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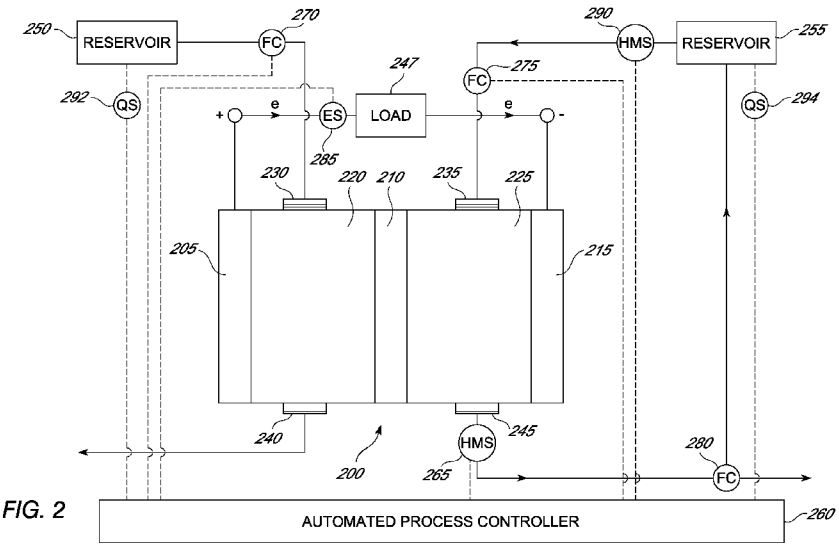


FIG. 2

(57) **Abstract**: Methods for treating wastewater containing one or more heavy metals are disclosed. The methods can include providing a fuel cell, the fuel cell including: an anode having a catalyst; a cathode electrically coupled to the anode; and an ion-exchange membrane disposed between the anode and the cathode. The methods may also include contacting a fuel to the anode to oxidize the fuel and contacting the wastewater to the cathode to reduce at least a portion of the heavy metals in the wastewater. The methods for treating wastewater may advantageously provide an efficient means for treating the wastewater while producing electricity. Systems for treating wastewater are also disclosed.

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SYSTEMS AND METHODS FOR TREATING HEAVY METAL WASTEWATER

BACKGROUND

[0001] Pollution of aqueous solutions and air is an expanding issue in the modern world. An ever-growing number of toxic pollutants are produced by industries, such as, for example, textile industries, chemical industries, pharmaceutical industries, pulp and paper industries, and food processing plants. The majority of these toxic pollutants are released within two primary fluid physical states: water and air. As the scope of water and air-borne pollutant production increases worldwide, the concerns over the risks imposed by these released pollutants on the environment also increases. Additionally, environmental regulations are requiring that these released fluid streams contain less and less pollutants. In fact, some treatment processes that were acceptable options at one point in time are now obsolete because more stringent treatment standards are required as new environmental regulations are implemented on the state and federal level

[0002] A variety of wastewater purification methods have been developed. Some techniques for removing the contaminants involve use of strong oxidants, which may themselves be hazardous. Other techniques remove the contaminant from the fluid but then release the contaminant into the air or produce a contaminant output, which must be disposed of.

SUMMARY

[0003] Some embodiments disclosed herein include a method for treating wastewater containing one or more heavy metals. The method may include: providing a fuel cell having an anode containing a catalyst, a cathode electrically coupled to the anode, and an ion-exchange membrane disposed between the anode and the cathode; contacting a fuel to the anode to oxidize the fuel; contacting the wastewater to the cathode to reduce at least a portion of the heavy metals in the wastewater. In some embodiments, an electrical current flows between the anode and the cathode.

[0004] Some embodiments disclosed herein include a system for treating wastewater. The system including: an anode having a catalyst; a cathode electrically coupled to the anode; an ion-exchange membrane disposed between the anode and the cathode; a first

input port configured to provide a fuel to the anode; a second input port configured to provide a wastewater to the cathode; and a heavy metal sensor configured to measure an amount of one or more heavy metal ions in the wastewater.

[0005] The foregoing summary is illustrative only and is not intended to be in any way limiting. In addition to the illustrative aspects, embodiments, and features described above, further aspects, embodiments, and features will become apparent by reference to the drawings and the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The foregoing and other features of the present disclosure will become more fully apparent from the following description and appended claims, taken in conjunction with the accompanying drawings. Understanding that these drawings depict only several embodiments in accordance with the disclosure and are not to be considered limiting of its scope, the disclosure will be described with additional specificity and detail through use of the accompanying drawings.

[0007] **FIGURE 1** is one example of a fuel cell that may be used in a method for treating wastewater that is within the scope of the present application.

[0008] **FIGURE 2** is one example of a system for treating wastewater that is within the scope of the present application.

DETAILED DESCRIPTION

[0009] In the following detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be used, and other changes may be made, without departing from the spirit or scope of the subject matter presented here. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the Figures, can be arranged, substituted, combined, and designed in a wide variety of different configurations, all of which are explicitly contemplated and make part of this disclosure.

[0010] Some embodiments disclosed herein include a method for treating wastewater containing one or more heavy metals. The method can include providing a fuel cell, the fuel cell including: an anode having a catalyst; a cathode electrically coupled to the anode; and an ion-exchange membrane disposed between the anode and the cathode. The method may also include contacting a fuel to the anode to oxidize the fuel and contacting the wastewater to the cathode to reduce at least a portion of the heavy metals in the wastewater. In some embodiments, an electrical current flows between the anode and the cathode. The method for treating wastewater may, in some embodiments, advantageously provide an efficient means for treating the wastewater while producing electricity. Also disclosed are systems for treating wastewater.

[0011] **FIGURE 1** is one example of a fuel cell that may be used in a method for treating wastewater that is within the scope of the present application. Fuel cell **100** includes anode **110**, cathode **120**, and ion-exchange membrane **130**. Anode **110** can include at least one catalyst **140** configured to catalyze oxidation of a fuel. First chamber **150** can be disposed between ion-exchange membrane **130** and anode **110**, and configured to receive at least one fuel that can contact anode **110**. Similarly, second chamber **160** can be disposed between ion-exchange membrane **130** and cathode **120**, and configured to receive wastewater that can contact cathode **120**. Anode **110** and cathode **120** may be electrically coupled together via load **190**. Fuel cell **100** can also include first input port **170** and second input port **175** configured to supply a fuel to first chamber **150** and wastewater to second chamber **160**, respectively. Fuel cell **100** may also optionally include first output port **180** and second output port **185** configured to receive an oxidized fuel that has contacted anode **110** and treated wastewater that has contacted cathode **120**, respectively.

[0012] Numerous fuel cell configurations are known in the art, and the present application is not limited to fuel cell **100** depicted in **FIGURE 1**. For example, the relative location of the anode, the ion-exchange membrane, and the first chamber configured to receive the oxidized fuel can vary so long as the fuel can contact the anode and an appropriate ion can be exchanged between the ion-exchange membrane and the fuel. Thus, in some embodiments, the anode may be disposed between the ion-exchange membrane and the first chamber configured to receiving the fuel. Similarly, the cathode, the ion-exchange membrane,

and the second chamber for receiving the wastewater can vary so long as the wastewater can contact the cathode and an appropriate ion can be exchanged between the ion-exchange membrane and the fuel. In some embodiments, the anode, the cathode, and the ion-exchange membrane are hot-pressed together in the fuel cell.

[0013] The anode (e.g. anode **110** depicted in **FIGURE 1**) is not particularly limited, and various anodes are known in the art. The anode may be composed of an inert material that generally does not react with fuel that is oxidized. The anode can be composed of, for example, one or more of carbon cloth, glassy carbon, graphite, nickel foam, and the like. The cathode (e.g. cathode **120** depicted in **FIGURE 1**) can similarly be composed of inert materials such as those described above with regard to the anode.

[0014] The anode may include at least one catalyst (e.g. catalyst **140** depicted in **FIGURE 1**) to catalyze oxidation of the fuel. In some embodiments, the catalyst is a metal or a metal oxide. Non-limiting examples of catalysts include Pt, Ru, Rh, Os, combinations thereof, or alloys thereof (e.g., Pt-Ru or Pt-Sn). The catalyst may vary depending on the fuel that is supplied to the anode. For example, Pt/C catalyst may be selected for oxidizing hydrogen, while Pt-Ru/C catalyst may be selected for oxidizing methanol. As another example, Pt-Ru/C catalyst may be selected for oxidizing ethanol. The amount of catalyst on the anode may be an amount effective to catalyze the fuel when contacting the anode. The amount of catalyst on the anode may be, for example, at least about 0.01 mg/cm^2; at least about 0.1 mg/cm^2; at least about 0.5 mg/cm^2; at least about 0.8 mg/cm^2; or at least about 1.5 mg/cm^2.

[0015] The methods for treating wastewater use catalysts rather than microorganisms (e.g. as typically found in a microbial fuel cell). In some embodiments, a majority of the fuel is catalytically oxidized using a metal or metal oxide catalyst. In some embodiments, the fuel cell is substantially free of microorganisms configured to oxidize the fuel.

[0016] The ion-exchange membrane is not particularly limited, and numerous ion-exchange membranes are known in the art. The ion-exchange membrane can be, for example, a cation-conducting membrane, an anion-conducting membrane, or a bipolar membrane. The bipolar membrane typically is a composite including a cation-conducting membrane and a anion-conducting membrane. When using the bipolar membrane, the cation-exchange

membrane typically faces the cathode, while the anion-exchange membrane faces the anode. These membranes can be commercially available. For example, NAFION is one example of a cation-exchange membrane commercially available from DuPont. As another example, FUMASEP FBM is one example of a bipolar membrane available from Fumatech. The ion-exchange membrane can be selected, in part, based on the fuel supplied to the anode. For example, a cation-exchange membrane may be selected for exchanging protons from oxidized hydrogen to the chamber containing the wastewater (e.g. second chamber **160** depicted in **FIGURE 1**).

[0017] The anode and the cathode can be electrically coupled together. Thus, in some embodiments, an electrical current may flow between the anode and the cathode during operation of the fuel cell. A load (e.g. load **190** depicted in **FIGURE 1**) may be electrically coupled between the anode and the cathode. The load can be, for example, a battery configured to be charged by the voltage between the anode and the cathode. As another example, the load may be a motor powered by the electrical current between the anode and the cathode. A power output from the fuel cell relative to an area of the anode may be, for example, at least about 10 W/m^2; at least about 25 W/m^2; the least about 50 W/m^2; the least 75 W/m^2; at least about 100 W/m^2; or least about 120 W/m^2.

[0018] The method can include supplying at least one fuel to contact the anode. For example, referring to **FIGURE 1**, the fuel may be supplied via first input port **170** into first chamber **150** so that the fuel can contact anode **110**. The fuel may be any material that can be oxidized when contacting the anode. Numerous fuels are known in the art for use in fuel cells, and any of these fuels are within the scope of the present application. A mixture of two or more different fuels may optionally be used. In some embodiments, the fuel can be a saturated or unsaturated, branched or unbranched hydrocarbon, such as methane, ethane, propylene, or isopentane. In some embodiments, the fuel can be an alcohol, such as methanol, ethanol, isopropanol, or glycerol. The alcohol may, for example, be an alkanol having about 1 to about 20 carbon atoms, or about 1 to about eight carbons. In some embodiments, the fuel is hydrogen. As noted above, the catalysts on the anode may vary depending upon the fuel supplied to the anode.

[0019] The method also includes contacting the wastewater having one or more heavy metals with the cathode. For example, referring to **FIGURE 1**, wastewater can be supplied via first input port **175** into second chamber **160** so that the wastewater can contact the cathode. The wastewater may contain one or more oxidized heavy metals. These heavy metals may, in some embodiments, be environmentally undesirable or toxic. Thus, in some embodiments, the methods disclosed herein may reduce the heavy metals into an environmentally friendlier or less toxic oxidation state. In some embodiments, the methods disclosed herein may reduce the heavy metals so that they separate from the wastewater (e.g., precipitate from the wastewater or deposit on the cathode). Non-limiting examples of heavy metals that may be included in the wastewater as an oxidized form are Cr, Cu, Cd, Hg, Au, and Ag. Examples of oxidized forms include, but are not limited to, Cu^{2+}, Au^{3+}, Au^{+}, Cr^{6+}, Ag^{+}, and Hg^{2+}. A plurality of heavy metals (e.g. two, three, or, or more heavy metals) may be present in the wastewater. The oxidized heavy metals in the wastewater may, for example, be in the form of a complex, a metal oxide, or a salt. Non-limiting examples of complexes that may be present in the wastewater include $Au(CN)_2^-$, $Ag(CN)_2^-$, $Ag(NH_3)_2^+$, AgCN, $Cu(NH_3)_4^{2+}$, $Cu(NH_3)_2^+$, $Cu(EDTA)^{2-}$, and $HgCl_4^{2+}$. Copper sulfate is one example of a salt form of a heavy metal that may be present in the wastewater.

[0020] The total amount of heavy metals in the wastewater before contacting the cathode can vary. The total amount of heavy metals in the wastewater before contacting the cathode can be, for example, at least about 1 ppb; at least about 100 ppb; at least about 1 ppm; at least about 5 ppm; at least about 10 ppm; at least about 0.01% by weight; or at least about 0.1% by weight. The total amount of heavy metals in the wastewater before contacting the cathode can be, for example, no more than about 5% by weight; no more than about 1% by weight; no more than about 0.1% by weight; or no more than about 500 ppm. In some embodiments, the total amount of heavy metals in the wastewater before contacting the cathode can be from about 1 ppb to about 5% by weight, or from about 1 ppm to about 0.1% by weight.

[0021] The amount of at least one heavy metal (e.g., one, two, three, or more of Cu^{2+}, Au^{3+}, Au^{+}, Cr^{6+}, Ag^{+}, or Hg^{2+}) in the wastewater before contacting the cathode can vary. The amount of any single heavy metal in the wastewater can be, for example, at least about 1

ppb; at least about 100 ppb; at least about 1 ppm; at least about 5 ppm; at least about 10 ppm; at least about 0.01% by weight; or at least about 0.1% by weight. The amount of any single heavy metal in the wastewater before contacting the cathode can be, for example, no more than about 5% by weight; no more than about 1% by weight; no more than about 0.1% by weight; or no more than about 500 ppm. In some embodiments, the amount of any single heavy metal in the wastewater before contacting the cathode can be from about 1 ppb to about 5% by weight, or from about 1 ppm to about 0.1% by weight.

[0022] The method may include, in some embodiments, contacting the fuel with the anode at about the same time as the wastewater contacts the cathode. Without being bound to any particular theory, it is believed that oxidizing the fuel produces an electrical current between the anode and the cathode, while the wastewater or fuel receives an ion from the ion-exchange membrane. This process can result in reducing the heavy metals in the wastewater. For example, Cr^{6+} may be reduced to Cr^{3+}, which is believed to exhibit lower toxicity. The chemical reaction when treating wastewater with Cr^{6+} and using methanol as the fuel may be:

$$\textbf{Cathode: } Cr_2O_4^{2-} + 8H^+ + 6e^- \rightarrow 2Cr^{3+} + 4H_2O$$

$$\textbf{Anode: } CH_3OH + OH^- \rightarrow CO_2 + 5H^+ + 6e^-$$

[0023] The wastewater can be any source of water having an undesirable amount of oxidized heavy metals. The wastewater can include, but is not limited to, electroplating waste, mining waste, silver plating waste, industrial chemical waste, metallurgy waste, textile manufacturing waste, leather processing waste, or pesticide manufacturing waste.

[0024] The fuel and wastewater may be processed in a batch process, a continuous process, or a combination of both a batch and a continuous process. For example, referring to **FIGURE 1**, a fixed volume of fuel may be disposed in first chamber **150**, and a fixed volume of wastewater may be disposed in second chamber **160**. The oxidation of the fuel and reduction of the wastewater can continue until the reaction is complete or when an amount of one or more heavy metals reaches acceptable levels. As another example, the fuel may continuously flow into first chamber **150** via first input port **170** and exit via first output port **180**. The wastewater may also continuously flow into second chamber **160** via second input port **175** and exit via second output port **185**. As another example, a fixed volume of

wastewater may be disposed in second chamber **160**, while a fuel continuously flows through first chamber **150**. The rate or volume of the fuel or wastewater being delivered into the fuel cell may vary according to numerous factors, such as size of the fuel cell, the type of fuel, and the contents of the wastewater (e.g., the amount of heavy metals in the wastewater).

[0025] The process may result in at least a portion of at least one heavy metal in the wastewater being reduced (e.g., one, two, three, or more of Cu^{2+}, Au^{3+}, Au^{+}, Cr^{6+}, Ag^{+}, or Hg^{2+} in the wastewater can be reduced). The amount of the at least one heavy metal in the wastewater that is reduced may be, for example, at least about 50% by weight; at least about 70% by weight; at least about 90% by weight; or at least about 95% by weight. In some embodiments, the amount of Cu^{2+} in the wastewater after contacting the cathode is no more than about 10 ppm, no more than about 1 ppm, or no more than about 1 ppb. In some embodiments, the amount of Au^{+} in the wastewater after contacting the cathode is no more than about 10 ppm, no more than about 1 ppm, or no more than about 1 ppb. In some embodiments, the amount of Au^{3+} in the wastewater after contacting the cathode is no more than about 10 ppm, no more than about 1 ppm, or no more than about 1 ppb. In some embodiments, the amount of Cr^{6+} in the wastewater after contacting the cathode is no more than about 10 ppm, no more than about 1 ppm, or no more than about 1 ppb. In some embodiments, the amount of Hg^{2+} in the wastewater after contacting the cathode is no more than about 10 ppm, no more than about 1 ppm, or no more than about 1 ppb.

[0026] The method may also optionally include measuring an amount of at least one of the heavy metals in the wastewater. The measurement may occur before the wastewater contacts the cathode, after the wastewater contacts the cathode, or at about the same time as the wastewater contacts the cathode. In some embodiments, the wastewater is maintained in contact with the cathode or within a chamber containing the cathode (e.g. second chamber **160** depicted in **FIGURE 1**) until an amount of at least one oxidized form of a heavy metal is below a predetermined amount. In some embodiments, the wastewater is recirculated into the chamber containing the cathode one or more times until an amount of at least one oxidized form of a heavy metal is below a predetermined amount.

[0027] The temperature of the fuel cell while treating the wastewater can have varying temperatures. The fuel cell may have a temperature of, for example, at least about -

5°C; at least about 10°C; at least about 20°C; at least about 30°C; or least about 40°C. The fuel cell may have a temperature of, for example, no more than about 50°C; no more than about 40°C; no more than about 30°C; no more than about 20°C; or no more than about 10°C. The methods of the present application may, in some embodiments, advantageously operate at a wide range of temperatures relative to those used with microbial fuel cells. Thus, for example, the temperature of the fuel cell may be less than about 20°C or more than about 30°C.

[0028] The method may optionally include harvesting at least a portion of the reduced metals produced by contacting the cathode. For example, Au^{+} may be reduced to elemental Au that deposits on the cathode. The Au can be removed from the cathode using, for example, leaching. As another example, Hg^{2+} may be reduced to elemental form and precipitate from the wastewater (e.g. precipitate as a powder). The precipitate may be collected by filtration, centrifugation, and the like. Although heavy metals may be harvested from the wastewater, in some embodiments, at least a portion of the reduced heavy metals remain in the wastewater after processing. In some embodiments, the method does not include harvesting a heavy metal that is reduced at the cathode.

[0029] At least one electrolyte may, in some embodiments, be combined with the fuel or the wastewater to improve ionic conductivity during processing. In some embodiments, both the fuel and the wastewater are combined with an electrolyte. Non-limiting examples of electrolytes that may be included with the fuel or the wastewater include H_2SO_4, H_3PO_4, KOH, Na_2SO_4, K_2SO_4, Na_2CO_3, K_2CO_3, and the like.

[0030] Some embodiments disclosed herein include a method of treating a sample suspected of containing one or more heavy metals. The method can include providing a fuel cell. The fuel cell may have any of the characteristics disclosed in the present application (e.g. the fuel cell can be fuel cell **100** as depicted in **FIGURE 1**). The method also includes contacting a fuel to the anode to oxidize the fuel, and contacting the sample to the cathode to reduce at least a portion of any heavy metals in the sample. The fuel can be any of those disclosed above. For example, the fuel can be an alkanol, such as methanol or ethanol.

[0031] The sample suspected of containing one or more heavy metal may be wastewater. In some embodiments, the wastewater can be at least one of electroplating waste,

mining waste, silver plating waste, industrial chemical waste, metallurgical waste, textile manufacturing waste, whether processing waste, or pesticide manufacturing waste. In some embodiments, an amount of at least one oxidized heavy metal can be measured in the sample after contacting the cathode. For example, an amount of at least one of Cu^{2+}, Au^{3+}, Au^{+}, Cr^{6+}, Ag^{+}, or Hg^{2+} (e.g., one, two, three, or more these oxidized heavy metals) can be measured in the sample after contacting the cathode.

[0032] Some embodiments disclosed herein include a system for treating wastewater. The system may, in some embodiments, be configured to perform any of the methods disclosed in the present application. **FIGURE 2** is one example of a system for treating wastewater that is within the scope of the present application. Although various components are shown for the system depicted in **FIGURE 2**, it will be appreciated that the systems within the scope of the present location may not include all of these components.

[0033] Fuel cell **200** can include generally the same components as those described above with respect to the fuel cell for the method of treating wastewater. Thus, fuel cell **200** includes anode **205**, ion-exchange membrane **210**, cathode **215**, first chamber **220**, second chamber **225**, first inlet port **230**, second inlet port **235**, first outlet port **240**, second outlet port **245**, and load **247**. These components may generally correspond to anode **110**, ion-exchange membrane **130**, cathode **120**, first chamber **150**, second chamber **160**, first inlet port **170**, second inlet port **175**, first outlet port **180**, second outlet port **185**, and load **190** depicted in **FIGURE 1**. Anode **205** can include a catalyst such as catalyst **140** depicted in **FIGURE 1** (not shown).

[0034] The system may include first reservoir **250** which is configured to contain the fuel and fluidly coupled to first input port **230**. The fuel contained within first reservoir **250** can be any of the fuels described in the present application with regard to the method for treating wastewater having heavy metals or samples suspected of containing heavy metals. For example, first reservoir **250** may contain methanol and be fluidly coupled to first inlet port **230** via a conduit (e.g., one or more pipes). Thus, the fuel can be stored and delivered to anode **205** at an appropriate time.

[0035] The system may include second reservoir **255** which is configured to contain the wastewater and fluidly coupled to second input port **235**. The wastewater

contained within second reservoir **255** can be any of the wastewaters described above with regard to the methods. For example, second reservoir **255** may contain electroplating waste having oxidized heavy metals and be fluidly coupled to second inlet port **235** via a conduit (e.g. one or more pipes). Thus, the wastewater can be stored and delivered to cathode **215** at an appropriate time.

[0036] The system can include at least one automated process controller **260**, which can be configured to execute instructions for treating the wastewater. In some embodiments, the automated process controller is configured to perform instructions for executing any of the methods for treating wastewater or treating a sample suspected of containing heavy metals disclosed in the present application. Automated process controller **260** can be in communication with the various components in the system to control treating the wastewater.

[0037] The system may include at least one heavy metal sensor **265** configured to measure an amount of one or more heavy metal ions in the wastewater. In some embodiments, heavy metal sensor **265** can be configured to measure an amount of one or more heavy metal ions in the treated wastewater that exits second outlet port **245**. In some embodiments, heavy metal sensor **265** can be configured to measure an amount of at least one of Cu^{2+}, Au^{3+}, Au^{+}, Cr^{6+}, Ag^{+}, or Hg^{2+} (e.g., one, two, three, or more of these oxidized heavy metals). Heavy metal sensor **265** can be, for example, a fluorometer, a spectrophotometer, and the like. Heavy metal sensor **265** may be in communication with automated process controller **260** and provide measurement results for the heavy metals. Automated process controller **260** may adjust certain operating conditions based on these measurements.

[0038] The system also includes first flow control device **270** fluidly coupled to first input port **230** and configured to adjust the flow of the fuel through first input port **230** (e.g., flow from first reservoir **250** to second input port **230**). Automated process controller **260** may be in communication with first flow control device **270** and can adjust the flow of fuel to anode **205**. For example, automated process controller **260** may receive measurement data from heavy metal sensor **265** indicating an amount of one or more heavy metals is above a pre-determined threshold. Automated process controller **260** may increase the flow of fuel from first reservoir **250** to first input port **230** using first flow control device **270**, which may

increase the rate that heavy metals are reduced in the fuel cell. As another example, the flow of fuel to the anode may be decreased when the amount of heavy metals is below a pre-determined threshold. First flow control device **270** may be, for example, a valve or a pump.

[0039] Second flow control device **275** may be fluidly coupled to second input port **235** and configured to adjust a flow of the wastewater through second input port **235** (e.g., flow from second reservoir **255** to second input port **235**). Automated process controller **260** may be in communication with second flow control device **275** and can adjust the flow of wastewater to cathode **215**. For example, automated process controller **260** may receive measurement data from heavy metal sensor **265** indicating an amount of one or more heavy metals is above a pre-determined threshold. Automated process controller **260** may decrease the flow of wastewater from second reservoir **255** to second input port **235** using second flow control device **275**, which may increase exposure time of the wastewater to the cathode to further lower the amount of one or more oxidized heavy metals in the wastewater. Second flow control device **275** may be, for example, a valve or a pump.

[0040] Third flow control device **280** may be fluidly coupled between second outlet port **245** and second input port **235**. Third flow control device **280** can be configured to adjust the flow of the treated wastewater that is recycled for further treatment. As shown in **FIGURE 2**, third flow control device **280** can be configured to adjust a flow of treated wastewater from second output port **245** to second reservoir **255**. The amount of treated wastewater sent to second reservoir **255** may be controlled by automated process controller **260** in communication with third flow control device **280**. As an example, automated process controller **260** may receive measurement data from heavy metal sensor **265** indicating an amount of one or more heavy metals is above a pre-determined threshold. Automated process controller **260** may increase a flow of the treated wastewater to second reservoir **255** for further treatment. Also, when the amount of one or more oxidized heavy metals is below a threshold, the flow to second reservoir **255** can be decreased or discontinued. Although **FIGURE 2** shows third flow control device **280** fluidly coupled to second reservoir **255**, third flow control device **280** can be fluidly coupled to second input port **235** in a configuration that bypasses second reservoir **255** (not shown). For example, a conduit may directly connect

third flow control device **280** and second input port **235**. Third flow control device **280** may be, for example, a valve or a pump.

[0041] The system may also include electrical sensor **285** electrically coupled to anode **205** and cathode **215**. Electrical sensor **285** can be configured to measure at least one of a voltage or a current between anode **205** and cathode **215**. Electrical sensor **285** may be in communication with automated process controller **260** and provide measurement results for the electric current between anode **205** and cathode **215**. Automated process controller **260** may adjust certain operating conditions for the fuel cell based on these measurements. For example, automated process controller **260** may decrease a flow of wastewater to cathode **215** using second flow control device **275** when a current or voltage is below a pre-determined threshold. As another example, automated process controller **260** may increase a flow of fuel to anode **205** using first flow control device **270** when a current or voltage is below a pre-determined threshold. Electrical sensor **285** can be, for example, a voltmeter or an ammeter.

[0042] Second heavy metal sensor **290** can be configured to measure an amount of one or more oxidized heavy metals in the wastewater received at second input port **275**. For example, second heavy metal sensor **290** can be fluidly coupled between second reservoir **255** and second input port **235**. Second heavy metal sensor **290** can be, for example, a fluorometer, a spectrophotometer, and the like. Second heavy metal sensor **290** may be in communication with automated process controller **260** and provide measurement results for the heavy metals. Automated process controller **260** may adjust certain operating conditions based on these measurements. For example, automated process controller **260** may decrease a flow of wastewater to cathode **215** when an amount of one or more heavy metals is above a pre-determined threshold. Similarly, automated process controller **260** may increase a flow of wastewater to cathode **215** when an amount of one or more heavy metals is below a pre-determined threshold. As another example, automated process controller **260** may increase a flow of fuel to anode **205** when an amount of one or more heavy metals is above a pre-determined threshold. Similarly, automated process controller **260** may decrease a flow of fuel to anode **205** when an amount of one or more heavy metals in the wastewater is below a pre-determined threshold.

[0043] The system can also include first quantity sensor **292** configured to measure an amount of fuel in first reservoir **250**. Automated process controller **260** may receive measurement results from first quantity sensor **292** and can be configured to adjust the process accordingly. For example, automated process controller **260** may stop processing wastewater when an amount of fuel in the reservoir is below a pre-determined threshold. First quantity sensor **292** can be, for example, a weighing device, a pressure sensor, or a volumetric sensor.

[0044] The system can also include second quantity sensor **294** configured to measure an amount of wastewater in second reservoir **255**. Automated process controller **260** may receive measurement results from second quantity sensor **292** and can be configured to adjust the process accordingly. For example, automated process controller **260** may stop processing wastewater when an amount of fuel in the reservoir is at or below a pre-determined threshold. As another example, automated process controller **260** may stop or decrease a flow of treated wastewater to second reservoir **255** using third flow control device **280** when an amount of wastewater is above a pre-determined threshold (e.g., when second reservoir **255** is full or almost full). Second quantity sensor **294** can be, for example, a weighing device, a pressure sensor, or a volumetric sensor.

[0045] Automated process controller **260** may optionally be coupled to a display screen (not shown) for displaying various characteristics of the process. Non-limiting examples for the display screen include a CRT monitor, an LCD screen, a touch-screen, an LED display, and the like. Automated process controller **260** may display characteristics, such as an amount of one or more heavy metals in the wastewater before or after contacting the cathode, a flow rate of fuel to the anode, a flow rate of wastewater to the cathode, an amount of fuel in the first reservoir, an amount of wastewater in the second reservoir, a current or voltage between the anode and the cathode, and the like. Automated process controller **260** may also be optionally coupled to an input device, such as a keyboard, mouse, touchscreen, etc. The input device may allow a user to adjust various settings or variables for automated process controller **260** that modifies the how the system performs the method for processing organic material. Automated process controller **260** can include any type of a microprocessor (μP), a microcontroller (μC), a digital signal processor (DSP), or any

combination thereof. Automated process controller **260** may also include system memory, such as any type of volatile memory (such as RAM), non-volatile memory (such as ROM, flash memory, etc.), or any combination thereof. The system memory may store instructions for performing the methods disclosed herein.

[0046] The systems and methods described in connection with the embodiments disclosed herein may be embodied directly in hardware, in a software module executed by a processor, or in a combination of the two. A software module may reside in RAM memory, flash memory, ROM memory, EPROM memory, EEPROM memory, registers, hard disk, a removable disk, a CD-ROM, or any other form of storage medium known in the art. An exemplary storage medium is coupled to the processor such the processor can read information from, and write information to, the storage medium. In the alternative, the storage medium may be integral to the processor. The processor and the storage medium may reside in an ASIC. The ASIC may reside in a user terminal. In the alternative, the processor and the storage medium may reside as discrete components in a user terminal.

[0047] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to volume of wastewater can be received in the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0048] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (e.g., bodies of the appended claims) are generally intended as "open" terms (e.g., the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or

"an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (e.g., “a” and/or “an” should be interpreted to mean “at least one” or “one or more”); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (e.g., the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to “at least one of A, B, and C, etc.” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., “ a system having at least one of A, B, and C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to “at least one of A, B, or C, etc.” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., “ a system having at least one of A, B, or C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase “A or B” will be understood to include the possibilities of “A” or “B” or “A and B.”

[0049] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0050] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible sub-ranges and combinations of sub-ranges thereof. Any listed range can

be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," and the like include the number recited and refer to ranges which can be subsequently broken down into sub-ranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 articles refers to groups having 1, 2, or 3 articles. Similarly, a group having 1-5 articles refers to groups having 1, 2, 3, 4, or 5 articles, and so forth.

[0051] While various aspects and embodiments have been disclosed herein, other aspects and embodiments will be apparent to those skilled in the art. The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting, with the true scope and spirit being indicated by the following claims.

[0052] One skilled in the art will appreciate that, for this and other processes and methods disclosed herein, the functions performed in the processes and methods may be implemented in differing order. Furthermore, the outlined steps and operations are only provided as examples, and some of the steps and operations may be optional, combined into fewer steps and operations, or expanded into additional steps and operations without detracting from the essence of the disclosed embodiments.

EXAMPLES

[0053] Additional embodiments are disclosed in further detail, which are not intended in any way to limit the scope of the claims.

Example 1

[0054] An electrochemical cell was constructed as shown in **FIGURE 1**. A square commercial carbon cloth having an area of 0.5 cm^2 and coated with 10% Pt/C catalyst with Pt load of 1 mg/cm^2 was used as the anode. A square graphite sheet with an area of 1 cm^2 was used as cathode. The anode chamber contained 20 mL mixture of 20 mol/L methanol and 0.2 mol/L sodium hydroxide solution, whereas the cathode chamber was filled with 20 mL heavy

metal wastewater containing 0.1 mol/L (5200 mg/L) of hexavalent chromium ions and 0.1M sodium sulphate. The cathode chamber and the anode chamber were separated by a bipolar membrane. The positive side of the membrane faces to the cathode and the negative side of the membrane faces to the anode. The electrochemical cell can supply electric power outwards. When connected to an external 50 ohm resistor, the voltage across the resistor was 0.557 V. Based on the area of the anode, the power density of the electricity output is calculated to be 124 W/m^2. The hexavalent chromium ions were reduced to low toxic trivalent chromium. The concentration of hexavalent chromium ions was monitored by spectrophotometry using diphenylcarbazide (Chinese National Standard GB7467-87) and was about 1 ppm.

[0055] These results demonstrate successfully reducing toxic hexavalent chromium ions to trivalent chromium having significantly lower toxicity.

Example 2

[0056] The process in Example 1 was repeated except that 2 mg/cm^2 of 20% Pt/C catalyst was coated on the anode. The voltage across the resistor was 0.599 V, while the power density was 144 W/m^2. The final concentration of hexavalent chromium ions was about 1 ppm.

[0057] These results demonstrate that a greater amount of catalyst on the anode can improve power output while still successfully reducing toxic hexavalent chromium ions to trivalent chromium having significantly lower toxicity.

Example 3

[0058] The process in Example 1 was repeated except that 0.1 mol/L (6400 mg/L) copper sulfate was supplied to the cathode rather than hexavalent chromium. When a 500 ohm resistor was connected to the anode the cathode, the voltage across the resistor was 0.7 V, while the power density was 20 W/m^2. The copper ions were reduced to elemental copper that deposited on the cathode. The concentration of copper ions was monitored using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) and was about 1 ppm. These results demonstrate toxic copper ions can be successfully removed.

Example 4

[0059] The process in Example 3 was repeated except that 2 mg/cm^2 of 20% Pt/C catalyst was coated on the anode. When a 75 ohm resistor was connected to the anode the cathode, the voltage across the resistor was 0.321 V, while the power density is 27 W/m^2. The copper ions were completely reduced to elemental copper that deposited on the cathode. The concentration of copper ions was about 1 ppm.

[0060] These results demonstrate that a greater amount of catalyst on the anode can improve power output while still successfully removing toxic copper ions from the wastewater.

WHAT IS CLAIMED IS:

1. A method for treating wastewater containing one or more heavy metals, the method comprising:

providing a fuel cell comprising:

an anode comprising a catalyst;

a cathode electrically coupled to the anode; and

an ion-exchange membrane disposed between the anode and the cathode;

contacting a fuel to the anode to oxidize the fuel;

contacting the wastewater to the cathode to reduce at least a portion of the heavy metals in the wastewater, wherein an electrical current flows between the anode and the cathode.

2. The method of Claim 1, wherein the catalyst comprises at least one of Pt, Ru, Rh, Os, or an alloy thereof.

3. The method of any one of Claims 1-2, wherein the catalyst comprises at least one of Pt-Ru or Pt-Sn.

4. The method of any one of Claims 1-3, wherein the fuel comprises at least one of a hydrocarbon, an alcohol, or hydrogen.

5. The method of any one of Claims 1-4, wherein the fuel comprises at least one of ethanol, methanol, isopropanol, or glycerol.

6. The method of any one of Claims 1-5, wherein the heavy metals comprise at least one oxidized form of Cr, Cu, Cd, Hg, Au, or Ag.

7. The method of Claim 6, wherein the heavy metals comprise at least one of Cu^{2+}, Au^{3+}, Au^{+}, Cr^{6+}, Ag^{+}, or Hg^{2+}.

8. The method of any one of Claims 1-7, wherein the wastewater comprises at least about 1 ppm of the heavy metals.

9. The method of any one of Claims 1-8, wherein at least about 50% by weight of at least one of the heavy metals are reduced in the wastewater.

10. The method of Claim 9, wherein at least about 50% by weight of Cu^{2+}, Au^{3+}, Au^{+}, Cr^{6+}, Ag^{+}, or Hg^{2+} is reduced in the wastewater.

11. The method of any one of Claims 1-10, wherein a load is electrically coupled between the anode and the cathode.

12. The method of any one of Claims 1-11, wherein a power output from the fuel cell relative to an area of the anode is at least about 10 W/m^2.

13. The method of any one of Claims 1-12, wherein the wastewater comprises at least one of electroplating waste, mining waste, silver plating waste, industrial chemical waste, metallurgy waste, textile manufacturing waste, leather processing waste, or pesticide manufacturing waste.

14. The method of any one of Claims 1-13, wherein the fuel cell has a temperature of at least about -5° C.

15. The method of any one of Claims 1-13, wherein the fuel has a temperature of no more than about 50° C.

16. The method of any one of Claims 1-15, where the fuel cell is substantially free of microorganisms configured to oxidize the fuel.

17. The method of any one of Claims 1-16, wherein the ion exchange membrane is a cation exchange membrane, anion exchange membrane, or a bipolar membrane.

18. The method of any one of Claims 1-17, further comprising measuring an amount of at least one of the heavy metals in the wastewater.

19. The method of any one of Claims 1-18, further comprising harvesting at least a portion of the heavy metals reduced by the cathode.

20. A method of treating a sample suspected of containing one or more heavy metals, the method comprising:

providing a fuel cell comprising:

an anode comprising a catalyst;

a cathode electrically coupled to the anode; and

an ion-exchange membrane disposed between the anode and the cathode;

contacting a fuel to the anode to oxidize the fuel; and

contacting the sample to the cathode to reduce at least a portion of any heavy metals in the sample.

21. The method of Claim 20, wherein the sample is wastewater.

22. The method of Claim 21, wherein the wastewater comprises at least one of electroplating waste, mining waste, silver plating waste, industrial chemical waste, metallurgical waste, textile manufacturing waste, leather processing waste, or pesticide manufacturing waste.

23. A system for treating wastewater, the system comprising:

an anode comprising a catalyst;

a cathode electrically coupled to the anode;

an ion-exchange membrane disposed between the anode and the cathode;

a first input port configured to provide a fuel to the anode;

a second input port configured to provide a wastewater to the cathode; and

a heavy metal sensor configured to measure an amount of one or more heavy metal ions in the wastewater.

24. The system of Claim 23, further comprising a first output port configured to receive oxidized fuel from the anode.

25. The system of any one of Claims 23-24, further comprising a second output port configured to receive the wastewater after the wastewater contacts the cathode.

26. The system of Claim 25, wherein the heavy metal sensor is configured to measure an amount of one or more heavy metal ions in the wastewater received by the second output port.

27. The system of any one of Claims 23-26, further comprising a second heavy metal sensor configured to measure an amount of one or more heavy metal ions in the wastewater provided by the second input port.

28. The system of any one of Claims 23-27, further comprising a first reservoir fluidly coupled to the first input port, the first reservoir containing the fuel.

29. The system of any one of Claims 23-28, wherein the fuel comprises at least one of a hydrocarbon, an alcohol, or hydrogen.

30. The system of any one of Claims 23-29, further comprising a second reservoir fluidly coupled to the second input port, the second reservoir containing the wastewater.

31. The system of any one of Claims 23-30, wherein the wastewater comprises at least one of electroplating waste, mining waste, silver plating waste, industrial chemical waste, metallurgy waste, textile manufacturing waste, leather processing waste, or pesticide manufacturing waste.

32. The system of any one of Claims 23-31, further comprising a first flow control device fluidly coupled to the first input port, the first flow control device configured to adjust a flow of the fuel through the first input port.

33. The system of any one of Claims 23-32, further comprising a second flow control device fluidly coupled to the second input port, the second flow control device configured to adjust a flow of the wastewater through the second input port.

34. The system of any one of Claims 23-33, wherein the second output port is fluidly coupled to the second input port via a third flow control device, the third flow control configured to adjust a flow of the wastewater from the second output port to the second input port.

35. The system of any one of Claims 23-34, further comprising a load electrically coupled between the anode and the cathode.

36. The system of any one of Claims 23-35, further comprising an electrical sensor electrically coupled to the anode and the cathode, the electrical sensor configured to measure at least one of a voltage or a current between the anode and the cathode.

37. The system of Claims 35, further comprising an automated process controller configured to execute instructions for treating the wastewater, the automated process controller is in communication with at least one of the first flow control device, the second flow control device, the third flow control device, the first heavy metal sensor, the second heavy metal sensor, or the electrical sensor.

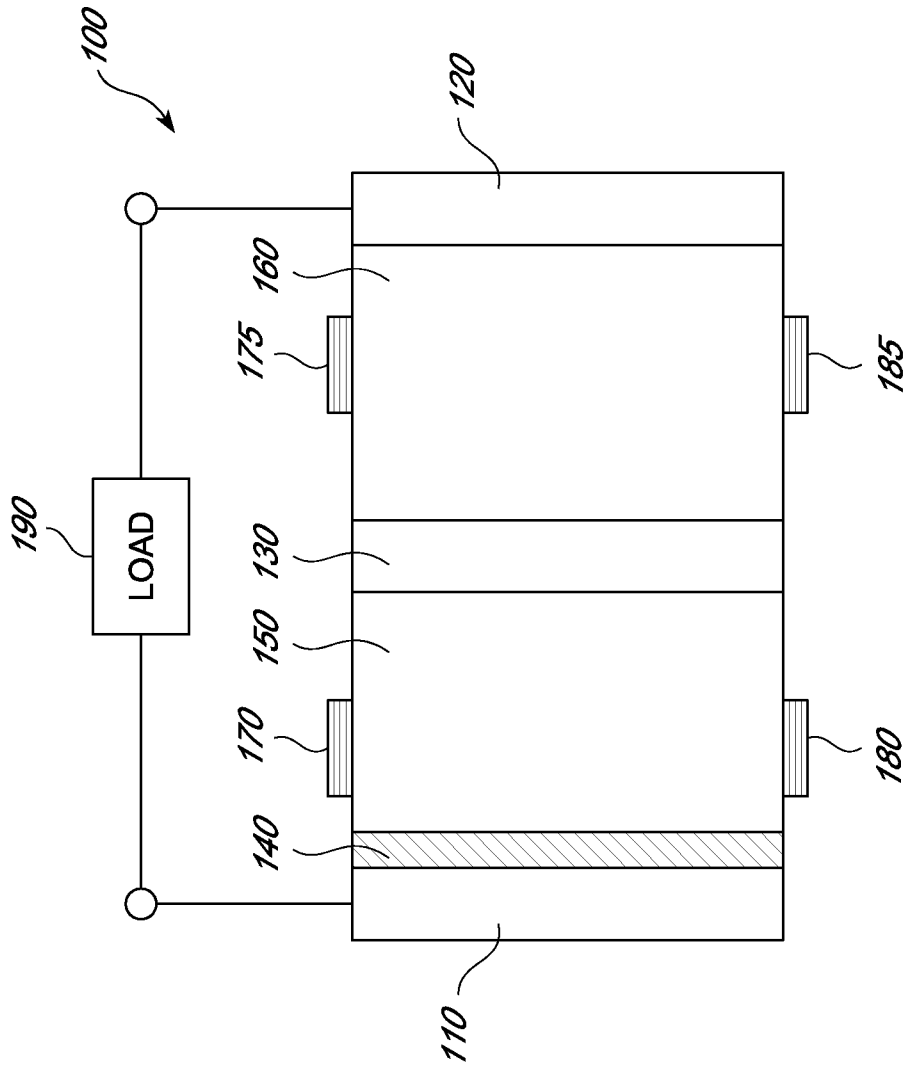


FIG. 1

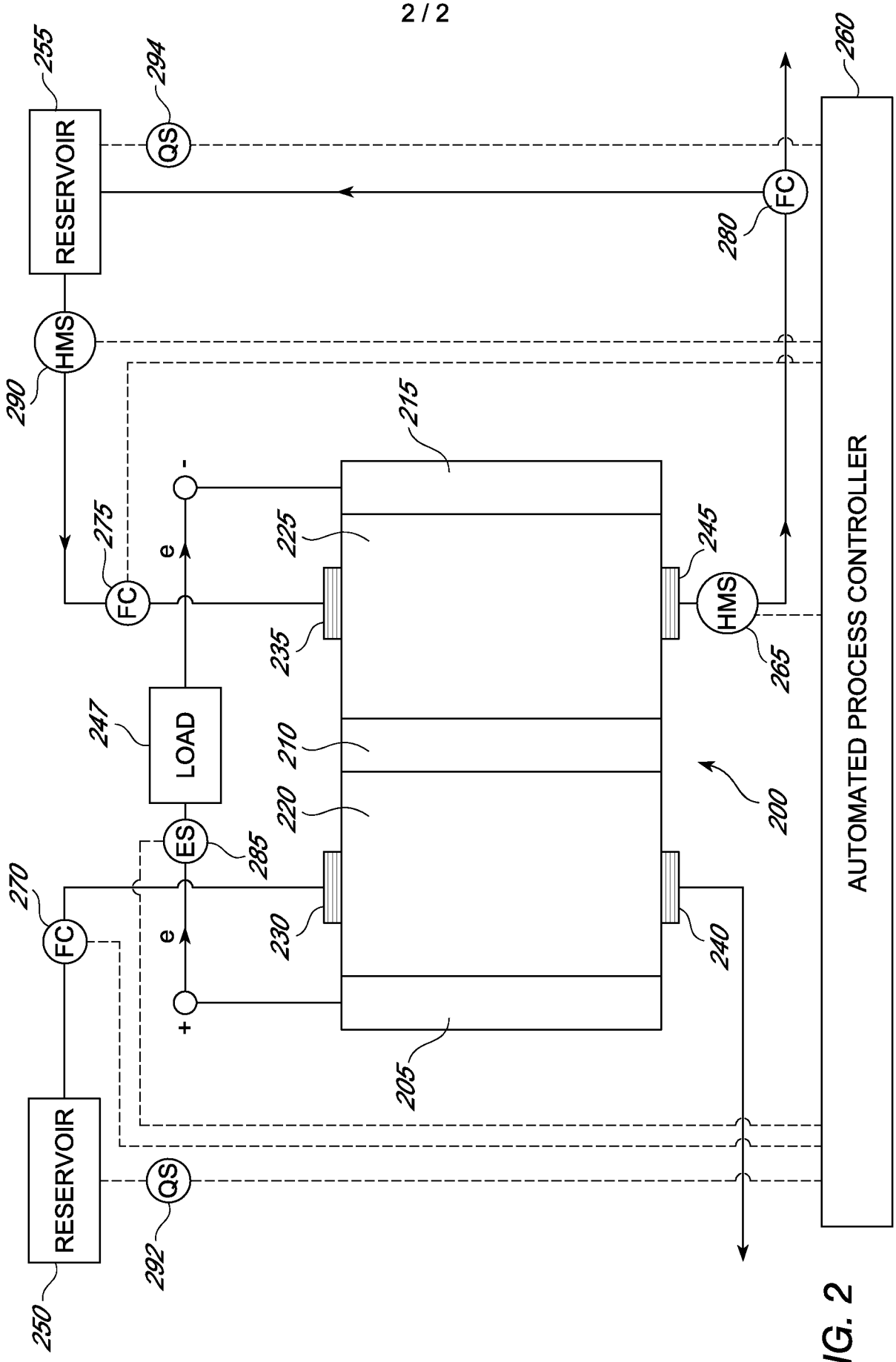

RESERVOIR
255
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215
-
275
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225
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HMS
235
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247
LOAD
210
220
200
ES
285
270
FC
e
230
240
+
205
AUTOMATED PROCESS CONTROLLER
RESERVOIR
QS
292
250

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/078809

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC:H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNKI; CNPAT; WPI; EPODOC: fuel? 2d cell?, wastewater, heavy 2d metal+, cataly+, ion d exchang+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 101710625 A (PEKING UNIVERSITY SHENZHEN GRADUATE SCHOOL) 19 May 2010 (19.05.2010) paragraphs [0021]-[0058], figures 1-2	1-15,17-37
Y	US 2006099482 A1 (SCOTT, Keith et al.) 11 May 2006 (11.05.2006) paragraphs [0049]- [0102], figures 1-5	1-15,17-37
A	CN 102324542 A (XI'AN JIAOTONG UNIVERSITY) 18 Jan. 2012 (18.01.2012) the whole document	1-37

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 Mar. 2013 (28.03.2013)	**25 Apr. 2013 (25.04.2013)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer ZHAO, Shixin Telephone No. (86-10)62413994

Form PCT/ISA /210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2012/078809

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 101710625 A	19.05.2010	CN 101710625B	25.07.2012
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		KR 20050083660 A	26.08.2005
		WO 2004021486 A3	24.03.2005
CN 102324542 A	18.01.2012	None	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/078809

CLASSIFICATION OF SUBJECT MATTER

H01M8/06 (2006.01) i
H01M8/08 (2006.01) i