Overlooked carbon transformation via photo-induced generation of reactive oxygen species at clay mineral-organic matter interface

Li, Biao; Wang, Song; Zhang, Yifeng

Published in:
Chemical Engineering Journal

Link to article, DOI:
10.1016/j.cej.2024.152982

Publication date:
2024

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Overlooked carbon transformation via photo-induced generation of reactive oxygen species at clay mineral-organic matter interface

Biao Li, Song Wang, Yifeng Zhang*

Department of Environmental and Resource Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

ARTICLE INFO

Keywords:
Clay mineral
Dissolved organic matter
Photolysis
Reactive oxygen species
Carbon cycle

ABSTRACT

Photolysis-induced generation of reactive oxygen species (ROS) is a crucial aspect of environmental processes, yet the photoactivity of natural clay minerals (CMs) and the carbon cycle involved remain unclear. Here, we discovered the light wavelength-dependent photoactivity of CMs in ROS generation and deeply elaborated the transformation of DOM on the CM’s surface. Our results reveal that CMs exhibit varying adsorption capabilities and a preference for highly unsaturated phenolic and aliphatic compounds within DOM, possibly related to their physical properties e.g., surface area. The formed CM-DOM aggregates result in photolysis ROS redistribution and DOM transformation at the CM-DOM interface, leading to the generation of saturated and oxidized smaller molecules. Moreover, we uncovered the previously overlooked release of transformed DOM from the CM-DOM interface. These findings unveil new environmental ROS generation and distribution through the photolysis of CMs and DOM, shedding light on previously neglected carbon cycling at the CM-DOM interface.

1. Introduction

Clay minerals (CMs) are ubiquitous on the Earth’s surface and play crucial roles in microbial metabolism, elemental cycling, and the transformation of diverse organic/inorganic compounds [1–3]. Our recent research has linked reactive Fe(II)-bearing CMs to the generation of reactive oxygen species (ROS) across the oxic-anoxic interface of soil or sediment-a phenomenon referred to as “dark ROS generation” [4]. Traditionally, naturally occurring ROS has been attributed to photochemical processes on the Earth’s surface [5,6]. For example, oxide minerals (e.g., hematite) and sulfide minerals (e.g., sphalerite) have demonstrated semiconducting properties that can separate photogenerated electrons and holes to generate ROS [3,7]. However, despite being an abundant mineral group with unique properties, it remains uncertain whether natural CMs can induce ROS generation under light.

While several studies have reported the ability of certain CMs to promote the photochemical degradation of organics in aqueous, the use of unnatural CMs (e.g., synthetic nontronite) and various light sources (e.g., visible and UV light) have resulted in diverse pollutant removal mechanisms (e.g., the interaction between CMs and pollutants or the formation of organic free radicals) [8–12]. Additionally, CMs are frequently employed as supporting materials for semiconductors due to their larger surface area, albeit with lower photoactivity compared to synthesized catalysts [13,14]. An effective strategy to enhance their photoactivity for ROS generation involves introducing Fe species. Consequently, Fe(III)-saturated CMs are extensively prepared to degrade various pollutants under light [10,12,15,16]. These prompt a fundamental question: what are the key factors for ROS generation during photolysis of CMs?

Dissolved organic matter (DOM) represents a complex mixture of organic species in terrestrial carbon pools [17,18]. The photoactivity of DOM to generate ROS has been extensively reported. On the one hand, owing to the presence of light-absorbing functional groups (e.g., aromatic groups), DOM exhibits photoactivity under solar radiation, generating various reactive species (e.g., \( \cdot \mathrm{O}_2, \cdot \mathrm{O}_2^-, \) and 3DOM*) [19–22]. These reactive species may not only influence the environmental fate of DOM itself but also coexisting organic compounds, given their high oxidation potential. Evidence suggests that the photo- transformation of DOM can yield bioavailable low molecular weight carbon or even emit CO\(_2\) into the air [22,23]. On the other hand, conflicting reports propose that DOM can block light penetration or function as a radical quencher, impeding the ROS yield [24,25]. While DOM can bind to CMs, protecting itself from degradation and fostering carbon persistence in soils and sediments [26], few studies have focused on the impact of their interactions under light on their respective ROS-generating abilities and...
DOM transformation. One report suggested that DOM can act as a photosensitizer to reduce Fe(III) to Fe(II) via interfacial electron transfer, thereby enhancing ROS generation [27]. Therefore, we speculate that the interaction between CMs and DOM under light could affect ROS generation and the involved carbon cycle.

To address the above questions, we selected various natural CMs and representative DOM to explore (i) their photoactivity in generating ROS under diverse light conditions, including simulated sunlight and UV light; (ii) the key factors influencing the photoactivity of CMs and DOM; (iii) the effect of interaction between CMs and DOM on ROS generation and distribution; and (iv) the molecule changes within DOM during the interaction under light. This study elucidates unidentified natural ROS generation and distribution by CM-DOM interactions, enriching our understanding of the carbon cycle associated with adsorption and ROS generation at the CM-DOM interface.

2. Materials and methods

2.1. Preparation of clay minerals and DOM

Six naturally occurring complex clay minerals, denoted as CM-n (n = 1–6), were sourced from the Netherlands (More information and characteristics of these CMs were summarized in Table S1). Three standard clay minerals, namely nontronite (NAu-2), montmorillonite (SWy-2), and illite–smectite mixed layer (70/30 ordered, IScz-1) were acquired from the Clay Minerals Society (Indiana, USA). Three standard CMs underwent grinding and were subsequently sieved through a 63 µm mesh, followed by Na⁺-homogenization in 0.1 M NaCl solution. The resulting samples were then categorized into CMs (<0.05 µm), CMs (<2 µm), and silt (<2 µm) according to previous studies [28]. Humic acid (HA, Sigma-Aldrich) and fulvic acid (FA, Klamar, Shanghai) were selected as representative DOM. The preparation process for both HA and FA was consistent with our previous study [4].

2.2. Photolysis of clay minerals and DOM

A xenon lamp (CEL-HXF300, Beijing) was used to conduct simulated sunlight experiments, with a current range of 14–21 A (light intensity range of 19.23–50.63 W/m²). In a typical batch run, a specific complex CM or standard CM (1.0 g/L) was dispersed in deionized water in a cylindrical glass vessel with a rubber lid and placed in a continuous water bath with approximately 25º in the water tank. The pH was maintained at 7.0 throughout the process. At specified time intervals, the solution was extracted and then filtered through a 0.22 µm membrane for subsequent analysis. Photolysis of DOM followed a similar procedure, with CM initially replaced by DOM (0–100 mg C/L). Visible light experiments involved the application of a UV filter (λ ≤ 420 nm) to the xenon lamp. Moreover, a customized UV light-emitting diode (LED) strip (24 V, 14.4 W/meter, Buyledstrip, Netherlands) was wrapped around the inner wall of an inverted beaker (1 L, Simax) to serve as the light source (the outer wall was covered by aluminum paper). To study the wavelength dependence of ROS generation by CMs and DOM, LED strips emitting at distinct wavelengths (400, 370, and 280 nm) and UVC lamp (254 nm, 9 W) were employed. The working voltage of these LED strips was in the range of 19–24 V (light intensity range of 0.58–3.79 W/m²). Additionally, the impact of light on the interaction between CM and DOM was studied under UV (λ > 380 nm). Four groups of samples were collected for analysis, including initial CMs and DOM, DOM-adsorbed CMs, direct photolysis of DOM, and photolysis of DOM-adsorbed CM (Text S1). The effects of pH (4–9), O₂ concentration, DOM concentration (0–100 mg C/L), and standard CM’s size on photolysis of CMs were also investigated (Text S2).

2.3. Assessment of ROS generation

To evaluate the production of ROS from CMs or DOM, various chemical probes were used. Specifically, furfuryl alcohol (FFA, 0.1 mM) was selected to quantify the generation of •O₂. The generation of O₂⁻ was detected by nitroblue tetrazolium (NBT, 0.1 mM). The concentration of H₂O₂ was measured by a peroxide assay kit (Sigma-Aldrich). The concentration of HO• was determined by quantifying 7-hydroxycoumarin (7-COU), a fluorescence product resulting from the reaction of HO• and coumarin (Text S3) [29]. To further validate ROS generation, electron spin resonance (ESR) tests were conducted using Bruker EMX PLUS spectrometer. The distribution of ROS in aqueous solution and on the CM’s surface was visualized using 2,7’-dichlorodihydrofluorescein diacetate as a ROS capturer on a confocal laser scanning microscopy (CLSM, Leica TCS SP5) [4]. In addition, we introduced methanol (MeOH), Ag ions, ascorbic acid, 2,4,6-trimethylphenol (TMP) as reactive species scavengers to confirm the presence of HO•, photogenerated electrons, photogenerated holes, and the excited triplet state of DOM (3DOM*) respectively [3].

2.4. Characterisation and analysis

Photocurrent generation was assessed by an electrochemical workstation (PalmSens4) equipped with a three-electrode electrochemical cell using CM-modified fluorine doped tin oxide (FTO), Pt foil, and Ag/AgCl as working, counter, and reference electrodes, respectively (Text S3). The Mott-Schottky tests were performed using the above electrochemical system at 1000–2000 Hz to study the conduction band (CB) of CMs [3]. Physichemical properties of CMs were characterized by UV–vis diffuse reflectance spectroscopy (UV–vis DRS, UV3600, Shimadzu), HAADF–STEM (FEI Talos F200X, Thermofisher), XPS, and BET analysis. Additionally, the surface area of these CMs was estimated using a specific surface area analyser (ESI-FE-ICR-MS analysis, SlariX, Bruker, Test S4).

3. Results and discussion

3.1. Photolysis property of CMs

We selected various CMs (two complex CMs and three standard CMs) to investigate their photolysis properties. Although all complex CMs showed similar mineralogical and elemental compositions (Table S1), their differences in structure, surface area, and zeta potential might contribute to differences in photoactivity. The UV–vis DRS spectrum revealed a notable light absorption capacity for all five CMs, with absorbance levels arranged in the following order: CM-5 > NAu-2 > CM-4 > SWy-2 > IScz-1 (Fig. 1a). Remarkably, complex CMs exhibited more efficient photo adsorption than standard CMs, even within the visible-light spectrum, suggesting a narrower band gap conducive to photocarrier generation. The band gaps (Eg) were determined as 1.95 (CM-4), 2.54 (NAu-2), 3.02 (SWy-2), and 3.31 eV (IScz-1). Note that CM-5 exhibited strong absorption across the entire spectrum without a distinct tangent point, and thus its Eg was assumed in a similar range as CM-4. The CB of these CMs was −0.37 to −0.62 V vs. Ag/AgCl (Fig. 1b). Integration of Eg enabled the quantification of the valence band (VB) of these semiconductors: 1.53 (CM-4), 1.72 (CM-5), 2.14 (NAu-2), 2.67 (SWy-2), 3.14 V (IScz-1, Fig. 1c).

Photocurrent generation was evaluated under simulated sunlight and visible light by employing a light on–off mode. As illustrated, five CMs exhibited substantial photoactivity under simulated sunlight, with the resulting photocurrent showed a similar trend to DRS absorbance (Fig. 1d). Notably, the photocurrent demonstrated light dependence, reaching levels between 1.0 and 2.5 µA/cm² under simulated light, but rapidly diminished to near-zero when the light was turn off. Despite multiple light on–off cycles, the photocurrent consistently maintained...
high levels, underscoring their remarkable stability in photoelectric conversion. In contrast, the photocurrent generated under visible light (\( \lambda \geq 420 \text{ nm} \)) was notably lower compared to simulated light. Especially, standard CMs produced photocurrent less than 0.5 \( \mu \text{A/cm}^2 \), despite exhibiting high stability over several cycles. These results suggest that CM semiconductors differ in their ability to separate photogenerated

Fig. 2. Changes in the concentrations of (a) FFA and (b) NBT (inset of ESR of O$_2^•$) during photolysis of NAu-2 and FA. Generation of (c) H$_2$O$_2$ and (d) HO• during photolysis of various CMs. Generation of HO• during photolysis of (e) CM and DOM in the presence of different scavengers. Experiment conditions: concentrations of CMs (1 g/L), DOM (50 mg C/L), FFA (0.1 mM), coumarin (1 g/L), NBT (0.1 mM), TMP (0.1 mM), Ag$^+$ (10 mM), and MeOH (0.1 M).
electrons and holes, especially in the UV range.

3.2. Photolysis generation of ROS from CMs and DOM

3.2.1. CM-involved different pathways for HO• generation

Total ROS generation and distribution were evaluated via CLSM. In general, the ROS intensity on the CM’s surface was higher than in the solution, among which CM-4, CM-5, and NAu-2 generated higher intensity both in solid and aqueous phases (Fig. 1e). Photolysis of CMs to generate O2•−, H2O2, and HO• was further studied respectively. FFA, a O2− capturer, maintained at the same level throughout the photolysis of five CMs (Fig. 2a and 3a), implying negligible generation of O2•−. The ESR spectrum confirmed this result as no characteristic peaks of O2•− were found (data not shown). Conversely, apparent peaks of O2•− and variations in the concentration of NBT, an O2− capturer, were observed in the photolysis of CMs (Fig. 2b and S1b), indicating their disparate ability in generating O2•−. Additionally, CM-4 and CM-5 accumulated higher levels of H2O2 (11.30 and 12.91 µM, respectively) compared to NAu-2, SWY-1, and ISCe-1 (7.26, 6.99, and 0.5 µM, respectively) within 4 h (Fig. 2c).

The order of H2O2 generation did not align precisely with that of O2•− generation but was consistent with their CB positions, suggesting that O2•− might be rapidly transformed to H2O2 via photogenerated electrons. The measurement of HO• followed a similar order, with CM-4 (2.25 µM) and NAu-2 (0.40 µM) produced the highest HO• among complex CMs and CMs, respectively (Fig. 2d). Under photolysis, HO• can be generated through three pathways. Firstly, the one-electron transfer pathway, where O2 accepts an electron to form O2•−, followed by the acceptance of electrons to form H2O2 and HO• in sequence (First pathway). The photolysis of CM-4 and CM-5 was likely to follow this pathway due to their low VB values (<1.98 V, a potential for oxidation of OH•) and high CB values. The generation of HO• by these CMs seems to be consistent with their surface area, suggesting their role in promoting electron transfer. Secondly, the direct VB oxidation of OH•, a pathway potentially followed by three standard CMs with high VB positions (>1.98 V) (Second pathway). Lastly, the Fenton process, involving the activation of formed H2O2 by Fe or other reactive metals, was ruled out (Third pathway, discussed below).

To further determine the dominant pathway for HO• generation, we assessed the impact of various scavengers on the process. The introduction of MeOH resulted in a notable decrease in HO• generation, while Ag+ decreased the HO• by complex CMs (e.g., CM-5) rather than some standard CMs (e.g., ISCe-1, Fig. 2e). A possible reason is that Ag+ consumed the photogenerated electrons for O2 reduction instead of holes for OH• oxidation [3]. In comparison, the introduction of ascorbic acid, a hole scavenger, had a minimal impact on ISCe-1, but increased HO• generation for CM-5 and NAu-2 (Fig. S1c). This enhancement is likely attributed to hole capture, promoting charge separation and providing more photogenerated electrons for HO• generation. These are consistent with the above findings that complex CMs (CM-4 and CM-5) primarily generate HO• through the first pathway, whereas other standard CMs (ISCe-1) follow the second pathway. In addition, the presence of NBT inhibited the generation of HO•, confirming the involvement of O2•− in the one-electron transfer pathway for HO• generation (Fig. 2f).

All in all, these findings indicate that complex and standard CMs may favor distinct pathways for HO• generation under photolysis.

3.2.2. HO• as a dominant ROS in photolysis of DOM

DOM can absorb photons and transitions to form an excited state of 3DOM* (Eq. (1)–(2)), which further induces the generation of various ROS (Eq. (3)–(5)). However, the lack of a decline in FFA suggests the negligible generation of O2•− within 4 h. In contrast, the decrease in NBT and the appearance of characteristic peaks of O2•− confirm the generation of O2•−. Following these steps, HO• can be generated not only through the oxidation of H2O by 3DOM*, but also through the one-electron transfer pathway (Eq. (6)–(7)). Consequently, the photolysis of FA and HA accumulated 3.60 and 3.25 µM of HO•, significantly higher than the concentration observed for CMs (Fig. 2e and 3c). The decrease in HO• concentration upon the introduction of MeOH, Ag+, and NBT provided additional evidence for electron transfer-involved HO• generation, with O2•− and H2O2 serving as intermediates. By introducing TMP, a typical 3DOM* scavenger, we obtained a significant decrease in HO• generation compared to the decrease caused by NBT (Fig. 2d), supporting the higher contribution of H2O2 oxidation by 3DOM* in HO• generation.

\[
\begin{align*}
\text{DOM} + \text{hv} & \rightarrow \text{3DOM*} \\
\text{3DOM*} & \rightarrow \text{3DOM}^* \\
\text{3DOM}^* + \text{O}_2 & \rightarrow \text{3DOM} + \text{O}_2^\cdot \\
\text{3DOM}^* + \text{O}_2 & \rightarrow \text{DOM}^\cdot + \text{O}_2^\cdot \\
\text{3DOM}^\cdot + \text{H}_2\text{O} & \rightarrow \text{DOM-H} + \text{HO•} \\
\text{2O}_2^\cdot + 2\text{H}^\cdot & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{H}_2\text{O}_2 + \text{e}^- & \rightarrow \text{HO•} + \text{OH}^- 
\end{align*}
\]

3.3. Crucial factors in photolysis generation of HO•

3.3.1. Various Fe-containing CMs

Fig. 2d shows that CM-4 and CM-5 accumulated higher HO• than other complex and standard CMs under simulated sunlight. Notably, the obtained complex CMs comprise various standard CMs, but they were found to have undetectable impurities, such as heavy metals [4]. An intriguing difference between these CMs lies in the content of Fe species. Among three standard CMs, the Fe content ranked in the order of NAu-2 (21.2 wt%) > SWY-2 (2.3 wt%) > ISCe-1 (1.1 wt%) [28]. However, the photoactivity of these standard CMs in HO• production did not consistently align with their Fe content (Fig. S1d). Similarly, the inconsistency between the generated HO• and the Fe content in complex CMs was found, suggesting that Fe content is not the decisive factor influencing photolysis ROS generation. Moreover, our previous studies also confirmed that although these CMs contain high concentrations of Fe, most of them (e.g., structural Fe(III)) are not reactive [4]. Thus, the photo Fenton process, initiated by the reaction of reactive Fe species (such as structural Fe(II)) and the generated H2O2, may be ruled out as the primary mechanism for HO• generation.

3.3.2. Various light wavelengths

We found that the generation of HO• by both CMs and DOM was dependent on light wavelength. When a UV filter was employed during simulated sunlight exposure, the HO• generated by complex and standard CMs notably decreased to the range of 0.12–0.41 and 0.02–0.05 µM, respectively (Fig. S2a). This underscores the dominant role of UV light in HO• generation-a correlation further supported by results in photocurrent generation. To confirm this light dependency, we conducted experiments under LED lights with different wavelengths. At an equivalent light intensity, CM-5 (0.63–1.30 µM) generated higher HO• than CM-4 (0.11–0.13 µM) in the UVA range (370 and 400 nm, Fig. 3a). Additionally, both CM-5 and CM-4 exhibited lower HO• accumulation in the UVB (280 nm, 0.060–0.065 µM) and UVC range (254 nm, 0.09–0.15 µM), despite the higher intensity of UV254 light. Standard CMs also followed the same trend in HO• generation under varying UV wavelengths, with UV400 > UV370 > UV254 (Fig. 3b). These findings highlight the wavelength sensitivity of these natural semiconductors, with higher UV wavelengths leading to higher HO• generation activity. In comparison, DOM can only generate HO• under UV light but also under visible light, as significant HO• in the range of 1.51–1.79 µM was still detected when a UV filter was applied (Fig. 3c). However, similar to CMs, the generation of HO• by DOM also followed the same wavelength order (Fig. 3d).
5

Fig. 3. Generation of HO• during photolysis of CMs under different UV wavelengths (a) without and (b) with the presence of DOM. Generation of HO• during photolysis of DOM (c) under simulated sunlight and visible light and (d) different UV wavelengths. Generation of HO• during photolysis of CMs in the solutions with different (e) gases and (f) pH conditions. Experiment conditions: concentrations of CMs (1 g/L) and DOM (50 mg C/L), pH (4–9).

3.3.3. Solution conditions

To explore the photolysis of CMs under different solution conditions, we utilized UV400 as the light source, given its ability to generate the highest level of HO•. Initially, when changing from an air-exposed solution to N2-saturated and O2-saturated solutions, the HO• generated by CMs decreased and increased, respectively (Fig. 3e). This reinforces the notion that photogenerated electrons were involved in the ROS generation triggered by O2 reduction. pH is another important factor influencing photolysis process. At low pH levels, an abundance of HO• was produced. This is likely due to the formation of HO• radicals from the photolysis of water. Consequently, the photolysis of DOM-DOM, coupled with ROS generation, involves electron transfer from DOM* to O•2, instead of the energy transfer pathway to generate O•2- and HO•, instead of the energy transfer pathway to generate 1O2. Compared with CMs, DOM showed similar light-wavelength dependence, with higher activity detected in the high UV range.Interestingly, moderate concentrations of ROS were found even in the visible light range during the photolysis of DOM instead of CMs. This underscores the substantial impact of photo-induced ROS from DOM on the associated geochemical processes.

3.4. Unique properties of CMs and DOM

The natural production of ROS has been linked to the photochemical activity of diverse organic compounds (e.g., DOM [30]), inorganic compounds (e.g., nitrate [31]), and organic–inorganic complexes (e.g., hematite-oxalate [32]). Our study presents a pioneering exploration into the semiconducting properties of various CMs for ROS generation, which possess several unique properties compared to previously reported natural species. Firstly, in contrast to typical oxide minerals that predominantly generate HO• through direct VB oxidation of OH• (pathway I) [3], our CMs demonstrate the capability to generate HO• through pathway II and the one-electron transfer pathway involving O2•- and H2O2 as intermediates (pathway I). Secondly, CMs can accumulate higher HO• concentration (0.2–2.25 µM) than oxide minerals (0.02–0.3 µM) within several hours. Thirdly, unlike hematite and magnetite which generate HO• solely within UVA range, with greater photoactivity at lower wavelengths [3], our CMs exhibit HO• generation across the entire UV range, with heightened activity at higher wavelengths. One possible reason is that we obtained the highest light intensity at UV400. Lastly, our results reveal that Fe content does not dictate the photoactivity of CMs in generating ROS, possibly due to the absence of reactive Fe species.

Similar to prior studies, the introduced DOM can adsorb light to form excited states of DOM* and further ROS. Notably, our study revealed a distinct phenomenon—the absence of high concentrations of 1O2. This suggests that the dominant pathway for ROS generation involves electron transfer from DOM* to O2 or H2O to generate O2•- and HO•, instead of the energy transfer pathway to generate 1O2. Compared with CMs, DOM showed similar light-wavelength dependence, with higher activity detected in the high UV range. Interestingly, moderate concentrations of ROS were found even in the visible light range during the photolysis of DOM instead of CMs. This underscores the substantial impact of photo-induced ROS from DOM on the associated geochemical processes.

3.5. Dynamics on the CM-DOM interface

In nature environments, CMs and DOM are generally combined to form CM-DOM aggregates through diverse adsorption, such as electrostatic, complexation and hydrophobic interactions [26]. This phenomenon, commonly observed in soils, sediments, and seabeds, represents a fundamental pathway for carbon storage on the Earth’s surface [26]. Consequently, the photolysis of CM-DOM, coupled with ROS generation, can be conceptualized in four key steps: adsorption of DOM on the CM’s surface (first), ROS generation at CM-DOM interface (second), DOM transformation by ROS (third), and release of the reacted DOM from CM-
DOM interface (fourth).

3.5.1. First step—adsorption

The capacity of CMs to adsorb DOM varies, as evidenced by the differential decrease in absorbance of FA when interacted with different CMs (Fig. S3b). The decline in COD supported the adsorption of FA from the solution onto the surface of CMs (Fig. S3b). 3D-EEM analysis demonstrated that the adsorbed FA (decrease in the fluorescence intensity) followed the order of ISCz-1 > CM-4 > CM-5 > NAu-2 > SWy-2 (Fig. S4). We further employed HAADF-STEM technical to visualize the distribution of adsorbed DOM on CMs. Initially, the surface of CM-5 exhibited an even distribution and high intensity of Fe and Al, while the C element showed weak intensity (Fig. 4a). In contrast, the intensity of C significantly increased on the CM’s surface after adsorption (Fig. 4b). Further element quantification through linear scanning revealed the order of intensity as Al > Fe > C initially. Following adsorption, the intensity of C reached a level comparable to that of Fe.

To further evaluate the interaction between DOM and CMs, we measured the changes in zeta potential and Z-average size of CMs before and after adsorption. As shown in Fig. S5a, the adsorption of more negatively charged FA resulted in more negative zeta potential of CMs. In addition, the difference in adsorption capability may related to the surface area or pore area of these CMs due to the positive correlation between them. It is known that a higher charged surface potential can enhance the formation of more stable particles, thus reducing particle aggregation [4]. Consequently, the Z-average size of the particles exhibited a decrease following the adsorption process (Fig. S5b).

3.5.2. Second step—ROS generation

Decreased ROS generation was observed in aqueous solution containing DOM after mixing CMs and DOM. Fig. S7a shows that the accumulated HO• by HA and FA substantially decreased from 1.45 and 2.23 µM to 0.82 and 1.18 µM, respectively, after mixture. Similar decreases in HO• generation were observed in the mixture of standard CMs and DOM compared to the existence of solely DOM under different UV wavelengths (Fig. 3b). One reason could be that the existence of CM particles hinder the photo emission and adsorption by DOM. Additionally, DOM transfer from aqueous solution to solid surfaces could contribute to reducing the detected aqueous HO•. Supporting this notion, the residual FA after adsorption exhibited diminished photoactivity in HO• generation (Fig. S7b). Interestingly, the accumulated HO• (0.9–1.3 µM) followed the opposite order of the adsorption ability of CMs (ISCz-1 > CM-4 > CM-5 > NAu-2 > SWy-2), suggesting that these CMs possess selective capability in interacting with the reactive molecules within DOM. This also confirms the relationship between their properties (e.g., surface area) and their capabilities in adsorption or ROS generation.

Enhanced ROS generation was found at the CM-DOM interface. After mixing DOM with CM, the generated photocurrent density significant increased from 0.2 to 0.5 to 2.0–3.5 µA/cm² (Fig. S8a). This improvement can be attributed to the heightened generation and separation of photoelectrons resulting from the interaction between CMs and DOM. To further investigate this phenomenon, CM was combined with varying concentrations of DOM, and the resulting solids were separated as semiconductors for ROS generation. The results showed that with an increase in DOM concentration from 25 to 100 mg C/L, the HO• generated by DOM-adsorbed CM increased from 0.46 to 0.77 µM (Fig. S8b). Moreover, we observed high fluorescence intensity on the particle surface after adsorption, confirming the increased ROS generation at the CM-DOM interface (Fig. 4f).

All in all, after adsorbing DOM from the solution to the CM’s surface, the ROS generation on the CM’s surface increased, but in the solution decreased. The changes in ROS production and distribution suggest that the adsorption behavior significantly influences the photoactivity of DOM given their role as primary photosensitizers. This parallels earlier studies where aromatic-rich compounds were preferentially sequestered by ferrihydrite, leading to a significant decline in ROS generation [33].

3.5.3. Third step—DOM transformation

Direct photolysis alone demonstrated limited effectiveness in
removing DOM from the solution within several hours. Specially, we observed a slight decrease in absorbance after photolysis of low concentrations of FA, but negligible changes in high concentrations of FA (Fig. S9a). However, the existence of CM significantly increased the removal of DOM. As shown in Fig. 4d, more than half of FA was removed after photolysis of the mixture of FA and CM-4 or SWy-2 (the intensity values were collected from the center of the fluorescent areas in Fig. S4). Additionally, while photolysis did not change the zeta potential of the mixture of CMs and DOM, it apparently induced particle aggregation (Fig. S5). The transformation of DOM was also affected by different aquatic parameters, such as dissolved O\textsubscript{2} concentration, pH, and salinity (Fig. S6). For instance, low pH and high O\textsubscript{2} of the solution are beneficial for the generation of high concentrations of ROS, facilitating DOM transformation.

3.5.4. Fourth step–DOM release
Considering the adsorption process increased ROS generation on the CM’s surface, we speculated that the redistributed ROS could, in turn, affect the fate of the adsorbed DOM. To explore this dynamic, we examined the changes in adsorbed DOM with and without subsequent photolysis. As shown, upon introducing DOM-adsorbed CMs into the solution without photolysis, 3D-EEM exhibited minimal changes in the characteristic peak of FA after 48 h (Fig. S10). However, a significant peak was observed in all separated solutions when UV\textsubscript{400} light was applied, suggesting the release of adsorbed DOM. More importantly, the characteristic peak decreased in intensity and shifted left compared to initial DOM, suggesting the changes in the concentration and composition of the released DOM. Similarly, when changing FA with HA, we still observed negligible release of DOM under dark, but substantial release under photolysis (Fig. S11). In both cases, the released DOM did not follow the same order as the initially adsorbed DOM. For instance, while CM-4 and ISCz-1 adsorbed high concentrations of DOM, they released relatively low amount after photolysis. This may be related to the different adsorption mechanisms between different CMs and DOM, resulting in different binding forces during the release process. In addition, the released DOM exhibited lower TOC concentration compared to the adsorbed DOM (Fig. S9c), suggesting the presence of residual DOM on the CM’s surface. Therefore, although the intensity of generated ROS decreased compared with that after adsorption, it was still higher than the initial CMs.

The release of the transformed DOM has been overlooked in previous studies and should be comprehensively evaluated in the future due to its close association with multiple carbon cycles on the Earth’s surface. For example, these released small DOM molecules could be easily utilized by microorganisms or plants as a source of carbon. Furthermore, considering the optical wavelength and intensity dependence of ROS production from CM-DOM, we infer its spatiotemporal dependence due to the widespread distribution of CM-DOM on Earth.

3.5.5. Molecular changes of DOM
The dynamics of DOM induced by adsorption and photolysis were further analyzed by FT-ICR-MS. In the initial sample, a total of 2357 peaks were identified in the mass range of 200–700 Da, with the primary peaks distributed within 300–500 Da (Fig. 5a and S12a). The magnitude-weighted H/C\textsubscript{w}, O/C\textsubscript{w}, and aromaticity index (AI\textsubscript{w}) were 0.82, 0.46, and 0.51, respectively. Direct photolysis of DOM resulted in a decrease in 200–450 Da molecules. AI\textsubscript{w} value remained consistent (0.51), but the abundance of H/C increased significantly (Fig. 5b), implying the removal of unsaturated compounds. Adsorption process also resulted in a slight decrease in 200–450 Da molecules. The decreased double bond equivalence (DBE) indicate that compounds with higher unsaturation levels could be preferentially sequestered by CMs (Fig. S12 b). Comparatively, the photolysis of DOM-adsorbed CM led to more pronounced changes. The percentage of 300–350 Da molecules significantly increased, accounting for over 55 %, indicating the release of mainly smaller molecules from CM’s surface. The decreased DBE and
increased H/C suggest these leached compounds had high saturation levels.

By integrating Al and H/C, all formulas were categorized into four groups on the van Krevelen diagram (Test S4) [34]. The remaining and disappeared molecules signify those still exist in the solution and those transformed after adsorption or photolysis, respectively. In the initial DOM, the ratios of molecules in the four groups were 33.2 %, 30.9 %, 29.7 % and 6.3 %, respectively (Fig. S5f). Following direct photolysis, the molecules in the groups (3) and (4) significantly decreased to 31.2 % and 3.9 %, respectively. In comparison, the remained molecules maintained the same order of the initial DOM (group (1) > group (2) > group (3) > group (4), Fig. S13). Analysis of the generated molecules after photolysis revealed a new array in the four groups. These results suggest that direct photolysis can only transform a small ratio of highly unsaturated compounds to some new compounds. Adsorption process led to a decrease in groups (4) and (3) but less change in groups (2) and (1), indicating a preferential sequestration of highly unsaturated and phenolic and aliphatic compounds by CMs. In contrast, the photolysis of DOM-adsorbed CM resulted in a relatively even distribution of the four group molecules in the solution (23.8 %–27.1 %).

The degrees of unsaturation and redox state of DOM molecules were further evaluated. Larger positive values in (DBE-O)/C and nominal oxidation state of carbon (NOSC) signify higher unsaturation and oxidation, respectively [33]. We found that after direct photolysis of DOM, (DBE-O)/C slightly decreased (Fig. S14), accompanied by an increase in molecules within the positive range of NOSC. These observations suggest that unsaturated and reduced compounds were preferentially decomposed, emphasizing the role of oxidation during photolysis. Similarly, the photolysis of DOM-adsorbed CM also resulted in a decrease in (DBE-O)/C but an increase in NOSC. The change in the number of confirmed oxygen addition reactions induced by photolysis.

4. Conclusion

This study investigated the photoactivity of natural CMs on ROS generation and its involvement in DOM transformation. Our findings unveil that CMs exhibit different ROS generation pathways and different photoactivities in different UV wavelength ranges. In comparison, DOM can generate ROS across the full wavelengths, yet its photoactivity remains wavelength-dependent. The interaction between CMs and DOM results in selective adsorption of unsaturated and phenolic compounds onto the surface of CMs, which might related to surface area and the presence of functional groups of CMs. This selective fractionation led to ROS redistribution from the aqueous solution to the CM’s surface. Significantly, we uncovered the overlooked release of reacted DOM molecules returning from the CM’s surface to the aqueous phase, a crucial aspect of carbon transformation. These results deep our understanding of natural ROS generation by natural species and their geochemical behavior especially for carbon cycles.

CRediT authorship contribution statement

Biao Li: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Song Wang: Writing – review & editing, Methodology, Formal analysis. Yifeng Zhang: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

Acknowledgements

The authors thank The Carlsberg Foundation (Distinguished Fellowships, CF18-0084, Denmark), The Ministry of Foreign Affairs of Denmark (No. 21-08-DTU, Denmark), VILLUM FONDEN (No.40828, Denmark), and Independent Research Fund Denmark (Project 1, No.171114, Denmark) for partly funding the research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2024.152982.

References


