Activation of Cadmium Under Simulated Solar Illumination and Its Impact on the Mobility of Cd in Flooded Soils

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Abstract

In waterlogged paddy soils, cadmium (Cd) can be precipitated as cadmium sulfide (CdS) under reductive environment, thereby limiting the absorption of Cd by plants. Multiple environmental factors (such as water, pH, Eh, etc.) played a role in the control of Cd mobility and bioavailability. In this study, we investigated the influence of the solar irradiation on the photo-dissolution of synthetic CdS-montmorillonite composites (CdS-M) in solution and the stability of Cd in natural soil. The release kinetic of Cd^{2+} showed that after the irradiation of simulated sunlight, CdS-M composites became less stable compared to the dark control. The solar irradiation seemed to enhance the release of Cd^{2+} from CdS significantly and continuously. Electron paramagnetic resonance (EPR) and quenching experiments confirmed that the photogenerated holes, $\text{O}_2^{\cdot -}$ and $\cdot\text{OH}$ were possibly involved in the photo-induced release of Cd^{2+} , while the holes were primarily responsible for the reaction.

Irradiation under alkaline solution or the presence of DOM, PO_4^{3-} , CO_3^{2-} and urea markedly inhibited the photodissolution process of CdS. The photo-mediated activation of Cd was further confirmed in paddy soil under natural sunlight, with a nearly 3-fold increase in concentration of extractable Cd during the 15 days irradiation. This study highlights the importance of photochemical transformation of Cd in the environmental water and soil.

1. Introduction

Cadmium (Cd) is a non-essential biological element with high-potential toxicity, mobility and bioaccumulation. Anthropogenic activities, such as mineral exploitation, sewage irrigation, and fertilizer application have greatly increased Cd levels in the water and soil environment (Saini and Dhaniala, 2020). Among all the surveyed contaminants, Cd ranks first in the percentage of soil samples (7.0%) exceeding the soil quality standards in China (Mahar et al., 2016). It is also one of the most harmful and widespread metals in agricultural soil of south China, which is readily absorbed by crop plants and threatens human health through the food chain (Wang et al., 2021).

When Cd enters the soil, it is first adsorbed on soil particles surface and then can be changed into other forms through various physicochemical or biological processes. In fact, the different forms of Cd often change with environmental conditions, such as soil pH, Eh, DOM, CEC and organic matter content, etc., thus influencing its fate and bioavailability (Lu, 2000; Niu et al., 2013). At present, there are several methods to classify the occurrence forms of heavy metals in soil, and the most widely used and representative morphological analysis method is sequential extraction procedure (BCR) proposed by the European Community Bureau of Reference (Ure et al., 1993), which divides the element in soil or sediment into four fractions: the acid-exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3), and residual fraction (F4). Among them, cadmium associated with organic matter or sulfide (CdS) belongs to the oxidizable fraction (F3). Rice is one of the most important cereal crops in the world and the main food crop in Asia (Carrijo et al., 2017). Because the paddy are continuously flooded or irrigated until

harvesting, the soil is usually under anaerobic and reductive conditions. S^{2-} produced in soil can deposit soluble Cd^{2+} in the form of CdS , or transform the refractory $Cd(OH)_2$ and CdO into more refractory sulfide, decreasing the mobility and bioavailability of Cd .

CdS is also one of the widely used cadmium pigments with the band gap of 2.5 eV, which is highly photoactive under sunlight (Liu et al., 2017; Swafford et al., 2006). Upon illumination, photoelectrons are excited from their valence band to the conduction band of CdS , forming photoelectron-hole pairs and triggering a series of redox reaction. In previous studies, photocatalysis driven by CdS has received considerable attention as it can be used for environmental remediation and solar energy conversion (Mohan et al., 2021; Zhang et al., 2020). Furthermore, photo corrosion of CdS nanoparticles or quantum dots and subsequent release of Cd^{2+} ions have also been reported (Matsumoto et al., 1996). Nevertheless, our understanding of the photo-transformation processes of CdS in soil under sunlight illumination is still limited. Such information reveals the presence of a photo-electrochemical system involved in the migration and transformation of Cd in paddy soils, which may increase the release risk of organic binding state Cd .

Herein, in order to simulate CdS in natural soil, the montmorillonite was applied as a carrier to load the prepared CdS particles (CdS -M). The photo-mediated release of Cd^{2+} and SO_4^{2-} from CdS was examined under simulated sunlight. The effect of factors including pH, DOM, phosphate, carbonate, urea, ferrous and ferric ion on the photo dissolution dynamics were further explored to inform the natural release process. Electron paramagnetic resonance (EPR) and quenching experiments were carried out to infer the possible mechanism of photo dissolution. In addition, the photo-mediated transformation of CdS in paddy samples was investigated under natural sunlight to support our findings.

2 Materials And Methods

2.1. Chemicals

In this research, all the chemical reagents were analytical grade or higher purity. Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$), sodium sulfide (Na_2S), trisodium phosphate ($Na_3(PO_4)$), sodium carbonate (Na_2CO_3), montmorillonite (MMT), urea (H_2NCONH_2), and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Both humic acid (HA) and fulvic acid (FA) were provided by Shanghai Macklin Biochemical Co.,Ltd. Methyl iologen dichloride hydrate (MV^{2+}) was obtained from Merck (Germany). All solutions were prepared using ultrapure water purified by the Mili-Q system (18 M Ω cm).

2.2. Preparation of MMT loaded CdS

The CdS -M composites were synthesized through the following steps: (i) Na-MMT was prepared by treating 9 g of MMT with 1 M $NaCl$ solution under mechanical stirring for 24 h. This procedure was repeated 5 times in order to obtain maximum saturation. Then, it was separated from the solution and washed several times with distilled water. (ii) The Na-MMT was mixed with 100 mL of 0.2 M $CdCl_2$

solution for 2 h at 60°C in a magnetic mixer. The mixture was then separated from the suspension through centrifugation and rinsed with deionized water several times to remove the excess Cd^{2+} . (iii) The Cd^{2+} -MMT was redispersed in 100 mL of 0.2 mol/L Na_2S solution, and the mixture was stirred at 25°C for 2 h. Clay particles in the solution immediately turned yellow. After that, the obtained CdS-M composites were centrifuged and rinsed three times with absolute ethanol, and then dried in 50°C oven under vacuum overnight. Dried samples were stored in an anaerobic chamber filled with pure N_2 gas prior for use.

2.2. Simulated illumination experiments

Solar irradiation was simulated by a 50 W xenon lamp (CELHXF300, AULTT, China). The CdS-M stock suspension was prepared by dispersing 0.02 g CdS-M powder into 100 mL deionized water by ultrasonication for 2 min, and then the resulting solution was placed in a water-circulating jacket beaker at $20 \pm 1^\circ\text{C}$ and irradiated by the Xe lamp from the top without stir. The unadjusted pH of the suspension was 6.0 ± 0.2 . At a regular interval, 5 mL sample was withdrawn from the beaker and filtered through a $0.22 \mu\text{m}$ -pore-size membrane filter to remove particles for further analysis. To guarantee precise data, all of the experiments were performed at least threefold and average values were recorded. Dark control experiments were carried out in the same experimental setting with the Xe lamp off and the beaker wrapped with aluminium foil.

The effect of pH on Cd^{2+} photo-mediated release was studied in the pH range of 3.98-8.11, with solutions adjusted using 0.1 M HCl and NaOH. To examine the role of different reagents in the reactions, DOM, PO_4^{3-} , CO_3^{2-} , and urea were added in the simulated illumination experiments.

2.3. Reactive oxygen species detection

The generation of ROS by CdS under simulated solar irradiation was determined by electron paramagnetic resonance method (EPR, A300-10/12, Bruker, Germany) and quenching experiment. The EPR were tested at room temperature with a microwave power of 20 mW, resonance frequency of 9.77 GHz, center field of 3480 G, sweep width of 200 G, modulation frequency of 100 kHz, and modulation width of 1 G. The 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was used as a spin-trapping agent for $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, and the dimethyl sulfoxide (DMSO, 65%) was used as the $\cdot\text{OH}$ scavengers during the detection of $\cdot\text{O}_2^-$.

The ROS involved in the photoreactions were examined via the quenching experiments using $\text{Na}_2\text{S}_2\text{O}_3$ as the hole scavenger, MV^{2+} as the electron scavenger, DMSO as the hydroxyl radical scavenger, and benzoquinone (BQ) as the peroxy radical scavenger.

2.4. Soil illumination experiments

To explore the effect of sunlight on soil Cd forms, the photo-mediated transformation of CdS in natural soil under sunlight was also examined. The soil samples were collected from a paddy field in Changsha, China (113.10°E , 28.38°N) by five-spot sampling method. The depth of the topsoil was 0-20 cm. Soil samples were air-dried, ground, sieved through a 2-mm nylon sieve. 50 g of soil sample were completely

mixed with 0.2 g CdS-M composite, which was then added in a serum bottle and submerged by water (1:3 w/v). The serum bottles were sealed by microporous membrane filter and placed outdoors, while the bottles for dark control experiment were wrapped with aluminium foil and protected from light during the experiments. Three replicates were performed for each group. At the interval of every 3 days, the water and soil samples were taken out at 7 p.m. for analysis. Extractable Cd in soil was determined by diethylene triamine pentaacetic acid (DTPA) extraction by shaking for 16 h at 25°C. BCR sequential chemical extraction was used to determine the different fractions of Cd in soil.

2.5. Analytical method

The Cd²⁺ concentration was detected by Optima 8300 ICP-OES (PerkinElmer, USA). The SO₄²⁻ concentration was determined by ion chromatography (ICS-1000, Dionex, USA) with a Dionex IonPac AS11-HC analytical column (250 × 4 mm). Reagent blanks and sample replicates were used to ensure analytical quality.

The phase composition and crystallinity of CdS-M composite were examined by X-ray diffractometer (XRD, Bruker D8-advance, Germany) with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The particles morphology was observed on a transmission electron microscopy (TEM, JEM-1230, JEOL, Japan). The surface chemistry of the CdS-M sample was examined using the X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo Scientific, USA) equipped with an Al K α X-ray radiation at 150 W. The element composition of the CdS-M was determined via a FE-SEM (FEI, QUANTA250, USA) equipped with an energy-dispersive X-ray spectroscope (EDX).

3 Results And Discussion

3.1 Characterization of CdS-M composites

To confirm the successful incorporation of CdS in MMT, the crystalline structure of the MMT and CdS-M composites were characterized by XRD (Fig. 1). The main peak in the diffraction pattern of MMT ($2\theta = 5.9^\circ$) can be attributed to the regular stacking of the silicate layers along the [001] direction, which is normal for montmorillonites (Krauskopf, 1967). The diffraction peaks occurring in the CdS-M composites at 2θ of 24.7° , 26.3° , 28.0° , 43.3° and 51.3° were ascribed to the Cd [100], [002], [101], [110], and [112] planes, respectively, according to JCPDS file No. 41-1049 (Chen et al., 2020). Furthermore, compared to the natural MMT, that peak of the CdS-M was less obvious and some peaks have disappeared, which indicated the ordered layered structure of CdS-M was disrupted during loading.

The morphology and particle distribution of CdS on clay were analyzed by HR-TEM. Figure 2a and b provide the images of CdS-M samples containing some darker spots, the putative CdS particles with a few nanometers in diameter. Considering that the cation-exchange only occurred in the MMT layers, CdS oligomers mostly bound in the interlayers of clays, which were not distinguishable. The EDX elemental mapping of the CdS-M composites confirmed the presence of CdS on the MMT support (Fig. 2c). As shown in Fig. 2d, the HR-TEM image showed crystal spacings of 0.34 and 0.36 nm on the CdS-M

composites, which were ascribed to the [002] and [100] crystal planes of the hexagonal CdS, respectively. Due to the distinct lattice fringes, CdS particles are easily differentiated from the clay background. EDX element analysis demonstrates that Si, Al, Na, and O from the MMT are presented (Fig. 2e), and distinct peaks of Cd and S from the CdS are also observed. Quantitative analysis results revealed that the CdS-M composite contains Cd (12.92 wt.%) and S (7.00 wt.%).

The XPS was utilized to elucidate the chemical structure and composition of the CdS-M sample. In addition to the high response of Al and Si in montmorillonite, Cd 3d and S 2p signals were detected in the XPS spectra (Fig. 3a). The deconvoluted high-resolution spectra showed double peaks at 411.4 eV (Cd 3d_{3/2}) and 404.7 eV (Cd 3d_{5/2}), which were considered the characteristic peaks of the Cd²⁺ species, whereas the peaks at 168.6 eV (S 2p_{1/2}) and 161.1 (S 2p_{3/2}) were assigned to the spin-orbit double of S²⁻ (Fig. 3b and c) (Huang et al., 2018). As a result, the characterization by XRD, TEM, EDX and XPS verified that the CdS was loaded into the MMT layers successfully with the procedures.

3.2 Release kinetics of Cd²⁺ from CdS-M composite

The release of Cd²⁺ and SO₄²⁻ from the CdS-M composite was examined under both dark and simulated solar irradiation (Fig. 4a and b). There are small amount of Cd²⁺ and SO₄²⁻ release from the CdS-M suspension in the dark condition within 240 min, which can be ascribed to the ions release during the dispersion process by sonication. This indicated an insignificant oxidative dissolution of CdS in the dark condition. In contrast, the presence of simulated solar irradiation was found to lead to significant and continuous enhance in the release of Cd²⁺ and SO₄²⁻ in the solution. The concentration of Cd²⁺ increased to 7.60 ± 0.38 mg/L within a 100-mins irradiation, and to 9.11 ± 0.23 mg/L after 240 mins of irradiation; meanwhile, the concentration of SO₄²⁻ reached 20.09 ± 0.30 mg/L at the end of the test.

The release kinetics of Cd²⁺ can be well described by the pseudo-second order equation. The pseudo-second-rate constants (*k*, L/mmol·h) was determined by fitting data to the following kinetic equation:

$$\frac{1}{[CdS]_t} - \frac{1}{[CdS]_0} = kt$$

The calculated *k* of Cd²⁺ was 0.126 L/mmol·h (*R*² = 0.97), which was 6.3 times higher than that under dark condition (*k* = 0.020 L/mmol·h, *R*² = 0.90). These results revealed that sunlight played a key role in promoting the release of Cd²⁺ from CdS.

3.3 Mechanisms for the photo dissolution of CdS

The EPR and radicals quenching experiments were carried out to detect the photo transients (such as ·OH and ·O₂⁻, etc.) generated by the CdS under simulated solar irradiation. The EPR spectrum of the CdS under irradiation showed a six-lines signals with the intensity ratio of 1:1:1:1:1:1 (Fig. 5a), which is the hallmark for the DMPO·OO(H) adduct, confirming the formation of ·O₂⁻ (Fang et al., 2017). As illustrated in Fig. 5b,

the characteristic intensity 1:2:2:1 of the DMPO-OH adduct was observed in the CdS suspension under simulated solar, suggesting the generation of $\cdot\text{OH}$ (Makino et al., 1991). Additionally, there were no EPR peaks in the same sample without simulated solar irradiation.

As previously reported by Gu et al. (Gu et al., 2015), the band gap energy (E_g) of CdS was 2.4 eV, and its conduction and valence bands (CB and VB) edge potentials are located at about -0.505 and +1.895 eV, respectively. Therefore, CdS could be excited by the visible-light irradiation and produce the photogenerated electron-hole pairs (Eqs. (1)). The CB potential of CdS is more negative than the redox potential of $\text{O}_2/\text{O}_2^{\cdot-}$ (-0.33 eV), indicating the agminated electrons in the CB can reduce O_2 into $\text{O}_2^{\cdot-}$ and other active species (Eqs. (2), (3) and (4)). Meanwhile, the photogenerated holes in the VB of CdS is not positive enough to oxidize H_2O or OH^- into $\cdot\text{OH}$ ($\cdot\text{OH}/\text{H}_2\text{O} = +2.27$ eV; $\cdot\text{OH}/\text{OH}^- = +1.99$ eV, respectively) (Luo et al., 2017). In consequence, the formation of $\cdot\text{OH}$ was most likely generated through the H_2O_2 reduction pathway (Eqs. (5) and (6)).

To determine the contribution of holes, electrons, $\cdot\text{OH}$, and $\cdot\text{O}_2^-$, scavengers including $\text{Na}_2\text{S}_2\text{O}_3$, MV^{2+} , DMSO and BQ were added into the CdS-MMT photoreaction system, respectively. As shown in Fig. 5c, the photodissolution of CdS under simulated solar were all inhibited after the addition of $\text{Na}_2\text{S}_2\text{O}_3$, DMSO and BQ, which decreased from 9.11 mg/L to 3.04, 7.38 and 5.54 mg/L, respectively, after 240 mins. However, the presence of MV^{2+} exerted an obviously promoting effect on the photodissolution of Cd^{2+} . MV^{2+} can react with photogenerated electrons, reducing the recombination probability of photogenerated electron-hole pairs and consequently leaving more holes involved in the photocatalysis system. This is consistent with the observations in the previous studies (Liu et al., 2017; Matsumoto et al., 1996). Furthermore, the photodissolution of CdS was also significantly inhibited under the anaerobic condition. Deficient oxygen can not combine with electrons to yield $\cdot\text{O}_2^-$, leading to more electron recombined with the holes and the inhibited release of Cd^{2+} accordingly. The above results showed that the photogenerated reactive species (h^+ , $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, etc) were possibly involved in the photo-induced release of

Cd^{2+} (Ge et al., 2015; Hu et al., 2018; Liu et al., 2017; Liu et al., 2020; Zhang et al., 2018), while the reaction was predominated by the holes. Based on these, the possible mechanism for the solar-mediated Cd^{2+} release from CdS is as follows (Eqs. (7)-(9)):

3.4 Influence of environmental factors on the photodissolution of CdS

To further understand the environmentally realistic release process, the effects of environmental factors including pH, DOM, PO_4^{3-} , CO_3^{2-} and urea on the photodissolution of CdS were examined.

3.4.1 pH

As is shown in Fig. 6a, the solution pH has an important effect on the photolysis of CdS. The photodissolution rate increased with increasing the initial pH in acidic conditions (from 3.98 to 6.00), yet the photodissolution drastically decreased as the initial pH increased to 8.11. Under alkaline conditions, the formation of $\text{Cd}(\text{OH})_2$ precipitates (K_{sp} , $\text{Cd}(\text{OH})_2 = 7.2 \times 10^{-15}$) (Lide, 2004) or adsorption of OH^- on the CdS-M surfaces (Torimoto et al., 1998) could effectively blocked the sites for trapping holes, leading to higher recombination of photogenerated electron-hole pairs and consequently less reaction with trapped holes (Spanhel et al., 1987). On the other hand, as the pH increased from 6.00 to 8.11, the VB edge of CdS was also decreased, resulting in the reduced photooxidation of CdS and inhibited photo-induced release of Cd^{2+} in the solution. Accordingly, the impact of initial pH on the photodissolution of CdS further supported the proposed mechanism of hole predomination.

3.4.2 DOM

The presence of DOM in natural waters (usually more than 2%) plays an important role in the fate and transformation of metal ions through direct complexation or activation, or oxidation with photogenerated ROS (Li et al., 2014; Pokhrel et al., 2014). To explore the effect of DOM on the photodissolution of CdS, experiments were conducted in the presence of 5 mg C/L HA and FA. A DOM-mediated inhibition of Cd^{2+} release can be observed in Fig. 6b, especially in the presence of FA. The inhibition effect could be ascribed to three possible mechanisms: (i) HA and FA molecules could absorb the light energy due to their photosensitivity and then reduced the receipt of irradiation by CdS (Xue et al., 2021); (ii) The complex formed by DOM and Cd could control the stability of Cd (Jia et al., 2019); (iii) HA

and FA could also compete for the photons and holes, mitigating the oxidation dissolution of CdS. However, photoactive DOM can generate ROS, which could promote the photo-oxidation of CdS. The overall effect of DOM depended on the interplay of the above mechanisms.

3.4.3 PO_4^{3-} and CO_3^{2-}

Phosphate and carbonate are well-known abundant anions in environmental media, which could affected the photo-oxidation process. Significantly inhibited release of Cd^{2+} was observed during simulated solar irradiation with the addition of 10 mg/L PO_4^{3-} or CO_3^{2-} (Fig. 6c). Especially, in the presence of CO_3^{2-} , the concentration of Cd^{2+} remained between 0.4 mg/L and 0.7 mg/L, much lower than that of the control. The main inhibition mechanism is the formation of insoluble and photostable $\text{Cd}_3(\text{PO}_4)_2$ and CdCO_3 salts (K_{sp} , $\text{Cd}_3(\text{PO}_4)_2 = 2.5 \times 10^{-33}$, and K_{sp} , $\text{Cd CO}_3 = 5.7 \times 10^{-13}$) (Jia et al., 2019), which cannot be oxidized by photogeneration holes or ROS in solution. Meanwhile, the solution pH value would increase correspondingly by the addition of PO_4^{3-} and CO_3^{2-} , generating cadmium hydroxide precipitation under alkaline conditions consequent affecting the photolysis of CdS (Luo et al., 2017; Matsumoto et al., 1996). Therefore, the passivation of the CdS surface by the cadmium salts or cadmium hydroxide precipitation leaded to the inhibited release of Cd^{2+} . Phosphate and carbonate played a negative role in photodissolution of CdS.

3.4.4 Urea

Urea is the most commonly used nitrogen fertilizer in rice production in South China. Figure 6d showed that the release rate of Cd^{2+} from CdS was markedly inhibited with the addition of 2 mmol/L urea. It has been documented that urea and N-containing compounds could be photodegraded in aqueous solutions under near-UV or visible radiation using the catalysts (such TiO_2 and so on), forming NH_4^+ and NO_3^- ions (Makino et al., 1991; Nohara et al., 1997). Furthermore, the photocomposition of urea was mainly attributed to the generated $\cdot\text{OH}$ in the system as a strong oxidant. The competition of $\cdot\text{OH}$ appears to explain the inhibition effects of urea on the photodissolution of CdS. Therefore, the release of Cd^{2+} should be slower in water with the application of urea.

3.5 Photo-mediated transformation of CdS in soil under sunlight

In order to obtain further insight into the natural photodissolution process of CdS in soil, a solar irradiation experiment of paddy topsoil sample was performed on the campus of Hunan Agricultural University from 27/08/2020-10/09/2020. The basic physical and chemical properties of the soil were introduced in Table 1.

Table 1
Physico-chemical properties of the tested soil sample

Soil type	pH	CEC (cmol(+)/kg)	Organic matter (g/kg)	Total Cd (mg/kg)	Total N (g/kg)
Paddy soil	5.98	4.5	23	0.36	0.05

3.5.1 Concentrations of soil extractable Cd and Cd²⁺ in surface water

Figure 7a shows the concentrations of DTPA-extractable Cd in the topsoil sampled on days 3, 6, 9, 12 and 15. In natural solar irradiation group, the contents of extractable Cd in soil increased markedly with time, nevertheless, there were insignificant changes of extractable Cd under the dark condition. Meanwhile, enhanced release of Cd²⁺ was observed in the surface water sample under solar condition (Fig. 7b), while the increase of Cd²⁺ under dark was slight. During the 15 days irradiation, the concentrations of DTPA-extractable Cd in soil increased from 0.81 mg/kg to 2.18 mg/kg. The above results indicate that sunlight plays an important role in the mobility and bioavailability of Cd in natural soil even in waterlogged paddy soil, which might be attributed to the photodissolution of CdS in topsoils. Furthermore, the soil pH increased and Eh decreased in both of the light and dark groups, the first day been taken as a control (Fig. S1). These changes could be related to the waterlogging treatment, and similar results have been reported in previous study (Zhang et al., 2019).

3.5.2 Distribution of Cd fractions in soils

The distributions of Cd among different fractions in the soil are presented in Fig. 8. The acid-extractable fraction (F1) Cd has the greatest mobility and bioavailability, whereas the residual fraction (F4) Cd is the most stable form and was unavailable to biota. The reducible fraction (F2) is mainly consist of Cd bound to amorphous Fe-Mn oxides and hydroxides, whereas the oxidizable fraction (F3) Cd is predominantly associated with organic matter and sulfides (Wang et al., 2021).

As shown in Fig. 8, acid-extractable Cd was the largest fraction, followed by the oxidizable, residual and reducible fraction. F1 accounted for 42.49% and 34.97% of Cd in light group and dark group soil samples, respectively, compared to 38.92% in initial soil. The proportions of the oxidizable and residual Cd fractions in three soil samples were similar. Notably, the reducible fraction in light group (20.76%) was lower than that in the initial soil (23.45%), indicating the transformation of Cd associated with organic matter and sulfides to other fractions in soils under natural sunlight. These results showed that the Cd fractions was affected by solar irradiation, as the acid-extractable Cd increased, whereas the oxidizable Cd decreased in the light group. It was suggested that natural sunlight can activate soil Cd and increase its bioavailability and environmental risk. Moreover, the waterlogging treatment can reduce the Cd mobility in soil, consistent with previous observations (Zhang et al., 2019).

4. Conclusions

CdS is a stable form of Cd in natural soil environments, which belongs to the oxidizable fraction. We herein investigated the effect of the sunlight on the Cd stability and activity. The kinetic experiments showed that simulated solar irradiation enhanced the release of Cd^{2+} from CdS-M significantly. The Cd^{2+} release rate increased from 3.98 to 6.00, while drastically decreased as the initial pH increased to 8.11. In addition, all of the co-existing DOM, PO_4^{3-} , CO_3^{2-} and urea negatively affected the photodissolution of CdS in solution. The possible mechanism of the solar-mediated Cd^{2+} release from CdS was predominated by the holes, besides, the photogenerated $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ were also possibly involved in the photo-induced reaction. The soil illumination experiment results showed that natural sunlight can activate soil Cd, lead to the increase of its bioavailability and environmental risk. These findings indicate that the solar irradiation may play an important role in shaping Cd species, to increase its mobility and bioavailability in natural soils. However, the irradiation exposure was only performed in laboratory settings under simulated conditions. The complexity of the environmental medium calls for studies under field or field-like conditions.

Declarations

Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Ethical Approval and Consent to Participate

Not applicable.

Consent for publication

Not applicable.

Competing Interests

The authors declare no competing interests.

Authors Contribution

Bihao Luo: Conceptualization, Methodology, Software, Investigation

Chenfeng Xiao: Data curation, Writing- original draft preparation.

Yuling Liu: Validation, Formal analysis, Visualization.

Li Li: Validation, Formal analysis, Visualization.

Liang Peng: Software, Writing - Review & Editing, Supervision.

Qingru Zeng: Software, Writing - Review & Editing, Supervision.

Si Luo: Funding acquisition, Writing-review & editing, Supervision.

All authors have reviewed and approved the final version for submission.

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Figures

Figure 1

XRD patterns of the MMT and CdS-M composites

Figure 2

(a-c) TEM images and EDX elemental mapping of CdS-M; (d) HR-TEM images and (e) EDX analysis results of CdS-M.

Figure 3

(a) XPS spectrum of montmorillonite loaded with cadmium sulfide; (b) XPS spectrum of S2p scan; (c) XPS spectrum of S2p scan of CdS-M.

Figure 4

(a) Cd^{2+} Concentration between sunlight and dark conditions; (b) SO_4^{2-} Concentration between sunlight and dark conditions.

Figure 5

(a) EPR detection results of hydroxyl radical under different light conditions; (b) EPR detection results of superoxide anions under different light conditions; (c) Cd²⁺ concentration in mechanism exploration experiment.

Figure 6

Effects of (a) initial pH; (b) DOM; (c) CO_3^{2-} and PO_4^{3-} ; (d) urea on release of Cd^{2+} in the solution.

Figure 7

(a) Changes of DTPA-extractable Cd in soil and (b) Cd²⁺ concentration in surface water.

Figure 8

Sequential chemical extraction of Cd in the initial topsoil and soils after 15 days treatment. (F1: acid-extractable, F2: reducible fraction, F3: oxidizable fraction, F4: residual fraction).

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