Applying Anodic Stripping Voltammetry to Complex Wastewater Streams for Rapid Metal Detection

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MOTIVATION

- As traditional water supplies for thermoelectric power plants are coming under increased stress there is an increased interest in exploiting marginal water sources, such as municipal wastewater
- Municipal wastewater, in particular, is of interest because of its widespread availability and relatively consistent quality (Figure 1)
- However, the complex nature of municipal wastewater, and the high metal contaminant loads found in wastewater streams makes their use in thermoelectric power plants challenging
- An accurate heavy metal detection method that can operate autonomously and accurately will enable the safer use of these marginal waters for cooling and other power plant-related activities
- Current metal detection methods rely on grab-sampling and analysis on complicated analytical chemistry instruments, often requiring dedicated technical staff
- There in imperative to develop small, independent and reliable heavy metal detection platforms

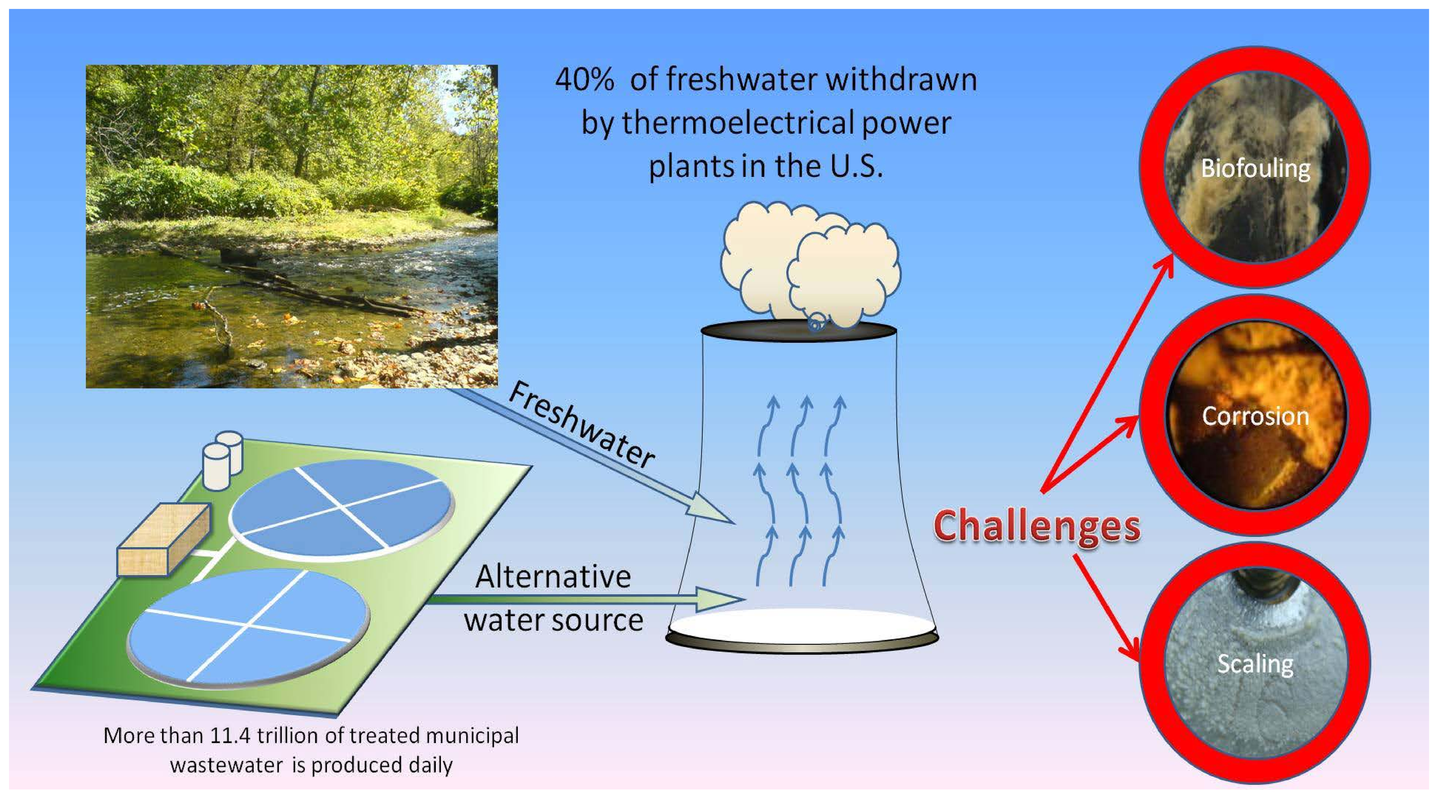

Figure 1. Challenges and opportunities for reusing wastewater in thermal power-plants (D. Dzombak, 2013; aaees.org)

OBJECTIVES

- The overall objective of this project is the development of a lab-on-a-chip (LOC) electrochemical sensor capable of accurately measuring heavy metal (lead (Pb), cadmium (Cd), and arsenic (As)) concentrations in complex wastewater streams (Figure 2)
- The sensor technology relies on anodic stripping voltammetry (ASV), which has been demonstrated to be able to detect extremely low (sub ppm) concentrations of these metals
- Using open-source hardware and software tools, we will construct sensor technology that operates with minimal human intervention, and which will be able to autonomously perform all of the needed pre-treatment steps for metal measurement activities
- The technology could be used for the detection of other metals of concern, such as chromium

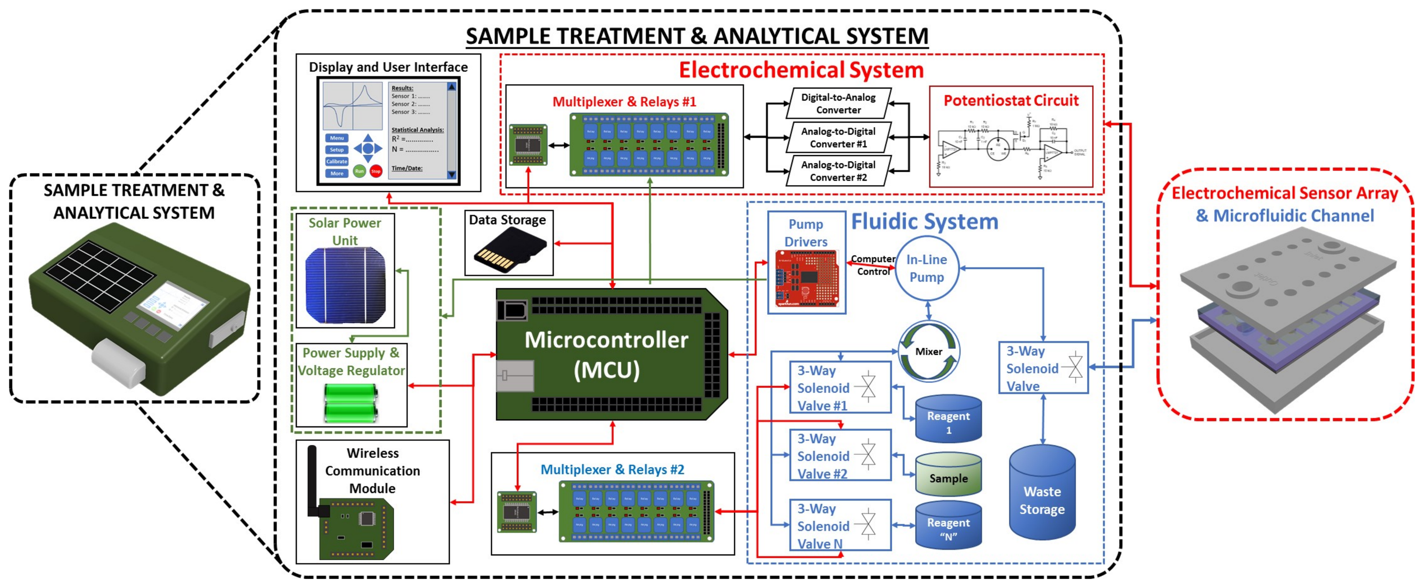

Figure 2. Schematic illustration of an on-site automated sampling and measurement device for heavy metals in water

ANODIC STRIPPING VOLTAMMETRY

Four steps to the process (Figure 3):

A. Electrooxidative cleaning (positive/anodic potentials)
  - Burn off any deposited "gunk"

B. Electro-deposition step (negative/cathodic potentials)
  - Reduce dissolved metals (to zero-valent form) onto electrode

C. Equilibration step (negative/cathodic potentials)
  - Allow metal to equilibrate on electrode

D. Stripping step (positive/anodic potentials)
  - Specific metals oxidize at specific potentials
  - Manifests as a spike in electrical current
  - Current during stripping corresponds to concentration of metals in water

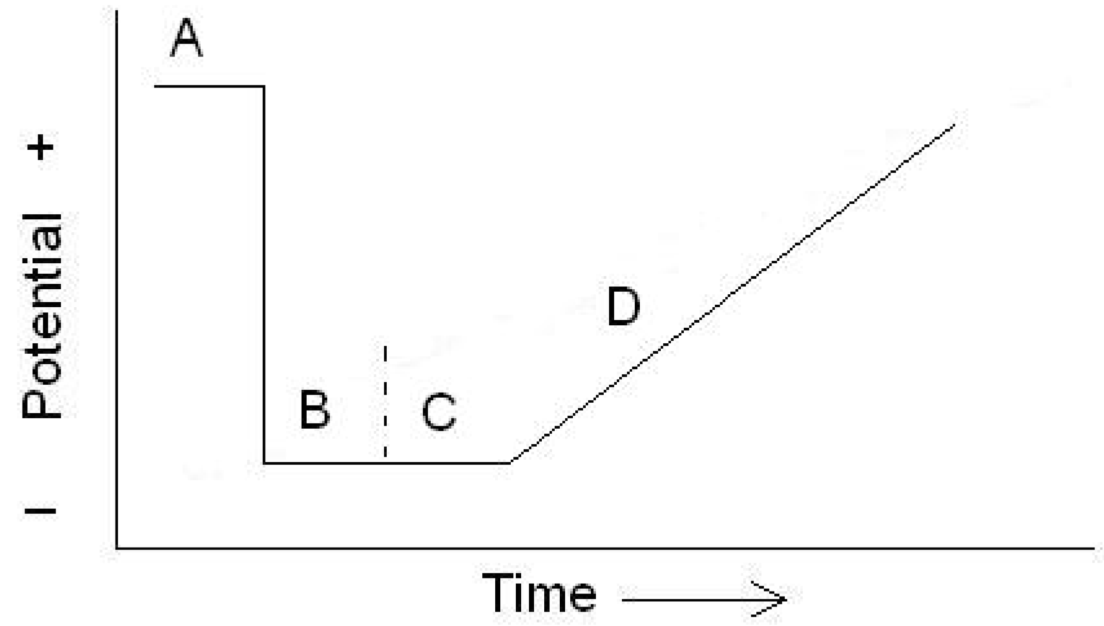

Figure 3. The four steps of ASV.

PROJECT TASKS

1. <u>Characterize Metal Speciation in Different Synthetic Wastewater</u>

In this Task, we will evaluate how different wastewater characteristics impact the speciation and form of heavy metals (Pb, Cd, and As). In addition, we will investigate how different wastewater treatment steps (primary, secondary, tertiary) impact the speciation and form of heavy metals.

2. <u>Fabricate and Test Electrodes for ASV</u>

In this Task, we will fabricate a range of electrode materials tailored towards the specific detection of Pb, Cd, and As. These electrode materials are known to facilitate specific interactions between the analytes and the electrode surface, which promotes sensitivity and selectivity of the ASV measurements. The electrodes are based on the unique chemistry and surface properties of reduced graphene oxide (rGO).

Two electrode materials will be used:

a. rGO/Bi nanocomposite for Pb and Cd detection
b. rGO/Fe_3O_4 nanocomposite for As detection

3. <u>Identify Optimal Operating Conditions for Metal Detection using ASV</u>

Different pre-treatment steps will be applied to heavy-metal contaminated wastewater taken from different stages of the wastewater treatment train. We will then apply ASV to wastewater that was pre-treated to determine how the measurement method responds to the degree of pre-treatment.

4. <u>Fabricate a microfluidic electrochemical cell with sensor arrays for ASV and evaluate its electrochemical performance</u>

In this task, we will fabricate a microfluidic electrochemical cell consisting of an array of four (two sensors of rGO/Bi and two of rGO/Fe3O4) sets of three electrode sensors for ASV analysis of metals. The microanalyzer system will be fabricated using traditional photolithography to pattern four sets of the three electrodes for two sensor arrays and soft lithography to make the flow channel (Figure 4). The fabricated sensor arrays microanalyzer will be tested for electrochemical performance.

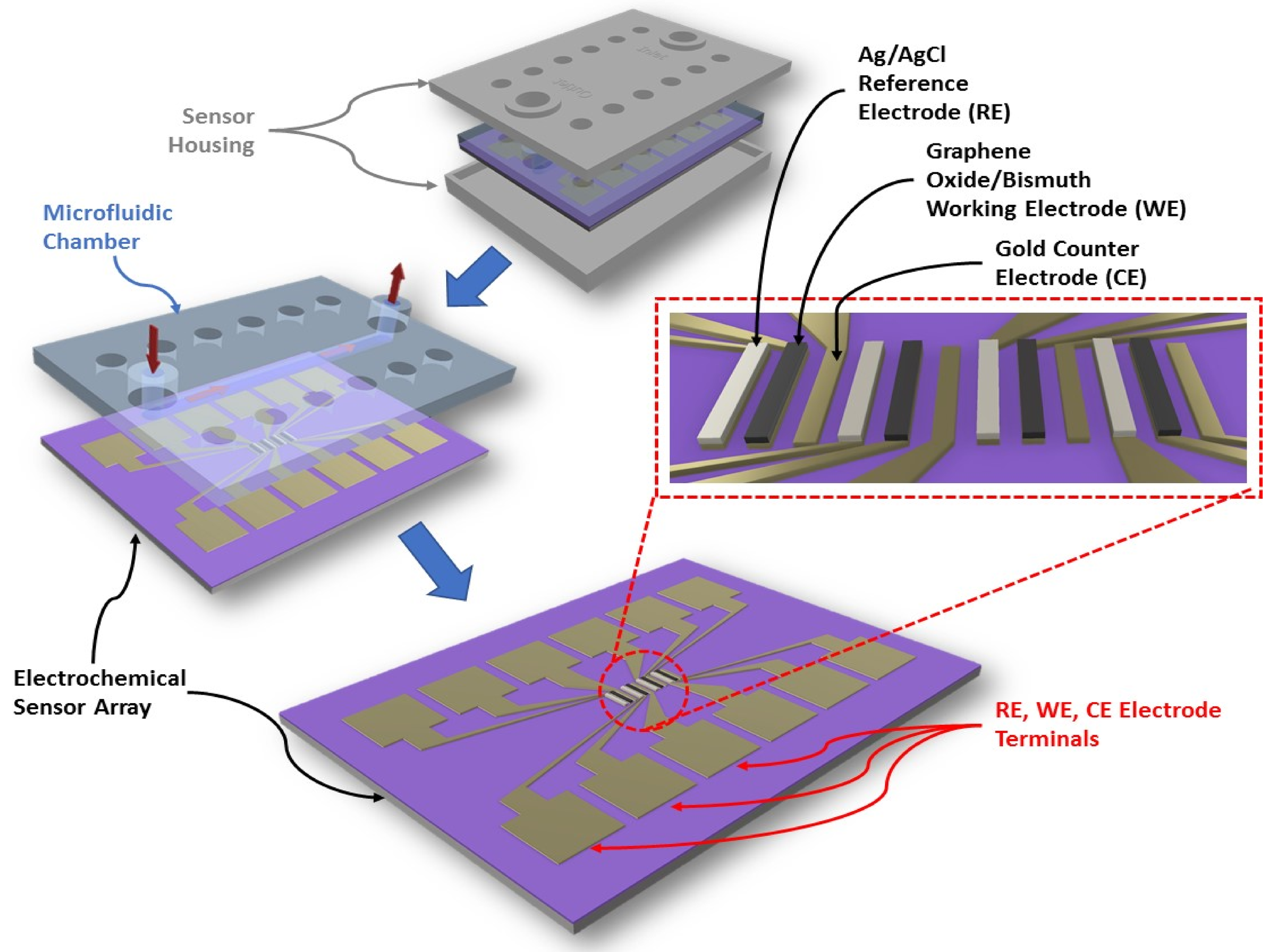

Figure 4. Schematic of electrochemical sensor array microanalyzer system

5. <u>Construct and Test LOC Anodic Stripping Voltammetry Device</u>

A salient feature of an ASV microfluidic analyzer for heavy metals is that the sensor signal output can be amplified by employing a continuous flow sensing. In such a process the sample can be passed continuously through the chip at controlled flow rate during deposition and stopped during stripping. By doing this, the deposition efficiency can be increased due to the enhanced mass transfer rate of the target analyte to the working electrode surface compared with static measurement method. Another advantage of a flow system is that a larger volume of analyte sample can be pumped through the channel during the electrodeposition cycle to achieve detection in stripping for samples with low metal ion concentration and thereby achieving a high sensitivity.