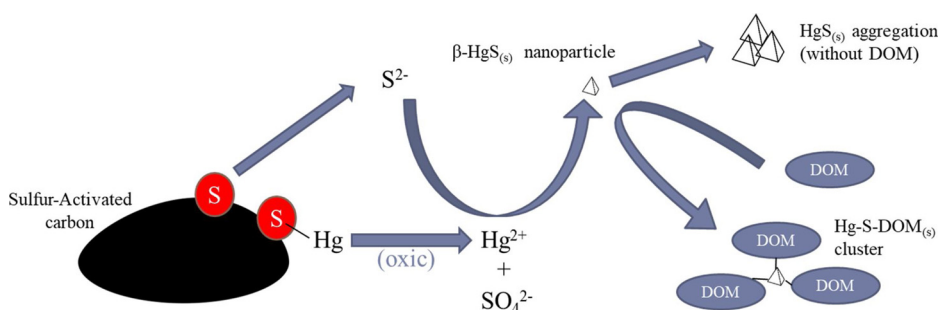# Using raw and sulfur-impregnated activated carbon as active cap for leaching inhibition of mercury and methylmercury from contaminated sediment

Yu Ting, Chi Chen, Boon-Lek Ch'ng, Ying-Lin Wang, Hsing-Cheng Hsi*

*Graduate Institute of Environmental Engineering, National Taiwan University, No. 71, Chou-Shan Rd., Taipei 106, Taiwan*

GRAPHICAL ABSTRACT

ABSTRACT

Sulfur-impregnated activated carbon (SAC) has been reported with a high affinity to Hg, but little research has done on understanding its potential as active cap for inhibition of Hg release from contaminated sediments. In this study, high-quality coconut-shell activated carbon (AC) and its derived SAC were examined and shown to have great affinity to both aqueous $Hg^{2+}$ and methylmercury (MeHg). SAC had greater partitioning coefficients for $Hg^{2+}$ ($K_D = 9.42 \times 10^4$) and MeHg ($K_D = 7.661 \times 10^5$) as compared to those for AC ($K_D = 3.69 \times 10^4$ and $2.25 \times 10^5$, respectively). However, AC appeared to have greater inhibition in total Hg (THg) leaching from sediment (14.2–235.8 mg-Hg/kg-sediment) to porewater phase as compared to SAC. 3 wt% AC amendment in sediment (235.8 mg/kg Hg) was the optimum dosage causing the porewater THg reduction by 99.88%. Moreover, significant inhibition in both THg and MeHg releases within the 83-d trial microcosm tests was demonstrated with active caps composed of SAC + bentonite, SAC + clean sediment, and AC + bentonite. While both AC and SAC successfully reduce the porewater Hg in sediment environment, the smaller inhibition in Hg release by SAC as compared to that by raw AC may suggest that possibly formed HgS nanoparticles could be released into the porewater that elevates the porewater Hg concentration.

## 1. Introduction

With high neurotoxicity, volatility, and bioaccumulation ability, mercury (Hg) has been considered as one of the most toxic heavy metal in the environment. Hg in general exists in the form of divalent Hg (i.e., $Hg^{2+}$) in the aqueous phase and may transform to methylmercury (MeHg), which is one of the most toxic Hg forms via biomethylation under an anoxic sediment environment [1]. With high affinity in

organism tissue [2], MeHg has high tendency to accumulate in biota and biomagnify through food chains, thus causing adverse effects to biota or human. Although ex-situ strategies have been proven promising in removing Hg out of sediment [3,4], problems such as unfeasible cost [5], resuspension of contaminants [6,7], and production of contaminated sediment residues [6,7] may discourage their application. Therefore, development of novel and feasible techniques in remediating Hg-contaminated sediment is highly needed.

Active capping is a newly emerged in-situ remediation concept that can be applied to remediate Hg-contaminated sediment. Active capping involves the use of active materials to sequestrate contaminant in sediment, therefore achieving remediation goal of reducing uptake of contaminants by biota and subsequently by human. It has been shown that active capping using activated carbon (AC) could be a promising treatment in reducing organic contaminant bioavailability in sediment, and has been demonstrated either in full-scale studies [8–13] or long-term prediction models [14,15]. As for Hg-contaminated sediment, however, fewer studies have been conducted [13,16,17], the reason may be because that AC generally has higher affinity to organic pollutant (log $K_D \approx 7.0$–10.0) than Hg (log $K_D \approx 3.0$–7.0) [18]. Therefore, seeking effective active materials with higher affinity to Hg is an important step to adopt the active capping technique to Hg-contaminated sediment.

Sulfur-impregnated activated carbon (SAC) has been verified to enhance Hg adsorption capacity than its raw AC precursor in aqueous adsorption tests [19–21]. The results were reasonable considering its reaction thermodynamics, for which Hg has high affinity to sulfur (i.e., log K $\approx$ 52.7–53.3) [22], as compared to that for Hg to organic matter (i.e., log K = 22–28) [2]. Wang et al. [19] demonstrated that an increase in Hg adsorption capacity of coconut AC from 150 to 820 mg/g by sulfurization with sulfur powder (C/S ratio: 1:2) was shown. Furthermore, Li et al. [20] increased Hg adsorption capacity of coke from 315.8 to 694.9 mg/g by impregnated the coke with sulfuric acid (80 °C, 13 h).

Based on the previous research, we expected that SAC may have strong potential as active capping material to remediate Hg contaminated sediment. However, studies on using SAC as the active capping material for inhibiting the release of Hg and MeHg from sediment environment are not done and presented. In this research, aqueous adsorption tests, sediment competition adsorption tests, and microcosm experiments were carried out to verify the Hg adsorption abilities of SAC and its raw AC counterpart. The feasibility of using SAC as the active capping material for inhibiting the release of Hg and MeHg from sediment environment was further evaluated. The results obtained in this study are practically critical, because a highly Hg-contaminated site in Southern Taiwan is currently remediated, for which active capping has been considered as one of the feasible approaches for limiting the accessibility of biota to the Hg present in the contaminated seawater ponds.

## 2. Materials and methods

### 2.1. Materials

The actual sediment used in the study, designated as TY03, was sampled from Taoyuan irrigation channel, Taiwan, acquired according to Taiwan Environmental Protection Administration (TEPA) standard method (NIEA S104.32B) [23]. Sediment within 0–15 cm depth was collected using a stainless crab bucket. Sampled sediment was immediately measured for oxidation reduction potential (ORP) and then sealed in bags and transported back to laboratory within 4 h. Wet sediment was air-dried in laboratory hood, picked out branches and benthic biota, then ground and sieved to pass through 20 mesh sieve. Dry sediment was stored in room temperature without sunlight. Commercial AC was obtained as raw AC material (10–18 mesh). Received AC was first rinsed with DI water for several times and dried in 60 °C for

24 h, then stored in a drying kettle. SAC was prepared by mixing 20 g of AC and 4 g of sulfur powder in a heating boat, heated to 400 °C for 1 h and maintained for 2 h in a tubular furnace (Lindberg/Blue-M model STF55346C); 50 mL/min of nitrogen gas was constantly flowed through the furnace tube to maintain an oxygen-free environment. The prepared SAC was then sieved to 10–18 mesh and stored under the same condition as that for AC.

### 2.2. Physical and chemical analysis of materials

Sediment pH was measured by pH meter (SunTex SP-2300) based on TEPA standard method (NIEA S410.62 C) [24]; readings of pH value were recorded after adding 20 g of dried sediment and 20 mL DI water in a 50 mL beaker and set for 1 h. The texture of sediment was measured using a bouyoucos hydrometer [25]. The cation exchangeable capacity (CEC) of sediment was measured by available K, Na, Ca, and Mg, which were extracted by leaching dry sediment through 1 N $NH_4OAc$ solution, based on TEPA standard method (NIEA S201.61C) [26]. Other elements including Fe, Mn, Al, K, Na, Ca, and Mg were extracted by citrate bicarbonate buffer solution [27] and then measured by ICP-OES (Agilent 710 Series, Agilent Technology). Sediment organic content was measured through Walkley-Black wet oxidation [28]. The concentrations of $NH_4^+$-N and $NO_3^-$-N were measured by steam distillation using MgO and the Devarda's alloy [29].

The specific surface area and pore size distribution of the adsorbents (AC and SAC) were measured using a physisorption analyzer (ASAP 2020 M, Micromeritics Inc.). Nitrogen adsorption-desorption isotherm at 77 K was obtained using a Micromeritics ASAP 2020; the Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area at relative pressure ($P/P_0$) within 0.05–0.3 based on ASTM D4820-96a. Micropore size distribution was determined by the quenched solid density functional theory (QSDFT) model. The surface morphology of adsorbent was measured by a scanning electron microscope (SEM, JSM-7600F, JOEL). X-ray photoelectron spectra (XPS) were recorded using a ULVAC PHI-5000 VersaProbe spectrometer with monochromatic Al Kα radiation. Element analysis was carried out by an elemental analyzer (Flash 2000, Thermo Scientific™) to measure elements including C, H, O, N, and S in the adsorbents.

### 2.3. Aqueous mercury adsorption experiment

The aqueous adsorption experiment was performed resembling to Wang et al. [19]. In brief, analysis-grade AAS Hg standard (1000 mg/L Hg, J.T.Baker) and MeHg standard (1 mg/L, BrooksRand) were used as Hg stocks and diluted to prepare $Hg^{2+}$ and MeHg solution, respectively. Hg solution was adjusted to pH = 7.0 $\pm$ 0.1 using NaOH (0.01–0.1 M) and HCl (0.01–0.1 M) solution. Adsorbent (AC or SAC) of 50 mg and 50 mL Hg solution were added into clean 100 mL HDPE bottles. The HDPE bottles was then placed in a water bath shaker (30 °C, 125 rpm). After the adsorption tests, water samples were collected for analysis of THg and MeHg.

### 2.4. Sediment competition adsorption experiment

Hg-containing sediment in this study was prepared by spiking Hg solution in the sampled sediment. Hg stock solution (5000 mg-Hg/L) was prepared by dissolving $HgCl_2$ in DI water with 0.2% HCl. The spiking procedure was carried out by adding 200 g of dried sediment into a clean 400 mL glass jar; Hg stock was diluted with DI water and added to the glass jar to an anticipated Hg sediment concentration of 15 − 250 mg/kg. The glass jar was then filled with DI water, capped with stainless steels caps and sealed with parafilm. Spiked sediment jars were incubated for 117 d. After incubation, overlying water was removed, and sediment was freeze-dried and stored in a 4 °C refrigerator.

Sediment competition adsorption experiments were carried out by adding 5 g of dried Hg sediment, 50 mg of adsorbent, and 50 mL of DI