

**(12) STANDARD PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

(11) Application No. **AU 2016301347 B2**

(54) Title  
**Filter media for respiratory protection comprising iron-doped manganese oxide**

(51) International Patent Classification(s)  
**A62B 18/00** (2006.01)                      **B01J 20/02** (2006.01)  
**A62B 19/00** (2006.01)                      **B01J 20/28** (2006.01)  
**B01D 53/02** (2006.01)

(21) Application No: **2016301347**                      (22) Date of Filing: **2016.08.04**

(87) WIPO No: **WO17/024116**

(30) Priority Data

(31) Number	(32) Date	(33) Country
<b>62/201,691</b>	<b>2015.08.06</b>	<b>US</b>

(43) Publication Date: **2017.02.09**

(44) Accepted Journal Date: **2019.03.07**

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(56) Related Art  
**US 2005/0074380 A1**



(51) International Patent Classification:

*B01D 53/02* (2006.01)      *B01J 20/02* (2006.01)  
*A62B 18/00* (2006.01)      *B01J 20/28* (2006.01)  
*A62B 19/00* (2006.01)

(21) International Application Number:

PCT/US2016/045514

(22) International Filing Date:

4 August 2016 (04.08.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/201,691      6 August 2015 (06.08.2015)      US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,

HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(88) Date of publication of the international search report:

16 March 2017

(54) Title: FILTER MEDIA FOR RESPIRATORY PROTECTION COMPRISING IRON-DOPED MANGANESE OXIDE

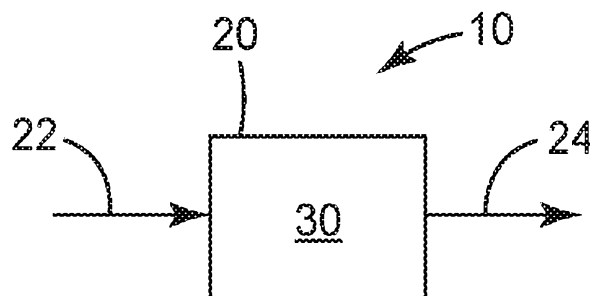


FIG. 1

(57) Abstract: A respiratory protection filter includes filtration media. The filtration media includes an iron-doped manganese oxide material having an average pore size (BJH method) in a range from 1 to 4 nm and a surface area (BET) of at least 300 m<sup>2</sup>/g, or at least 350 m<sup>2</sup>/g, or at least 400 m<sup>2</sup>/g.

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## FILTER MEDIA FOR RESPIRATORY PROTECTION

### BACKGROUND

5 Sorbents used in respiratory filter cartridges are typically based upon activated carbon. An attribute of activated carbon is its high surface area and ability to adsorb organic vapors. Activated carbons generally only poorly adsorb low boiling point polar compounds such as ammonia, and therefore additional materials are added to the surface to remove these contaminants by chemical reaction.

10 To filter hazardous gases, such as acidic gases, ammonia, cyanides, or aldehydes, specific chemicals are added to the activated carbon in a process known as impregnation. For example, the Lewis acid transition metal salt zinc chloride is added to carbon to produce a sorbent for ammonia removal. Impregnation of any support (such as activated carbon) involves a balance of loading a sufficient amount of the reactive impregnant without destroying the high surface area of the support.

15 When considering impregnant materials as sorbent components, factors such as toxicity, stability under relevant conditions, and reactivity represent key attributes. Traditional carbon impregnant based upon copper and zinc are often oxides in the 2+ oxidation state, formed via thermolysis (at ca. 180-200°C) of activated carbons treated with Cu and/or Zn salts that are soluble in aqueous or ammoniacal solutions. However, when these inorganic oxides are not  
20 supported on materials such as activated carbon, each commonly suffer from low porosity and surface area.

25 Reference to any prior art in the specification is not, and should not be taken as, an acknowledgment or any form of suggestion that this prior art forms part of the common general knowledge in Australia or any other jurisdiction or that this prior art could reasonably be expected to be understood, regarded as relevant and/or combined with other pieces of prior art by a person skilled in the art.

### SUMMARY

30 The present disclosure relates to filter media for respiratory protection. In particular the filter media is a manganese oxide material such as an iron-doped manganese oxide material that is capable of removing hazardous gases from a respiratory airstream. The iron-doped manganese oxide material may be prepared using either a low temperature aqueous redox co-precipitation method or an oxalate thermolysis method.

35 In one aspect of the present invention there is provided a respiratory protection filter comprising: a housing having an air stream inlet and an air stream outlet and containing an amount of filtration media in fluid connection and between the air stream inlet and the air stream

outlet, the filtration media comprising: iron-doped manganese oxide material having an average pore size (BJH method) in a range from 1 to 4 nm and a surface area (BET) of at least 300 m<sup>2</sup>/g, or at least 350 m<sup>2</sup>/g, or at least 400 m<sup>2</sup>/g.

In a further embodiment of the present disclosure there is provided a method, comprising: combining an iron (III) salt with manganese (II) salt in water to form an aqueous salt mixture; blending a permanganate solution with the aqueous salt mixture to form a wet precipitate; isolating and drying the precipitate to form an iron-doped manganese oxide material.

In a further embodiment of the present disclosure there is provided a method, comprising: combining an iron (II) salt with manganese (II) salt in water to form an aqueous salt mixture; forming an ammonium oxalate solution with a pH in a range from 7 to 8; blending the ammonium oxalate solution with the aqueous salt mixture to form a wet Fe/Mn oxalate precipitate; drying the wet Fe/Mn oxalate precipitate to remove water and form a dry Fe/Mn oxalate precipitate; heating the dry Fe/Mn oxalate precipitate at a temperature in range from 200 to 250 degrees Celsius to form an iron-doped manganese oxide material.

These and various other features and advantages will be apparent from a reading of the following detailed description.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawings, in which:

**FIG. 1** is a schematic drawing of an illustrative respiratory protection filter;

**FIG. 2** is a flow diagram of an illustrative method; and

**FIG. 3** is a flow diagram of another illustrative method.

#### DETAILED DESCRIPTION

In the following detailed description, reference is made to the accompanying drawings that form a part hereof, and in which are shown by way of illustration several specific embodiments. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present disclosure. The following detailed description, therefore, is not to be taken in a limiting sense.

All scientific and technical terms used herein have meanings commonly used in the art unless otherwise specified. The definitions provided herein are to facilitate understanding of certain terms used frequently herein and are not meant to limit the scope of the present disclosure.

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Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical

parameters set forth in the foregoing specification and attached claims are approximations that may vary depending upon the properties desired by those skilled in the art utilizing the teachings disclosed herein.

5 The recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

As used in this specification and the appended claims, the singular forms “a”, “an”, and “the” encompass embodiments having plural referents, unless the content clearly dictates otherwise.

10 As used in this specification and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

As used herein, “have”, “having”, “include”, “including”, “comprise”, “comprising” or the like are used in their open ended sense, and generally mean “including, but not limited to”. It will be understood that “consisting essentially of”, “consisting of”, and the like are subsumed in “comprising,” and the like.

15 The present disclosure relates to filter media for respiratory protection. Like activated carbons, transition metal oxides may have high surface area and porosity, and may be doped with other transition metals to potentially enhance adsorption of hazardous gases. In particular the filter media in the present disclosure is a manganese oxide material such as an iron-doped manganese oxide material that is capable of removing hazardous gases from a respiratory  
20 airstream. The manganese oxide material such as an iron-doped manganese oxide material has an average pore size in a range from 1 to 4 nm (BJH method) and a surface area of at least 300 m<sup>2</sup>/g, or at least 350 m<sup>2</sup>/g, or at least 400 m<sup>2</sup>/g (BET method). The iron-doped manganese oxide material may be prepared using either a low temperature aqueous redox co-precipitation method or an oxalate thermolysis method. The iron-doped manganese oxide material is granulated to a  
25 mesh size in a range from 12 to 50 U.S. standard sieve series. The iron-doped manganese oxide material may then be disposed in a respiratory protection filter element. While the present disclosure is not so limited, an appreciation of various aspects of the disclosure will be gained through a discussion of the examples provided below.

**FIG. 1** is a schematic drawing of an illustrative respiratory protection filter **10**. The  
30 respiratory protection filter **10** includes a housing **20** having an air stream inlet **22** and an air stream outlet **24** and containing an amount of filtration media **30** in fluid connection and between the air stream inlet **22** and the air stream outlet **24**. The filtration media **30** includes iron-doped manganese oxide material.

The filtration media **30** may include one or more additional types of filtration material,  
35 such as, activated carbon, for example. In many embodiments the filtration media **30** includes

free-standing granular iron-doped manganese oxide material. The filtration media **30** may include at least 20% wt, or at least 30% wt, or at least 50% wt free-standing granular iron-doped manganese oxide material.

The filtration media **30** may include iron-doped manganese oxide material described herein or manganese oxide material or a combination of iron-doped manganese oxide material and manganese oxide material.

The iron-doped manganese oxide material or manganese oxide material is capable of removing one or more hazardous gas from an air stream passing through the filtration media **30** at ambient conditions or atmospheric pressure and -20 to 40 degrees Celsius and 5% to 95% relative humidity. These hazardous gases include examples from acidic or basic gas groups, such as sulfur dioxide, ammonia, and formaldehyde vapour.

The iron-doped manganese oxide material or manganese oxide material described herein has an average pore size (BJH method) in a range from 1 to 4 nm, or 1 to 3.5 nm, or 1 to 3.0 nm and a surface area (BET) of at least 300 m<sup>2</sup>/g, or at least 350 m<sup>2</sup>/g, or at least 400 m<sup>2</sup>/g. The iron-doped manganese oxide material is prepared from chemical reactions with a molar ratio of manganese:iron in a range from 95:5 to 70:30, or preferably in a range from 85:15 to 80:20.

In many embodiments, the iron-doped manganese oxide material or manganese oxide material is granulated to define granules having a mesh size in a range from 12 to 50, or from 20 to 40 U.S. standard sieve series. Any useful granulation process may be utilized. In many embodiments, the granules are formed with compression and without the use of a binder. In many embodiments, the iron-doped manganese oxide granules or manganese oxide granules have a moisture content of less than 10% wt, or less than 5% wt.

In many embodiments, the iron-doped manganese oxide material particles or granules or manganese oxide material particles or granules may have an apparent or bulk density of less than 1.3 g/mL, or less than 1 g/mL, or less than 0.8 g/mL, or less than 0.7 g/mL.

**FIG. 2** is a flow diagram of an illustrative method **100**. This illustrative method is a low temperature aqueous redox co-precipitation method. The method **100** forms an iron-doped manganese oxide material. The method includes combining an iron (III) salt with manganese (II) salt in water to form an aqueous salt mixture (step **110**) and blending a permanganate solution with the aqueous salt mixture (step **120**) to form a wet precipitate. Then the method includes isolating and drying the precipitate (steps **140** and **150**) to form an iron-doped manganese oxide material (step **160**).

The blended permanganate solution with the aqueous salt mixture may be stirred or agitated at an ambient temperature for a set period of time (step **130**). The set period of time may be any useful time duration. In many embodiments the set period of time is at least a few hours

to 48 hours or from 10 hours to 30 hours or from 20 to 24 hours. Isolating the precipitate (steps **140**) may include any useful isolation technique to separate a solid from a liquid, such as, filtration, centrifuging and washing, for example.

Drying the precipitate (step **150**) occurs at a relatively low temperature to remove water from the precipitate. The drying step **150** may raise the temperature of the precipitate or air surrounding the precipitate to a temperature at or above 100 degrees Celsius but less than 150 degrees Celsius, or less than 125 degrees Celsius, or no greater than 120 degrees Celsius, or no greater than 115 degrees Celsius, or in a range from 100 to 110 degrees Celsius. In many embodiments the method **100** has a processing temperature for all the steps that is no greater than 115 degrees Celsius, or no greater than 110 degrees Celsius. In many embodiments, the drying steps **130**, **150** remove only water or moisture from the wet iron-doped manganese oxide material.

In many embodiments, the method **100** occurs at a temperature of less than 125 degrees Celsius, or less than 120 degrees Celsius, or less than 115 degrees Celsius. In particular the blending a permanganate solution with the aqueous salt mixture (step **120**) and stirring the mixture step **130** occurs at ambient temperatures such as from 20 to 30 degrees Celsius.

The method may include combining a hydrated iron (III) salt with the manganese (II) salt in water to form an aqueous salt mixture (step **110**). In many embodiments the manganese (II) salt is a hydrated manganese (II) salt. Illustrative salts include nitrate, acetate, sulfate and the like. Examples of hydrated manganese (II) salt include manganese (II) acetate tetrahydrate and manganese (II) sulfate monohydrate. Examples of hydrated iron (III) salt include iron (III) nitrate nonahydrate and iron (III) sulfate pentahydrate.

The combining step may include combining a molar ratio of manganese (II) salt:iron (III) salt in a range from 95:5 to 70:30, or preferably in a range from 80:20 to 85:15. In many embodiments, the method **100** may further include granulating or compressing the iron-doped manganese oxide material into granules (step **170**) having a mesh size in a range from 12 to 50, or from 20 to 40 U.S. standard sieve series. The iron-doped manganese oxide granules may then be placed into a respiratory protection filter.

**FIG. 3** is a flow diagram of an illustrative method **200** of forming an iron-doped manganese oxide material. The illustrated method is an oxalate thermolysis method. The method **200** includes combining an iron (II) salt with manganese (II) salt in water to form an aqueous salt mixture (step **210**). Then forming an ammonium oxalate solution with a pH in a range from 7 to 8 (step **220**), and blending the ammonium oxalate solution with the aqueous salt mixture (step **230**) to form a wet Fe/Mn oxalate precipitate. Then the method includes drying the wet Fe/Mn oxalate precipitate (step **250**) to remove water and form a dry Fe/Mn oxalate precipitate (step

**260**), and then heating the dry Fe/Mn oxalate precipitate at a temperature in range from 200 to 250 degrees Celsius (step **270**) to form an iron-doped manganese oxide material (step **280**).

After the ammonium oxalate solution is blended with the aqueous salt mixture (step **230**), the blended mixture may be sonicated (ultrasonic agitation). Ultrasonic agitation (step **240**) may provide a number of surprising advantages such as providing a comparatively smaller particle size and narrower particle size distribution, among others. In some embodiments, ultrasonic agitation may not be preformed.

The blended solution aqueous salt mixture (step **230**) may be agitated, such as magnetic stirring for example, (step **240**) at an ambient temperature for a set period of time. The set period of time may be any useful time duration. In many embodiments the set period of time is at least 30 minutes to 4 hours, or from 1 hour to 3 hours, or about 2 hours. Isolating the precipitate (steps **250**) may include any useful isolation technique to separate a solid from a liquid, such as, filtration, centrifuging and washing, for example.

Drying the precipitate (step **260**) occurs at a relatively low temperature to remove water from the precipitate. The drying step **260** may raise the temperature of the precipitate or gas surrounding the precipitate to a temperature at or above 40 degrees Celsius but less than 100 degrees Celsius, or in a range from 40 to 80 degrees Celsius, or about 60 degrees Celsius. The dry precipitate may have a moisture content of less than 30%, or less than 25%, or less than 20% by weight.

The dry precipitate (from step **260**) is then calcined at a low temperature sufficient to remove carbon dioxide and water. The calcining temperature is from 200 to 250 degrees Celsius, or from 220 to 240 degrees Celsius, or about 225 degrees Celsius for a set period of time is at least 1 hour to 12 hours, or from 3 hour to 8 hours, or about 6 hours. In some embodiments the drying step **260** and the calcining step **270** may be combined into a single calcining step **270** as described above.

The iron-doped manganese oxide material (step **280**) may have a uniform size that ranges from 100 to 500 nm, or from 200 to 300 nm.

The method **200** may include combining a hydrated iron (II) salt with the manganese (II) salt in water to form an aqueous salt mixture (step **210**). In many embodiments the manganese (II) salt is a hydrated manganese (II) salt. Illustrative salts include nitrate, acetate, sulfate and the like. Examples of hydrated iron (II) salt include iron (II) sulfate heptahydrate. Examples of hydrated manganese (II) salt include manganese (II) acetate tetrahydrate and manganese (II) sulfate monohydrate.

The combining step may include combining a molar ratio of (manganese (II) salt):(iron (II) salt) in a range from 95:5 to 70:30, or preferably in a range from 80:20 to 85:15. In many

embodiments, the method **200** may further include granulating or compressing the iron-doped manganese oxide material into granules (step **290**) having a mesh size in a range from 12 to 50, or from 20 to 40 U.S. standard sieve series, for example. The iron-doped manganese oxide granules may then be placed into a respiratory protection filter.

5 Objects and advantages of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure.

### Examples

10 All parts, percentages, ratios, etc. in the examples are by weight, unless noted otherwise. Solvents and other reagents used are obtained from Sigma-Aldrich Corp., St. Louis, Missouri unless specified differently.

### Material Listing

Table 1. Material Listing

Chemical Name	Supplier
Manganese (II) acetate tetrahydrate	Sigma-Aldrich
Manganese (II) sulfate monohydrate	Alfa Aesar
Potassium permanganate	Fisher Scientific
Zinc nitrate hexahydrate	Sigma-Aldrich
Copper (II) nitrate hemi(pentahydrate)	Sigma-Aldrich
Copper (II) sulfate pentahydrate	Anachemia
Paraformaldehyde	TDI Chemicals
Iron (III) nitrate nonahydrate	Sigma-Aldrich
Iron (II) sulfate heptahydrate	Alfa Aesar
Ammonium oxalate monohydrate	Alfa Aesar
Ammonium hydroxide	BDH

### 15 Preparative Procedures for Method 1: Examples 1-5.

Doped manganese oxide samples are named according to the molar ratio of metals in the complete reaction mixture. For example, 80Mn20FeO<sub>x</sub> refers to a material obtained from a reaction mixture that contained a 4:1 molar ratio of Mn-containing reagents to Fe-containing reagents.

20 Preparations were modular in that the proportions of KMnO<sub>4</sub> and Mn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O remained constant, but the molar amount of iron added to the reaction mixture was changed.

- Example 1 is 100:0 Mn:Fe
- Example 2 is 90:10 Mn:Fe
- Example 3 is 85:15 Mn:Fe
- Example 4 is 80:20 Mn:Fe
- 5 • Example 5 is 75:25 Mn:Fe.

Described below is a representative procedure for the preparation of Example 3: In a 2L Erlenmeyer flask,  $\text{KMnO}_4$  (19.0g, 0.12mol) was treated with 200 mL of deionized water and the mixture was stirred magnetically. In a separate beaker,  $\text{Mn}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$  (44.1g, 0.18mol) was dissolved in 100 mL of deionized water. To this pink solution was added  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  10 (30.3g, 0.075mol), which produced a brown solution. This solution was then added to the Erlenmeyer flask containing permanganate, the first 50 mL via Pasteur pipette, followed by a slow pour for the remaining 50 mL. The mixture was observed to thicken and stirring became impeded, so 200 mL of deionized water was added to resume efficient stirring. The solution was then left to stir magnetically for 22 hours. The dark precipitate was then isolated by vacuum 15 filtration, and washed with 300 mL deionized water in 4 portions. The washed solid was then transferred to a pyrex dish for drying at  $100^\circ\text{C}$  for 20 hours. After this time, the solid was broken up to smaller pieces with the use of a spatula, and then dried again at  $110^\circ\text{C}$  for 1.5 hours or until the moisture content was  $<5$  wt%. The dried solid was then crushed with a mortar and pestle and sized to 20 x 40 U.S. Standard Sieve Series granules. The remaining fines were then formed into 20 pellets using a 13 mm die and Carver press using a pressure of 70000 PSI. The pellets were then crushed and sized to 20 x 40 U.S. Standard Sieve Series granules. Granules were washed a second time with deionized water (150 mL in 4 portions) and dried at  $100^\circ\text{C}$  for 3 hours. Example 4-Cu and 4-Zn were prepared as above using  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in place of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

## 25 **Preparative Procedures for Method 2: Examples 6-8.**

[001]  $\text{MnSO}_4/\text{FeSO}_4$  mixed solutions (0.25M) were prepared by dissolving  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in molar Mn:Fe ratios of:

- Example 6 is 100:0 Mn:Fe
- Example 7 is 90:10 Mn:Fe
- 30 • Example 8 is 80:20 Mn:Fe

in 400 mL deionized water.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution (0.25M) was prepared by dissolving 14.2 g  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (Alfa Aesar) in 400 mL deionized water. The pH of the  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution was adjusted to between 7~8 using 8% (vol.)  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . Using a Masterflex peristaltic pump, the resulting  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution was added slowly to the  $\text{MnSO}_4/\text{FeSO}_4$  solution over a period of 2

hours while mild sonication (Branson Sonifier 450, 20W) was applied. Precipitated solids were observed to form during the 2 hour time period. After the complete addition of the  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution, the precipitate was isolated by centrifugation and washed with deionized water repeatedly until the pH reached  $\sim 7$ . The product was then dried overnight in an oven at  $60^\circ\text{C}$  in air. The dried oxalate precipitate was then ground with a mortar and pestle and heated at  $225^\circ\text{C}$  for 6 hours in air to obtain the final powder. The powder was then formed into pellets using a 17mm die and hydraulic press using a pressure of 8000 PSI. The pellets were then crushed and sized to 20 x 40 granules. Example 8-Cu was prepared as above using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in place of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , with another exception that the final heating period was  $250^\circ\text{C}$  for 5 hours.

## 10 Test Methods

### *Tube Testing*

A tube testing apparatus was used for breakthrough testing. The sample tubes employed are composed of polyvinylchloride (PVC) (inner diameter = 6.5mm) with a fine stainless steel mesh near the base. These tubes are loaded with a specified volume of filter media granules for testing and are packed to a constant volume by repeatedly tapping the lower end against a hard surface. The sample tube is connected to flexible Teflon tubing using ultra-torr (Swagelok) fittings. Challenge gases of desired concentrations are then delivered through the vertical tube through the top (inlet) portion of the tube at a specified flow rate and the effluent gas that exits the sorbent bed through the lower end of the tube (outlet) is then transported to a detector for analysis.

### *Sulfur Dioxide Breakthrough Testing:*

A sample of filter media granules, either obtained from a commercial vendor or prepared according to a given example, equating to a volume of 1.7 cc was transferred to the tube testing apparatus outlined above and weighed. The filter media granules were tapped until no significant reduction in volume was observed by the human eye. The sample in the tube was then exposed to a test stream of approximately 200 mL/minutes that contained  $1000 \pm 10\%$  ppm of sulfur dioxide ( $\text{SO}_2$ ) in air from a certified gas mixture from Linde (Whitby, ON, Canada). The air downstream from the filter media granules was monitored for breakthrough using either a MIRAN SapphIRe IR portable air analyzer or by pH changes (Fortier et al. *Appl. Surf. Sci.* **2007**, 253, 3201-3207). The breakthrough time was defined as the time at which a concentration of 20 ppm was observed downstream from the sample.

*Ammonia Breakthrough Testing:*

A sample of filter media granules, either obtained from a commercial vendor or prepared according to a given example, equating to a volume of 1.7 cc was transferred to the tube testing apparatus outlined above and weighed. The filter media granules were tapped until no significant reduction in volume was observed by the human eye. The sample in the tube was then exposed to a test stream of approximately 200 mL/minutes that contained 1000±10% ppm of ammonia (NH<sub>3</sub>) in air from a certified gas mixture from Linde (Whitby, ON, Canada). The air downstream from the filter media granules was monitored for breakthrough using either a MIRAN SapphIRe IR portable air analyzer or by pH changes (Fortier et al. *J. Coll. Interf. Sci.* **2008**, 320, 423-435). The breakthrough time was defined as the time at which a concentration of 20 ppm was observed downstream from the sample.

*Formaldehyde Breakthrough Testing:*

The sample tubes employed are composed of glass (inner diameter = 9 mm) with an ASTM A glass frit (145-175 µm) near the base. These tubes are loaded to a volume of 0.9 cc of filter media granules for testing. They are packed to a constant volume by repeatedly tapping the lower end against a hard surface. The sample tube is connected to flexible Teflon tubing using ultra-torr (Swagelok) fittings. Formaldehyde of a desired concentration was then delivered through the vertical tube through the top (inlet) portion of the tube at a specified flow rate, and the effluent gas that exits the sorbent bed through the lower end of the tube (outlet) is then transported to a detector. In this case the outlet gas stream was analyzed by an SRI gas chromatograph (GC) using a methanizer to convert carbon dioxide (CO<sub>2</sub>), and formaldehyde (HCHO) into methane (CH<sub>4</sub>). A flame ionization detector (FID) was used to detect the methane when it came through at distinct times for CO<sub>2</sub> and HCHO. The column in the GC was a 30 m, 0.53 mm inner diameter RT U-Bond (Restek). The sample in the tube was then exposed to a test stream of approximately 250 mL/min of that contained about 250 ppm of HCHO in air from a volatilized sample of paraformaldehyde that was prepared using paraformaldehyde powder. The air downstream to the filter media granules was monitored for breakthrough using the SRI GC. The breakthrough time was defined as the time at which a concentration of 1 ppm was observed downstream to the sample.

*Powder X-ray Diffraction:*

Powder X-ray diffraction patterns were collected using a Phillips PW 1720 X-ray generator operated at a voltage of 40 kV and a current of 30 mA. The system is equipped with a Cu K $\alpha$  radiation source (wavelength = 1.54178 Å) and a diffracted beam monochromator.

Typical conditions were a scan rate of 0.05°/step and a dwell time of 40 s/step. The samples were ground into fine powder and mounted on an aluminum sample holder.

*Surface Area and Pore Size Measurements:*

N<sub>2</sub> adsorption isotherm and the pore size distribution were determined using a Micromeritics ASAP2010 at 77K. Samples were degassed at 150°C for 2-3 days before the measurement to remove residual moisture. Pore size distributions were determined using the BJH method (1-300nm) using software supplied by Micromeritics (ASAP 2010 V5.03 C). The BJH method is a known method and is described at E.P. Barrett, L.G. Joyner, P.H. Halenda, J. Am. Chem. Soc. 73 (1951) 373.

10 **Table 2. Selected Characterization Data for Examples 1, 3, 4, 6, and 8.**

Example	Material	Method	Phase by XRD	BET Surface Area (m <sup>2</sup> /g)	BJH Average Pore Volume (cm <sup>3</sup> /g)	BJH Pore Size (nm)
1	MnO <sub>x</sub>	1	Amorphous MnO <sub>x</sub>	214	0.23	4.4
3	85Mn15FeO <sub>x</sub>	1	Amorphous MnO <sub>x</sub>	348	0.23	3.1
4	80Mn20FeO <sub>x</sub>	1	Amorphous MnO <sub>x</sub>	382	0.18	2.6
6	MnO <sub>x</sub>	2	Amorphous MnO <sub>x</sub>	451	0.29	2.3
8	80Mn20FeO <sub>x</sub>	2	Amorphous MnO <sub>x</sub>	487	0.30	2.3

The samples of Examples 1-8 were challenged with vapors or gases using the test methods described above. The test results are shown below in Table 3 along with the test results from commercially available Calgon URC, a whetlerite multigas adsorbent prepared by impregnation of activated carbon with copper compounds, molybdenum compounds and salts of sulfuric acid.

**Table 3. Breakthrough Test Results**

Example <sup>1,2,3</sup>	Material	Method	Breakthrough Time (minutes)		
			SO <sub>2</sub> (±10%)	NH <sub>3</sub> (±10%)	HCHO (±10%)
	Calgon URC <sup>4</sup>	N/A	83	113	306
	Carulite <sup>5</sup>	N/A	175	189	N <sup>6</sup>
1	MnO <sub>x</sub>	1	278	190	465
4-Cu	80Mn20CuO <sub>x</sub>	1	231	277	N
4-Zn	80Mn20ZnO <sub>x</sub>	1	213	273	N

2	90Mn10FeOx	1	221	203	N
3	85Mn15FeOx	1	365	535	495
4	80Mn20FeOx	1	358	503	506
5	75Mn25FeOx	1	289	523	N
6	MnOx	2	380	175	N
8-Cu	80Mn20CuOx	2	229	130	N
7	90Mn10FeOx	2	340	156	N
8	80Mn20FeOx	2	410	180	N

<sup>1</sup>All filter media granules tested at 20x40 mesh size.

<sup>2</sup>Sample volume: 1.7 cc (SO<sub>2</sub>, NH<sub>3</sub>); 0.9 cc (HCHO)

<sup>3</sup>Average of 2-3 tests for breakthrough times

<sup>4</sup>Calgon URC (as received), commercially available from Calgon Carbon Company, Pittsburgh, PA, USA.

<sup>5</sup>Carulite (as received, sized to 20 x 40 mesh granules), commercially available from Carus Corporation, Peru, IL, USA.

<sup>6</sup>N signifies test was not undertaken.

## 10 Preparative Procedures for Method 2: Examples 9-10.

MnSO<sub>4</sub>/FeSO<sub>4</sub> mixed solutions (0.25M) were prepared by dissolving MnSO<sub>4</sub>•H<sub>2</sub>O and FeSO<sub>4</sub>•7H<sub>2</sub>O in molar Mn:Fe ratios of:

- Example 9 is 80:20 Mn:Fe
- Example 10 is 90:10 Mn:Cu

15 Example 9 was prepared using magnetic stirring with no sonication (ultrasonic mixing). A MnSO<sub>4</sub>/FeSO<sub>4</sub> mixed solution (0.25M) and (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (0.25M) solution were prepared as above. The pH of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution was adjusted to ~10 using 8% (vol.) NH<sub>3</sub>•H<sub>2</sub>O. Using a Masterflex peristaltic pump, the resulting (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution was added slowly to the MnSO<sub>4</sub>/FeSO<sub>4</sub> solution over a period of 15 hours with vigorous magnetic stirring. After the  
20 complete addition of the (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution, the precipitate was isolated by filtration and washed with deionized water repeatedly until the pH reached ~7. The product was then dried overnight in an oven at 60°C in air. The dried oxalate precipitate was then ground with a mortar and pestle and heated at 225 °C for 6 hours in air to obtain the final powder. The powder was then formed into pellets using a 17mm die and hydraulic press using a pressure of 8000 PSI. The  
25 pellets were then crushed and sized to 20 x 40 mesh granules. Example 10 was prepared in the same fashion as Example 9 using CuSO<sub>4</sub>•5H<sub>2</sub>O in place of FeSO<sub>4</sub>•7H<sub>2</sub>O, with another exception that the final heating period was 250 °C for 5 hours.

**Table 4. Selected Characterization Data for Examples 9 and 10.**

Example	Material	Method	Phase by XRD	BET Surface Area (m <sup>2</sup> /g)	BJH Average Pore Volume (cm <sup>3</sup> /g)	BJH Pore Size (nm)
9	80Mn20FeOx	2	Amorphous MnOx	445	N <sup>1</sup>	N
10	90Mn10CuOx	2	Amorphous MnOx	434	N	N

<sup>1</sup>N signifies analysis was not undertaken.

**Table 5. Breakthrough Test Results**

Example <sup>1,2,3</sup>	Material	Method	Breakthrough Time (minutes)		
			SO <sub>2</sub> (±10%)	NH <sub>3</sub> (±10%)	HCHO (±10%)
9	80Mn20FeOx	2	270	146	N <sup>4</sup>
10	90Mn10CuOx	2	295	150	N

<sup>1</sup>All filter media granules tested at 20x40 mesh size.

<sup>2</sup>Sample volume: 1.7 cc (SO<sub>2</sub>, NH<sub>3</sub>); 0.9 cc (HCHO)

<sup>3</sup>Average of 2-3 tests for breakthrough times

<sup>4</sup>N signifies test was not undertaken.

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Thus, embodiments of FILTER MEDIA FOR RESPIRATORY PROTECTION are disclosed.

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All references and publications cited herein are expressly incorporated herein by reference in their entirety into this disclosure, except to the extent they may directly contradict this disclosure. Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that a variety of alternate and/or equivalent implementations may be substituted for the specific embodiments shown and described without departing from the scope of the present disclosure. This application is intended to cover any adaptations or variations of the specific embodiments discussed herein. Therefore, it is intended that this disclosure be limited only by the claims and the equivalents thereof. The disclosed embodiments are presented for purposes of illustration and not limitation.

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What is claimed is:

1. A respiratory protection filter comprising:  
a housing having an air stream inlet and an air stream outlet and containing an amount of  
filtration media in fluid connection and between the air stream inlet and the air stream  
outlet, the filtration media comprising:  
iron-doped manganese oxide material having an average pore size (BJH method)  
in a range from 1 to 4 nm and a surface area (BET) of at least 300 m<sup>2</sup>/g, or at  
least 350 m<sup>2</sup>/g, or at least 400 m<sup>2</sup>/g.
2. The respiratory protection filter according to claim 1, wherein the iron-doped manganese  
oxide material is capable of removing a hazardous gas from an air stream passing through the  
filtration media at ambient conditions or atmospheric pressure and -20 to 40 degrees Celsius and  
5% to 95% relative humidity.
3. The respiratory protection filter according to claim 1 or 2, wherein the iron-doped  
manganese oxide material is produced from a chemical reaction that has a molar ratio of  
manganese:iron in a range from 95:5 to 70:30, or preferably in a range from 80:20 to 85:15.
4. The respiratory protection filter according to any preceding claim, wherein the iron-  
doped manganese oxide material defines granules having a mesh size in a range from 12 to 50,  
or from 20 to 40 U.S. standard sieve series.
5. The respiratory protection filter according to any preceding claim, wherein the iron-  
doped manganese oxide material has an apparent or bulk density of less than 1.3 g/mL, or less  
than 1 g/mL, or less than 0.8 g/mL, or less than 0.7 g/mL.
6. The respiratory protection filter according to any preceding claim, wherein the iron-  
doped manganese oxide material is in a form of compression derived granules.
7. A method for making the respiratory filter of claim 1, the method comprising:  
combining an iron (III) salt with manganese (II) salt in water to form an aqueous salt  
mixture;  
blending a permanganate solution with the aqueous salt mixture to form a wet precipitate;  
isolating and drying the precipitate to form an iron-doped manganese oxide material.

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8. The method according to claim 7, wherein the method has a processing temperature for all method steps that is no greater than 115 degrees Celsius.

9. The method according to any one of claims 7 to 8, wherein the blending step has a processing temperature in a range from 20 to 30 degrees Celsius.

10. The method according to any one of claims 7 to 9, wherein the combining step comprises combining a molar ratio of manganese (II) salt:iron (III) salt in a range from 95:5 to 70:30, or preferably in a range from 80:20 to 85:15.

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11. The method according to any one of claims 7 to 10, further comprising the step of granulating or compressing the iron-doped manganese oxide material into granules having a mesh size in a range from 12 to 50, or from 20 to 40 U.S. standard sieve series.

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12. The method according to any one of claims 7 to 11, further comprising placing the iron-doped manganese oxide material into a respiratory protection filter.

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13. A method for making the respiratory filter of claim 1, the method comprising:  
combining an iron (II) salt with manganese (II) salt in water to form an aqueous salt mixture;  
forming an ammonium oxalate solution with a pH in a range from 7 to 8;  
blending the ammonium oxalate solution with the aqueous salt mixture to form a wet Fe/Mn oxalate precipitate;  
drying the wet Fe/Mn oxalate precipitate to remove water and form a dry Fe/Mn oxalate precipitate;  
heating the dry Fe/Mn oxalate precipitate at a temperature in range from 200 to 250 degrees Celsius to form an iron-doped manganese oxide material.

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14. The method according to claim 13, wherein the blending step comprises ultrasonic mixing.

15. The method according to any one of claims 13 to 14, wherein the combining step comprises combining a molar ratio of manganese (II) salt:iron (II) salt in a range from 95:5 to 70:30, or preferably in a range from 80:20 to 85:15.

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16. The method according to any one of claims 13 to 15, further comprising the step of granulating or compressing the iron-doped manganese oxide material into granules having a mesh size in a range from 12 to 50, or from 20 to 40 U.S. standard sieve series.

5 17. The method according to any one of claims 13 to 16, further comprising placing the iron-doped manganese oxide material into a respiratory protection filter.

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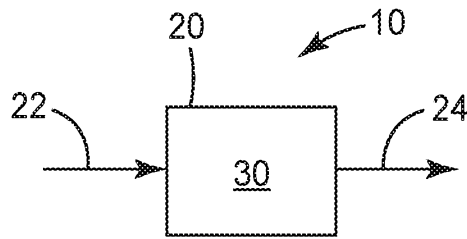


FIG. 1

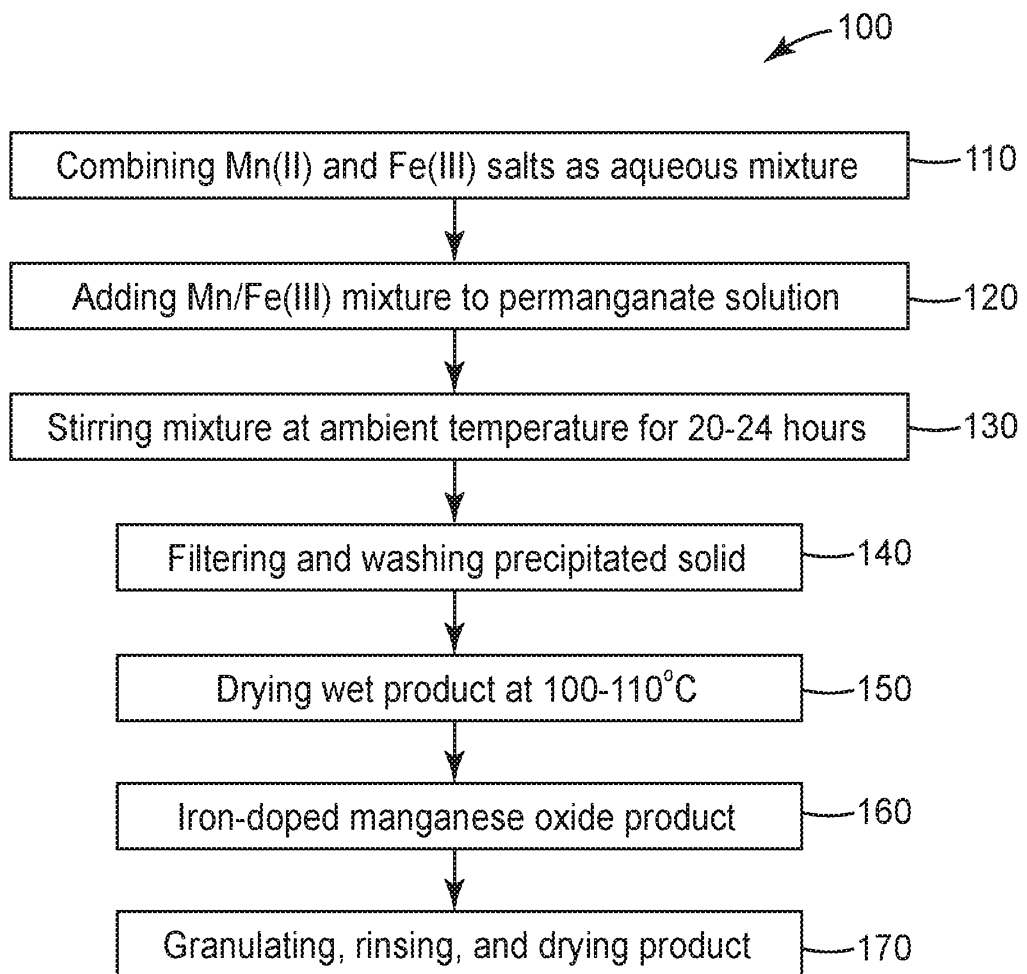
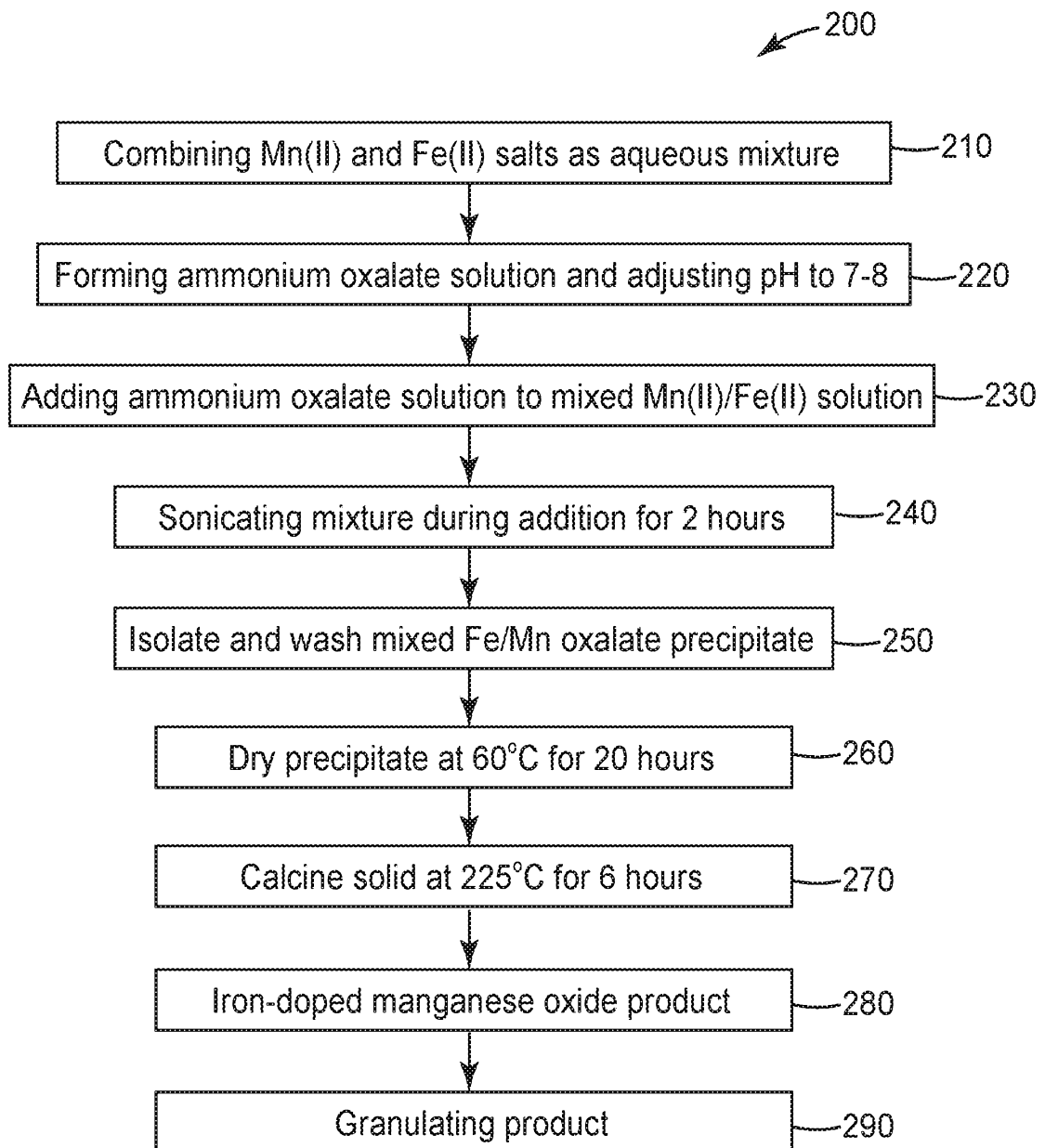


FIG. 2

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*FIG. 3*