

# Toward Rapid Detection of Trace Lead and Cadmium by Anodic Stripping Voltammetry in Complex Wastewater Streams

Shengcun Ma,<sup>#</sup> Guo Zhao,<sup>#</sup> Mona Elsayed,<sup>#</sup> Mohammed Sedki, Xingyu Chen, Dong Wu, Ximin He, Ashok Mulchandani,<sup>\*</sup> and David Jassby<sup>\*</sup>



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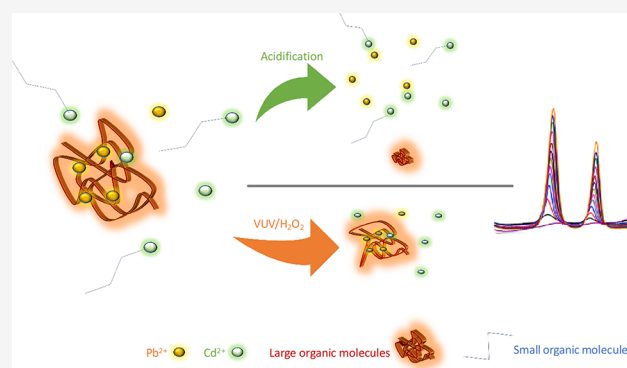
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**ABSTRACT:** Heavy metals (HMs), such as lead (Pb) and cadmium (Cd), in municipal wastewater (MWW) limit its use as an alternative water resource. Therefore, monitoring HM concentrations in MWW is critical to evaluating potential reuse applications. However, current metal detection methods rely on grab-sampling and analysis on complicated laboratory-based analytical chemistry instruments, limiting sampling frequency. Anodic stripping voltammetry (ASV) is a promising measurement alternative. However, HMs in MWW are found as complexes and/or sorbed onto particles, and are thus not detectable by ASV. In this study, we develop a processing method that enables the detection of HMs using ASV. In this method, HM-containing MWW is pretreated by either vacuum ultraviolet (VUV)/H<sub>2</sub>O<sub>2</sub> (Cd) or a strong acid (Pb), which releases the bound HMs. HMs are then accurately detected and quantified using ASV by utilizing a bismuth subcarbonate/reduced graphene oxide nanocomposite incorporated in a Nafion matrix electrode. The resulting sensing process is able to detect trace concentrations of Cd and Pb in both synthetic and real MWW samples. Detection results were benchmarked against state-of-the-art metal detection methods, and were found to be highly accurate (>88%). This pretreatment and detection method enables utilities and end-users to frequently monitor HM concentrations in complex streams.

**KEYWORDS:** heavy metal sensing, anodic stripping voltammetry, wastewater reuse, pretreatment



## 1. INTRODUCTION

Exposure to heavy metals (HMs) is known to lead to negative impacts on humans and the environment.<sup>1</sup> As a result, various advanced measurement techniques have been developed to measure HMs concentrations, including inductively coupled plasma-mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS).<sup>2</sup> However, these advanced methods rely on expensive instrumentation and highly trained technicians. Because of this, the measurement of HMs is a costly and infrequent process.<sup>2</sup> However, the increasing interest in the reuse of municipal wastewater (MWW), which can be rich in HMs, is raising the risk of exposure to HMs, which is driving the interest in developing robust, high-frequency, and low-cost HM sensing technologies.

Anodic stripping voltammetry (ASV) is an attractive sensing technique that can measure a wide range of metal contaminants at ppb levels.<sup>3</sup> Importantly, ASV can be miniaturized and integrated into a lab-on-a-chip device that can conduct frequent metal measurements in a highly automated manner. While ASV is a highly sensitive detection method and has been successfully demonstrated in simple water matrixes (e.g., synthetic tap water, deionized water, and

refined sugar solution<sup>4</sup>), it can only detect metals in their ionic form. Some studies have taken advantage of this limitation to differentiate between free metals, which could be detected via ASV, and nonfree metals, which are not detected.<sup>5</sup> Unfortunately, many HMs are found as complexed species (e.g., with natural organic matter (NOM), carbonates,<sup>6</sup> and oxides) or sorbed onto particulate matter in wastewater,<sup>7</sup> making them invisible to ASV.<sup>8</sup> In addition, certain aqueous species, such as NOM, can react with and/or damage the ASV electrodes.<sup>8</sup> Furthermore, some electrochemically active substances (e.g., oxygen and nontarget metals) could screen or overlap target signals, and thus interfere with ASV detection.<sup>8</sup> To detect and quantify the total metal concentrations, current state-of-the-art detection methods, such as ICP-MS, utilize extreme conditions (highly acidic conditions

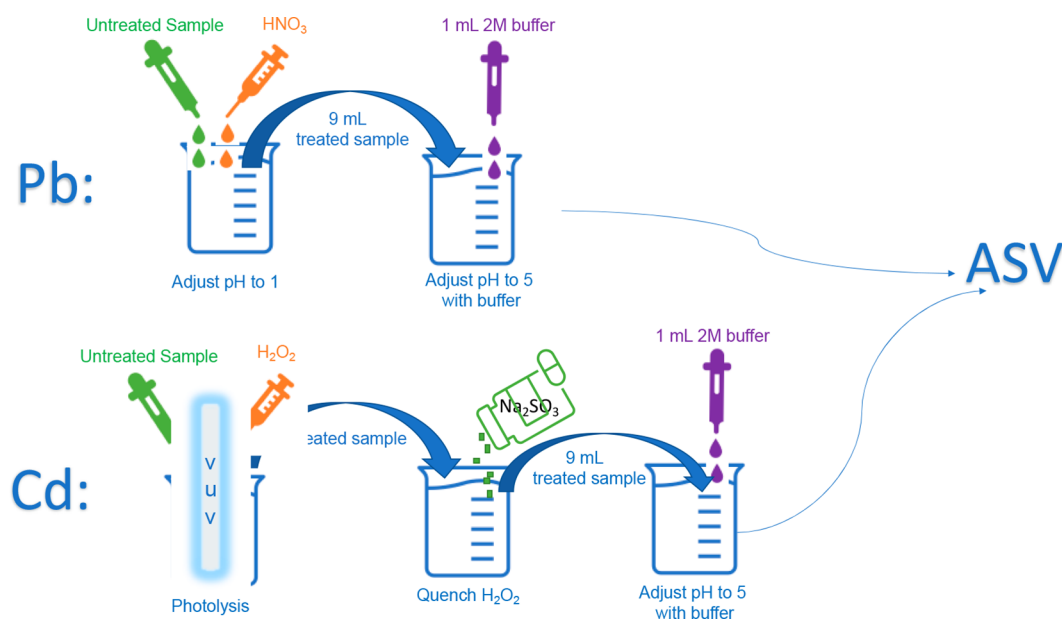
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**Figure 1.** Sample processing steps for Pb and Cd detection.

followed by plasma treatment) to convert metals to their atomic form.<sup>9</sup> In a similar manner, enabling ASV to detect total metal concentrations in complex aqueous streams requires the transformation of the target metal to its ionic form. However, the extreme conditions used in ICP-MS make such pretreatment processes difficult to implement in a cost-effective manner. Therefore, the development of simple pretreatment steps that are specifically targeted toward particular metal species would enable the use of ASV as an alternative sensing platform for the detection of trace HMs in complex aqueous streams. Ultraviolet (UV) based processes have been used to photolyze cadmium-containing organic molecules (e.g., cadmium dimethyl<sup>10</sup>) or to release metals in MWW for ASV detection.<sup>11,12</sup> However, long processing times and high temperatures make these approaches difficult to implement for routine Pb and Cd detection. Importantly, previous ASV measurements in MWW were not validated by ICP-MS or AAS measurements.<sup>12,13</sup>

Recently, we reported a bismuth subcarbonate ((BiO)<sub>2</sub>CO<sub>3</sub>)/reduced graphene oxide (rGO) nanocomposite incorporated in a Nafion matrix ((BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion) modified glassy carbon electrode (GCE) for ASV detection of trace lead (Pb) and cadmium (Cd) in simulated river water.<sup>13</sup> In this study, we applied the above electrode to detect Pb and Cd concentrations in synthetic and real MWW samples. When samples were pretreated using a strong acid or vacuum UV (VUV)/H<sub>2</sub>O<sub>2</sub>, the ASV method was able to detect trace concentrations of these HMs, with results matching those obtained using ICP-MS. The combination of appropriate pretreatment and excellent electrode sensitivity and selectivity paves the way toward the development of cost-effective and automated sensor packages capable of generating frequent and automated results (once per hour).

## 2. MATERIALS AND METHODS

### 2.1. Chemicals and Instruments.

Unless indicated, all chemicals used in this research were ACS grade. Lead nitrate, cadmium nitrate, sodium acetate, ammonium acetate, monopotassium phosphate, sodium bicarbonate, manganese sulfate,

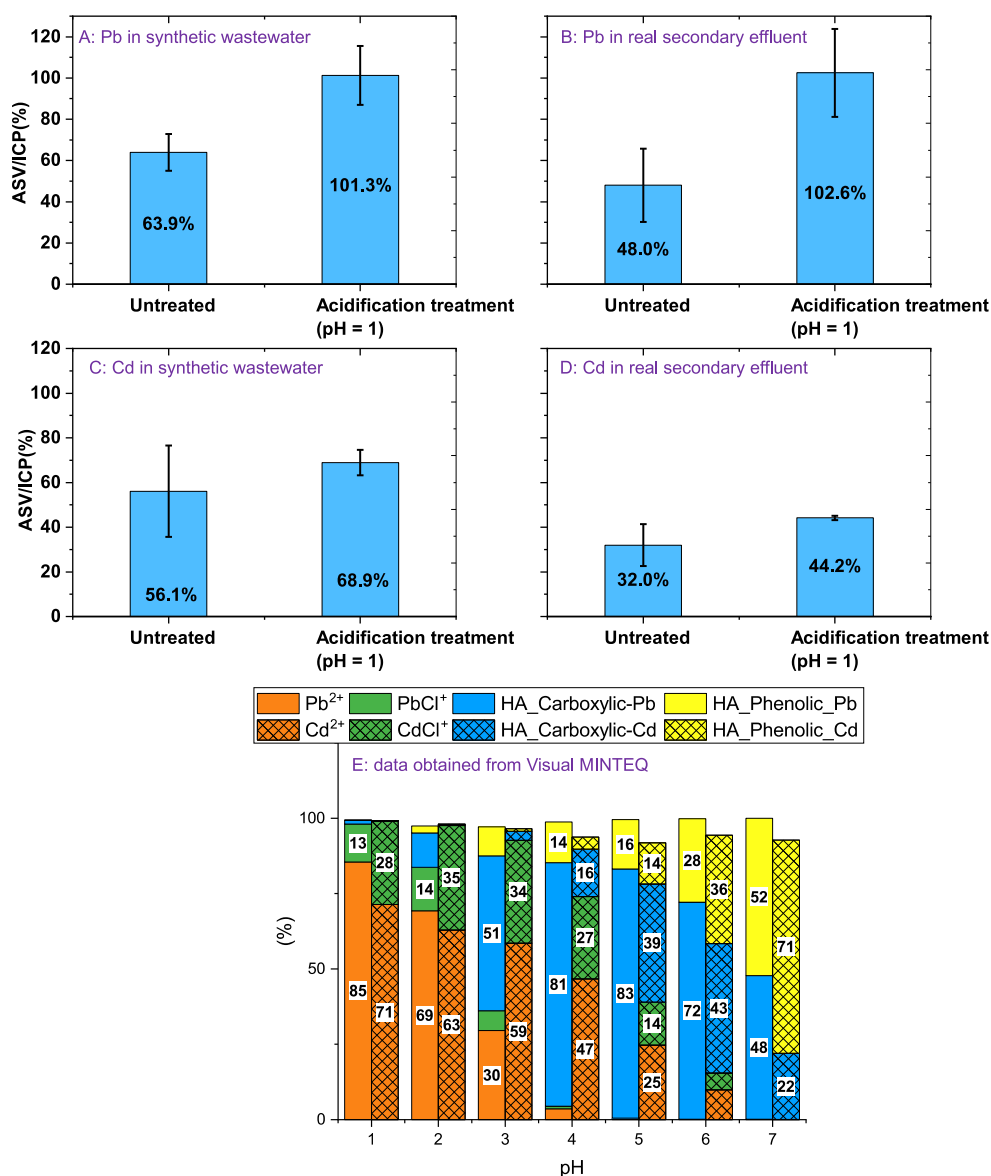
manganese chloride, zinc chloride, zinc sulfate, magnesium sulfate, hydrogen peroxide (30%, Optima grade), nitric acid (67% ~ 69%, Optima grade), graphite powder, bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O), *N,N*-dimethylformamide (DMF), ethylene glycol, sodium acetate trihydrate, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%), potassium permanganates (KMnO<sub>4</sub>), hydrochloric acid (HCl, 37%), and calcium chloride were ordered from Fisher. Nafion, Pb(NO<sub>3</sub>)<sub>2</sub> and Cd(NO<sub>3</sub>)<sub>2</sub> standard solutions (1 mg/mL), and humic acid sodium salt (Technical grade) were purchased from Sigma-Aldrich (St. Louis, MO). Dissolved organic carbon (DOC) was measured with a total organic carbon analyzer (Shimadzu TOC-LCSN) after samples were filtered with 0.45 μm filters.

### 2.2. SWW Composition and Sources of Real MWW.

Synthetic MWW, a modification of a recipe used by other studies,<sup>7,14</sup> was spiked with Cd and Pb. In short, the synthetic MWW contained (in 1 L of DI water): CH<sub>3</sub>COONa, 256.41 mg; CH<sub>3</sub>COONH<sub>4</sub>, 240.88 mg; KH<sub>2</sub>PO<sub>4</sub>, 43.94 mg; NaHCO<sub>3</sub>, 125 mg; FeCl<sub>2</sub>, 0.375 mg; MnSO<sub>4</sub>, 0.038 mg; ZnSO<sub>4</sub>, 0.035 mg; NaCl, 585 mg; humic acid sodium salt, 50 mg; MgSO<sub>4</sub>, 25 mg; CaCl<sub>2</sub>, 10 mg. Real secondary effluent (i.e., from an activated sludge process) and real tertiary effluent (i.e., chemically enhanced filtration, which consists of coagulant addition (FeCl<sub>3</sub>), and rapid sand filtration) were obtained from the West Basin Municipal Water District in Southern California. Neither Pb or Cd were detectable in the real wastewater samples using ICP-MS, and as a result, we spiked Pb and Cd into these samples. These real wastewater samples were filtered with filter papers (Whatman, grade 4) before being spiked with Cd and Pb. After the addition of metals, both synthetic wastewater samples and real wastewater samples were stirred for 24 h at ambient temperature (23 °C).

### 2.3. Fabrication of Electrodes and ASV Detection/Measurement of Cd and Pb.

The ((BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion)-modified GCE was fabricated according to our previously reported protocol.<sup>13</sup> In brief, a GCE was polished on a MicroCloth pad using alumina powder (0.05 μm), followed by sequential washing in nitric acid (50% w/v), ethanol, and deionized water. Eight microliters of a suspension



**Figure 2.** Detection of trace Pb (A, B) and Cd (C, D) by ASV and ICP-MS in synthetic wastewater (A, C) and real secondary treatment wastewater (B, D) before and after acidification; E shows the influence of pH on the metal speciation distribution in synthetic wastewater predicted by Visual MINTEQ 3.1; Fractions lower than 3% were ignored and fractions lower than 10% were not labeled with an exact number in this figure. The NICA-Donnan model was chosen to calculate the complex between metal and humic substances.

consisting of 4 mL of *N,N*-dimethylformamide (DMF), 800  $\mu\text{L}$  of 0.5% (w/v) of Nafion in ethanol, and 1 mg of  $(\text{BiO})_2\text{CO}_3$ -rGO (synthesized as reported previously)<sup>13</sup> was deposited and dried at 60 °C in an oven.

A complete analysis cycle consisted of (1) holding the WE at 0.3 V (vs Ag/AgCl) for 120 s to remove all metals from the surface, which is achieved by keeping the voltage constant using a CHI 760C electrochemical station, (2) applying a potential of  $-1.2$  V (vs Ag/AgCl) for 2 min to reduce Pb and Cd cations to zerovalent under stirred condition, followed by equilibrating without stirring for 10 s, and (3) sweeping the potential from  $-1.1$  to  $-0.3$  V at 5 mV potential step, 25 mV amplitude, and 25 Hz frequency.

The procedure of measuring the concentrations of Pb and Cd in MWWs consisted of two steps: (1) Generating plots of peak anodic stripping current as a function of known concentration of Pb and Cd in 0.2 M, pH 5, acetate buffer<sup>13</sup> and fitting a linear relationship between anodic current and

metal ion concentration. (2) Performing ASV of MWW samples and estimating Pb and Cd concentrations. This process is started by adding 1 mL of 2 M, pH 5, acetate buffer to 9 mL of MWW and performing ASV; each measurement was repeated three times. This was followed by estimating the concentrations using the linear correlations from the calibration plots generated in step 1.

Measurement/detection of Pb and Cd by ASV was performed according to the protocol reported previously,<sup>13</sup> with the current peak height used to evaluate HM concentrations. In short, measurements were performed in a 20 mL, three-electrode cell consisting of a  $(\text{BiO})_2\text{CO}_3$ -rGO-Nafion)-modified GCE working electrode (WE), Ag/AgCl (3 M KCl) reference electrode, and Pt wire counter electrode using a CHI 760C (CH Instrument, Austin, TX, USA) electrochemical station. Each newly fabricated/calibrated electrode was used for analyses of up to 10 MWW samples.

All measurements were at least duplicated. A sample of typical ASV raw data are shown in Figure S1.

**2.4. Sample Processing Methods.** A brief summary of the sample processing steps is shown Figure 1, and detailed protocol was provided in Text S1. For acidification, 50 mL of sample was added to a beaker and 0.3 mL of nitric acid (67% ~ 69%, Optima grade) was added to adjust the pH to 1. HNO<sub>3</sub> was chosen because HNO<sub>3</sub> is commonly used for ICP-MS sample preparations. A customized UV reactor made of polyvinyl chloride (PVC) was used to expose 100 mL of sample to VUV light (Figure S2A). To generate hydroxyl radicals, 0.33 mL of 30% H<sub>2</sub>O<sub>2</sub> was added to the reactor. Samples containing high-concentration metals (i.e., 100 ppb Cd and 1058 ppb Pb) were photolyzed for 30 min, while those containing low-concentration metals (i.e., 3.5 ppb Cd and 12.5 ppb Pb) were photolyzed for 1 h. After photolysis, Na<sub>2</sub>SO<sub>3</sub> was added to quench the remaining H<sub>2</sub>O<sub>2</sub> in the reactor. A 10 W VUV lamp (Sterilight S212ROL Lamp) with an emission peak of 185 nm, was purchased from HomePlus Products Inc. (this product is advertised as a total organic carbon (TOC) removal and ozone generation lamp, and is used in under-the-sink water treatment systems). The spectrum of this lamp (Figure S2B) was measured by a spectrometer (USB2000+UV-vis-FS, Ocean Insight, FL, USA), which shows that this lamp also emits at 254, 310, and 365 nm (it is noted that this spectrometer could not measure the spectrum at 185 nm). Although these pretreatment methods may introduce some impurities, (e.g., anions released from H<sub>2</sub>O<sub>2</sub> reacting with organic matter),<sup>12</sup> our results show that these impurities had little impact on ASV detections (shown below). Samples for ICP-MS measurements were treated with 5% HNO<sub>3</sub> solution.

**2.5. Model Verification.** Visual MINTEQ 3.1 and the NICA-Donnan model were used to calculate the theoretical speciation of HMs in synthetic wastewater.

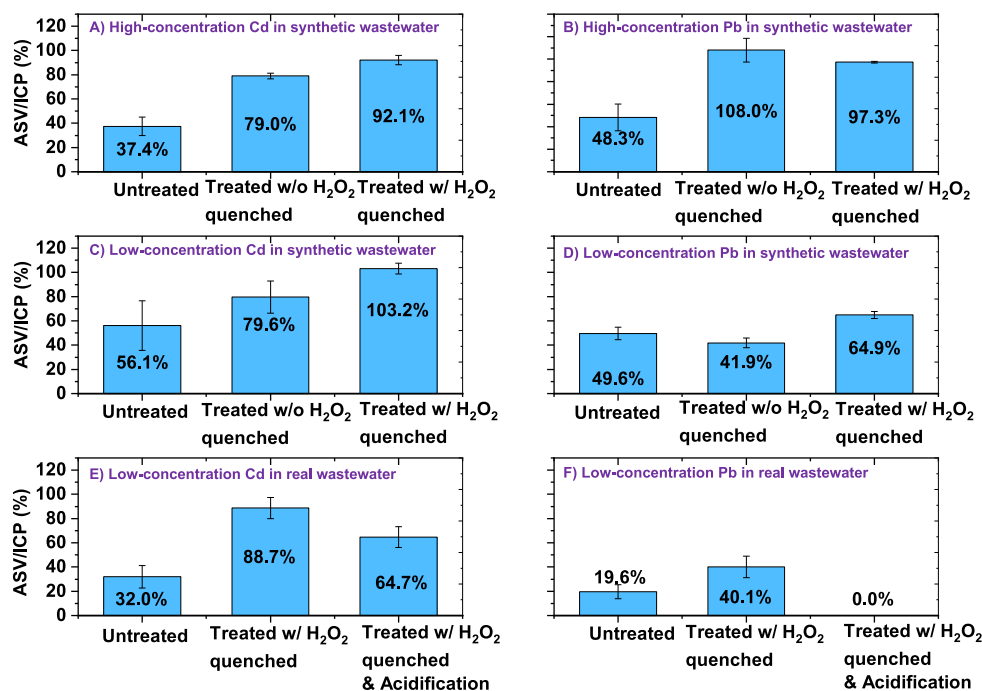
### 3. RESULTS AND DISCUSSION

**3.1. Analytical Characterization of (BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion/GCE for Pb and Cd Detection in Buffer.** In a recent publication, we demonstrated ASV detection of Pb and Cd using the (BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion/GCE WE with a limit of quantitation of 0.694 ppb for Pb(II) and 0.544 ppb for Cd(II) and a limit of detection (LOD) of 0.208 ppb Pb(II) and 0.164 ppb Cd(II).<sup>13</sup> This LOD is comparable to previous research (i.e., 0.25 ppb Pb(II) and 0.4 ppb Cd(II)).<sup>15</sup> The details of the calculations are listed in the Supporting Information (section Text S2). Figure S4 presents calibration curves for the detection of Pb and Cd in 0.2 M, pH 5 acetate buffer generated prior to the analyses of the MWW samples to estimate their concentrations in the MWW samples. It is worth noting that all processed samples were ultimately measured by ASV at a pH of 5 (Figure 1). As a result, we used calibration curves at pH 5 (in acetate buffer) to calculate metal concentrations. The sensitivity (slope of the calibration plot) for metals corresponded well with the reported values. There was no interference from 10-ppm ions (Na<sup>+</sup>, K<sup>+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>)<sup>13</sup> (Table S1). All ions listed in Table S1 were spiked in DI water. It is noted that although Cu<sup>2+</sup> may interfere with ASV measurements of Pb, the interferences of Cu<sup>2+</sup> can be easily addressed by selectively precipitating Cu<sup>2+</sup> with ferrocyanides.<sup>16–18</sup> Although 10-ppm Zn(II) resulted in ~17% and ~41% current increase for Cd and Pb,<sup>13</sup> respectively (Table S1), it is reasonable to assume that Zn(II) would not significantly influence the detections of

Pb and Cd in MWW because the concentrations of Zn(II) MWW are generally in the range of 10–650 ppb.<sup>19</sup> Specifically, in our experiments, the concentration of Zn(II) measured in our real wastewater samples was  $8.7 \pm 2.1$  ppb, which was measured by ICP-MS, and did not influence the detection of Pb or Cd, as shown in section 3.2.1 and section 3.2.2. Importantly, the (BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion/GCE electrode was stable/reusable for at least 10 cycles,<sup>13</sup> which is a desired property for sensing applications in the field and real time monitoring (Figure S3).

**3.2. Performances of (BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion/GCE with Coupled Pretreatment Methods in Synthetic and Real MWW Samples.** ASV with (BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion/GCE electrodes failed to detect Pb and Cd when they were spiked into synthetic and real MWW samples, while ICP-MS was able to accurately determine their concentrations (Figure 2 and Figure S5). To enable the detection of HMs using ASV, we investigated the impact of two pretreatment methods: acidification and VUV/H<sub>2</sub>O<sub>2</sub>.

**3.2.1. Acidification Coupled with (BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion/GCE to Detect Low-Concentration Metals.** Figure 2 and Figure S5 show the impact of acidification (pH 1) on the detection of low-concentration Cd (i.e., 3.5 ppb) and Pb (i.e., 12.5 ppb) by ASV (the results in Figure 2 are normalized to the concentrations measured using ICP-MS, while Figure S5 shows the absolute value measured by ASV and ICP-MS). While ASV was able to detect only 64% and 48% of Pb in synthetic and real secondary treatment wastewater, respectively, in untreated samples, acidification dramatically enhanced ASV detection of Pb, enabling ASV to achieve similar detection results to ICP-MS in both synthetic raw wastewater ( $101\% \pm 14\%$  in Figure 2A and Figure SSA) and real secondary treatment wastewater ( $102\% \pm 21\%$  in Figure 2B and Figure SSB); these results are largely in-line with data calculated by Visual MINTEQ, which predicted that 85% of Pb should be present in its ionic form at pH = 1 (Figure 2E). It is worth noting that despite its success at pH = 1, this model severely underestimated free Pb (i.e., ASV detectable Pb) at pH = 7. This underestimation of free metals was also reported in another study.<sup>20</sup> Previous studies have reported that acidic conditions can facilitate metal release from humic acid as well.<sup>21</sup> However, the minimum pH set by other studies are generally larger than 2, which could not completely release metals.<sup>21–24</sup> The improved ASV detection of Pb is attributed to the destruction of the Pb-NOM complex, due to protonation of carboxylic binding sites on NOM. In the synthetic wastewater, the main NOM was humic acid, which precipitated significantly (based on visual examination) when the pH was decreased to 1. In addition to humic acid, real secondary effluent likely contained many other organic molecules, including fulvic acid, synthetic organic compounds, and microbial products.<sup>25</sup> It has been reported that DOM in some wastewater effluents is composed primarily of fulvic acid.<sup>26</sup> The calculation from Visual MINTEQ shows that although metal speciation is different in the presence of fulvic acid compared to humic acid within a pH range of 3 to 7, the speciation was nearly identical when the pH was decreased to 1 (Figure S6), which potentially explains why acidification worked well in both synthetic wastewater and real wastewater samples. In addition to the protonation of acidic groups, a low pH can facilitate the dissolution of inorganic species, such as carbonates and oxides, that are known to sorb Pb,<sup>7,27</sup> which will result in the release of ionic Pb into the solution. Overall,



**Figure 3.** Detection of high (A, B) and low (C, D, E, F) concentration of Pb (B, D, F) and Cd (A, C, E) by ASV and ICP-MS in synthetic wastewater and real secondary effluent before and after VUV/H<sub>2</sub>O<sub>2</sub> treatment. Photolysis conditions: pH was around 7, initial H<sub>2</sub>O<sub>2</sub> concentration was 1 g/L, temperature was 25 °C (temperature increased to around 40 °C during photolysis due to heat dissipated from the lamp); 0.5-h photolysis for high-concentration metals, 1-h photolysis for low-concentration metals; residue H<sub>2</sub>O<sub>2</sub> was quenched by Na<sub>2</sub>SO<sub>3</sub>.

acidification results indicate that Pb(II) is bound to carboxylic groups in NOM or inorganic particles, which generally cannot pass through 5 kDa membranes. This is supported by a fact that most of complexed Pb(II) in wastewater is rejected by 5 kDa membranes.<sup>7</sup>

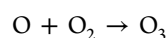
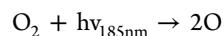
Acidification had only a slight impact on Cd detection by ASV in both synthetic wastewater (from 56% ± 20% to 69% ± 5% in Figure 2C and Figure S5C) and real secondary treatment wastewater (from 32% ± 9% to 44% ± 1% in Figure 2D and Figure S5D). The percent detection of Cd by ASV in synthetic wastewater following acid treatment corresponds well with the Visual MINTEQ model predictions; the model predicted that at pH 1, 71% of Cd would be in ionic form (ASV results yielded 69% ± 5%). However, the model showed that Cd is able to complex with Cl<sup>-</sup> at low pH (Figure 2E). This complexation has been shown to shift the half-wave potential of Cd.<sup>28</sup> However, we did not observe a distinguishable shift in the Cd signal. While decreasing the pH to 1 was supposed to dissolve the majority of inorganic substances, our results show that acidification had a relatively minor impact on the amount of Cd available for ASV detection, suggesting that the majority of Cd(II) is not bound to inorganic particles or carboxylic groups in NOM, which corresponds well with previous research stating that compared to Pb(II), it is harder for Cd(II) to complex with NOM.<sup>29</sup> We speculate that Cd(II) is bound to nonhumic DOC, which generally has a lower molecular weight than NOM. This speculation was supported by the fact that most of the complexed Cd in wastewater could pass through membranes with a pore size of 5 kDa.<sup>7</sup>

Overall, it was found that acidification to pH 1 enabled the efficient detection by ASV of trace Pb concentrations (12.5 ppb) in both synthetic and real wastewater; however, it failed to make trace (3.5 ppb) Cd detectable by ASV.

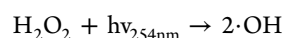
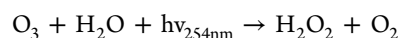
**3.2.2. VUV/H<sub>2</sub>O<sub>2</sub> Coupled with (BiO)<sub>2</sub>CO<sub>3</sub>-rGO-Nafion/GCE.** Figure 3 and Figure S7 (the results in Figure 3 are normalized to the concentrations measured using ICP-MS, while Figure S7 shows the absolute value measured by ASV and ICP-MS) show the ASV and ICP-MS detection of high-concentration metals (i.e., 100 ± 9 ppb Cd and 1058 ± 113 ppb Pb) in synthetic wastewater samples before and after VUV/H<sub>2</sub>O<sub>2</sub> treatment. A 0.5 h VUV/H<sub>2</sub>O<sub>2</sub> treatment significantly enhanced the amount of metals available for ASV detection (from 37% ± 8% to 92% ± 4% for Cd and from 48% ± 11% to 97% ± 0.7% for Pb), indicating that VUV/H<sub>2</sub>O<sub>2</sub> is a robust process to release high-concentration metals (Figure 3A,B and Figure S7A,B). It is noted that the pH of the solution after treatment was 7.2 ± 0.3, a level at which HMs are not expected to be complexed with Cl<sup>-</sup>, but rather be primarily complexed with organic matter (Figure 2E). However, the presence of residual H<sub>2</sub>O<sub>2</sub> remaining in the solution was found to interfere with Cd detection by ASV (Figure 3A and Figure S7A). Therefore, to eliminate this interference, we added 1200 ppm of Na<sub>2</sub>SO<sub>3</sub> to quench residual H<sub>2</sub>O<sub>2</sub>, which enabled ASV to achieve comparable results to ICP-MS (Figure 3A and Figure S7A). Interestingly, ASV detection of high-concentration Pb was insensitive to residual H<sub>2</sub>O<sub>2</sub> (Figure 3B and Figure S7B). We speculate that this is because the concentration of Pb in this case was high enough to have a sufficiently high signal-to-noise ratio, and thus be resistant to the presence of residual H<sub>2</sub>O<sub>2</sub>. However, the impact of residual H<sub>2</sub>O<sub>2</sub> on the detection of low-concentration Pb was observed, and quenching of H<sub>2</sub>O<sub>2</sub> was necessary (more on this below).

VUV/H<sub>2</sub>O<sub>2</sub> is a complex photolysis process that can involve multiple reactive pathways responsible for the degradation of DOC.<sup>30,31</sup> Overall, VUV/H<sub>2</sub>O<sub>2</sub> mechanisms can be classified into direct photolysis (i.e., by VUV), indirect photolysis (by

radicals induced by VUV,<sup>31</sup> and direct oxidation by the H<sub>2</sub>O<sub>2</sub> or ozone<sup>32</sup> (ozone can be generated by VUV irradiation).<sup>33</sup> Under VUV (i.e., UV with wavelength = 185 nm), ozone would be produced from oxygen.<sup>33</sup>



The produced ozone could oxidize organics directly; however, ozone would form hydroxyl radicals under UV radiation in aqueous solutions.<sup>33</sup>



Hydroxyl radicals ( $\cdot\text{OH}$ ) are nontarget oxidants that are powerful to degrade organics.<sup>33</sup> In our case, DOC in synthetic raw MWW decreased 48.7% and 64.3% (see Table S2) after 30 min and 60 min photolysis, respectively, suggesting that the VUV/H<sub>2</sub>O<sub>2</sub> treatment led to partial mineralization. However, the DOC of real secondary effluent only dropped 10.5% and 11.1% (see Table S2) after 30 min and 60 min photolysis, respectively, likely because easily degraded DOC was removed during the activated sludge process.

After validation of the effectiveness of VUV/H<sub>2</sub>O<sub>2</sub> pretreatment for the detection of high-concentration HMs, we further evaluated the effectiveness of VUV/H<sub>2</sub>O<sub>2</sub> on low-concentration HM samples. With a 1-h VUV/H<sub>2</sub>O<sub>2</sub> treatment, 103%  $\pm$  4% and 89%  $\pm$  9% of Cd was detected by ASV in synthetic and real secondary treatment samples, respectively (Figure 3C,E). This is because Cd(II) ions are likely bound to small organic molecules, evidenced by the fact that most of the complexed Cd(II) in wastewater could pass through membranes with a pore size of 5 kDa.<sup>7</sup> These small organic molecules are more readily mineralized by the VUV/H<sub>2</sub>O<sub>2</sub> treatment compared to NOM,<sup>34</sup> which releases the Cd(II), making it available to ASV detection.

However, some loss of Cd was observed after VUV/H<sub>2</sub>O<sub>2</sub> treatment in both ICP-MS and ASV measurements (Figure S7C,E), where the total amount of Cd in real secondary treatment effluent decreased  $0.22 \pm 0.01 \mu\text{g}$  (from  $4.46 \pm 0.09$  ppb to  $2.22 \pm 0.23$  ppb in 100 mL of solution) (Figure S7E). It is noted that similar Cd loss (i.e., from  $4.30 \pm 0.08$  ppb to  $2.48 \pm 0.07$  ppb in 100 mL of solution) was also observed in the control group (i.e., solutions containing only DI water and cadmium), indicating that these errors were systematic. Similar losses were observed in real tertiary treated wastewater (decrease from  $4.21 \pm 0.02$  ppb to  $2.34 \pm 0.43$  ppb), with ASV achieving similar results with ICP-MS after VUV/H<sub>2</sub>O<sub>2</sub> (Figure S8). These systematic errors are likely because of Cd sorption on the PVC reactor.<sup>35</sup> Therefore, we conclude that VUV/H<sub>2</sub>O<sub>2</sub> is an effective pretreatment step for enabling Cd detection by ASV. One hour of VUV/H<sub>2</sub>O<sub>2</sub> pretreatment slightly increased the amount of Pb available for ASV detections in synthetic wastewater (from  $49.6\% \pm 5\%$  to  $65\% \pm 3\%$  in Figure 3D and Figure S7D) and real secondary effluent (from  $20\% \pm 5\%$  to  $40\% \pm 9\%$  in Figure 3F and Figure S7F). To explore whether adsorption to inorganic particles was preventing the complete detection of trace Pb concentrations, HNO<sub>3</sub> was used to adjust the solution pH to 2 after the VUV/H<sub>2</sub>O<sub>2</sub> treatment. However, the acidic pH led to a decreased amount of detectable Pb and Cd available for ASV detection (Figure 3E,F and Figure S7E,F). We speculate that the

impaired metal detection at low pH resulted from interferences from SO<sub>2</sub>, which is electrochemically active.<sup>36</sup> SO<sub>2</sub> can be produced from the hydrolysis of HSO<sub>3</sub><sup>-</sup> (originating from Na<sub>2</sub>SO<sub>3</sub> used to quench H<sub>2</sub>O<sub>2</sub>) at low pH (pK<sub>a1</sub> for SO<sub>2</sub>/H<sub>2</sub>SO<sub>3</sub> is 1.91). As a result, it is impractical to follow the VUV/H<sub>2</sub>O<sub>2</sub> treatment with acidification.

Overall, 30 min of VUV/H<sub>2</sub>O<sub>2</sub> is a robust technique to make high-concentration (100 ppb) Cd and (1058 ppb) Pb available for ASV detection. Furthermore, although a systematic error was observed in VUV/H<sub>2</sub>O<sub>2</sub> treated samples containing trace (3–4 ppb) Cd, this systematic error can be eliminated by using inert reactor materials that do not absorb Cd (e.g., glass material).

## 4. CONCLUSION

ASV is an attractive on-site, low-cost metal detection technique capable of performing frequent and highly accurate measurements with little user input (i.e., the system can be readily automated). We demonstrated that appropriate pretreatment (acidification for Pb and VUV/H<sub>2</sub>O<sub>2</sub> + Na<sub>2</sub>SO<sub>3</sub> quenching for Cd) enables the sensitive detection of Cd and Pb in complex waste stream down to low ppb levels. Detection was enabled by using novel electrodes that are easily processable and scalable, and enabled very low LODs (0.208 and 0.164 ppb for Cd and Pb). The deployment of the method described here (pretreatment + ASV) has the potential of enabling the low-cost and frequent detection of HMs in complex wastewater streams, which will reduce the reliance on expensive and time-consuming ICP-based methods. The low-cost and frequent monitoring of HMs in wastewater could enable its more widespread use in various recycling activities, such as cooling and agricultural irrigation.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestengg.1c00161>.

Figures for (i) typical ASV current vs voltage graph before and after VUV/H<sub>2</sub>O<sub>2</sub> treatment, (ii) reactor picture and spectrum of the lamp; (iii) typical calibration curves for ASV measurements; (iv) the absolute metal value measured by ICP-MS and ASV; and (v) metal species calculated by visual MINTEQ. Tables for (i) decreases of DOC after photolysis and (ii) influence of water matrix on ASV measurements of Pb and Cd (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

David Jassby – Department of Civil and Environmental Engineering, Los Angeles, California 90095, United States; [orcid.org/0000-0002-2133-2536](https://orcid.org/0000-0002-2133-2536); Email: [jassby@ucla.edu](mailto:jassby@ucla.edu)

Ashok Mulchandani – Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521, United States; Center for Environmental Research and Technology (CE\_CERT), University of California, Riverside, California 92507, United States; [orcid.org/0000-0002-2831-4154](https://orcid.org/0000-0002-2831-4154); Email: [adani@engr.ucr.edu](mailto:adani@engr.ucr.edu)

## Authors

Shengcun Ma – Department of Civil and Environmental Engineering, Los Angeles, California 90095, United States; [orcid.org/0000-0001-5560-9612](https://orcid.org/0000-0001-5560-9612)

Guo Zhao – Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521, United States; Present Address: College of Artificial Intelligence, Nanjing Agricultural University, Nanjing, 210031, China

Mona Elsayed – Department of Materials Science and Engineering, University of California, Riverside, California 92521, United States

Mohammed Sedki – Department of Materials Science and Engineering, University of California, Riverside, California 92521, United States; [orcid.org/0000-0002-9830-8972](https://orcid.org/0000-0002-9830-8972)

Xingyu Chen – Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521, United States

Dong Wu – Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States

Ximin He – Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States; [orcid.org/0000-0001-8845-4637](https://orcid.org/0000-0001-8845-4637)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsestengg.1c00161>

## Author Contributions

#These authors contributed to this work equally.

## Notes

The authors declare no competing financial interest.

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