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# Release behavior of heavy metals during treatment of dredged sediment by microwave-assisted hydrogen peroxide oxidation

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## HIGHLIGHTS

- Chemical oxidation is used to remediate river sediment.
- The oxidation reduction potential of sediment slurry was greatly increased.
- The final pH of sediment slurry was markedly decreased.
- High release of metals was found during microwave-assisted $H_2O_2$ oxidation.
- Metals in residue were found higher stability and lower risk to the environment.

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## ABSTRACT

Chemical oxidation is often used to remediate river sediment contaminated with organic contaminants, which might cause the release of heavy metals. However, the mechanisms of the heavy metals release are not fully understood. In this work, dredged sediment was collected from Xiawan River in Hunan province, China, and the release behavior of heavy metals from the sediment treated with microwave-assisted hydrogen peroxide oxidation (MW-$H_2O_2$) process was investigated. The release efficiency of Cu, Cd and Zn was stable with pH varying from 0 to 4.0 and declined dramatically when the pH went higher than 4.0. $H_2O_2$ was advantageous to improve the release efficiency for Cu, Zn and Pb with $H_2O_2$ concentration from 0 M to 0.2 M, and from 0 M to 0.1 M for Cd. The release efficiency of Cu and Pb increased significantly with increasing microwave temperature from 25 °C to 85 °C and microwave time from 0 min to 6 min. After treatment by MW-$H_2O_2$ process, the metals in the sediment have higher stability and thus lower risk to the environment.



## 1. Introduction

Dredging activities are necessary for maintenance of existing navigation channels, and construction of new port and harbor facilities [1]. The sediments of harbors, lakes or rivers situated in industrial areas may be highly polluted with organic and inorganic contaminants, depending on the type of activity present in the area [2]. As these sediments are regarded as hazardous waste, it is necessary to detoxify them before they are sent to landfill or other application [3]. Different approaches can be used when dealing with contaminated sediments depending on the types of hazardous substances and characteristics of sediments [4]. Ex situ remediation technologies for dredged sediment, aiming at heavy metals, mainly include washing, electrochemical remediation, flotation and immobilization [5]. For organic contaminants, such as total polycyclic aromatic hydrocarbons (PAHs), chemical oxidation using ozone, hydrogen peroxide ($H_2O_2$), Fenton's reagent, etc. is applied to destroy organic pollutants [4].

Oxidation processes have been widely studied and applied to degrade refractory organic compounds, and the mechanisms of oxidation processes are well understood [6–17]. However, chemical oxidation may cause the release of heavy metals when it is used to remediate sediment contaminated with organic contaminants.

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There is little information on the effectiveness of oxidation process for heavy metals release from dredged sediment.

A microwave-assisted hydrogen peroxide (MW-$H_2O_2$) oxidation process, known as an advanced oxidation process (AOP), is an efficient and promising oxidation technology for the treatment of organic contaminants [8–10,12,13,15–20]. MW-$H_2O_2$ generates active species of hydroxyl radicals ($HO^{\cdot}$) with a redox potential of +2.8 eV that can non-selectively degrade most organic compounds [11,15]. Due to the unique heating mechanism, microwave has been widely applied to accelerating the heating process, enhancing chemical catalytic degradation activity [21]. As a supplement to heavy metals extraction method, microwave can efficiently cause the release of heavy metals from sewage sludge, fly ash and industrial dust, and meanwhile, shorten extraction time and reduce agent concentrations [3,22,23]. However, to the best of our knowledge, research on the release behavior of heavy metals in dredged sediment by MW-$H_2O_2$ process has not been reported.

The heavy metals in sediment exist in various chemical species and generally exhibit different physical and chemical behaviors in terms of chemical interaction, mobility, bio-availability, and potential toxicity [24]. The total content of heavy metals in sediment provides, in most cases, limited information on the mobility and bio-availability of heavy metals and could mislead the result of risk assessment [25]. For an accurate assessment on the risk of MW-$H_2O_2$ technique for dredged sediment treatment, the study of chemical speciation of the heavy metals is of great importance. The objective of this study is to explore the release behavior of heavy metals in dredged sediment during the process of MW-$H_2O_2$, and the effect of such treatment on the chemical speciation of the heavy metals.

## 2. Materials and methods

### 2.1. Sample collection, preparation and characterization

Sediment samples were collected from Xiawan River in Hunan province, China. All sediment samples with high moisture content were sieved through a 2 mm nylon sieve to remove coarse debris. The sediment was then dried at 105 °C for 24 h. The dried sediment was ground and sieved through a 150 μm sieve. Sample was stored at 4 °C prior to use. All chemicals used are of analytical reagent grade. Water used throughout the experiment was ultrapure water (18.25 MΩ cm). All glassware and plastic containers were washed with 15% (v/v) nitric acid solution and rinsed thoroughly with ultrapure water [26].

The pH of sediment was obtained by mixing the sediment with ultrapure water at the ratio of 1:2.5 and measuring the pH of the aqueous solution using a pH meter (PHSJ-5, China) [27]. The loss on ignition was measured by gravimetric method. Briefly, a portion of the sample was ignited by muffle for 4 h at 550 °C. The mass loss during bakeout and ignition was determined as indirect index of organic matter content [27]. Total carbon (TC) was measured using an elemental analyzer (EA3000, Euro Vector, Italy) [26].

For the analysis of total heavy metal concentrations, 0.1 g sediment sample was placed in Teflon tube and digested with $HNO_3$, HF and $HClO_4$. Then the solutions were diluted with 2% (v/v) nitric acid solution to 50 ml, and analyzed with an atomic absorption spectrophotometer (AAnalyst700, Perkin–Elmer, US) [27,28].

The selected properties of sediment and the concentrations of metals in raw sediment sample are listed in Table 1. For comparative purposes, the Control Standard for Agricultural Use (MEP of China, GB15618-1995) of China is also shown in Table 1. It can be seen that the total concentrations of heavy metals in sediment of Xiawan River were much higher than the limits specified in the standards.

**Table 1**
Select properties, total concentrations of metals in raw sediment sample and permitted values in discharge standards. (mean ± standard deviation, $n = 3$).

| Metals | (mg/kg) | Maximum permitted values | | |
|---|---|---|---|---|
| | | pH < 6.5 | pH 6.5 ~ 7.5 | pH > 7.5 |
| Cu | 209.5 ± 7.3 | 50 | 100 | 100 |
| Cd | 318.0 ± 11.4 | 0.30 | 0.30 | 0.60 |
| Zn | 10800 ± 163 | 200 | 250 | 300 |
| Pb | 602.5 ± 18.7 | 250 | 300 | 350 |
| Fe | 46400 ± 274 | – | – | – |
| pH | 7.79 ± 0.05 | – | – | – |
| Total carbon | 10.84 ± 0.12% | – | – | – |
| Loss on ignition | 10.56 ± 0.14% | – | – | – |

### 2.2. Experimental setup

All experiments were batch type and were performed using an Open-ended Microwave Chemical Reactor (MCR-3, China) which had a Pt-temperature transmitter (Fig. 1). The frequency of microwave irradiation was 2450 MHz ± 50 Hz and the maximum output power of microwave irradiation was 800 W. The reaction vessel was a 150 ml two-neck round-bottom flask (RF20, Chem Focus, US). The Pt-temperature transmitter was utilized to detect the temperature of sediment slurry. During the rising phase of temperature, the built-in microcomputer would adjust the power output of the reactor to have stable increase of temperature. When the temperature of sediment slurry reached to the pre-set reaction temperature, the built-in microcomputer would adjust the power output of the reactor so that the temperature of sediment slurry could be maintained. In this way the reaction temperature and time in the reactor could be controlled. Meanwhile, the sediment slurry was stirred by a magnetic stirrer at 250 rpm. A glass tube was used to connect a water-cool condenser on top of the reaction vessel so that water vapor loss in the reactor could be prevented.

### 2.3. MW-$H_2O_2$ oxidation process

MW-$H_2O_2$ oxidation experiments were carried out by using a series of 150 ml round-bottom flasks which contained 5.0 ± 0.0005 g sediment and 50 ml ultrapure water. 65–68% (v/v)

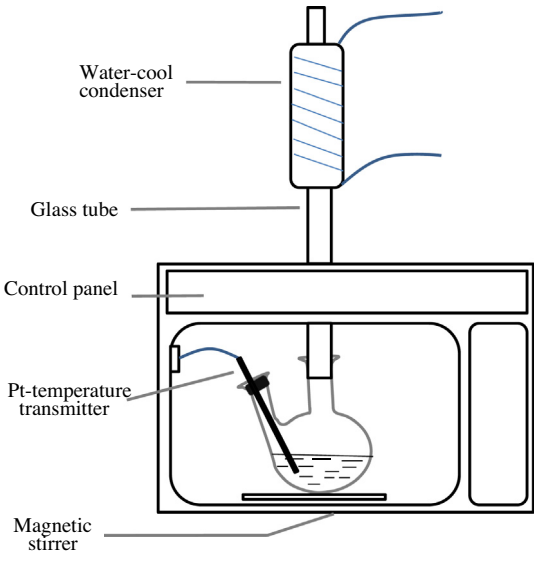


**Fig. 1.** Schematic diagram of reaction in Microwave Reactor.