25 mM) on the removal of ATZ was studied and the results are shown in Figure 5(a) and 5(b). With the addition of HCO\(_3\)\(^–\) increasing, the removal of ATZ decreased from >99% to 87.6%, 57.9%, 54.6%, and the corresponding \(k_{\text{obs}}\) value significantly declined from 0.160 to 0.070, 0.030, 0.027 min\(^–1\), respectively. The results could be explained by the fact that HCO\(_3\)\(^–\) can react with SO\(_4\)\(^2–\) and HO\(^–\), producing HCO\(_3\)\(^–\) (Equations (4) and (5)) (Ji et al. 2015; He et al. 2019) which had a lower redox potential. Supplementary Material, Figure S4 shows the pH change of CuCo\(_2\)O\(_4\)/PMS system during the reaction after the addition of HCO\(_3\)\(^–\). As can be seen in Supplementary Material, Figure S4, when HCO\(_3\)\(^–\) was added to the CuCo\(_2\)O\(_4\)/PMS system, the solution became weakly alkaline, which was not conducive to the activation of PMS. This factor might be the reason for the inhibition in the ATZ removal.

\[
\begin{align*}
\text{HO}^\ast + \text{HCO}_3^- & \rightarrow \text{OH}^- + \text{HCO}_3^- \\
\text{SO}_4^{2–} + \text{HCO}_3^- & \rightarrow \text{HCO}_3^- + \text{SO}_4^{2–}
\end{align*}
\]

(4)\n(5)

The influence of the NO\(_3\)\(^–\) (0, 1, 10, and 25 mM) inorganic anion on the removal of ATZ was investigated in Figure 5(c) and 5(d). The ATZ removal remained at >99% with little change of the \(k_{\text{obs}}\) when the concentration of NO\(_3\)\(^–\) increased from 0 to 25 mM. This result reveals that concentration of NO\(_3\) less than 25 mM had a slight influence on the ATZ removal.
Furthermore, NO$_3^-$ at the concentration of 25 mM showed little inhibition of the removal of ATZ. The results could be interpreted as ATZ removal is not affected by a small amount of NO$_3^-$ in the CuCo$_2$O$_4$/PMS system, which is consistent with the degradation of ATZ by the CoFe$_2$O$_4$/PMS system (Li et al. 2018).

Figure 5(e) and 5(f) show the influence of HPO$_4^{2-}$ (0, 1, 10, and 25 mM) on the removal of ATZ. Compared to no HPO$_4^{2-}$ addition, the ATZ removal decreased from >99% to 25.6% with adding 1 mM HPO$_4^{2-}$ to the reaction solution in the CuCo$_2$O$_4$/PMS system. Meanwhile, the $k_{obs}$ for ATZ removal showed a distinct reduction (from 0.160 to 0.009 min$^{-1}$) when the addition concentration of HPO$_4^{2-}$ changed from 0 to 1 mM. Nevertheless, the ATZ removal did not show a further decrease when the addition concentration of HPO$_4^{2-}$ increased from 1 to 10 and 25 mM. On the contrary, the ATZ removal increased from 25.6% to 38.2% and 39.5% and the $k_{obs}$ also increased slightly from 0.09 min$^{-1}$ to 0.015 min$^{-1}$ and

**Figure 5** | Influences of (a and b) HCO$_3^-$, (c and d) NO$_3^-$, (e and f) HPO$_4^{2-}$, (g and h) Cl$^-$, and (i and j) HA on the removal of ATZ. Experiment conditions: [ATZ]$_0$ = 5 mg/L, [CuCo$_2$O$_4$]$_0$ = 150 mg/L, [PMS]$_0$ = 0.2 mM, initial pH = 6.8, and reaction time = 30 min. (Continued.)
With increasing the addition concentration of \( \text{HPO}_4^{2-}/C_0 \), the inhibition of ATZ removal increased initially, followed by a decrease. The inhibition of ATZ removal could be explained as \( \text{SO}_4^{2-}/C_0 \) and \( \text{HO}^+ \) would react with \( \text{HPO}_4^{2-}/C_0 \) and produce some species with lower redox potential according to Equations (6) and (7) (Buxton et al. 1988; Neta et al. 1988). The reason for the reduction of the inhibition was as follows: when \( \text{HPO}_4^{2-}/C_0 \) was excessive, some of the \( \text{HPO}_4^{2-}/C_0 \) could scavenge \( \text{SO}_4^{2-}/C_0 \) and \( \text{HO}^+ \), and the rest would activate PMS to produce \( \text{SO}_4^{2-}/C_0 \) and \( \text{HO}^+ \). The activation of \( \text{HPO}_4^{2-}/C_0 \) for PMS was demonstrated in a previous study by Lou et al. (2014). Therefore, the inhibition of ATZ removal was still in existence but reduced when the concentration of \( \text{HPO}_4^{2-}/C_0 \) was higher than 1 mM.

\[
\text{HO}^+ + \text{HPO}_4^{2-} \rightarrow \text{HPO}_4^{2-} + \text{OH}^- \quad (6)
\]

\[
\text{SO}_4^{2-} + \text{HPO}_4^{2-} \rightarrow \text{HPO}_4^{2-} + \text{SO}_4^{2-} \quad (7)
\]

The effect of different concentrations of \( \text{Cl}^- \) (0, 1, 10, and 25 mM) on ATZ removal was investigated. As exhibited in Figure 5(g) and 5(h), low concentration of \( \text{Cl}^- \) significantly inhibited the removal of ATZ. On the contrary, an increase in the concentration of \( \text{Cl}^- \) decreased the degree of inhibition. When the concentration of \( \text{Cl}^- \) increased to 25 mM, the \( k_{\text{obs}} \) for ATZ removal increased to 0.525 min\(^{-1}\), suggesting that high concentration of \( \text{Cl}^- \) promoted the removal of ATZ to a certain extent. The results can be explained as follows: (1) at low concentration, \( \text{Cl}^- \) would compete with ATZ for \( \text{SO}_4^{2-}/C_0 \) and \( \text{HO}^+ \) to generate less reactive chlorine species such as \( \text{Cl}^- \) (2.4 V) and \( \text{Cl}_2^- \) (2.1 V) (Equations (8)–(10)), causing the reduction of the removal of ATZ; (2) when the concentration of \( \text{Cl}^- \) increased to 25 mM, \( \text{Cl}^- \) would react with PMS to form HClO (Equation (11)). Although the redox potential of HClO (1.63 V) was low, HClO had a much longer lifetime as

\[
\text{HO}^+ + \text{Cl}_2^- \rightarrow \text{HClO} + \text{Cl}^- \quad (11)
\]
compared to radicals, and can become the main oxidant in high Cl⁻/C₉ conditions (Lutze et al. 2015; Lee et al. 2020).

\[
\text{HO}^* + \text{Cl}^- \rightarrow \text{Cl}^* + \text{OH}^- \quad (8)
\]

\[
\text{SO}_4^{2-} + \text{Cl}^- \rightarrow \text{Cl}^* + \text{SO}_4^{2-} \quad (9)
\]

\[
\text{Cl}^* + \text{Cl}^- \rightarrow \text{Cl}_2^* \quad (10)
\]

\[
\text{HSO}_5^- + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{HClO} \quad (11)
\]

As the model compounds of natural organic matter, different concentrations of humic acid (0, 1, 5, and 10 mg/L) were introduced to study its effect on ATZ removal (Figure 5(i) and 5(j)). An apparent inhibition in the removal of ATZ was observed. With the increase of HA, the inhibition for the removal of ATZ also increased. When the addition of HA increased from 0 mM to 1, 5, and 10 mg/L, the removal of ATZ decreased from >99% to 41.9%, 34.5, and 0%. Similar results were also found in Sharma et al. (2015) study. HA has often been applied as quencher for free radicals (Sharma et al. 2015). Therefore, HA may compete with ATZ for SO₄²⁻ and HO·, resulting in the decrease of the removal of ATZ.

Control experiments
To prove the activation performance of the CuCo₂O₄/PMS system, PMS alone, CuCo₂O₄ alone, CuO/PMS, and Co₂O₃/PMS systems were set up. Figure 6 shows that the removal of ATZ can achieve 20.9% when only PMS was present in aqueous solution. The results inferred that ATZ could be removed by PMS for direct oxidation. Meanwhile, the 150 mg/L CuCo₂O₄ alone system had little adsorption to ATZ. Nevertheless, the removal of ATZ was signally improved in the CuCo₂O₄/PMS system. The above results indicated the CuCo₂O₄/PMS system had a significant effect on the removal of ATZ because PMS activated by CuCo₂O₄ produced large amounts of radicals (i.e., SO₄²⁻ and HO·). Moreover, the performance of CuO and Co₂O₃ was evaluated under the same conditions. As can be seen in Figure 6, the ATZ removal by CuO/PMS could achieve 23.7% and that by Co₂O₃/PMS could reach 50.9%, both of which were far lower than with CuCo₂O₄/PMS. The results suggested that CuCo₂O₄ NPs had a better performance in catalytic activity than CuO or Co₂O₃ alone.

As shown in Supplementary Material, Figure S5, the pH value in the three systems was recorded. The pH value showed slight fluctuations when only CuCo₂O₄ was added to the aqueous solution. However, the pH decreased to 4.00 and 4.30 in PMS alone and CuCo₂O₄/PMS system, respectively, which was contributed to by the production of amount of H⁺ according to Equations (12) and (13):

\[
\text{HSO}_5^- + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{SO}_4^{2-} \quad (12)
\]

\[
\text{HSO}_5^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{HSO}_4^- \quad (13)
\]
Actual application
To study the ATZ removal ability of the CuCo$_2$O$_4$/PMS system in actual wastewater, four ATZ solutions were prepared with ultrapure water, tap water, river water, and lake water, respectively. The samples of tap water and lake water were taken from Sichuan University, and river water was taken from the Fuhe river in Chengdu. Supplementary Material, Table S1 shows the characteristics of various water matrices. The river and lake water were suction filtered and then used as the solvent for atrazine. The removal of ATZ in these four solutions by CuCo$_2$O$_4$/PMS system is illustrated in Supplementary Material, Figure S6. The removal of ATZ reduced in order of deionized water, tap water, river water, and lake water. However, the biodegradability of all solutions after the reaction was improved. As shown in Supplementary Material, Figure S7, the biodegradability of lake water increased slightly from 0.820 to 0.848 (expressed as BOD/COD). This might be because the actual water contained a large number of pollutants that could compete with ATZ for radicals.

Reusability of CuCo$_2$O$_4$ NPs
Supplementary Material, Table S2 shows the leaching concentration of cobalt and copper iron during reaction in the CuCo$_2$O$_4$/PMS system. The leaching concentration of the cobalt and copper iron increased with the increase of reaction time. The maximum leaching of Co and Cu was 0.035 mg/L and 0.062 mg/L at 30 min, respectively, which was much lower than the limit concentration (1 mg/L) required by Emission standard of pollutants for copper, nickel, cobalt industry of China (GB 25467-2010). Therefore, the influence of Co and Cu ion leaching was negligible.

Furthermore, as an engineering material, the stability and reusability of CuCo$_2$O$_4$ is a key factor of practical application. It was studied by using recycled CuCo$_2$O$_4$ NPs catalysts for ATZ removal under uniform operating conditions (i.e., 150 mg/L CuCo$_2$O$_4$, 0.2 mM PMS, 5 mg/L ATZ, and initial pH of 6.8). Figure 7 showed that the removal of ATZ gradually decreased from >99% to 97.1%, 96.5%, 90.4%, and 86.7%, in five consecutive experiments. The results show that the CuCo$_2$O$_4$ NPs had a gradual deactivation in these five recycle experiments because the absorbed intermediates occupied the active sites and small amounts of Co and Cu ions leached into the solution (Ding et al. 2017).

Identification of main radicals
Two radical quenching experiments were carried out to identify the main radicals for the removal of ATZ by adding quenching agent into the CuCo$_2$O$_4$/PMS system. As a quenching agent without $\alpha$ hydrogen, tert-butyl alcohol (TBA) could differentiate SO$_4^{\cdot}$ and HO$^\cdot$ because its reaction rate constant with HO$^\cdot$ $(3.8-7.6) \times 10^8 M^{-1} \cdot s^{-1}$ is three orders of magnitude greater than that with SO$_4^{\cdot}$ $((4-9.1) \times 10^8 M^{-1} \cdot s^{-1})$ (Li et al. 2017). As well, both SO$_4^{\cdot}$ and HO$^\cdot$ could actively react with ethanol (EtOH) which had $\alpha$ hydrogen (Li et al. 2017). The reaction rate constant of EtOH and HO$^\cdot$ is $(1.2-2.8) \times 10^9 M^{-1} \cdot s^{-1}$ which was almost as large as that of EtOH and SO$_4^{\cdot}$ $((1.6-7.7) \times 10^7 M^{-1} \cdot s^{-1})$ (Xu et al. 2016). Hence, TBA and EtOH can be applied as two kinds of radical scavengers. With the addition of 50 mM TBA, the removal of ATZ decreased from >99% to
79.7% in Figure 8(a). The results could prove that HO• made a certain contribution to the removal of ATZ. When 50 mM EtOH was added into aqueous solution, there was almost no ATZ removal because almost all HO• and SO4•/C0 were quenched by EtOH. It could be concluded from the above results that both HO• and SO4•/C0 could significantly promote the removal of ATZ and the dominant active radical is SO4•/C0 in this study.

The EPR spectra were utilized to identify HO• and SO4•/C0 by using DMPO as the spin trapping agent with the reaction time of 2 min, in order to confirm these two radicals were produced during the activation of PMS. As seen in Figure 8(b), a strong signal of DMPO-HO• with an intensity ratio of 1:2:2:1 was observed, which could confirm the existence of HO•. However, the signal of DMPO-SO4•/C0 was not obvious. The results could be interpreted as follows: DMPO-SO4•/C0 could be converted to DMPO-HO• via nucleophilic substitution (Equation (14)) (Kang et al. 2018), indicating that the produced DMPO-SO4•/C0 was rapidly consumed (Wang et al. 2015). This phenomenon further confirmed that the main radical in the system was SO4•/C0, which also verified the results of radical quenching experiments.

\[
\text{SO}_4^{\cdot-} + \text{N} \rightarrow \text{N} - \text{SO}_4^{\cdot-} \rightarrow \text{N} - \text{OH} \rightarrow \text{N} - \text{SO}_4^{\cdot-} \]

(14)

The possible catalytic mechanism of CuCo2O4/PMS system

The possible reaction mechanism of the CuCo2O4/PMS system for ATZ removal is illustrated in Figure 9. Based on the results of Figure 6, a part of ATZ could be directly oxidized by PMS but could not be removed by the adsorption of CuCo2O4 NPs. Furthermore, the metal ions which played the role of Lewis acid could react with H2O absorbed on the surface of CuCo2O4 NPs, producing a large number of active hydroxyls as described in Equations (15) and (16) (Ren et al. 2015). This process (Equations (15) and (16)) was the rate-limiting step in the activation of PMS (Ren et al. 2015). Next, with the addition of PMS into the reaction solution, HSO5• could bind to CuCo2O4 to form CuCo2O4-O-H-HSO5 for hydrogen bonding. Then, HSO5• could react with \( \equiv \text{Co}^{2+}-\text{OH}^- \) to produce SO4•/C0 and \( \equiv \text{CoO}^- \) (Equation (17)). The \( \equiv \text{CoO}^- \) could react with H\(^+\) to form \( \equiv \text{Co}^{3+} \) (Equation (18)). The cycle of Co was formed after the reaction between \( \equiv \text{Co}^{3+} \) and HSO5• (Equation (19)). Similarly, \( \equiv \text{Cu}^{+} \) would also bind to the active hydroxyl to form \( \equiv \text{Cu}^{+}-\text{OH}^- \) (Equation (16)) which could combine with HSO5• to produce SO4•/C0 and \( \equiv \text{Cu}^{2+}-\text{OH}^- \) (Equation (20)). Subsequently, \( \equiv \text{Cu}^{2+}-\text{OH}^- \) would continue to react with HSO5• to form \( \equiv \text{Cu}^{+} \) and SO5•/C0 (Equation (21)). Furthermore, the catalytic activity of CuCo2O4 could be improved by the reaction of Cu(I) and Co(III) as described in Equation (22), which reflected the strong synergistic effect of Cu and Co (Chen et al. 2020). The
HO' might be produced as shown in Equations (23) and (24) (Shen et al. 2020):

\[
\begin{align*}
\text{Co}^{2+} + H_2O & \rightarrow \text{Co}^{2+} - OH^- + H^+ \\
\text{Cu}^{+} + H_2O & \rightarrow \text{Cu}^{+} - OH^- + H^+ \\
\text{Co}^{2+} - OH^- + \text{HSO}_5^- & \rightarrow \text{CoO}^+ + \text{SO}_4^{2-} + H_2O \\
\text{CoO}^+ + 2H^+ & \rightarrow \text{Co}^{3+} + H_2O \\
\text{Co}^{3+} + \text{HSO}_5^- & \rightarrow \text{Co}^{2+} + \text{H}^+ + \text{SO}_5^{2-} \\
\text{Cu}^{+} - OH^- + \text{HSO}_5^- & \rightarrow \text{Cu}^{2+} - \text{OH}^- + \text{SO}_4^{2-} + OH^- \\
\text{Cu}^{2+} - \text{OH}^- + \text{HSO}_5^- & \rightarrow \text{Cu}^+ + \text{H}^+ + \text{SO}_4^{2-} \\
\text{Cu}^{3+} + \text{Cu}^+ & \rightarrow \text{Cu}^{2+} + \text{Cu}^{2+} \\
\text{SO}_4^{2-} + H_2O & \rightarrow \text{H}^+ + \text{HO}^+ + \text{SO}_4^{2-} \\
\text{SO}_4^{2-} + \text{OH}^- & \rightarrow \text{HO}^+ + \text{SO}_4^{2-}
\end{align*}
\]

Figure 9 | The possible reaction mechanism of CuCo$_2$O$_4$/PMS system for the ATZ removal.

Intermediates and possible removal pathways

To speculate on the removal pathway of ATZ, the intermediate products during the reaction process were detected by UPLC-QTOF-MS/MS. The molecular formula, chemical name, abbreviation, charges-to-mass ratio (m/z), the absolute error of m/z, and structural formula of 11 intermediates are listed in Supplementary Material, Table S3. The possible removal pathway of
ATZ is proposed in Figure 10. The removal pathway of ATZ included de-alkylation (path 1), dechlorination–hydroxylation (path 2), alkylic-hydroxylation (path 3), alkylic-oxidation (path 4), and olefination (path 5) as demonstrated in Figure 10.

In path 1, the side chain of ATZ was attacked by HO$^\cdot$ and SO4$^-$/Co, then H in the alkyl group was abstracted to form the carbon-based radical. Subsequently, oxygen would react with the carbon-based radical, resulting in forming the by-product containing peroxide radical, which would bring about the generation of de-alkylation intermediate (e.g., CAIT, CEAT, CAAT, OAIT, and OAAT) (Rejto et al. 1983; Acero et al. 2000). In path 2, the aromatic ring of ATZ reacted with the HO$^\cdot$ and SO4$^-$/Co to form radical adduct, which then reacted with water to generate hydroxylated intermediate (e.g., OEIT) (Antoniou et al. 2010; Song et al. 2012). In path 3, the H on the alkyl group of the side chain could be taken away by free radicals to form carbon-based radicals, which could continue to react with water to produce alkyl-hydroxylation intermediate (e.g., CNIT and ODIT). In path 4, under the action of HO$^\cdot$ and SO4$^-$/Co, the products of path 3 were converted to carbon-based radicals, which could react with oxygen to generate by-products containing peroxide radical. With water molecular break down, the by-product of the previous step became an alkyl-oxidation product (e.g., ONIT and CDIT). In path 5, alkyl-hydroxylation intermediates were dehydrated to form olefins by-product (e.g., OVIT).

**CONCLUSIONS**

In this study, the high ATZ removal (>99%) could be attained in the CuCo2O4/PMS system under the optimal experimental conditions of 150 mg/L CuCo2O4, 0.2 mM PMS, and initial pH of 6.8. The five co-existing ions (i.e., NO3$, $ HCO3$, HPO4$^{2-}$, Cl$, $ and HA) had some different effects on the removal of ATZ. The effects of these five ions on the ATZ removal were, in descending order, HA $>$ HPO4$^{2-}$ $>$ HCO3$^-$ $>$ Cl$^-$ $>$ NO3$. Furthermore, compared with PMS alone, CuCo2O4 alone, CuO/PMS and Co2O3/PMS systems, the excellent performance of CuCo2O4/PMS system was proved. Through five successive runs, on account of the reduction of active sites on the catalyst surface, the ATZ removal decreased from >99% to 97.1%, 96.5%, 90.4%, and 86.7% in turn. In the CuCo2O4/PMS system, SO4$^-$ was identified as the dominant radical. In addition, the possible catalytic mechanism of the CuCo2O4/PMS system was deduced. The removal pathway of ATZ was proposed according to the information of the detected intermediate. In a word, the CuCo2O4/PMS system is a potentially effective technique for the removal of ATZ.
ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from National Natural Science Foundation of China (No. 51878425), Student Innovation and Entrepreneurship Foundation of Sichuan University (No. 201810610418), and Sichuan Province Science and Technology Innovation Seedling Project (No. 2019084).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 2 June 2021; accepted in revised form 19 July 2021. Available online 5 November 2021