

# Efficient Removal of Mercury from Polluted Aqueous Solutions Using the Wireless Bipolar Electrochemistry Technique

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Mercury represents one of the major toxic pollutants in water that affect human and ecosystem. Extensive efforts have been globally invested to remove mercury using various chemical and electrochemical approaches. In this study, I propose the use of bipolar electrochemistry for the first time for mercury depollution process. Mercury(II) is removed from aqueous solutions by direct electrodeposition on millimeter scale graphite rods held in a bipolar setup. By adjusting the strength of the applied electric field and the number of the graphite rods the

efficiency of the system can be controlled. This wireless technique allows the use of multiple graphite rod arrays within the bulk cell which resulted in high removal efficiency (98%) of  $\text{Hg}^{2+}$  ions from the polluted solution. The method is straightforward, green, and efficient. The concept can be adapted to remove other heavy metal ions or electrochemically active contaminants from polluted water as long as their reduction potentials are within the water stability window.

## Introduction

Mercury (Hg) is one of the most toxic metals of concern to human, and has become a serious environmental issue due to its high rate of spreading and accumulation in natural waters.<sup>[1]</sup> Human activities in the industrial sector or, for example, in the consumption of fossil fuels prominently raised mercury levels in the environment over the course of the last centuries.<sup>[2]</sup> One of the leading worldwide reasons for human illnesses and deaths is water contamination with heavy metals like mercury.<sup>[3]</sup> Exposure to even trace concentrations of mercury is reported to be behind brain, lungs, and kidney damage,<sup>[4]</sup> with the divalent mercury ( $\text{Hg}^{2+}$ ) being responsible for the two latter cases.<sup>[5]</sup> Therefore, recovery of the mercury from the water sources is of great importance for community and environment. The classical methods of water depollution include adsorption, precipitation, ion exchange, oxidation and reduction, and extensive efforts have been devoted by researchers to develop new materials and techniques for detection and removal of mercury from water such as using nano-materials like carbon nanotubes, and magnetic nano-composites.<sup>[6-7]</sup> However, the majority of these methods have drawbacks due to the need to add chemicals<sup>[8]</sup> or nanoparticles<sup>[9-10]</sup> for decontamination process and conse-

quently to dispose the resulted precipitate or alloy (in precipitation and alloy formation methods, respectively) or to regenerate the contaminated adsorption material (in adsorption technique) which might be complex in addition to the high cost, hence, the scale up of some of these methods might be restricted.<sup>[6,11-12]</sup> Electrochemistry represents another attractive route for heavy metal retrieval. The nobility of mercury enables its electrodeposition from aqueous solution under the effect of applied potential,<sup>[13]</sup> and metallic mercury can later interact locally with some other metals and form amalgam. Thus, an obvious advantage of the electrochemical method is that no chemical reagents are required for the reduction of mercury as the applied potential will undertake that. This technique has been used to remove mercury ions from aqueous solutions by amalgam formation on copper,<sup>[14-15]</sup> or platinum<sup>[16-17]</sup> electrode.

In the frame of electrochemistry one interesting possibility would be to use the bipolar electrochemistry<sup>[18-19]</sup> to remove the heavy metals via direct electrodeposition.<sup>[20]</sup> Bipolar electrochemistry is a wireless technique in which a pair of feeder electrodes is used to generate an electric field in an electrolytic solution that accommodates conductive object (also called bipolar electrode) with no physical contact between the latter and the feeder electrodes. When a sufficient electric field is applied and in the presence of electroactive species, the two extremities of the bipolar electrode will be polarized with respect to the surrounding solution and provoke simultaneous cathodic and anodic reactions. The polarization potential difference ( $\Delta V$ ) between the two ends of the bipolar electrode follows the Equation (1):

$$\Delta V = E l \quad (1)$$

Where  $E$  is the value of the applied electric field and  $l$  is the length of the bipolar electrode.

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/open.202200231>

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The concept of bipolar electrochemistry has been adapted for metals electrodeposition on carbon substrates,<sup>[21–24]</sup> (Bio)electroanalysis,<sup>[25]</sup> electrocatalysis,<sup>[26–27]</sup> bioelectrocatalysis,<sup>[28]</sup> and electrosynthesis of various organic, inorganic,<sup>[29]</sup> and polymeric<sup>[30]</sup> materials. So far, bipolar electrochemistry has never been adapted for mercury depollution purposes. In this study, I describe for the first time the possibility to remove mercury(II) ions from synthetic polluted water by electrodeposition on the cathodic pole of multiple graphite rod arrays (GRAs) that are held in a bipolar electrochemistry setup. As a wireless technique, the efficiency of mercury removal can be easily controlled by adjusting the number of the bipolar electrodes and the strength of the applied electric field. I show mercury retrieval from aqueous solutions as a function of the number of graphite rods (GRs), GRAs, and as a function of the time.

## Results and Discussion

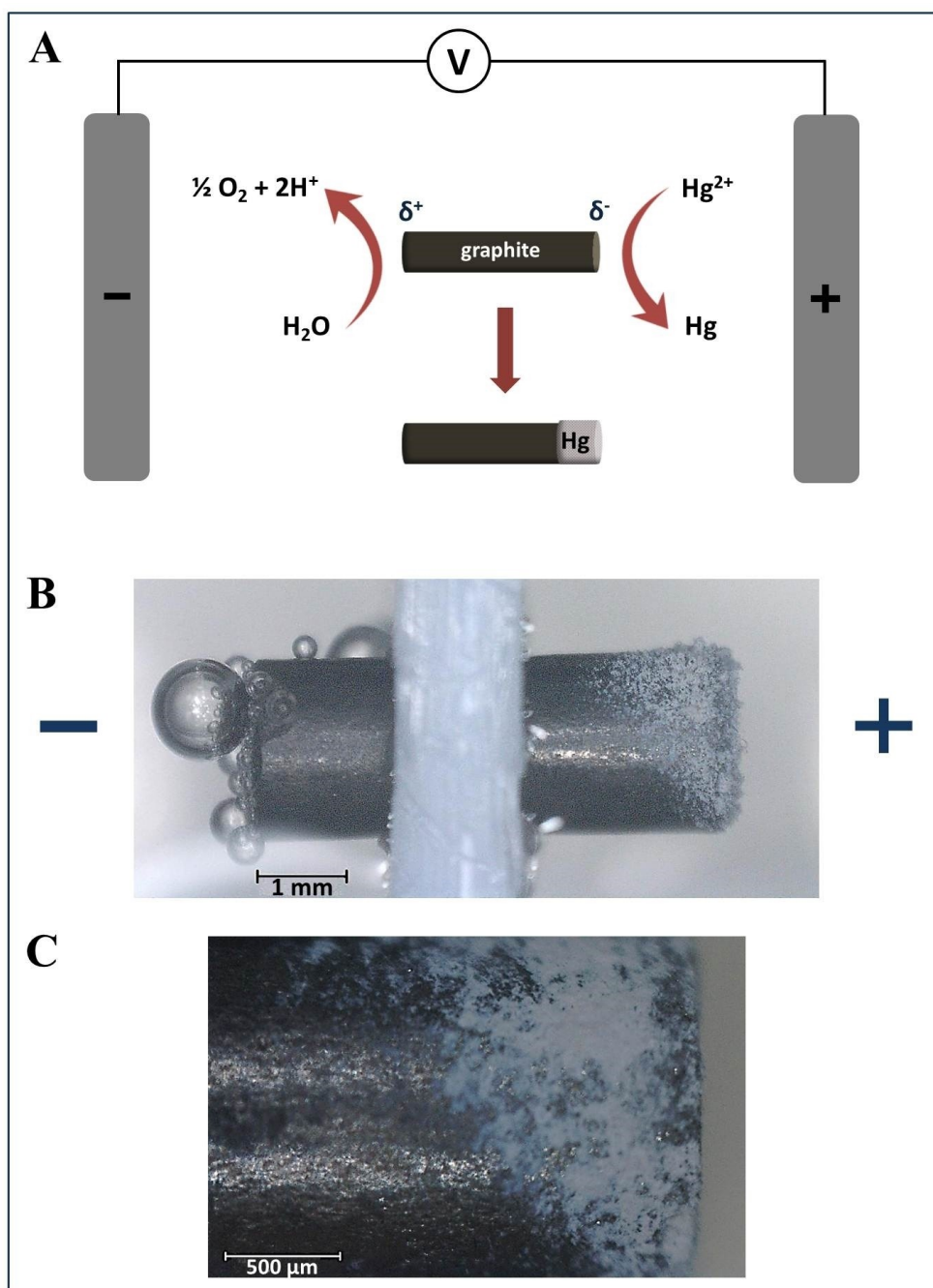
For electrodeposition of divalent mercury on GR, two redox reactions need to be considered at the extremities of the bipolar rod as illustrated in Figure 1A, oxidation of water at the anodic pole and reduction of mercury(II) ions at the cathodic pole. These reactions occur at formal potentials of  $E^0 = +1.23$  and  $E^0 = +0.85$  V versus NHE, respectively. This indicates to a minimum threshold value  $\Delta V_{\min} = |E_1^0 - E_2^0| = 0.38$  V which corresponds to an electric field of  $0.76$  Vcm<sup>-1</sup> that should be applied to achieve Hg electrodeposition on a 5 mm long GR based on Equation (1).

In a first experiment, a 5 mm long GR that was held by a plastic mesh was introduced into the bipolar cell which was then filled with a 50 mM HgCl<sub>2</sub> solution. Practically, an electric field of  $2.4$  Vcm<sup>-1</sup> was applied between the feeder electrodes which generates a 1.2 V potential difference (calculated from Equation (1)) between the two ends of this GR. This  $\Delta V$  is around 3 times higher than the required value (0.38 V) which is sufficient to overcome the overpotentials of both redox reactions on the graphite bipolar substrate, but still low enough to avoid hydrogen gas formation at the cathodic pole which may disturb the formation of Hg deposit. At this applied potential, oxidation of the anodic pole of the GR ( $E^0 = 0.207$  V vs. NHE) would be somehow limited as it requires a  $\Delta V_{\min}$  of 0.64 V to simultaneously occur with Hg<sup>2+</sup> electrodeposition at the cathodic pole, this value is 1.7 times higher than the calculated  $\Delta V_{\min}$  for Hg<sup>2+</sup>/Hg<sup>0</sup> and O<sub>2</sub>/H<sub>2</sub>O redox couples to occur. The relatively high concentration (50 mM) of the employed salt was to produce a clear image for Hg deposition with the concomitant oxygen gas production. Figure 1B shows these two redox reactions under the optical microscope while the voltage is on for a period of 38 min (see also Hg electrodeposition on a 6 mm long GR with an oblique cathodic pole (right end of the GR) in the Supporting Information Movie). As there is no generated hydrogen gas at the cathodic pole of the graphite rod, the Faraday efficiency must be quite high because all the liberated electrons by the production of O<sub>2</sub> gas at the anodic pole will be quantitatively used for the reduction of Hg<sup>2+</sup> ions at the cathodic pole of the rod. A zoom on the

cathodic pole of the GR (Figure 1C, right end) demonstrates the formation of Hg deposit as small accumulated thin films rather than a droplet which might be attributed to the small quantity of metal deposit. It might also be possible that some Hg<sub>2</sub>Cl<sub>2</sub> was formed ( $E_{\text{Hg}^{2+}/\text{Hg}^{1+}}^0 = 0.91$  V vs. NHE) at the cathodic pole under the effect of the applied potential, however, this should not affect the value of the present work as long as the main purpose (metal removal) has been achieved. This image was obtained after 40 min of voltage application then the rod has been washed for 5 times with deionized water. After this proof-of-principle experiment with a single bipolar GR, multiple GRs were employed in the following step.

For electrochemical investigations, mercury(II) iodide was used to prepare the polluted aqueous samples in this set of experiments. The dissolved HgI<sub>2</sub> complex in water showed two absorption peaks at 264 and 209.5 nm, respectively, by UV/Vis spectroscopy. Therefore, I could determine the remaining amount of mercury by following the decrease in these absorption peaks due to the removal of the free Hg<sup>2+</sup> ions from the solution under the applied voltage and the re-adjustment of HgI<sub>2</sub> complex dissociation. For investigating the depollution process I focused on the peak at 209.5 nm (Figure S2) as this peak is more pronounced and the remaining amount of mercury was quantified based on the calibration curve in Figure S2B. Figure 2 shows the experimental setup that has been used to investigate the electrochemical retrieval of mercury ions from aqueous solution. The feeder graphite electrodes, which were immersed in KNO<sub>3</sub> solution (0.1 mM) in the outer compartments of the cell, were connected to a power supply. Reinforced proton exchange membranes were introduced in the cell design to prevent the electrodeposition of Hg<sup>2+</sup> ions on the feeder cathode so that the metal electrodeposition only occurs on the bipolar GRs. The membranes can also decrease any possible generated effect at the two feeder electrodes such as bubble formation from electrolysis of water or changes in pH. 11 mL of 7.7 mgL<sup>-1</sup> HgI<sub>2</sub> solution was put in the reaction compartment and a GRA consists of 11 rods was introduced into the solution.

Two preliminary experiments have been conducted in order to investigate the influence of time at a given voltage on decreasing the metal concentration in solution. An electric field of  $2.4$  Vcm<sup>-1</sup> was applied for 30 min in the first experiment (Figure 3A, red curve), and 60 min in the second one (Figure 3A, blue curve). The decrease in the absorption peak of HgI<sub>2</sub> in Figure 3A with increasing the time of the experiment is a clear indication for the removal of freely existing Hg<sup>2+</sup> ions from the sample and the possibility to follow the depollution process by measuring the absorbance of the present HgI<sub>2</sub> complex. The effect of different applied potentials on the rate of metal ions removal was also tested using similar other conditions. An electric field of  $3.6$  Vcm<sup>-1</sup> was applied on the polluted sample for 30 min and the result (Figure 3B, blue curve) was compared with the previously treated solution under  $2.4$  Vcm<sup>-1</sup> electric field and for the same time duration (Figure 3B, red curve). The remaining amount of Hg<sup>2+</sup> ions was 7.17 mgL<sup>-1</sup> when  $2.4$  Vcm<sup>-1</sup> was applied, while 6.8 mgL<sup>-1</sup> was left using  $3.6$  Vcm<sup>-1</sup> which means a higher rate of depollution was



**Figure 1.** (A) Schematic representation of the redox reactions occurring at the ends of graphite bipolar electrode leading to  $\text{Hg}^{\text{II}}$  removal from the solution. Optical micrographs of a 5 mm long graphite rod (B) in situ in the experimental setup used for the mercury removal (the voltage is on), and (C) zoom on the cathodic pole with the Hg deposit obtained after applying an electric field of  $2.4 \text{ V cm}^{-1}$  in 50 mM  $\text{HgCl}_2$  solution for 40 min.

achieved using the higher potential. This is because at a higher voltage, a larger part of the GRs would have the sufficient polarization potential for  $\text{Hg}^{2+}$  ions electrodeposition (Equation (1)). It is noteworthy that the  $\text{Hg}^{\text{II}}$  electrodeposition was also possible at a lower electric field value ( $2 \text{ V cm}^{-1}$ ) and by using different experimental conditions and setup (result is not shown here), however, the removal required a longer time. Although the use of a higher voltage results in a faster removal of  $\text{Hg}^{2+}$  ions, the price to pay is to consume more energy.

Therefore, and in order to make a good compromise between the energy cost and the kinetic of depollution, the electric field of  $2.4 \text{ V cm}^{-1}$  has been selected as the optimum value to be used in the next experiments.

The influence of the number of GRs and GRAs on decontamination process has been studied in this set of experiments. The bipolar electrochemical treatment of the polluted samples was performed using a 12 mL of  $60.2 \text{ mg L}^{-1}$  mercury(II) chloride and the electric field of  $2.4 \text{ V cm}^{-1}$ .  $\text{HgCl}_2$

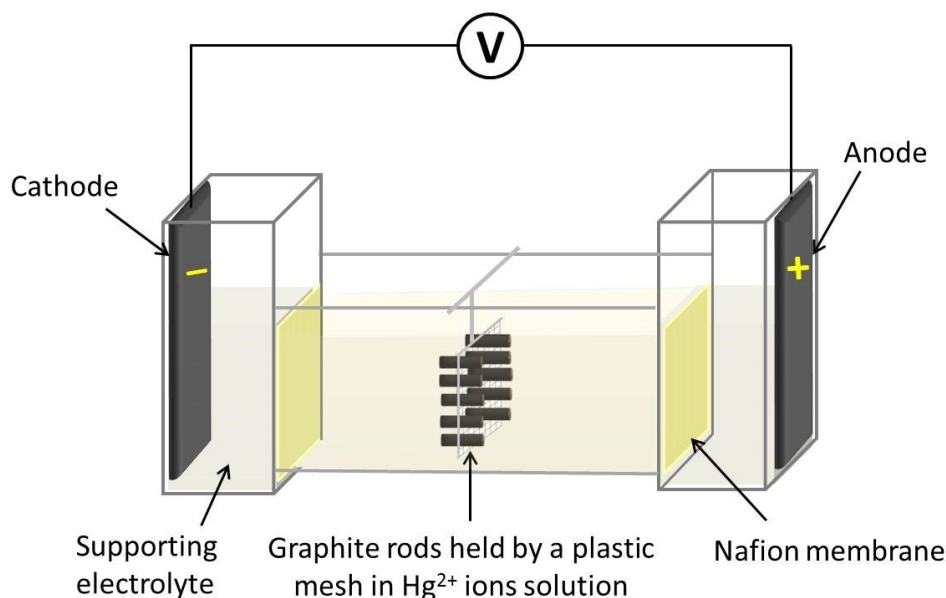


Figure 2. Scheme of the experimental setup used for  $\text{Hg}^{2+}$  ions removal by bipolar electrodeposition.

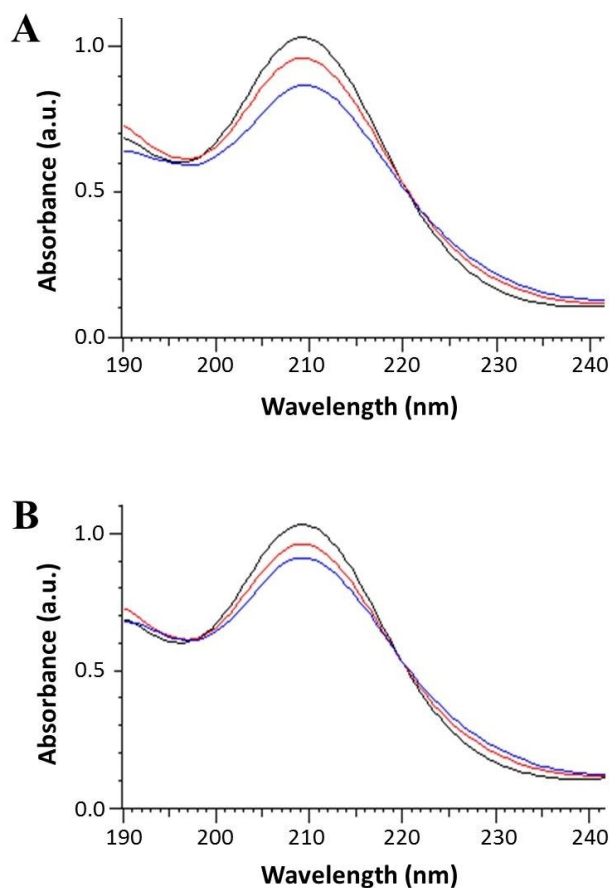
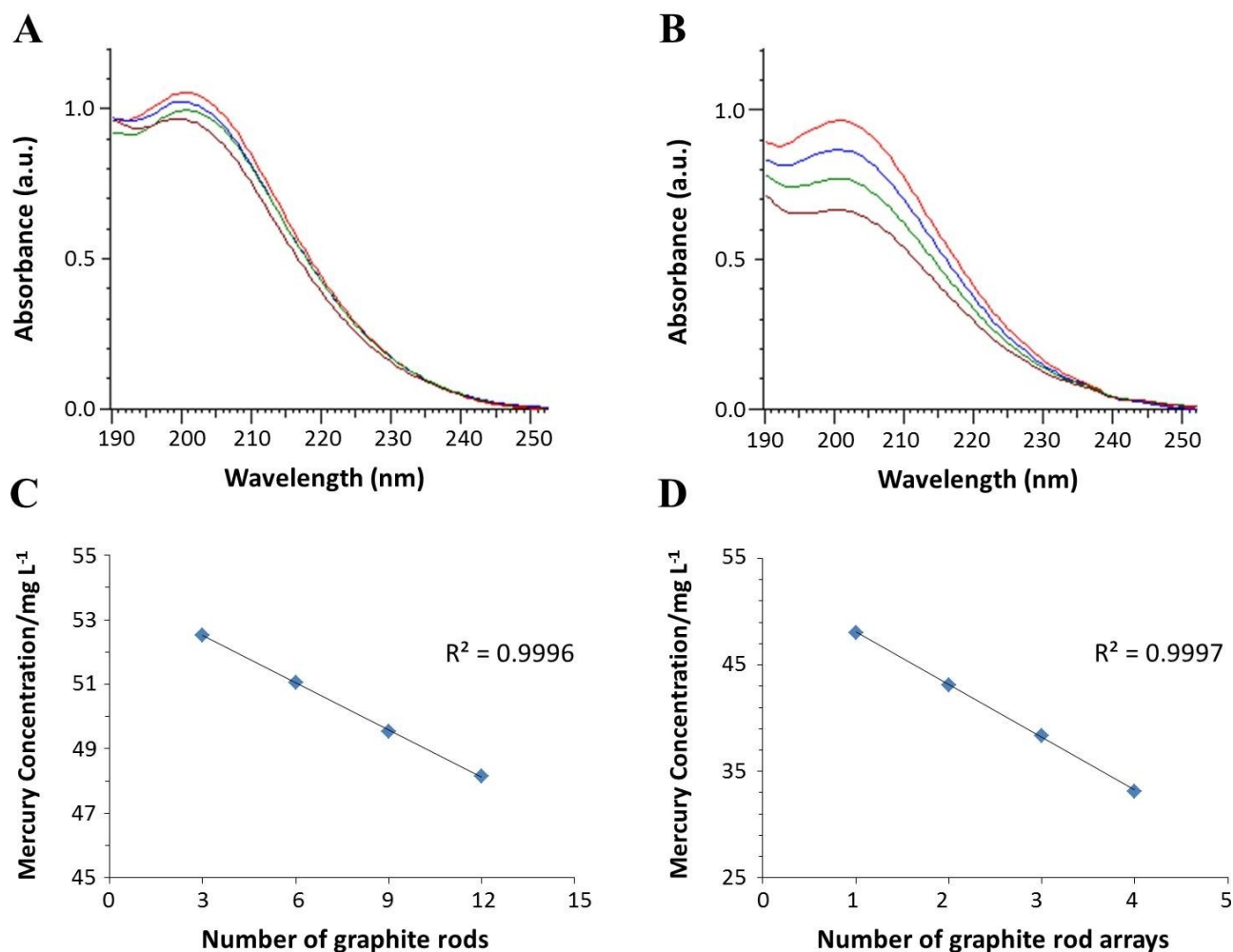


Figure 3. UV/Vis absorption spectra of  $7.7 \text{ mg L}^{-1} \text{ HgI}_2$  solution before (black curves), and (A) after applying an electric field of  $2.4 \text{ V cm}^{-1}$  for 30 min (red curve) and 60 min (blue curve), (B) after application of  $2.4 \text{ V cm}^{-1}$  (red curve) and  $3.6 \text{ V cm}^{-1}$  (blue curve) electric field in the polluted solution over 30 min.

has a unique absorption peak at 200 nm which allows to follow the remaining metal concentration (calculated by the calibration curve in Figure S3B) after the polluted sample was exposed to the electric field for 60 min.

By systematically changing the number of the GRs, 3, 6, 9, and 12 rods were employed in different experiments. The GRs were arranged as one array so that each rod feels the same potential gradient or electric field when introduced into the bipolar cell. Figure 4 shows the reduction of the absorption peak at 200 nm (Figure 4A) and the linear decrease of  $\text{HgCl}_2$  concentration as a function of the number of GRs (Figure 4C) with a high coefficient of determination ( $R^2 = 0.9996$ ), indicating that each rod participates independently in the metal electro-deposition process. For example, for every 3 GRs added, there was a  $1.5 \pm 0.1 \text{ mg L}^{-1} \text{ h}^{-1}$  decrease in the metal concentration. As the efficiency of the setup increased in a controlled manner when using more rods, GRAs that consisted of 15 rods were utilized in the next experiments. Furthermore, a transition from a two dimensional reaction plane (single GRA) into a 3D space (multiple GRAs) that is allowed with the bipolar electrochemistry was done. 1 to 4 GRAs were used through several experiments, with the same number (15) of GRs in each array. The GRAs were put in parallel and spaced by a 5 mm distance in order to avoid the impact of the GRs in one array in terms of electric field distribution on the GRs in the next array. Analysis of the treated solutions by UV/Vis spectroscopy shows a decline in the absorption peak (Figure 4B) and a linear decrease in  $\text{HgCl}_2$  quantity as a function of the number of GRAs (Figure 4D) with a high value of  $R^2 = 0.9997$ . The results show a decrease of  $5 \pm 0.2 \text{ mg L}^{-1} \text{ h}^{-1}$  in  $\text{HgCl}_2$  concentration for each an array added to the reaction compartment, which means an increase in the rate of the metal removal of slightly more than three times using the 3D setup compared to the 2D configuration.

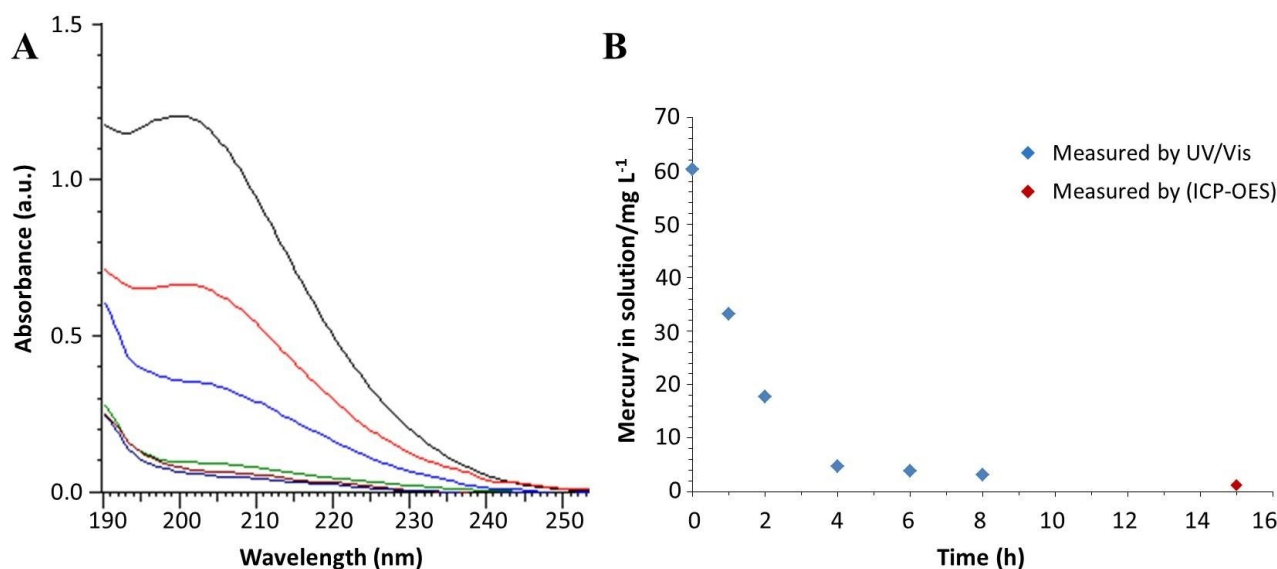


**Figure 4.** UV/Vis spectra of the remaining mercury in solution using different number of (A) GRs and (B) GRAs. Red, blue, green, and brown lines correspond to (A) 3, 6, 9, and 12 GRs, and (B) 1, 2, 3, and 4 GRAs, respectively. The remaining concentration of mercury (C) as a function of the number of GRs and (D) as a function of the number of GRAs. Applied electric field =  $2.4 \text{ V cm}^{-1}$  for 1 h in  $60.2 \text{ mg L}^{-1} \text{ HgCl}_2$  solution.

This confirms that the removal efficiency can be significantly improved by invasion of the volume of the reaction compartment by the GRAs. This is because when I multiply the number of the bipolar electrodes, the active surface area that will be available to remove the mercury ions from the bulk solution increases. However, a suitable distance must always present between the GRAs to prevent the screening effect of the electric field that might be generated by the rods. Hence, 4 GRAs were the maximum number that has been employed next for mercury retrieval experiments.

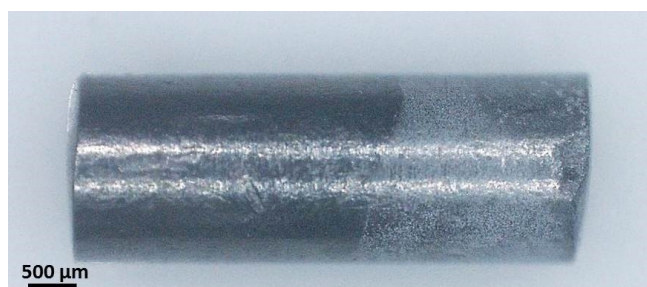
Mercury(II) retrieval from a 12 mL of  $60.2 \text{ mg L}^{-1} \text{ HgCl}_2$  sample has been studied as a function of the time under  $2.4 \text{ V cm}^{-1}$  electric field and using 4 GRAs. The polluted samples have been electrochemically treated over different periods of time (2 to 15 h), and with each sample a similar control experiment was run in which the  $\text{HgCl}_2$  solution was replaced by deionized water. This was to ensure that both the sample and the deionized water had the same treatment so that we use this water as a corresponding blank for the sample during the UV/Vis measurement. Figure 5A demonstrates the big drop

in the absorption peak within the first four hours (Figure 5A, green line) of the  $\text{Hg}^{\text{II}}$  electrodeposition, which corresponds to  $4.7 \text{ mg L}^{-1}$  (7.8%)  $\text{Hg}^{2+}$  ions present in the solution after 4 h (Figure 5B). Retrieval process slows down with time and this might be due to the low number of  $\text{Hg}^{2+}$  ions left and the difficulty to diffuse or migrate toward the cathodic pole of the GRs compared to the high initial concentration of ions presented close to the GRs which could be deposited faster. Stirring the solution can provide a higher rate for mass-transfer of the ions to the bipolar electrode surface and consequently increase the efficiency of  $\text{Hg}^{2+}$  electrodeposition.<sup>[13]</sup> The use of a higher concentration of  $\text{KNO}_3$  electrolyte in the feeder electrode compartments than the concentration of  $\text{HgCl}_2$  solution in the reaction compartment can also increase the efficiency of the electrodeposition as the major potential drop will occur in the reaction compartment.<sup>[31]</sup> The phenomenon of slow retrieval of ions with time was also reported for Hg electrochemical alloy formation on thin platinum layers by Tunsu et al.<sup>[17]</sup> For example, for a 50 mL sample they needed 235 h to remove ~98% of  $15 \text{ mg L}^{-1} \text{ Hg}^{2+}$  ions using different experimental



**Figure 5.** UV/Vis absorption spectra (A) and plot shows the decrease (B) of mercury(II) concentration with time upon electrochemical removal from 12 mL of 60.2 mg L<sup>-1</sup> HgCl<sub>2</sub> solution under 2.4 V cm<sup>-1</sup> electric field. The obtained spectra (A) correspond to 0 (black line), 1 (red line), 2 (blue line), 4 (green line), 6 (brown line), and 8 h (dark blue line) of removal. ICP-OES: Inductively Coupled Argon Plasma - Optical Emission Spectrometer.

conditions. The authors attributed such a long time to the slow diffusion of mercury in the alloy which they could significantly improve by using electrodes with a very high surface area. In the first set of experiments, I followed the decontamination process by measuring the absorbance of the samples, however, after 8 h of treatment (Figure 5A, dark blue line) the remaining concentration of Hg<sup>2+</sup> ions became very low so the UV/Vis spectroscopy started to be insensitive to measure such low amount of ions, hence, I switched to ICP-OES technique. Precise measurement by ICP-OES demonstrated that with a relatively prolonged treatment time (15 h) almost all the Hg<sup>2+</sup> ions (98%) could be removed from the solution (Figure 5B, red diamond). Working with lower initial concentrations of the metal ions obviously required a shorter time of retrieval using classic electrochemistry,<sup>[17]</sup> thus, one can predict even a much faster kinetic of depollution when using the bulk bipolar electrochemical cell to treat these low concentrations. Figure 6 shows an optical micrograph of a GR with Hg deposit (~ 2 mm long) at the cathodic pole (right end) obtained after application of the

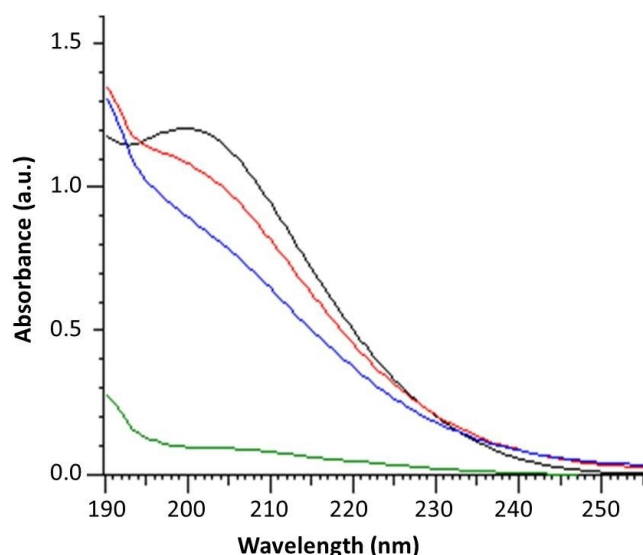


**Figure 6.** Optical image of a 5 mm long GR with Hg deposit at the cathodic (right) end obtained by application of an electric field of 2.4 V cm<sup>-1</sup> in 60.2 mg L<sup>-1</sup> HgCl<sub>2</sub> solution for 9 h. Three GRAs (15 rods/array) were used in this experiment.

electric field in HgCl<sub>2</sub> solution for 9 h. Only three GRAs (15 rods/array) were used in this experiment in order to get an adequate deposit for imaging.

To investigate the effect of any possible adsorption of mercury ions on the graphite rods, I have performed two experiments using the same experimental conditions that have been used for the complete removal of Hg<sup>2+</sup> ions under potential except that no electric field was applied in this case. HgCl<sub>2</sub> solution was left in the bipolar setup for 4 h in the first experiment and 15 h in the second one, then the solutions were collected and the absorbance was measured. Quantitative analysis of the remaining amount of Hg<sup>2+</sup> ions showed that 54 mg L<sup>-1</sup> (90%) of the metal ions was remained in the solution after 4 h (Figure 7, red line) in the absence of the electric field compared to only 4.7 mg L<sup>-1</sup> (7.8%) of Hg<sup>2+</sup> ions left in the solution when the voltage was applied for the same time duration (Figure 7, green line). When the experiment time was increased to 15 h, 44.7 mg L<sup>-1</sup> (74.5%) of Hg<sup>2+</sup> ions was remained (Figure 7, blue line) compared to only 1.2 mg L<sup>-1</sup> (< 2%) of metal ions presented when the solution was exposed to the electric field over 15 h (Figure 5B, red diamond). These results demonstrate that there is a certain fraction of the metal ions that have been removed by a simple physical adsorption, however, with the application of the electric field, I could remove rather quickly almost all (>98%) the metal ions from the solution, while a much longer characteristics time is required for removing a substantial amount of the metal ions when no electric field is applied.

The nature of Hg deposit formed on the GRs during metal removal was indirectly investigated for an experiment that has been run for 13 h using 4 GRAs. The collected GRAs from this experiment and from the corresponding blank were each immersed in a 12 mL pure water for 40 h. UV/Vis analysis of the recovered water from the sample arrays versus the blank



**Figure 7.** UV/Vis absorption spectra of 60.2 mg L<sup>-1</sup> HgCl<sub>2</sub> solution (black curve) show the decrease in the absorption peak in the absence (red curve (after 4 h) and blue curve (after 15 h)) and presence (green curve (after 4 h)) of 2.4 V cm<sup>-1</sup> electric field.

(Figure S4) showed no peak at 200 nm where normally HgCl<sub>2</sub> absorption peak appears, which means there is no spontaneous release of ionic mercury from the GRs, so the deposit must be a metallic Hg and some insoluble Hg<sub>2</sub>Cl<sub>2</sub> may also exist.

In a control experiment, the re-use of the collected GRAs was assessed. GRAs that have been previously used for mercury retrieval over 6 h and loaded with 93.5% of Hg content were employed in a new experiment that has been run for the same period of time. Absorbance measurement for the recovered solution from both experiments versus pure water as a blank showed the same efficiency of the metal removal for the re-used as for the fresh GRAs (Section D, Supporting Information and Figure S5). Upon this interesting result, it might be possible to sufficiently re-use the loaded bipolar electrodes several times without further treatment before the need to be recycled. By using the Hg/GRAs as working electrodes in a classical electrochemistry setup, Hg deposit can basically be re-dissolved in a small volume of electrolyte by electrochemical oxidation (stripping). This enrichment mechanism of Hg<sup>2+</sup> ions and regeneration of bare GRs for re-use will be a good recycling strategy. The small enriched volume of the mercury can be then employed in any other appropriate field.

Toward an eco-friendlier bipolar setup for Hg<sup>II</sup> removal, a last experiment has been performed over 8 h using a 0.1 mM NaCl instead of KNO<sub>3</sub> as a supporting electrolyte in the feeder electrode compartments. The result showed a UV/Vis spectrum for the collected solution similar to the one previously obtained using KNO<sub>3</sub> and for the same time duration (Figure S6). NaCl is an abundant material in nature and a normal component of every water supply and also found in human body, therefore, it is a very cheap material and also highly safe to be used for the water decontamination purposes.

## Conclusions

Mercury(II) removal from synthetic polluted water is proposed using the wireless bipolar electrochemistry technique. The work was performed using two different types of mercury salts, HgI<sub>2</sub> and HgCl<sub>2</sub>. As a 3D technique, the depollution process was achieved through direct electrodeposition of metal ions at the negative end of numerous graphite rods. By changing the applied potential, the rate of electrodeposition can be controlled. The removal efficiency increased as the number of GRs increased, and by occupying the bulk volume of the cell with GRAs the increase is much more significant as the active surface area increases. Within 15 h, a 98% of Hg<sup>2+</sup> ions were successfully removed, and a removal efficiency of 100% should be possible in principle with a longer time of electrodeposition. When there is a small amount of Hg<sup>2+</sup> ions, we can also compensate a less fast kinetic by increasing the applied potential so that a longer section of the graphite rod is polarized to a potential where electrodeposition of Hg<sup>2+</sup> ions can happen. That means a higher overall removal efficiency and a better chance to remove still these small concentrations in a reasonable time, however, this will be at the expense of energy consumption. The employed bipolar setup is straightforward and cheap, and the GRAs can be recycled upon availability of voltammetry technique. In addition, the method is a very efficient and green, even no supporting electrolyte is required to add to the water sample in the reaction part, except in the feeder electrode compartments, a limited amount (4 mL) of supporting electrolyte is used. Furthermore, as a wireless technique with no limitation in term of size and shape of the conductive substrates, it can be adapted for different scales and configurations such as in confined micro/nano channels where conventional electrochemistry cannot be used. A possible benefit could also be when using a flow through the system, that the electrodes are easily exchanged with fresh GRs without the need to stop the process and to replace feeder electrodes. On the other hand, a limited oxidation of the anodic pole of the GRs might also occur in parallel with oxygen gas evolution; however, this can also be the case with classical two electrodes electrochemical setup.

This work has been done with graphite rods as substrates, however, different other conductive materials can also be used. For example, gold and platinum are good candidates as they form amalgam with the electrodeposited Hg, but being very expensive prohibits their practical application. Though graphite rods coated with a thin layer of either metal or copper (cheap and also forms amalgam) at the cathodic pole might be a good option. The kinetic of metal removal can be further enhanced by employing porous bipolar substrates with a high surface area, which could have an advantage over the nano-materials since the latter might leakage into the water and cause health and environmental problems.<sup>[7]</sup> The method can be adapted to remove for example cadmium ( $E^0 = -0.40$  V vs. NHE) or zinc ( $E^0 = -0.76$  V vs. NHE) ions, however, with the latter we will lose Faraday efficiency due to the hydrogen gas evolution at the cathodic pole of the substrate in addition to zinc electrodeposition. It might also be interesting to remove other water

contaminants than metal ions using this approach if they are electrochemically active and have reduction potentials within the water stability window.

## Experimental Section

### Chemicals and materials

Chemicals were used as received and deionized water was used to prepare all solutions. GRs (2 mm diameter, from BAILE) were purchased from local market. Mercury(II) chloride ( $\geq 99.5\%$ ) chemical reagent grade obtained from UNI-CHEM. Mercury(II) iodide ( $\geq 99\%$ ) purchased from Fluka garantie. Potassium nitrate ( $\geq 99\%$ ) laboratory chemical was supplied by Alpha Chemika. Sodium chloride ( $\geq 99.5\%$ ) laboratory reagent, purchased from Thomas Baker.

### Electrodeposition of divalent mercury on graphite rods

The obtained GRs were manually cut into 5 mm long rods (Section A, Supporting Information) and used as bipolar electrodes in the setup. Electrodeposition of divalent mercury was first tested in a home-built cell similar to the one that has been reported previously,<sup>[22]</sup> except that a plastic bridge connected the polyethylene cuvettes together. The bridge serves as a reaction compartment where the bipolar electrodes are introduced. A GR held by a plastic mesh was positioned in the bridge and the three compartments of the bipolar cell were filled with 50 mM  $\text{HgCl}_2$  solution. The feeder electrodes (graphite strips) were positioned in the cuvettes with a 6 cm distance between them and the potential was applied.

### Bipolar setup for mercury(II) removal and electrochemical investigations

All investigations and metal ions removal experiments were performed in two similar homemade plastic cells composed of three compartments (Figure 2); a centered inner compartment and two outer compartments separated by a fixed reinforced proton exchange membranes (Nafion® perfluorinated membrane (N115) with a thickness of 0.13 mm from Ion Power). The cell was filled with deionized water 2 h prior to the experiment to allow the membranes to be hydrated. The anode and cathode (graphite strips) were positioned in the outer compartments of the cell with a distance of 5 cm between both electrodes. A solution of potassium nitrate was used in the two outer compartments, except for a last experiment as indicated in results and discussion section; sodium chloride solution was used. Synthetic polluted water with  $\text{Hg}^{2+}$  ions was put in the inner part of the cell. Plastic meshes were used to hold the GRs (Figure S1) in the polluted water in the bipolar cell. For each case, a sufficient voltage was applied between the feeder electrodes for a given period of time using a DC power supply from Rainworm® RS232 130 V.

The first set of experiments was carried out using mercury(II) iodide solution to investigate the influence of time at a given voltage, and the effect of different applied potentials on metal ions removal from the solution.

### Mercury(II) removal as a function of the number of the graphite rods, graphite rod arrays, and as a function of the time

In the second set of experiments, mercury(II) chloride solution was used to study the influence of different number of GRs and GRAs on the depollution process. Mercury(II) removal from 60.2  $\text{mg L}^{-1}$   $\text{HgCl}_2$  solution (12 mL) was shown as a function of the time and with each sample a corresponding blank experiment was run in parallel with exactly the same conditions except that pure water was used instead of mercury solution. Adsorption effect on the metal ions removal was also investigated.

### Characterization of Hg deposit/graphite rods and analytical techniques

After the bipolar metal electrodeposition, the GRAs were removed from the cell, washed several times with deionized water and dried at room temperature. The Hg/GRs were characterized by optical microscopy (DNT Digimicro Profi). The treated aqueous samples were recovered and the amount of  $\text{Hg}^{2+}$  ions was quantitatively measured based on UV/Vis spectrophotometry (Jenway 6800 double beam spectrophotometer (190–1100 nm)) (see Figure S2B and Figure S3B for the calibration curves of  $\text{HgI}_2$  and  $\text{HgCl}_2$ , respectively). The sample that has been treated for 15 h was characterized with Inductively Coupled Argon Plasma - Optical Emission Spectrometer (ICP-OES) (model iCAP 7000 from Thermo Fisher Scientific Inc.).

## Acknowledgements

Chemistry Department, Duhok University is acknowledged for the equipment. The author gratefully acknowledges Prof. Alexander Kuhn for the valuable discussion. New Standard Co., Ibrahim Khalil Border, Iraq is acknowledged for the ICP-OES measurement.

## Conflict of Interest

The author declares no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** bipolar electrochemistry · graphite bipolar electrode · heavy metal removal · mercury electrodeposition · mercury(II) removal

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Manuscript received: October 30, 2022

Revised manuscript received: November 11, 2022