

A method and system for heavy metal immobilization

Technical Field

The present invention relates to a method and system for heavy metal immobilization.

5 Background

Due to increased industrial activity, many rivers, lakes, sea, other water sources and land are contaminated by toxic organic substances and heavy metals due to dumping. The contamination of water bodies and land posts high risks and hazards to human health and the environment.

- 10 General organic contaminants in soil include polyaromatic halides (PAHs), organophosphate pesticides (OPPs), organochloride pesticides (OCPs), polychlorinated biphenols (PCBs), phthalic acid esters (PAEs), just to name a few. These may include heavy metal contaminants.

- Most industrial waste treatment methods seek to remove or immobilize the heavy metal
15 contaminants. Removal methods may include washing and adsorption, electrochemical accumulation via electrophoresis, chelating, and precipitation. Immobilization methods may include adsorption, chelating, precipitation, bioaccumulation, and phytomediation. However, these methods often result in the leaching of the heavy metals over time and are associated with high cost due to solid-liquid separation, waste water treatment and
20 the reagents used in the treatment methods.

There is therefore a need for an improved method for heavy metal immobilization.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved method and system for heavy metal immobilization.

- 25 In general terms, the present invention relates to a simple method of immobilizing heavy metal in organic-containing media. The method is easily scalable. The end product of the method may also be used for various applications, such as fertilizers and construction materials. Further, the method is a fast, efficient and green method. The method also enables the media to be converted into biochar, which is free of any
30 biohazards, making it a useful and environmentally friendly end product.

According to a first aspect, the present invention provides a method for heavy metal immobilization, the method comprising:

- mixing organic-containing media comprising heavy metal with at least one additive to form a mixture; and
- 5 - torrefying the mixture to form biochar, wherein the biochar immobilizes the heavy metal.

The organic-containing media may be any suitable organic-containing media that comprises heavy metal.

- 10 According to a particular aspect, the torrefying may be under suitable conditions. For example, the torrefying may comprise torrefying in the presence of inert gas. The torrefying may be at a suitable temperature for the purposes of the present invention. For example, the torrefying may be at a temperature of 1-500°C.

The method may further comprise treating flue gas produced during the torrefying.

- 15 According to a particular aspect, the method may further comprise drying the mixture prior to the torrefying. The drying may be under suitable conditions. For example, the drying may comprise drying in the presence of inert gas. In particular, the drying may comprise drying at a suitable temperature. For example, the temperature may be 1-280°C.

- 20 According to a particular aspect, the organic-containing media may comprise ≥ 25 weight % organic content. In particular, when the organic-containing media comprises ≥ 25 weight % organic content, the at least one additive may comprise a reducing agent. The at least one additive may be any suitable reducing agent. For example, the at least one additive may be, but not limited to: sodium borohydride hydrazine,
- 25 aluminium powder, LiAlH_4 , or a mixture thereof.

- According to a particular aspect, the organic-containing media may comprise less than 25 weight % organic content. In particular, when the organic-containing media comprises less than 25 weight % organic content, the at least one additive may comprise an inorganic additive. The at least one additive may comprise any suitable
- 30 inorganic additive. For example, the at least one additive may comprise, but not limited

to: lime, limestone, FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , aluminium powder, iron powder, FeOOH , Fe_2O_3 , MgCO_3 , $\text{MgCa}(\text{CO}_3)_2$, NaOH , KOH , phosphate, monohydrogenphosphate, dihydrogenphosphate, rock phosphate, phosphoric acid, polyphosphate, hydroxyapatite, milorganite, bentonite, kaolinite, zeolite, manganese oxide, iron oxide,
5 or a mixture thereof.

The method may further comprise calcinating the biochar following the torrefying to form calcinated material. The calcinating may be under suitable conditions. For example, the calcinating may comprise calcinating in an oxidising atmosphere. In particular, the calcinating may comprise calcinating at a suitable temperature. For
10 example, the temperature may be 600-1200°C.

The method may further comprise treating flue gas produced during the calcinating.

The method may further comprise cooling the biochar following the torrefying and/or cooling the calcinated material.

According to a particular aspect, the method may further comprise:

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- mixing the biochar with at least one further additive to form a biochar mixture;
and
 - molding the biochar mixture,

wherein the mixing and the molding is prior to the calcinating.

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The at least one further additive may be any suitable additive. For example, the at least one further additive may comprise, but is not limited to: clay, sand, stone, fly ash, coal ash, furnace slag, incineration bottom ash, construction waste, egg shell, or a mixture thereof.

25 According to a second aspect, the present invention provides a system for heavy metal immobilization, the system comprising:

- an inlet for receiving organic-containing media comprising heavy metal and at least one additive;
- a mixing chamber coupled to the inlet for mixing the organic-containing
30 media comprising heavy metal and the at least one additive; and

- a torrefaction chamber for torrefying a mixture formed in the mixing chamber to form biochar.

The torrefaction chamber may comprise an inlet for receiving an inert gas.

- 5 The system may further comprise a drying chamber for drying the mixture formed in the mixing chamber.

According to a particular aspect, the system may further comprise a calcination chamber for calcinating biochar formed in the torrefaction chamber. The calcination chamber may comprise an inlet for receiving air.

- 10 The system may further comprise a heat source for heating the torrefaction chamber, the drying chamber and/or the calcination chamber.

- According to a particular aspect, the system may further comprise a flue gas treatment system in fluid communication with the torrefaction chamber and/or the calcination chamber for treating flue gas from the torrefaction chamber and/or calcination chamber.
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The system may further comprise a collection chamber for collecting the formed biochar and/or the calcinated material.

Brief Description of the Drawings

- In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:
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Figure 1 shows a schematic representation of a system according to one embodiment of the present invention;

- 25 Figure 2 shows a sealing system according to one embodiment of the present invention;

Figure 3 shows a schematic representation of a system according to one embodiment of the present invention;

Figure 4 shows the thermal gravity analysis (TGA) graph of the dried and grinded sample in which TGA was conducted in air and the weight loss was 16.5 wt. %; and

Figure 5 shows the thermal gravity analysis (TGA) graph of the dried and grinded sample in which TGA was conducted in purified nitrogen and the weight loss was 14.7 wt. %.

Detailed Description

As explained above, there is a need for an improved method and system for heavy metal immobilization.

In general terms, the invention relates to a method and system for immobilizing heavy metals in organic-containing media. The method of the present invention forms biochar which adsorbs and immobilizes either reduced zero valence heavy metals or precipitated heavy metal salts. The method of the present invention is a simple method which is able to convert contaminated organic-containing media into useful and beneficial products such as fertilizers and construction material. With the method of the present invention, the heavy metals are immobilised such that there is no leaching of the heavy metals even when the products of the method are used in further applications. This makes the method an environmentally friendly method.

The system of the present invention is a simple system which enables organic-containing media comprising heavy metals to be treated and converted into biochar-containing material which may then be used in further applications. The system also enables a rapid and green treatment of organic-containing media in order to immobilize the heavy metals comprised within the organic-containing media. With the system of the present invention, the heavy metal immobilization can be carried out on site, thus saving time and cost in transporting the organic-containing media to another location to carry out the heavy metal immobilization.

According to a first aspect, the present invention provides a method for heavy metal immobilization, the method comprising:

- mixing organic-containing media comprising heavy metal with at least one additive to form a mixture; and

- torrefying the mixture to form biochar, wherein the biochar immobilizes the heavy metal.

The organic-containing media may be any suitable organic-containing media that comprises heavy metal. In particular, the organic-containing media may comprise soil, sludge and/or solid waste. The organic-containing media may be industrial waste comprising heavy metals or hazardous waste comprising heavy metals. For example, the organic-containing media may comprise river sludge, lake sludge, pond sludge, sea sludge, sand, soil, agriculture soil, waste water treatment sludge, activated sludge, or any media with heavy metal contamination.

For the purposes of the present invention, heavy metal may be defined as any heavy metal which may be considered toxic or hazardous to life form. For example, to animals, including humans, microorganisms, or plants. Heavy metals may comprise, but is not limited to, metallic ions, metallic compounds, or metallic compound anions. Examples of heavy metals include, but is not limited to, antimony, arsenic, cadmium, chromium, cobalt, copper, gallium, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, silver, palladium, platinum, selenium, thallium, tin, tungsten, uranium, vanadium and zinc.

The mixing may comprise mixing the organic-containing media comprising heavy metals with any suitable additive to form a mixture. For example, the additive may be a reducing agent and/or an inorganic additive.

According to a particular aspect, the organic-containing media comprising heavy metals may comprise ≥ 25 weight % organic content. In particular, when the organic-containing media comprises ≥ 25 weight % organic content, the at least one additive may comprise a reducing agent. The at least one additive may be any suitable reducing agent. For example, the at least one additive may be, but not limited to: sodium borohydride, hydrazine, aluminium powder, LiAlH_4 , or a mixture thereof. In particular, the mixing may comprise reducing the heavy metal ions to zero valence metals.

According to a particular aspect, the organic-containing media may comprise less than 25 weight % organic content. In particular, when the organic-containing media comprises less than 25 weight % organic content, the at least one additive may

comprise an inorganic additive. The at least one additive may comprise any suitable inorganic additive. For example, the at least one additive may comprise, but not limited to: lime, limestone, FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , aluminium powder, iron powder, FeOOH , Fe_2O_3 , MgCO_3 , $\text{MgCa}(\text{CO}_3)_2$, NaOH , KOH , phosphate, monohydrogenphosphate, dihydrogenphosphate, rock phosphate, phosphoric acid, polyphosphate, hydroxyapatite, milorganite, bentonite, kaolinite, zeolite, manganese oxide, iron oxide, or a mixture thereof. The at least one additive may react with the heavy metal ions to form a metal salt precipitate.

The torrefying may be under suitable conditions. For example, the torrefying may comprise torrefying in the presence of inert gas. The inert gas may be any suitable inert gas, such as, but not limited to, nitrogen gas, argon, helium gas, carbon dioxide, or a combination thereof. In this way, the biochar produced from the torrefying may have a higher degree of carbon content.

The torrefying may be at any suitable temperature for the purposes of the present invention. For example, the torrefying may be at a temperature of 1-500°C. In particular, the torrefying may be at a temperature of 10-480°C, 25-450°C, 50-420°C, 100-400°C, 150-350°C, 200-300°C, 250-275°C. Even more in particular, the torrefying may be at a temperature of 300-400°C.

The torrefying may be for a suitable period of time. For example, the torrefying may be for ≥ 3 minutes. In particular, the torrefying may be for 3-60 minutes, 5-50 minutes, 10-45 minutes, 15-30 minutes. Even more in particular, the torrefying may be for 10-30 minutes.

According to a particular aspect, when the torrefying may transform the organic content of the organic-containing media into biochar which may adsorb and immobilize the heavy metals inside the biochar fibres and/or on the biochar fibres' surface due to the large surface area of the biochar fibres. In particular, the heavy metals adsorbed and immobilized may be solid heavy metal salts and/or the zero valence metals reduced from the heavy metals during the mixing. The immobilization of the heavy metals inside and/or on the biochar may be by physical and/or chemical adsorption. Once the heavy metals are immobilized, the heavy metals would be difficult to be adsorbed by plants and animals, or diffuse into the environment.

The method may further comprise drying the mixture prior to the torrefying. The drying may be under suitable conditions. For example, the drying may comprise drying in the presence of inert gas. The inert gas may be any suitable inert gas, such as, but not limited to, nitrogen gas, argon, helium gas, carbon dioxide, or a combination thereof.

- 5 The drying may comprise drying at a suitable temperature. For example, the temperature may be 1-280°C. In particular, the drying may be at a temperature of 1-280°C, 50-250°C, 80-220°C, 90-200°C, 100-175°C, 110-170°C, 120-150°C. Even more in particular, the drying may be at a temperature of 110-150°C.

- The drying may be for a suitable period of time. For example, the drying may be for ≥ 3 minutes. In particular, the torrefying may be for 3-60 minutes, 5-50 minutes, 10-45 minutes, 15-30 minutes. Even more in particular, the drying may be for 10-30 minutes.

- During the drying and/or the torrefying, moisture from the mixture may evaporate and therefore be discharged. The moisture may be ducted out and condensed to a liquid and subsequently discharged. The method may further comprise treating the condensed liquid in a liquid filtration system. Any suitable liquid filtration system may be used for the treating. In particular, the treating may comprise treating the condensed liquid according to local regulations before being discharged.

- During the torrefying, flue gas may be produced. For example, the flue gas may comprise, NO_x, SO₂, NH₃, H₂S, CO and/or CO₂. Accordingly, the method may further comprise treating flue gas produced during the torrefying. The treating may be in a flue gas treatment system. In this way, the gases from the method of the present invention may be adsorbed by the flue gas system, thereby minimising odourous and/or environmentally harmful gas emissions. In particular, the flue gas treatment system may comprise adsorbing solutions and/or solid cartridges for odour removal.

- 25 According to a particular aspect, the method may further comprise cooling the formed biochar following the torrefying. The method may then comprise collecting the formed biochar. For example, the formed biochar may be used as fertilizers. In particular, since the heavy metals immobilized in and/or on the biochar are zero valence heavy metals, these are not absorbed by plants, or are absorbed much lesser as compared to the absorption of mobile heavy metal ions. Accordingly, the use of the formed biochar as fertilizers will not be harmful to the plants on which the fertilizer is used.

According to another particular aspect, the method may further comprise calcinating the biochar formed from the torrefying to form calcinated material. The calcinating may be under suitable conditions. For example, the calcinating may comprise calcinating in an oxidising atmosphere. In particular, the calcinating may be in the presence of air or oxygen.

The calcinating may comprise calcinating at a suitable temperature. For example, the temperature may be 600-1200°C. In particular, the calcinating may be at a temperature of 650-1150°C, 700-1100°C, 800-1050°C, 850-1000°C, 900-950°C. Even more in particular, the calcinating may be at a temperature of 800-1000°C.

The calcinating may be for a suitable period of time. For example, the calcinating may be for ≥ 5 minutes. In particular, the calcinating may be for 5-120 minutes, 10-90 minutes, 15-60 minutes, 30-45 minutes. Even more in particular, the calcinating may be for 60-120 minutes.

In particular, the biochar formed from the torrefying may be used as a fuel in the calcinating. In this way, the calcinating may be performed at a lower temperature with lower energy input. While calcinating is generally associated with high energy consumption, in view of the biochar used in the calcinating in the method of the present invention, the overall energy consumption of the calcinating is reduced. Further, the calcinating may comprise oxidising the biochar to form calcinated material, thereby thermally decomposing the biochar into flue gas. Accordingly, the method may further comprise treating flue gas produced during the calcinating. The treating may be as described above in relation to the treating of flue gas produced during the torrefying.

The method may further comprise cooling the calcinated material following the calcinating.

According to a particular aspect, the method may further comprise:

- mixing the biochar with at least one further additive to form a biochar mixture;
and
- molding the biochar mixture,

wherein the mixing and the molding may be prior to the calcinating.

The at least one further additive may be any suitable additive. For example, the at least one further additive may comprise, but is not limited to: clay, sand, stone, fly ash, coal ash, furnace slag, incineration bottom ash, construction waste, egg shell, or a mixture thereof.

- 5 The molding may be under suitable conditions. For example, the molding may be at a suitable pressure. The molding may comprise molding the biochar mixture into suitable molded prototypes. For example, the molding may comprise molding the biochar mixture into construction material such as, but not limited to, bricks, road pavement material, or sea bed filler.
- 10 The molded prototype may then be subjected to the calcinating as described above. In view of the presence of the biochar in the molded prototype, heating during the calcinating would be uniform with each molded prototype, therefore resulting in improved and homogenized prototypes. In view of the method of the present invention, the prototypes comprising road pavement materials, bricks or sea reclamation fillers
- 15 may be used without fear of the heavy metals leaching out during use of the prototypes.

From the above, it can be seen that the method of the present invention immobilizes heavy metals and therefore, minimises heavy metals in leachate. The method also enables organic-containing media comprising heavy metals to be converted into

20 biochar which may be used as an adsorbent or fuel. In some aspects of the method, the organic content of the organic-containing media may be removed.

The present invention also provides a system for heavy metal immobilization. The system may be any suitable system. For example, the system may be one which is suitable for carrying out the method described above.

- 25 According to a second aspect of the present invention, there is provided a system for heavy metal immobilization, the system comprises:
- an inlet for receiving organic-containing media comprising heavy metal and at least one additive;
 - a mixing chamber coupled to the inlet for mixing the organic-containing
- 30 media comprising heavy metal and the at least one additive; and

- a torrefaction chamber for torrefying a mixture formed in the mixing chamber to form biochar.

The mixing chamber may comprise a seal to prevent any odour from the organic-containing media from escaping the system and into the atmosphere. In this way, the odour from the organic-containing media is contained within the system. In particular, the seal may be a rubber seal or a gasket.

The mixing chamber may comprise a mixer. The mixer may be any suitable mixer for mixing the organic-containing media comprising the heavy metal with the at least one additive. The mixing chamber may comprise an outlet for discharging the mixture formed in the mixing chamber.

The system may further comprise a drying chamber for drying the mixture formed in the mixing chamber. According to a particular aspect, the drying chamber may be in communication with the mixing chamber. For example, an outlet of the mixing chamber may be in communication with an inlet of the drying chamber. The drying chamber may further comprise an inlet for receiving an inert gas. The inert gas may be any suitable inert gas. The inert gas may be as described above.

The drying chamber may comprise an external heat source for heating the mixture received from the mixing chamber. The heat source may be any suitable heat source. For example, the heat source may be, but not limited to, an electric heater, microwave, gas-burner, or solar-powered panel.

The torrefaction chamber may be any chamber suitable for torrefying the mixture formed in the mixing chamber. According to a particular aspect, the torrefaction chamber may be in communication with the drying chamber. The torrefaction chamber may comprise an inlet for receiving an inert gas. The inert gas may be any suitable inert gas. The inert gas may be as described above.

The torrefaction chamber may comprise a temperature control device to adjust the temperature of the torrefaction chamber. For example, the temperature control device may be a cooling source for cooling the torrefaction chamber or an external heat source for heating the torrefaction chamber. The heat source may be any suitable heat

source. For example, the heat source may be, but not limited to, an electric heater, microwave, gas-burner, or solar-powered panel.

According to a particular aspect, the system may further comprise a calcination chamber for calcinating biochar formed in the torrefaction chamber. In particular, the calcination chamber may be in communication with the torrefaction chamber to receive the biochar formed in the torrefaction chamber. The calcination chamber may comprise an inlet for receiving air.

The calcination chamber may comprise an external heat source for heating the calcination chamber. The heat source may be any suitable heat source. For example, the heat source may be, but not limited to, an electric heater, microwave, gas-burner, or solar-powered panel.

According to a particular aspect, the system may further comprise a flue gas treatment system in fluid communication with the drying chamber, the torrefaction chamber and/or the calcination chamber for treating flue gas from the drying chamber, the torrefaction chamber and/or the calcination chamber. In use, the drying chamber, the torrefaction chamber and/or the calcination chamber may emit flue gas which may therefore be treated before being discharged into the atmosphere. In this way, the system of the present invention does not emit any harmful and/or odourful gas into the atmosphere, making the system an environmentally friendly system. The flue gas treatment system may be any suitable system for the purposes of the present invention.

The system may further comprise a collection chamber for collecting the formed biochar from the torrefaction chamber and/or the calcinated material from the calcination chamber.

The system may also comprise a liquid collection tank. The liquid collection tank may be in fluid communication with the drying chamber, the torrefaction chamber and/or the calcination chamber. For example, in use, moisture from the mixture and biochar treated in the drying chamber, the torrefaction chamber and/or the calcination chamber may evaporate from the mixture and biochar and subsequently condense and be collected in the liquid collection tank. The liquid collection tank may be in further

communication with or may comprise a liquid filtration system for treating and/or filtering the liquid collected in the liquid collection tank.

Figure 1 shows an example of a heavy metal immobilization system 100 according to one embodiment of the present invention. The system 100 comprises an inlet 102 into which organic-containing media comprising heavy metal is to be fed. At least one additive may also be fed via the inlet 102. The inlet 102 may be part of a feeding chamber 104.

The feeding chamber 104 may be in communication with a mixing chamber 106. In particular, an outlet of the feeding chamber 104 may be connected to an inlet 108 of the mixing chamber 106. The inlet 108 may comprise a mixing inlet sealing system, which may be as shown in Figure 2. There is also provided a mixer 110 comprised within the mixing chamber 106 to facilitate and improve the mixing between the organic-containing media comprising heavy metal and the at least one additive.

An outlet 112 of the mixing chamber 106 may be connected to a drying chamber 114 so that a mixture of the organic-containing media and the at least one additive mixed in the mixing chamber 106 may then be transferred to the drying chamber 114. The mixture may be dried in the drying chamber 114 under suitable conditions. For example, the conditions may be those as described above in relation to the method of the present invention. The drying chamber 114 may comprise an inlet 116. Further additives may be added into the drying chamber 114 via the inlet 116. In particular, the inlet 116 may be used for introducing an inert gas into the drying chamber 114.

The drying chamber 114 may further comprise a heater 118. The heater 118 may be any suitable heater, such as that described above. The heater 118 may raise the temperature of the inert gas within the drying chamber 114, thereby drying the mixture received from the mixing chamber 106. In this way, any liquid content within the mixture is evaporated and removed from the drying chamber 114 via outlet 120a.

An outlet 122 of the drying chamber 114 may be connected to a torrefaction chamber 124 so that the mixture that has been dried in the drying chamber 114 may be transferred from the drying chamber 114 to the torrefaction chamber 124 for torrefying into biochar.

The dried mixture may be torrefied in the torrefaction chamber 124 under suitable conditions. For example, the conditions may be those as described above in relation to the method of the present invention. The torrefaction chamber 124 may comprise an inlet 126. Further additives may be added into the torrefaction chamber 124 via the inlet 126. In particular, the inlet 126 may be used for introducing an inert gas into the torrefaction chamber 124.

The torrefaction chamber 124 may further comprise a heater 128. The heater 128 may be any suitable heater, such as that described above. The heater 128 may raise the temperature of the inert gas within the torrefaction chamber 124, thereby torrefying the dried mixture received from the drying chamber 114 to form biochar. During the torrefying in the torrefaction chamber 124, flue gases may be released. The flue gas may be channelled out of the torrefaction chamber 124 via outlet 120b.

Following torrefying of the dried mixture to form biochar, the biochar may be transferred to a storage chamber 130 via outlet 132 of the torrefaction chamber 124. The biochar may be cooled and stored in the storage chamber 130. The storage chamber 130 may comprise an outlet 120c for channelling any flue gas or evaporated moisture out of the storage chamber 130.

The outlets 120a, 120b and 120c may be in fluid communication with a flue gas treatment system 134 and a liquid collection tank 140. In particular, channel 136 connected to the outlets 120a, 120b and 120c enables gases from the drying chamber 114, the torrefaction chamber 124 and the storage chamber 130 to be channelled to the flue gas treatment system 134 before being vented out from outlet 138. The flue gas treatment system 134 may be any suitable system for treating flue gas.

The channel 136 also enables any liquid condensed in the channel 136 to be channelled to the liquid collection tank 140. The liquid collection tank 140 may comprise a liquid filtration system for treating the liquid collected. For example, the liquid collection tank 140 may further comprise a funnel 142 for filtering the liquid collected, and discharging only filtered liquid via outlet pipe 144.

Figure 2 shows an example of the mixing inlet sealing system at inlet 108 of the mixing chamber 106. The seal may be a horizontal cylinder which along its horizontal axis is divided into three equal portions by three tetragons. The horizontal cylinder seal has

two rounded sides, which the curved surface is removed. The cylinder is configured to rotate along its horizontal axis. When one portion of the cylinder is exposed to the inlet 108, any odour is prevented from escaping the system 100. When the cylinder rotates, the organic-containing media comprising heavy metal and the at least one additive fed into inlet 108 goes into the mixing chamber 106. In this way, the mixing chamber 106 is sealed at all times.

Figure 3 shows an example of a heavy metal immobilization system 200 according to another embodiment of the present invention. The system 200 and system 100 have many common components which are labelled with the same reference numerals.

In the system 200, following torrefying of the dried mixture to form biochar, the biochar may be transferred to a calcination chamber 202 via outlet 132 of the torrefaction chamber 124. The biochar may be calcined in the calcination chamber 202 to form calcinated material. The biochar in the calcination chamber 202 may be calcined under suitable conditions. For example, the conditions may be those as described above in relation to the method of the present invention. The calcination chamber 202 may comprise an inlet 204. Further additives may be added into the calcination chamber 202 via the inlet 204. In particular, the inlet 204 may be used for introducing air into the calcination chamber 202.

The calcination chamber 202 may further comprise a heater 206. The heater 206 may be any suitable heater, such as that described above. The heater 206 may raise the temperature of the air within the calcination chamber 202, thereby calcinating the biochar received from the torrefaction chamber 124. In particular, the biochar may be oxidised to form calcinated material. During the calcination, flue gas may be released. Accordingly, the flue gas released from the calcination of the biochar in the calcination chamber 202 may be channelled out of the calcination chamber 202 via outlet 220d.

Following calcination of the biochar, the calcinated material may be transferred to the storage chamber 130 via outlet 208 of the calcination chamber 202. The calcinated material may be cooled and stored in the storage chamber 130. The storage chamber 130 may comprise an outlet 120c for channelling any flue gas or evaporated moisture out of the storage chamber 130.

The outlet 220d may be in fluid communication with the flu gas treatment system 134 and the liquid collection tank 140. In particular, channel 136 connected to the outlet 220d, as well as outlets 120a, 120b and 120c, enables gases from the calcination chamber 202, as well as gases from the drying chamber 114, the torrefaction chamber 124 and the storage chamber 130 to be channelled to the flue gas treatment system 134 before being vented out from outlet 138.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention. Having now generally described the invention, the same will be more readily understood through reference to the following example which is provided by way of illustration, and is not intended to be limiting.

Example

A sludge sample from the bottom of a lake was dried and treated for elemental ingredients. The sample was dried at 110°C for 24 hours and then was grinded until uniform. For inductively coupled plasma mass spectrometry (ICP-MS) elemental analysis except Hg, 0.2 g of the dried and grinded sample was added to 9 ml of 85 wt.% HNO₃, then 2 ml of 37 wt. % HCl, 3 ml of 50 wt. % HF and 1 ml of 20 wt.% H₂O₂ were added and mixed well. The mixture was digested at 180°C for 20 minutes. After cooling down, DI water was added to it till the total volume was made up to 50 ml. The sample was then filtered through a 0.22 µm filter and was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES).

For Hg analysis by ICP-OES, 0.2 g of dried and grinded sample was added to 15 ml of 85 wt. % HNO₃, and then 0.85 ml of 37 wt. % HCl, 6.5 µL of 1000 ppm Au standard and 35 ml of DI water were added and mixed well. The sample was filtered through 0.22 µm filter and was analyzed by ICP-OES for Hg. The ICP-OES elemental results are summarized in Table 1. As can be seen, heavy metals of this sample, namely As, Hg, Pb, Zn, Sb, and Cu exceeded or were close to the upper limits of the standard. The major metal elements in this sample were Si (22.14 wt.%), Al (5.29 wt.%), Fe (2.87 wt.%), K (1.80 wt.%), and P (0.52 wt.%). Accordingly, a general formula of the inorganic silicate components in this sample may be $Al_{0.25}Fe_{0.06}K_{0.06}M_xSiO_{2.5+x}$, where M represents other metals (M is formalized to +2 valence).

Element	Concentration in solution (ppm)	Concentration in dry sludge sample (ppm)	Standard * (ppm)	Name of Oxide	Concentration (ppm)
Mg	8.46	1692		MgO	2806
Al	264.5	52900		Al ₂ O ₃	99951
Ca	2.05	410		CaO	574
Na	16.14	3228		Na ₂ O	4351
K	89.79	17958		K ₂ O	21632
Ba	0.74	148		BaO	165
Be	ND	ND		BeO	ND
Si	1107	221400		SiO ₂	473647
P	26.04	5208		P ₂ O ₅	11933
As	0.20	40	30	As ₂ O ₅	61
Se	ND	ND	3	SeO ₃	ND
Fe	143.4	28680		Fe ₂ O ₃	41005
Zn	0.98	196	200	ZnO	244
Cu	1.06	212	50	CuO	265
Cr	0.43	86	150	Cr ₂ O ₃	126
Mn	0.96	192	1200	MnO	248
Co	0.05	10	20	Co ₂ O ₃	14
Cd	ND	ND	0.3	CdO	ND
Pb	0.37	74	80	PbO ₂	85
Ni	0.11	22	40	Ni ₂ O ₃	31
V	0.21	42	140	V ₂ O ₅	75
Ti	ND	ND	1	TiO ₂	ND
Sn	0.07	14		SnO ₂	18
Sb	0.25	50	3	Sb ₂ O ₅	66
Mo	ND	ND	6	MoO ₃	ND
Hg	0.013	2.6	0.3	HgO	2.81

ND: Not detected

*: Standard refers to GB15618-201X Soil Environmental Quality Standard for Agriculture Land (China)

- 5 **Table 1: Elemental analysis of the dried, grinded and treated sludge sample by ICP-OES**

Elemental analysis results of C, H, N, and S are listed in Table 2.

Elements	Concentration in Dried Sample (%wt.)
C	5.37
H	1.51
N	0.25
S	0.25

Table 2: Elemental analysis of the dried and grinded sample

Thermal gravity analysis (TGA) graphs (in air or N₂) of the dried and grinded sample are shown in Figures 4 and 5. Weight loss values of the sample in air and in N₂ from 25°C to 900°C were 16.5 wt.% and 14.7 wt.%. Therefore, the organic content in the dried and grinded sample was 16.5 wt.% with most of them (i.e. 14.7 wt.%) thermally degradable and minor (1.8 wt.%) could only be thermally oxidized to gas. The total organic and inorganic contents of the dried sample were 16.5 wt.% and 83.5 wt.%, respectively.

Brick samples were prepared as follows: 1.1 ml of 3% H₃PO₄ or DI water was added to 2 g of dried and grinded sample and manually mixed well and aged for 1 hour. 0.8 g of the mixture was then pressed into a disc with a diameter of about 14 mm and thickness of 3 mm and dried at 60°C for 24 hours.

The dried disc was then torrefied and calcined in a tube furnace as follows: the torrefaction comprised heating from 25°C to 400°C with a ramp rate of 5°C/min with N₂ flow rate of 100 ml/min, followed by calcination comprising heating from 400°C to 1000°C with a ramp rate 1.7°C/min with 100 ml/min of air flow rate, and maintained at 1000°C for 300 minutes with the same air flow rate before natural cooling down with the same air flow rate. Before calcination, both discs with and without phosphoric acid additive were greenish grey, which turned to orange after calcination in the case of the disc without phosphoric acid additive and darker orange and some reddish at the edge for the disc with phosphoric acid additive. The colour change is mainly due to oxidation of ferrous or ferric compounds in soil at high temperature by air oxygen to reddish iron oxide.

Leaching tests were conducted to evaluate the leaching risk of heavy metals from the produced construction bricks using the process described above. The leaching test procedures were performed in accordance with GB5086.1, Test method standard for

leaching toxicity of solid wastes – Roll over leaching procedure (China). In particular, the test was conducted as follows: 0.7 g of dry sample was soaked in 10 ml DI water for 18 hours at room temperature with 30 rpm of agitation. The leachate was filtered through a 0.45 μm filter and analyzed for heavy metals As, Hg, Pb, Sb, Ni, Cu, Fe, Cr, Mn, and V by ICP-OES. The leaching test results are summarized in Table 3.

<u>Heavy metals</u>	<u>Leachate concentration (mg/L)</u>	<u>Standard (mg/L) *</u>
As	0	1.5
Fe	0.045	\
Zn	0.06	50
Cu	0.075	50
Cr	0	1.5
Mn	0	\
Pb	0	3
Ni	0.045	25
V	0.975	\
Sb	0.09	\
Hg	0	0.05

Table 3: Concentration of heavy metals in the leachate solution of the calcined brick sample

The results obtained were compared with a standard, HJxxx-2010, Technical guidelines of sludge treatment and disposal for municipal waste water treatment plant (China). Table 3 shows that the concentration of heavy metals in the leachate solution of the calcined brick sample were far below the upper limits of the standard. This demonstrates that the process of the present invention is highly efficient in immobilizing the heavy metals in the sludge sample.

Claims

1. A method for heavy metal immobilization, the method comprising:
 - mixing organic-containing media comprising heavy metal with at least one additive to form a mixture; and
 - 5 - torrefying the mixture to form biochar, wherein the biochar immobilizes the heavy metal.
2. The method according to claim 1, wherein the torrefying comprises torrefying in presence of inert gas.
- 10 3. The method according to claim 1 or 2, wherein the torrefying is at a temperature of 1-500°C.
4. The method according to any preceding claim, further comprising treating flue gas produced during the torrefying.
- 15 5. The method according to any preceding claim, further comprising drying the mixture prior to the torrefying.
- 20 6. The method according to claim 5, wherein the drying comprises drying in presence of inert gas.
7. The method according to claim 5 or 6, wherein the drying is at a temperature of 1-280°C.
- 25 8. The method according to any preceding claim, further comprising cooling the biochar following the torrefying.
9. The method according to any preceding claim, wherein the organic-containing media comprises ≥ 25 weight % organic content.
- 30 10. The method according to claim 9, wherein the at least one additive comprises a reducing agent.

11. The method according to claim 9 or 10, wherein the at least one additive comprises: sodium borohydride, hydrazine, aluminium powder, LiAlH_4 , or a mixture thereof.

5 12. The method according to any of claims 1 to 8, wherein the organic-containing media comprises less than 25 weight % organic content.

13. The method according to claim 12, wherein the at least one additive comprises an inorganic additive.

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14. The method according to claim 13, wherein the inorganic additive comprises: lime, limestone, FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , aluminium powder, iron powder, FeOOH , Fe_2O_3 , MgCO_3 , $\text{MgCa}(\text{CO}_3)_2$, NaOH , KOH , phosphate, monohydrogenphosphate, dihydrogenphosphate, rock phosphate, phosphoric acid, polyphosphate,
15 hydroxyapatite, milorganite, bentonite, kaolinite, zeolite, manganese oxide, iron oxide, or a mixture thereof.

15. The method according to any of claims 12 to 14, further comprising calcinating the biochar following the torrefying to form calcinated material.

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16. The method according to claim 15, wherein the calcinating comprises calcinating in an oxidising atmosphere.

17. The method according to claim 15 or 16, wherein the calcinating is at a
25 temperature of 600-1200°C.

18. The method according to any of claims 15 to 17, further comprising treating flue gas produced during the calcinating.

30 19. The method according to any of claims 15 to 18, further comprising cooling the calcinated material.

20. The method according to any of claims 15 to 19, further comprising:

- mixing the biochar with at least one further additive to form a biochar mixture; and
- molding the biochar mixture,

wherein the mixing and the molding is prior to the calcinating.

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21. The method according to claim 20, wherein the at least one further additive comprises: clay, sand, stone, fly ash, coal ash, furnace slag, incineration bottom ash, construction waste, egg shell, or a mixture thereof.

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22. A system for heavy metal immobilization, the system comprising:

- an inlet for receiving organic-containing media comprising heavy metal and at least one additive;
- a mixing chamber coupled to the inlet for mixing the organic-containing media comprising heavy metal and the at least one additive; and
- a torrefaction chamber for torrefying a mixture formed in the mixing chamber to form biochar.

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23. The system according to claim 22, wherein the torrefaction chamber comprises an inlet for receiving an inert gas.

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24. The system according to claim 22 or 23, further comprising a drying chamber for drying the mixture formed in the mixing chamber.

25. The system according to any of claims 22 to 24, further comprising a calcination chamber for calcinating biochar formed in the torrefaction chamber.

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26. The system according to claim 25, wherein the calcination chamber comprises an inlet for receiving air.

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27. The system according to any of claims 24 to 26, further comprising a heat source for heating the torrefaction chamber, the drying chamber and/or the calcination chamber.

28. The system according to any of claims 25 to 27, further comprising a flue gas treatment system in fluid communication with the torrefaction chamber and/or the calcination chamber for treating flue gas from the torrefaction chamber.

5 29. The system according to any of claims 25 to 28, further comprising a collection chamber for collecting calcinated material.

30. The system according to any of claims 22 to 24, further comprising a collection chamber for collecting the formed biochar.