

Article

Exploration of Influencing Factors and Generation Mechanism of EPFRs in Polycyclic Aromatic Hydrocarbon-Contaminated Soil

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Abstract: Environmentally persistent free radicals (EPFRs) are a new class of pollutants that have been identified as potential environmental contaminants due to their persistence and ability to generate reactive oxygen species (ROS) that cause oxidative stress in living organisms. This study investigates the formation and behavior of EPFRs during the photodegradation of organic pollutants, emphasizing the role of metal ions, precursor concentration, and environmental conditions. Results show that light exposure significantly enhances pollutant degradation rates, EPFR yield, and formation speed, though it simultaneously shortens EPFR lifespan due to reactive oxygen species (ROS) generation. In dark conditions, EPFR formation is slower but results in more stable radicals. Metal ions play a pivotal role, with Cu(II) exhibiting the highest EPFR generation capacity due to its strong electron-accepting properties, surpassing Zn(II) and Na(I), highlighting that metal ions with greater oxidizing potential enhance EPFR formation. The precursor, as both reaction product and reactant, plays a dual role in EPFR formation. Individual compounds like anthracene (ANT) yield stable carbon-centered radicals, while mixtures of polycyclic aromatic hydrocarbons (PAHs) produce more complex radical spectra. The study of the influencing factors and transformation mechanisms of EPFR generation in soil can provide a more comprehensive understanding of the environmental behavior of new pollutants, provide a scientific basis for sustainable development, and be of great significance for the assessment and management of environmental risks and the protection of the ecological environment.

Keywords: polycyclic aromatic hydrocarbons; environmental persistent free radicals; degradation patterns; soil; electron transfer



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1. Introduction

Environmentally persistent free radicals (EPFRs) are a class of hazardous substances characterized by their stronger electromagnetic resonance stabilization and longer lifetimes compared to traditional free radicals (i.e., $\cdot\text{OH}$, $\cdot\text{O}_2$, and HO_2 -radicals) [1]. EPFRs are ubiquitous across atmospheric, soil, and aqueous environments, where they are continuously transported and transformed [2–4]. Due to their persistence and potential health risks, particularly to the human respiratory and cardiovascular systems, EPFRs have garnered significant research attention. These radicals are capable of inducing reactive oxygen species (ROS), such as hydrogen peroxide, superoxide, and hydroxyl radicals, which can damage cell membranes, lipids, proteins, and DNA [5].

As the main precursor compounds of EPFRs, polycyclic aromatic hydrocarbons (PAHs) exist widely in soil. Studies on global soil PAH concentrations have reported levels ranging from <1 to 7840 ng g^{-1} dry weight, with significant implications for soil health and EPFR generation [6]. The distribution and degradation of PAHs in soil have a great impact on the environmental behaviors of EPFRs. EPFRs can be generated through a variety of natural processes, such as biodegradation, chemical transformation, and photolysis reactions [7,8]. Among the degradation processes, photodegradation has received growing attention, with montmorillonite clay emerging as a key factor in EPFR generation due to its unique structure and high affinity for organic contaminants [9,10]. Due to the highly delocalized π -electrons of PAH molecules, they can act as substantial electron donors and form “cation- π ” interactions with electron-deficient sites in the soil. This interaction promotes electron transfer, making the parent compound unstable and more prone to redox reactions, thus facilitating its transformation [11]. Although some have studied the transformation of selected ternary, quaternary, and quintet cyclic PAHs on transition metal ion-modified montmorillonite [12], most of the existing studies on multiple polycyclic PAHs have investigated their individual degradation mechanisms but have not been able to elucidate the degradation mechanisms when they coexist. Therefore, it is important to clarify when mixed PAHs contaminate soil, how they are degraded, and what properties of EPFRs are generated. This will enable improved source control and risk reduction of EPFRs.

Various environmental factors, such as light conditions, transition metal ion species, metal ion concentrations, and organic matter content, influence EPFR formation. Previous studies have shown that light irradiation promotes the direct electron transfer of ANT to the mineral surface and accelerates the formation of polycyclic aromatic hydrocarbon-type radical cations. Light irradiation induced the generation of reactive oxygen species, which facilitated the conversion of radical cations to oxygen-containing EPFRs, ultimately leading to ANT degradation [13]. Transition metal ions, in particular, affect the degradation of precursor pollutants and the generation of EPFRs through electron transfer processes. PAHs are rich in off-domain electrons and interact with metal ions. When the distances between each of the ANT-bonded cations and ANT is more minor, the cationic bonds are stronger, the stability is lower, and the photodegradation of ANT is higher [14]. EPFRs generated by substituted aromatics in different copper concentration loading systems have different spin concentrations, line widths, and g-values. Lucy W. Kiruri et al. found that 1,2-dichlorophenol formed radicals with lower g-values and narrower linewidths as the copper concentration decreased, and it gradually transformed from semiquinone radicals to chlorophenoxy radicals. It is speculated that the growth of metal clusters and spatial site resistance effects may be responsible for the different chemical behaviors of EPFRs [15]. Organic matter in the soil also plays a key role in the fate of PAHs, as PAHs are generally adsorbed onto organic matter, which in turn inhibits their interactions with underlying minerals and so reduces the rate of production of EPFRs [16,17]. Although some progress has been made in the study of factors affecting the generation of EPFRs, the effects of various soil properties on EPFRs is still unclear due to the late start of EPFR research.

In this study, we selected montmorillonite and PAHs as model compounds to investigate the factors influencing EPFR generation. Controlled experiments were conducted to examine variables such as light conditions, transition metal species, precursor compound concentrations, and copper loading concentration. The main objectives of this work are (1) to reveal the effects of different factors on the formation of EPFRs by PAHs on montmorillonite clay surfaces, (2) to study the photodegradation of mixed PAHs and the formation of their EPFRs in the Cu-MT/SiO₂ system at a concentration of 1.0 wt% Cu, and (3) to gain further insight into the mechanism of formation of PAH-induced EPFRs on Cu(II)

montmorillonite clay surfaces. By comparing the degradation of monomer ANT with that of mixed PAHs, we aimed to elucidate the mechanisms of EPFR generation under varying conditions in areas previously unexplored.

2. Materials and Methods

2.1. Preparation of Soil with Various Transition Metal Ion Loading

The preparation of montmorillonite with various transition metal ion loadings, as well as Cu-MT/SiO₂ composites, was conducted as follows: 5 g of montmorillonite was dispersed in deionized water at a soil-to-water ratio of 1:20. The pH of the solution was adjusted to 6.8 using a 0.5 mol/L sodium acetate buffer (pH 5.0–5.5). After a 2 h rest, the suspension was centrifuged (3800 rpm, 5 min), and 0.05 mol/L solutions of CuCl₂, ZnCl₂, and NaCl were added. For the Cu-MT/SiO₂ sample preparation, 5 g of montmorillonite and 5 g of silica gel powder were weighed, and 9.767 mL, 19.53 mL, 29.30 mL, 39.06 mL, 78.13 mL, 117.19 mL, and 195.31 mL of 0.02 M Cu(NO₃)₂·2.5H₂O were added to produce 0.5, 0.75, 1, 2, 3, and 5 wt% of copper content of Cu-MT/SiO₂. The soil-to-water ratio was maintained at 1:20, and the mixture was stirred for 8 h at ambient temperature. After stirring, the suspension was centrifuged to remove the supernatant, and this process was repeated three times. Deionized water was added to eliminate chloride ions (Cl[−]), and the mixture was stirred for 15 min. The supernatant was subsequently removed by centrifugation, and this step was repeated until no Cl[−] was detected, which was confirmed using a silver nitrate solution test. The resulting saturated montmorillonite samples were dried in an oven at 60 °C to remove moisture. The dried samples were removed and ground in a mortar until powdered, sieved through a 100-mesh sieve, and stored in a desiccator protected from light. Detailed information on the chemicals used in this study is supplied in Content S1.

2.2. Analytical Methods

For the contaminated soil samples, we weighed 30–50 mg of soil into the EPR quartz tube (internal diameter = 3 mm, external diameter = 4 mm, length = 25 cm) every 1 h for EPR analysis to monitor the spin concentration of free radicals. A total of 100 mg of soil was weighed every 4 h for GC-MS analysis to assess the degradation rate of PAHs and the formation of intermediate degradation products. The artificial climate chamber uses a color temperature of 4000 K, a white light close to natural light, which has a light intensity of 27,733 lm/m². The flow of the reaction design is presented in Content S1.

2.2.1. EPFR Measurements

EPR analysis was conducted using a Bruker electron resonance (ESR) spectrometer. The analysis parameters included a center magnetic field of 3520 G, a magnetic field width of 200 G, and a scan time of 20 s. The receiver gain was set to 30 dB, with a modulation frequency of 100 kHz, modulation amplitude of 1.0 G, microwave frequency of 9.8523 GHz, and microwave power of 0.2 mW. Data acquisition and processing were carried out using BRUKER EMX Xenon software.

2.2.2. PAH Measurements

Quantitative analysis of PAH degradation was performed using gas chromatography–mass spectrometry (GC-MS; Agilent, Beijing, China). The temperature program for GC-MS involved an initial increase from 80 °C to 180 °C at a rate of 20 °C per minute, holding at 180 °C for 5 min, followed by a rise to 290 °C at a rate of 10 °C per minute, and holding for an additional 5 min. PAH recovery ranged from 43.38% to 132%, within the acceptable range of variability. Data analysis was performed using the GC-MS software (Unknowns Analysis 10.0, Qualitative Analysis 10.0).

Other organic chemical compounds obtained after the photodegradation of anthracene were screened by gas chromatography (Agilent 8890 GC; Agilent Technologies, Santa Clara, CA, USA) quadrupole time-of-flight mass spectrometry (Agilent 7250 QTOF-MS; Agilent Technologies, Santa Clara, CA, USA) using an HP-5 ms Ultra Inert chromatographic column (15 m $\times$ 250 μ m $\times$ 0.25 μ m). The column temperature was programmed to increase from 60 $^{\circ}$ C to 120 $^{\circ}$ C at 40 $^{\circ}$ C min $^{-1}$ and then from 120 $^{\circ}$ C to 310 $^{\circ}$ C at 5 $^{\circ}$ C min $^{-1}$. The injection temperature was 280 $^{\circ}$ C. The compounds were identified by spectrum comparison with the NIST library.

2.3. Data Processing

Data visualization was carried out using Origin 2021 software, and both EPR data and XPS data were plotted in Origin 2021. Statistical analysis was performed using SPSS (<https://www.ibm.com/spss>, accessed on 4 November 2024), to verify whether there was a significant difference between the two data sets of free radicals produced by anthracene alone and those produced by mixed PAHs.

3. Results and Discussion

3.1. Influence of Environmental Factors on the Generation of EPFRs from Individual Pollutants

Various environmental factors influence the transformation of PAHs and the formation of EPFRs. This section selected ANT as a typical precursor pollutant to assess the generation and variations of EPFRs under different conditions, including light and dark environments, different transition metal ions, different concentrations of precursor contaminants, and varying Cu loading concentrations. In addition to these factors, ambient temperature is one of the factors that influence the environmental behavior of EPFRs. For example, the concentration of EPFRs in soil varies significantly with temperature (25–300 $^{\circ}$ C) [10,18]. However, when the room temperature is in the range 20–25 $^{\circ}$ C, there is no obvious change in EPFR contents. Therefore, in this study, the temperature of the experimental conditions was set at 20 $^{\circ}$ C and no temperature control experiments were performed. We will investigate the effect of temperature change on EPFRs in future studies.

3.1.1. Effects of Light and Darkness on EPFR Spin Concentration

Photo-induced electron transfer is a crucial mechanism for initiating oxidation-reduction reactions of organic precursors, including PAHs. EPFRs can be involved in the photochemical reactions of organic precursors and are formed by them. Therefore, light exposure is an essential external environmental factor. EPFR production was monitored under natural light and dark conditions (Figure 1a). Both untreated and ANT-spiked soils started with an initial spin density of 5.0×10^{14} spins/g. Under light exposure, the spin density peaked at 8 days, reaching 7.81 times the initial value. However, under dark conditions, the peak occurred at 25 days, reaching only 3.27 times the original spin density. The maximum spin density observed under light was 2.39 times higher than in the dark. This indicates that light alters the rate of EPFR formation and increases the total amount of free radicals produced. It is probable that light facilitates the breakdown of chemical bonds and electron transfer, thus promoting EPFR generation from precursor pollutants. Previous studies have found that light as a common energy driving force can promote the generation of EPFRs from parent pollutants in the soil by chemical bond breaking and electron transfer [18–20]. Our observations in this study support this.

Despite this, the decay rate in the dark was slower: after 35 days, spin density remained at 90.33% of its peak value, whereas light exposure resulted in a 61.21% reduction in just 4 days. Chen et al. have reported that atmospheric particulate matter can produce secondary EPFRs in visible light. Still, in seasons and regions of intense light, secondary

EPFRs may decay rapidly during sampling to form end products [1]. This might explain why EPFRs decay faster in the presence of light.

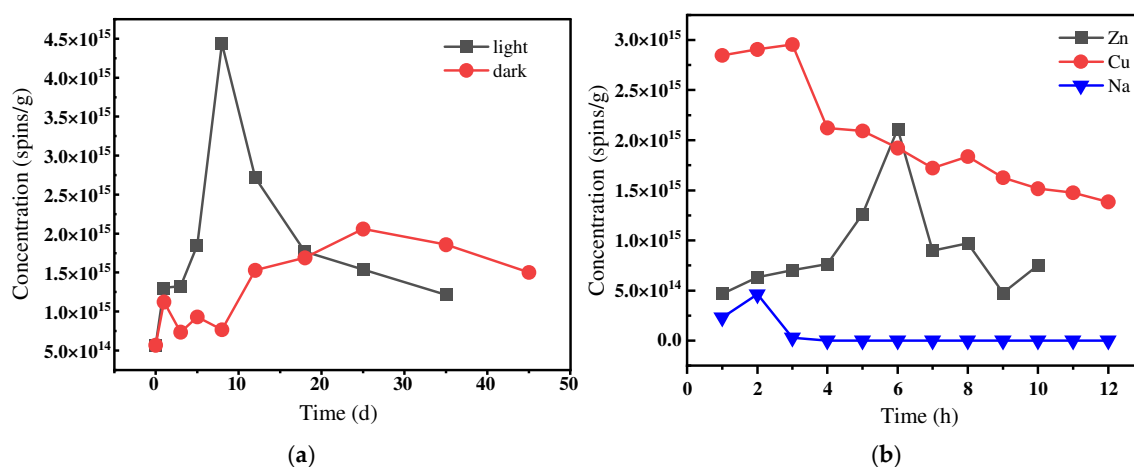


Figure 1. (a) EPFR spin density changes in brown soil with 0.1 mg/g ANT under light and dark conditions; (b) variation of spin density with different metal montmorillonite after 0.1 mg/g ANT exposure to xenon light.

3.1.2. Effects of Different Transition Metal Ions on EPFR Spin Concentration

The role of metal ions in promoting the generation of EPFRs is debated. The stronger the oxidizing potential of the metal ion, the more effectively it promotes EPFR formation. Some studies suggest that Cu(II) in soil plays a critical role in EPFR formation [21,22]. Typically, the ability of transition metal ions to promote the generation of EPFRs is consistent with the oxidizing ability of transition metal ions. However, a different finding has been proposed that the concentration of EPFRs formed on the surface of ZnO particles is higher than on the surface of CuO particles [23].

To further investigate this, Na(I), Cu(II), and Zn(II) were selected as representative metal ions loaded onto montmorillonite, taking ANT as the model contaminant. All metal-ion-loaded montmorillonites exhibited clear EPR signals after 1 h of light exposure (Figure 1b), with EPFRs generated ranked as Cu(II) > Zn(II) > Na(I). Unlike Cu(II)-montmorillonite and Zn(II)-montmorillonite, there was almost no EPFR generation on Na(I)-montmorillonite. A small amount of free radicals was formed in the initial three hours. Still, sodium ions (Na^+), with their high reactivity in the soil, tend to react with free radicals or other ions, neutralizing the charge and making it difficult for the radicals to maintain stability. As light exposure increases, EPFRs are gradually converted into final products, serving as intermediates in the degradation of organic pollutants. In contrast, Cu(II) and Zn(II), which are metals with high polarizability and significant electron deficiency, facilitate efficient energy or charge transfer between adsorbed pollutant molecules, such as ANT, and exchangeable cations [24].

However, differences were observed between Cu(II)- and Zn(II)-loaded systems. Compared with Cu(II)-montmorillonite, Zn(II)-montmorillonite had a faster decay rate, and the EPFRs formed were not as persistent as those of Cu(II)-montmorillonite. After 1 h of xenon light, the spin density of Cu(II)-montmorillonite was 2.847×10^{15} spins/g, an order of magnitude higher than Zn(II)-montmorillonite (4.673×10^{14} spins/g). Cu(II)-montmorillonite reached a peak value of 2.957×10^{15} spins/g after 3 h of exposure, while Zn(II)-montmorillonite peaked at 2.093×10^{15} spins/g after 5 h, which is 70.78% of the Cu(II) maximum. Zn(II)-montmorillonite exhibited a faster decay rate and less persistent EPFRs compared to Cu(II)-montmorillonite. This suggests Cu(II) is more effective in facilitating electron transfer from pollutant molecules to surface metal sites, producing

more stable and persistent EPFRs. As a common transition metal ion in soil, Cu has a stronger ability to bind to the functional groups of precursor compounds, and precursor compounds transfer electrons to the highly active Cu(II) in the soil, catalyze the degradation of precursor compounds, and promote the generation of intermediate EPFRs [25].

The redox potentials of Cu(II) ($\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$; $E^0 = +0.153 \text{ V}$) [26] and Zn(II) ($\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$; $E^0 = -0.76 \text{ V}$) [27] further corroborate these findings. Higher redox potentials are linked to more effective promotion of EPFR formation. Additionally, we found that $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$; $E^0 = +0.77 \text{ V}$, $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$; $E^0 = -0.257 \text{ V}$ [26,28], $\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$; $E^0 = -0.28 \text{ V}$ [26]. Based on redox potentials, metals like Ni(II), Co(II), and Fe(III) may generate EPFR concentrations comparable to Cu(II), and greater than Zn(II). This predictive model aligns with observed PAH decay rates, supporting the hypothesis that transition metals with higher oxidizing potentials more effectively catalyze the transformation of PAHs into EPFRs [12]. This is consistent with our experimental results, which further verify that the ability of transition metal ions to promote the production of EPFRs is positively correlated with their oxidizing ability. Such a pattern was found in the photodegradation of phenanthrene because Fe(III) has a stronger oxidizing ability than Cu(II), so the photolysis rate of phenanthrene in Fe^{3+} -smectite is greater than that in Cu^{2+} -smectite [18]. This insight links theoretical chemistry with practical environmental concerns, enabling more accurate predictions of pollutant behavior in contaminated soils with varying transition metals in real-world environments.

3.1.3. Effects of Precursor Concentration on Spin Concentration and g-Value of EPFRs

The effects of three precursor concentrations (0.05 mg/g, 0.1 mg/g, and 0.2 mg/g) on formation of EPFRs during light exposure were evaluated. The effects of different precursor concentrations on EPFR spin concentrations are shown in Figure 2a. For the lowest concentration (0.05 mg/g), no detectable EPR signals were observed from 1 to 12 h of light exposure. This may be due to the following two reasons: (1) based on chemical reaction collision theory, the frequency of collisions between reactant molecules is reduced at low concentrations, resulting in fewer chances of activation reactions and thus less free radical generation [29]; and (2) free radicals may be more likely to be inactivated by reacting with other substances at low concentrations, resulting in a shorter life span, and thus undetectable.

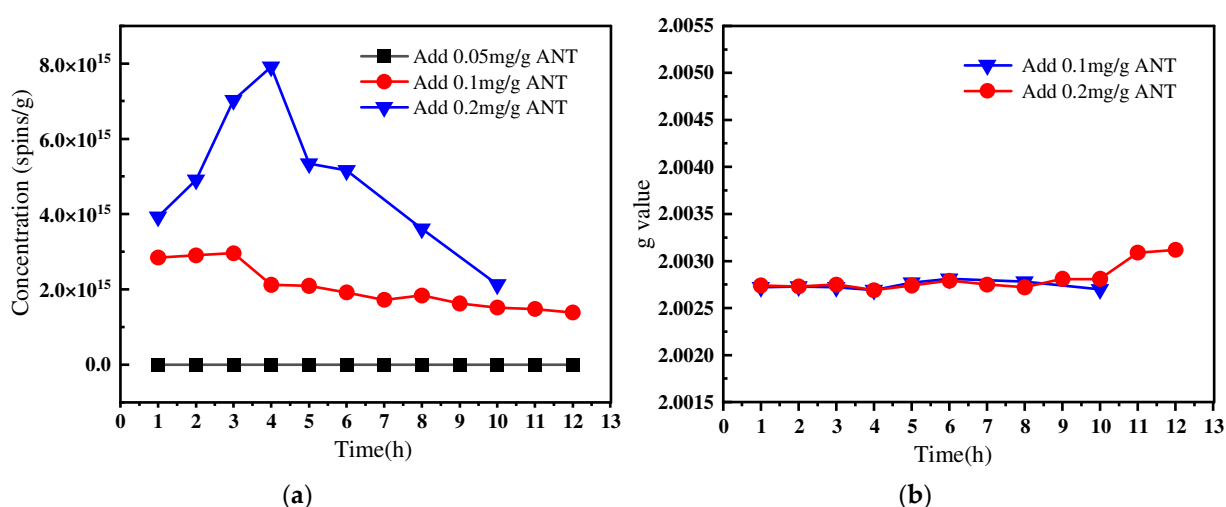


Figure 2. (a) Spin density changes of Cu(II)-montmorillonite with different ANT concentrations under xenon light; (b) g-value shifts with light exposure.

However, significant EPR signals were observed under similar conditions in the samples of 0.1 mg/g and 0.2 mg/g ANT-loaded Cu(II)-montmorillonite. The 0.2 mg/g concentration produced a maximum spin density 2.68 times higher than that of the 0.1 mg/g sample (Figure 2a), showing a clear positive correlation between precursor concentration and EPFR generation [14]. Interestingly, it is hypothesized that EPFR generation may be inhibited at very high pollutant concentrations. A possible reason for this is that precursor pollutants exhibit a double effect in forming EPFRs during light exposure. In conditions with lower precursor concentrations, transition metal ions likely act as oxidizers, promoting both pollutant degradation and EPFR formation [30,31]. At elevated concentrations, existing EPFRs may serve as electron shuttles to oxidize precursor pollutants, reducing the yield of new EPFRs [32]. This dual role of EPFRs—both as products and reactants—provides critical insights into the dynamics of contaminant behavior in the environment.

Regarding the type of radicals produced, the experiments showed that carbon-centered radicals dominated in both the 0.1 mg/g and 0.2 mg/g ANT-loaded montmorillonite samples (Figure 2b). The g-values of these radicals (ranging from 2.0020 to 2.0030) correspond to the off-domain electronic energy of the added ANT molecules [33,34]. After 10 h of light exposure, the g-value in the 0.1 mg/g ANT sample slightly increased, indicating a gradual shift from carbon-centered radicals toward a mixture of carbon-oxygen-centered radicals. This transformation is likely due to the oxidation of the more reactive carbon-centered radicals into more stable oxygen-centered radicals under sustained light exposure [15,35]. Additionally, the different conversion rates of individual PAHs can be linked to their varying ionization potential energies (or ionization energies). This further suggests that the specific type of EPFR generated strongly depends on the precursor pollutant's nature.

3.1.4. The Effect of Different Concentrations of Cu Loading Systems on the Generation of EPFRs

Transition metals, particularly Cu(II), demonstrated superior EPFR generation due to their electron-accepting capacity, which facilitates electron transfer. ANT produces different surface concentrations and densities of radicals in Cu-MT/SiO₂ loaded with varying concentrations of copper, the electron spin resonance spectra shown in Figure S1. As copper serves as the electron exchange site with anthracene, a linear relationship between radical yield and copper content would be expected.

However, it was found that this relationship was observed only for copper loading concentrations below 1%, where a positive linear correlation occurred, peaking at 1% copper loading, followed by an exponential decline at higher concentrations. The spin concentration of free radicals per mole of copper atoms—referred to here as the radical density—decreased with increasing copper content, as depicted by the dashed line in Figure 3. This indicates that, at copper concentrations greater than 1%, the aggregation of Cu atoms into clusters and the possible encapsulation of copper atoms within these clusters reduce the number of free radicals produced per copper atom. This encapsulation is the primary factor responsible for the decreased spin concentration [15]. When the Cu loading concentration is less than 1%, the Cu atom clusters become smaller, leading to an increase in radical density, but, due to the lower reactivity of the small clusters, leading to a decrease in the spin concentration of the radicals.

3.2. Generation of EPFRs in the PAH Mixtures and Degradation of Mixed PAHs

The type of precursor contaminant also influenced EPFRs formation. When different kinds of radicals are produced, the shape of the EPR spectral lines may broaden or split due to the superposition of various radicals. Single precursors like ANT produced stable radicals, but mixtures of PAHs led to broader and more complex EPR spectra. The EPR spectra show a significant difference between the radicals produced by ANT and those

produced by mixing PAHs, as shown in Figure 4a and Table 1. For ANT, the self-EPR signal was remarkably stable, with little change in signal intensity and linewidth as light exposure increased. The g-value remained relatively constant, indicating that the signal generated by ANT alone represented a single type of radical. Nevertheless, when the precursor pollutants were PAH mixtures, the EPR signal significantly changed. The spectrum became asymmetrical, and the linewidth increased to several times its original value, ranging from 10–12 G, suggesting the presence of more than one type of radical.

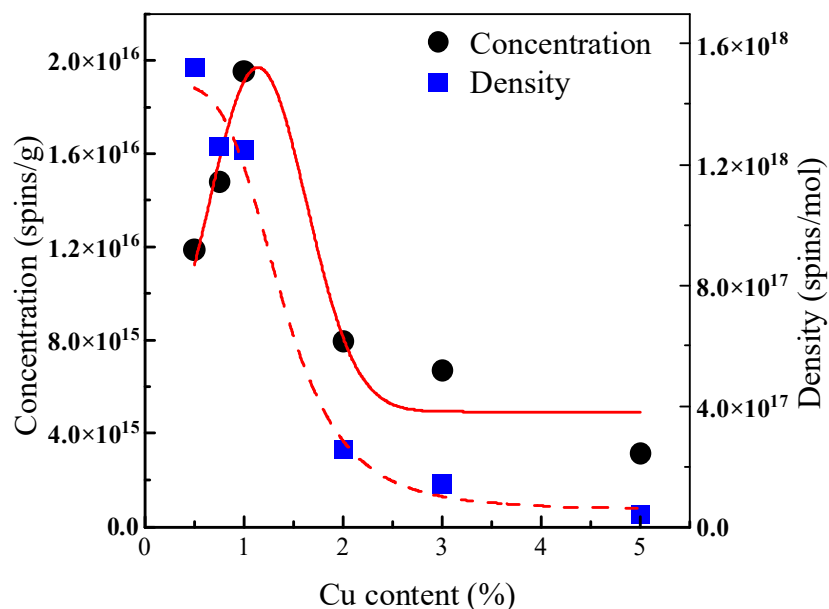


Figure 3. The concentration of EPFRs produced in ANT by Cu-MT/SiO₂ with different copper loading concentrations and the ratio of spin concentration to metal concentration.

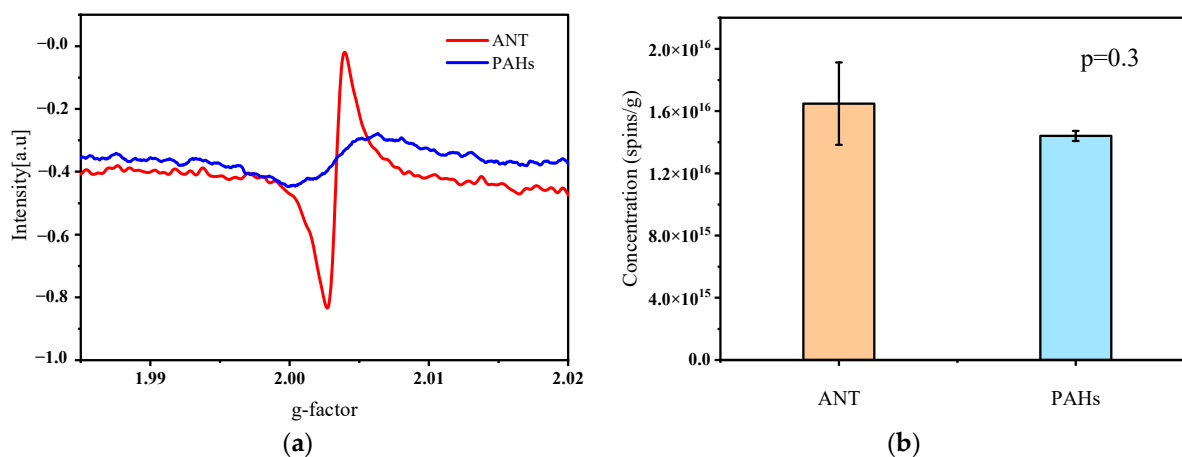


Figure 4. (a) Average EPR spectra of the EPFRs; (b) average EPFR concentration in spins/g.

Table 1. g value and ΔH_{p-p} for EPFRs produced by ANT and mixing of other PAHs.

Time (h)	0	1	2	3	4	5	6	7	8	9	10	11	12
g value	ANT 2.00315 2.00301	2.00310 2.00330	2.00310 2.00305	2.00307 2.00328	2.00308 2.00321	2.00309 2.00318	2.00308 2.00358	2.00308 2.00318	2.00306 2.00332	2.00305 2.00313	2.00305 2.00316	2.00307 2.00304	2.00308 2.00348
ΔH_{p-p} (G)	ANT 4.2 PAHs 10.3	2.2 11.6	2.1 10.2	2.0 11.1	2.3 12.8	1.8 10.3	2.1 11.0	2.2 12.4	2.3 9.6	2.3 10.1	2.6 10.1	2.0 11.1	2.1 11.4

The concentration of EPFRs generated by ANT monomers versus PAH mixtures is shown in Figure 4b. ANT alone produced a higher spin concentration than PAH mixtures,

which may be attributed to the dual role of precursor contaminants in EPFR formation. The p -value of 0.3 in the graph indicates a difference in the concentration of free radicals produced by the two. For lower concentrations of precursor contaminants, the formation of EPFRs is favored by electron transfer with metal ions. On the contrary, for higher concentrations of precursor contaminants, the already produced EPFRs may be consumed; EPFRs may act as electron shuttles to mediate the reduction of precursor contaminants [32]. Thus, further investigation is needed into the effect of synergism between different PAHs on the generation of EPFRs. This dual role of EPFRs—acting as products of electron transfer at low concentrations and as reactive intermediates at higher concentrations—highlights the complex dynamics of contaminant behavior in the environment.

Lower-ring PAHs in mixed pollutants showed faster degradation under light, further suggesting that precursor type critically determines EPFR characteristics. To further investigate the degradation of PAHs, a mixture of PAHs was used as model molecules and tested on Cu-MT/SiO₂ under controlled conditions (20 °C and 60% humidity). The evolution of the mixed PAHs over time is depicted in Figure 5. Four PAHs—NAP (Naphthalene), ANA (Acenaphthene), ANY (Acenaphthylene), and ANT—showed significant degradation within 12 h, with decreases to approximately 15%, 50%, 86%, and 84% of their original level, respectively. This degradation is likely due to their simpler ring structures, which react more readily under light exposure. As the molecular weight of PAHs increases, the intermolecular forces between the higher ring PAHs become stronger in the presence of van der Waals forces. The molecular weights of PAHs (i.e., >100) partially determine their stability [36]. In contrast, despite having a more complex structure with three benzene rings, ANT also exhibited notable degradation, to about 84% of the original value in the same timeframe. This can be explained by ANT's ability to act as a potent electron donor due to its delocalized π -electron system. PAHs with ionization potentials (IP) lower than 7.5 eV tend to undergo electron-transfer reactions. This property enables ANT to interact strongly with electron-deficient species, such as Cu²⁺ ions, on the montmorillonite clay surface. When Cu²⁺ binds to ANT in a symmetric binding approach, the cation- π distance is reduced, leading to stronger interactions and a higher degree of conversion or faster photodegradation of the precursor pollutants [37–39].

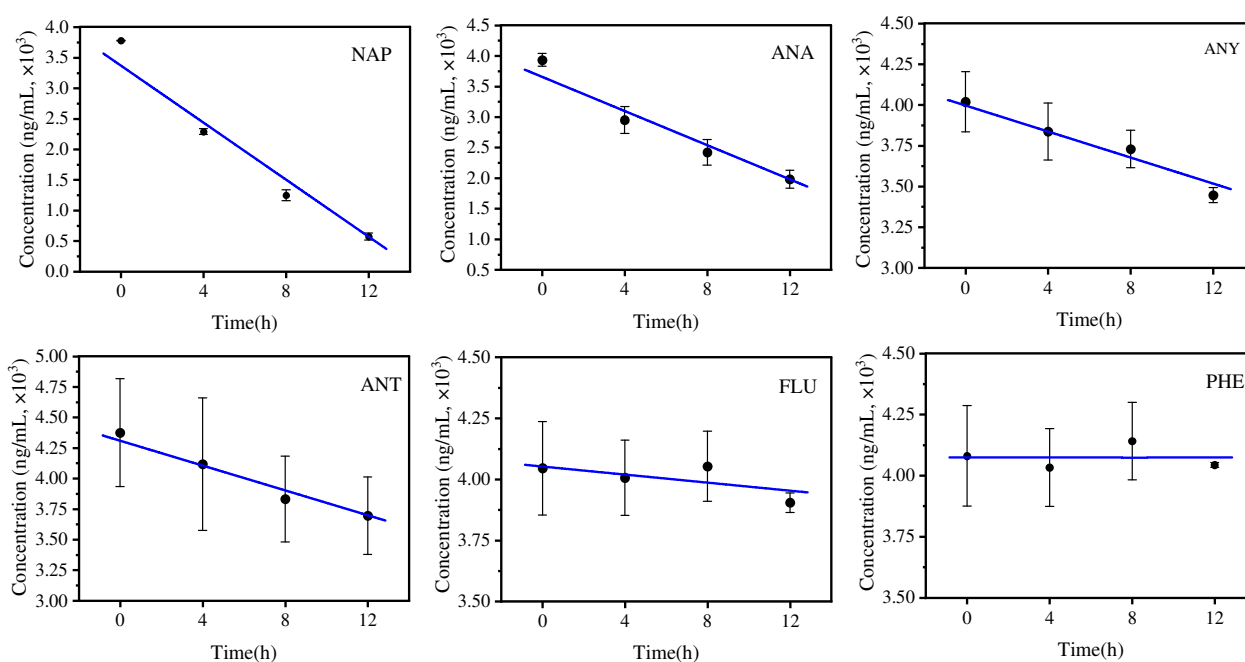


Figure 5. Cont.

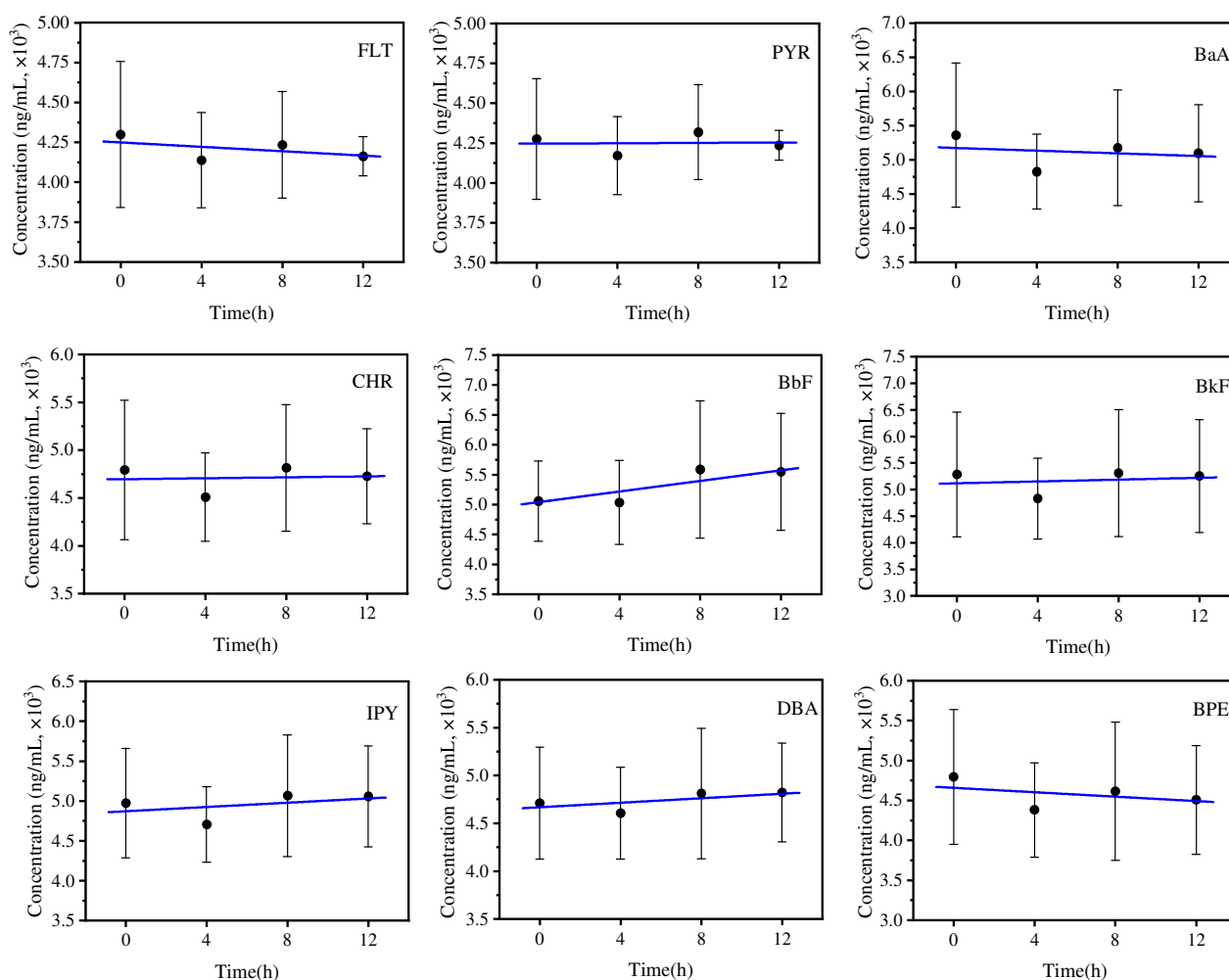


Figure 5. Degradation of various PAHs (Naphthalene (NAP), Acenaphthene (ANA), Acenaphthylene (ANY), Anthracene (ANT), Fluorene (FLU), Phenanthrene (PHE), Fluoranthene (FLT), Pyrene (PYR), Benzo[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Indeno[1,2,3-cd]pyrene (IPY), Dibenz[a, h]anthracene (DBA), Benzo[g, h, i]perylene (BPE)) in 0–12 h.

3.3. Free Radical-Mediated Formation Mechanism of Organic Pollutants from Photodegradation Reactions of Anthracene

The free radical-mediated mechanism of organic pollutant formation in the photodegradation reaction of ANT is a complex process involving the adsorption, excitation, radical formation, and product formation of anthracene on specific surfaces. The photoionization process for the formation of cationic radicals is due to the electron ejection of PAHs, demonstrating that the stabilized structure of PAHs can undergo electron transfer. Under light irradiation, anthracene molecules absorb photons, entering an excited state and thereby increasing their reactivity, making them prone to reactions with surrounding molecules or substrates. On the Cu-MT/SiO₂ surface, anthracene molecules interact with Cu(II) ions via “cation- π ” interactions, forming a pre-reaction complex. Due to the high frontier electron density at anthracene’s ninth and tenth carbon atoms, these carbons are less electronegative and thus more susceptible to C-H bond cleavage (Figure S3). This cleavage is promoted under light irradiation, and Cu(II) ions selectively target these two positions, leading to the formation of initial radicals [40,41]. By theoretical prediction, it was found that Fe(III) is added to the C9 or C10 atoms on the anthracene molecule via a transition state TS with a low activation barrier of 0.355 kcal/mol, and thus the reaction can be considered as a barrierless reaction pathway [42]. The electron transfer from anthracene

to Cu ions on the clay surface is further demonstrated by XPS spectroscopy (Figure S4), where the peaks at Cu 2p_{3/2} (933.2 eV) and peaks at Cu 2p_{1/2} (935.2 eV) indicate the presence of Cu(II) on the surface of the clay mineral. The peaks at 932.9 eV and 935.1 eV can be attributed to the presence of Cu(I). The results suggest that Cu(II) can accept electrons from the anthracene molecule to produce Cu(I) on the clay surface. As shown in Figure 6, first, photoinduced anthracene opens the ring in the reaction system to form product 1. It has been demonstrated that anthracene degradation on montmorillonite can form ring-opening products [43]. Meanwhile, Cu(II) attacks the C9 or C10 atom, interacts with ANT, and the associated electron transfer within the complex leads to the formation of Radical A and the reduction of the transition metal ion. At this stage, montmorillonite's negatively charged silicate layers effectively stabilize the positively charged radical cations on the interlayer surfaces, facilitating a stable initial radical, which provides a solid basis for subsequent reactions [42].

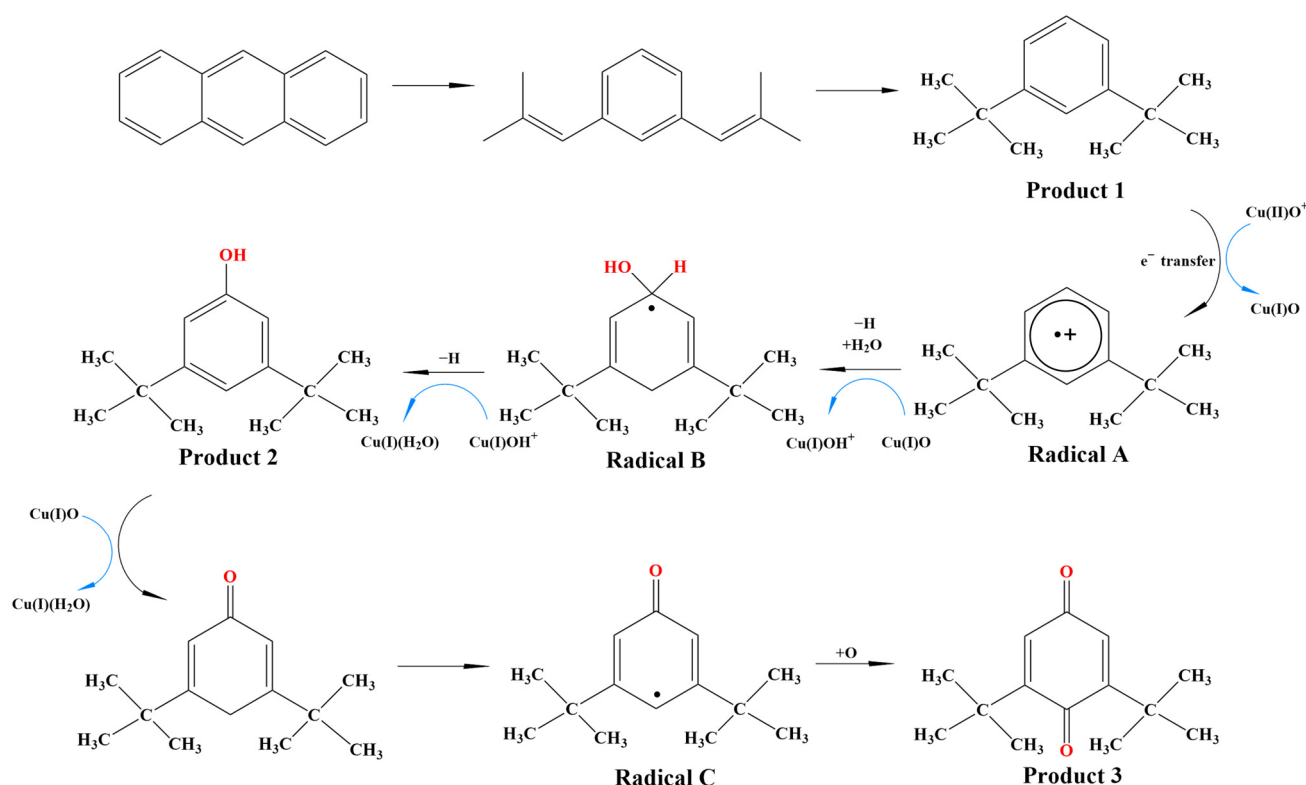


Figure 6. Proposed mechanism for the transformation of ANT and formation of EPFRs on Cu(II)-MT/SiO₂.

After the formation of the initial radical (Radical A), it exhibits high reactivity, easily reacting with water (H₂O) to produce a hydroxyanthracene-type radical (Radical B). This reaction occurs more readily than that between Radical A and oxygen (O₂) [42,44]. During this stage, the hydration reaction results in the attachment of water molecules to Radical A, leading to the formation of Radical B. Radical B then undergoes deprotonation to form Product 2. The hydroxyl group in Product 2 exhibits high reactivity and rapidly undergoes isomerization, transforming into a thermodynamically more stable ketone structure [45]. During this process, Cu(II)-montmorillonite catalyzes electron transfer, facilitating the formation of a keto radical (Radical C). Radical C is then further oxidized, resulting in Product 3. Throughout this sequence, electron transfer interactions and radical transformations on the Cu(II)-MT/SiO₂ surface lead to the gradual oxidation of intermediates and final products, illustrating the complex mechanism by which anthracene is converted into pollutants via radical chain reactions under photocatalytic conditions.

Gas chromatography-quadrupole time-of-flight mass spectrometry (GC/Q-TOF-MS) was employed to detect the intermediates generated during the degradation process. In the GC/Q-TOF-MS analysis, the quadrupole was set to select specific ions for transmission to the collision cell, where collision-induced dissociation (CID) generated product ions. These product ions were then analyzed using time-of-flight mass spectrometry to obtain high-precision mass data. By manually analyzing the GC/Q-TOF screening results, we identified three main intermediates with relative ion abundances that closely matched the library spectra, with match scores exceeding 80%, confirming the reliability of the detection results. Detailed information on the detected intermediates is provided in Table S1 and Figure S2, and the high degree of match between the GC/Q-TOF-MS spectra and the NIST library further validated the presence of these intermediates. In summary, the photodegradation of anthracene under light irradiation produces a series of radical intermediates and final pollutant products. The detection and confirmation of these products demonstrate the transformation pathways of anthracene in the photodegradation process and highlight its potential risks concerning environmental pollution.

4. Conclusions

This study highlights the significant role of environmental conditions in the generation and behavior of EPFRs. Our findings demonstrate that light exposure significantly enhances the degradation rate of organic pollutants, increases EPFR yield, and accelerates EPFR formation compared to dark conditions. However, light also promotes the generation of reactive oxygen species (ROS), accelerating EPFRs' decay and reducing their lifespan. In contrast, dark conditions facilitate slower but more stable EPFR generation, underscoring the importance of environmental factors in influencing EPFR dynamics and stability.

This study further reveals that the metal ions, precursor concentration, and precursor type are critical factors influencing EPFR formation. Specifically, Cu(II) shows a higher capacity to generate EPFRs due to its strong electron-accepting properties than Zn(II) and Na(I). The concentration of precursor pollutants has a direct impact on EPFR yield, with higher concentrations favoring greater EPFR formation. Notably, at elevated concentrations, previously generated EPFRs can act as electron shuttles, mediating precursor reduction and reducing net EPFR yield. This dual role of EPFRs—as both products and reactants—provides a deeper understanding of pollutant dynamics in environmental contexts. Moreover, the type of precursor contaminant also influences EPFR characteristics, and we innovatively investigated the mixed degradation of multiple pollutants and compared the environmental behavior of EPFRs in different pollutants. For instance, single precursors like ANT tend to produce stable, carbon-centered radicals, whereas complex mixtures of PAHs generate more diverse radicals, as indicated by broader EPR spectra. This will provide a basis for the treatment and remediation of mixed PAH-contaminated soils.

Overall, this research contributes to a deeper understanding of the environmental behavior of EPFRs by connecting metal ion chemistry, precursor concentrations and types, and environmental factors with EPFR formation and stability, providing a basis for assessing the potential environmental risk of EPFRs from mixed PAH-contaminated clay minerals. These insights are essential for developing targeted remediation strategies for polluted sites and mitigating the environmental and public health risks posed by EPFRs, which can promote the development of green remediation technologies to support sustainable environmental governance and resource utilization.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su17020663/s1>, Content S1: Experimental conditions; Figure S1: Changes in electron spin resonance spectra over time under continuous visible light irradiation for Cu-MT/SiO₂ of different copper loading concentrations loaded with ANT; Figure S2: The mass

spectra of major relevant products in the ANT degradation of Cu(II)-MT/SiO₂ system; Figure S3: The electronegative structure of ANT; Figure S4: (a) X-ray photoelectron spectroscopy (XPS) of ANT-contaminated clay without ANT; (b) after reaction, XPS of ANT-contaminated clay. Table S1: Intermediates of contaminant formation screened by GC/Q-TOF MS.

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