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PROCESS FOR TREATMENT OF WATERS CONTAINING IRON,
MANGANESE AND ARSENIC

The present invention relates to a method for treatment of water. More precisely, the invention relates to a process of making waters intended for human consumption drinkable, by reducing iron,
5 manganese and arsenic.

The principle of elimination of iron depends on its oxidation and on the retention of the insoluble oxides thus formed ($\text{Fe}(\text{OH})_3$, Fe_2O_3). Oxidation with oxygen, or with chemical oxidants which may be
10 considered such as chlorine, chlorine dioxide, potassium permanganate or ozone, is necessary to attain sufficient oxidation-reduction potentials. The oxidant most currently used in this context is potassium permanganate.

15 The principle of elimination of arsenic depends on its chemical oxidation and its adsorption on insoluble metallic hydroxides (iron or aluminum in general).

The traditional physicochemical method of manganese and iron removal from waters consists of
20 chemically oxidizing the manganese and/or the iron

contained in them by means of potassium permanganate, chlorine or ozone, then filtering them on a granular material such as sand, for example. This can become coated with precipitates of manganese dioxide at the
5 end of several months and form a so-called natural "greensand". This "greensand" can likewise be prepared by depositing beforehand a film of hydrated manganese dioxide on the surface of a support which may be sand, acid clay, anthracite, zeolite, a dolomitic material,
10 etc. The manganese dioxide is then considered as playing the part of a catalyst.

This type of method has the major disadvantage of necessitating the addition at the beginning of a powerful oxidant such as potassium permanganate, free
15 chlorine, or ozone.

A granular material can also be prepared starting from a mainly inert material. Combined with finely divided manganese dioxide and/or an oxide of iron (Fe_3O_4 , for example), the whole is bound by a cement in
20 order to obtain granules of 10-60 mesh size, such as described in the patents US 2,145,901 and GB 471 277.

This type of method does not require the addition of oxidant. On the other hand, it requires the specific manufacture of the granular material, entailing
25 particular equipment to do this and the consequential investment, to which has to be added the cost of preparing the granular material.

The invention has particularly as its object to remedy the disadvantages or deficiencies of the prior
30 art.

More precisely, the object of the invention is to propose a physicochemical water treatment method enabling efficient removal of iron, manganese and arsenic contained in waters, without the addition of powerful oxidants.

The invention also has the object of providing such a method for which the preparation of the filtering material is appreciably simplified with respect to the prior art.

The invention also has the object of providing such a physicochemical method which uses a filtering material not requiring chemical regeneration, particularly by an oxidant.

Another object of the invention is to propose such a method for water treatment which gives rise to no, or very small, loss of filtering material.

Another object of the invention is to propose such a method which makes use of a filtering material which may be a residue directly from the mining industry, for example, requiring only a simple mechanical treatment before use.

Yet another object of the invention is to provide such a water treatment method which may be used on waters having variable and seasonal dissolved contents of iron, manganese and arsenic.

The invention also has the object of proposing such a method which is economical and simple to use.

These objects, as well as others which will become apparent in what follows, are attained by means of a water treatment method in order particularly to reduce the content of iron, manganese and arsenic,

characterized in that it comprises a step of causing the said waters to pass over at least one bed of filtering materials comprising an association:

- of at least one divided material based on iron oxide or hydroxide, or iron in the metallic state, in the form of particles of dimensions 0.3-2 mm;
- of grains of manganese dioxide having an apparent density of the order of 2 and hardness greater than 6 on Moh's scale.

10 It will be noted that in the context of the present description "apparent density of the order of 2" denotes a density which may vary from 1.7 to 2.3.

 According to the invention, the iron-based divided material used may therefore be metallic iron (valence equal to 0) or iron oxide or hydroxide. In the first case, it may be in the form of iron filings, chips, foils, etc. In the second case, grains of ferric or ferrous hydroxide may be concerned.

 Such an association of iron and manganese dioxide could be in the form of a mixture of iron-based divided material and grains of manganese dioxide, but also in the form of a superposition of layer(s) of iron-based divided material and layer(s) of manganese dioxide grains. In the latter case, the iron-based layer of divided material is preferably in the upper position, while the layer of manganese dioxide grains is preferably in the lower position.

 When a layer of grains of ferric hydroxide and a layer of grains of manganese dioxide is used, the layer of ferric hydroxide will advantageously have an apparent density of the order of 1.2-1.5.

The chosen specifics of density and hardness of such materials enable two uniform, stable layers of manganese dioxide and ferric or ferrous hydroxide to be maintained. More precisely, the hardness greater than 6
5 on Moh's scale of the manganese dioxide grains enables the initial particle size distribution and the initial adsorption capacity of the material to be maintained. Because of this, a negligible or zero consumption of the materials is found, giving a particularly
10 advantageous result connected to the fact that the materials are not constituted as consumables.

The principle of the invention is thus based, for the elimination of iron, arsenic and manganese, on the use of an association of iron-based divided material
15 and on manganese dioxide grains, with a density and hardness enabling manganese to be retained without the addition of oxidant, and without having to effect a chemical regeneration of the materials by means of an oxidant compound.

20 Such a method enables waters loaded with iron, manganese and arsenic to be efficiently treated by means of these two materials, chosen for their characteristics and properties. The addition of strong oxidants such as potassium permanganate, free chlorine,
25 or ozone is not necessary, whether for the reduction of the iron, manganese and arsenic content of the waters, or for the regeneration of the filtering material; this is in opposition to current practice.

Furthermore, the method according to the invention
30 is found to be particularly effective without its being necessary to provide the specific preparation of the

filtering material consisting of coating, using a cement, an inert material with grains of manganese dioxide as is the case in the prior solutions.

According to a noteworthy characteristic, when the
5 iron-based divided material used is iron hydroxide, this acts as an adsorbent.

According to another noteworthy characteristic, the manganese dioxide chosen by the Applicant acts as a catalyst, and also as an oxidant. The principle of its
10 catalytic activity is similar to that of the catalytic effect obtained with a manganese-treated sand ("greensand"), to which is added the capability of the material for acting as a support for the adsorption of manganese dissolved in the water.

15 Furthermore, manganese dioxide has an oxidant action for dissolved manganese present in the water to be treated.

It will furthermore be noted that this manganese dioxide is not selective for manganese, and also
20 oxidizes iron, arsenic and selenium. The Mn^{2+} and Fe^{2+} ions are oxidized by MnO_2 , and are deposited on the surface of the grains of the filtering material.

The overall oxidation-reduction reaction taking place at the surface of the material at the solid-
25 liquid interface, leads to the formation of manganese sesquioxide, Mn_2O_3 (solid), both by oxidation of the dissolved manganese and by reduction of solid manganese dioxide. The Mn_2O_3 thus produced progressively coats the grains of material.

30 According to an advantageous solution, the method comprises, when necessary, a step of regeneration of

the said filter bed, performed by simple washing by means of a stream of water and/or of a gaseous fluid such as air.

5 This regeneration step could be performed periodically, in particular taking account of the volumes of water treated and the seasonal variation of their manganese concentration.

p 10 According to another embodiment, the said regeneration step could also be performed when the said filtering material bed reaches a predetermined loss of load.

Monitoring, continuously or by sampling, of the residual manganese concentration of the treated water may indicate a loss of load of the filtering material
15 and bring about a decision to regenerate the filter bed.

According to a first embodiment of the regeneration step, the said washing is performed counter-current to the flow of water to be treated
20 within the said filter bed.

ce According to a second embodiment of the regeneration step, the said washing is effected co-current with the flow of water to be treated within the said filter bed.

25 According to a preferred solution, the iron-based divided material and/or the said manganese dioxide grains are associated with at least one other material chosen from among the following materials:

- sand,
- 30 - anthracite,
- grains of active carbon,

- neutralizing material.

Advantageously, the method comprises a preliminary step of crushing and screening the manganese dioxide so as to obtain a particle size of 0.3-1 mm.

5 It will be noted that, according to other embodiments which may be envisaged, the crushing and screening could vary in order to obtain a different particle size according to the desired filtration.

The method preferably includes a supplementary
10 step of pH adjustment of the said water by a treatment with air, caustic soda, or lime water, upstream of the filtration step.

The said association advantageously comprises by volume, 5%-95% of iron-based divided material and 95%-
15 5% of manganese oxide grains.

The said association preferably comprises about 70% of iron-based divided material and about 30% of manganese dioxide grains,

According to an embodiment, the said step
20 consisting causing the water to pass through at least one filtering material bed is performed at atmospheric pressure, but this step could alternatively be performed under pressure, according to another embodiment.

25 The said step advantageously consisting of passing said water over at least one bed of filtering material is performed with a contact time of 30 seconds to 10 minutes.

The method may be used either by means of filters
30 operating at atmospheric pressure, or by means of filters operating under pressure.

Other characteristics and advantages of the invention will more clearly become apparent on reading the following description of several embodiments of the invention, given by way of illustrative examples and
5 without limitation, with reference to the accompanying drawings.

- Figure 1 shows a first embodiment of an industrial unit for removal of iron and manganese and for elimination of arsenic according to the invention,
10 in which the water to be treated ascends through the filter, and

- Figure 2 shows a second embodiment of a unit of the same type in which the water descends through the filter.

15 In the industrial water treatment unit shown schematically in Figure 1, the water is brought by a duct 1 into the filter 2, which is open in the present case, that is, at atmospheric pressure, but which may be of any other type in other embodiments.

20 The filter contains a filter bed consisting of a mixture of about 70% by volume of ferric hydroxide grains and about 30% by volume of manganese dioxide grains. It will also be noted that in other embodiments which may be considered, particularly as a function of
25 the iron and manganese contents of the water to be treated, these proportions could for example be reversed. More generally, the bed contains, by volume, 5-95% iron and 95-5% of manganese.

The filter medium 3 is supported by a perforated
30 or fringed floor 11. Furthermore, note that the filter 2 is provided with conventional emptying means 13.

In the case of the open filter shown in Figure 1, the water flows by gravity through the said filter bed 3 and is collected at the base of the filter by a treated water outlet duct 4. An overflow 10 is provided if needed.

Upstream of the filtration, the water undergoes if necessary a pH adjustment step by air treatment. This adjustment is performed if the pH of the water to be treated is below 7.2. Such an adjustment is performed using an air compressor 5 and an air filter 6 connected to the water input duct 1.

To proceed to filter material regeneration, the unit has a washing air booster 7 connected to a duct 8 opening into the base of the filter 2.

In this manner, the washing air is conveyed at the same time or separately from the washing water, into the filter bed 3, counter-current to the water to be treated. The washing water is collected by a drain duct 9.

To demonstrate the effectiveness of the method according to the invention, used with the unit shown in Figure 1, the course of the arsenic and manganese contents of the raw water and the treated water was observed for a first application of manganese removal and arsenic elimination in surface water.

In this unit, the contact time of the water with the filtration bed is of the order of 3 minutes. However, in other embodiments, the contact time could be between 30 seconds and 10 minutes, as a function of the required percentage reduction and the desired residual content.

While the manganese content of raw waters varies between 40 and 410 $\mu\text{g/l}$, the effectiveness of the method is observed with a residual content of the treated water constantly below 10 $\mu\text{g/l}$, or a reduction
5 of as much as 97.5%.

It is thus clearly shown that the method which has been described enables the reduction of manganese and arsenic content of waters to be treated, which may show considerable seasonal variations.

10 With results equivalent or superior to those of prior art techniques, the method of using a specific filtering material avoids:

- recourse to oxidants, both for the filtration step and for filter bed regeneration;
- 15 - recourse to an exacting and costly preparation of a filtering material, as is the case for the prior solutions.

Referring to Figure 2, in which reference numerals identical to those of Figure 1 denote structural
20 elements identical or similar to those of Figure 1, the water no longer passes on a descending but on an ascending path through the filter bed. For this purpose, the duct 1 arrives in the lower portion of the filter 2, while the drain duct 4 is provided in its
25 upper portion.

Washing of the filter takes place by co-current injection of air and/or of wash water.

The filter bed 3, composed of an upper layer 3a of ferric hydroxide grains of density about 1.2-1.5
30 representing about 30% of the total volume of the filter bed 3, and of a lower layer 3b of manganese

dioxide grains of density of the order of 4 and of hardness greater than 6 on Moh's scale, representing about 70% of the total volume of the filter bed.

CLAIMS

1. Method of treatment of waters, in particular to reduce their iron, manganese and arsenic content, characterized in that it comprises at least one step consisting of passing the said waters over at least one
5 bed of filter material (3) comprising an association:
- of at least one iron-based divided material in the hydroxide, oxide or metallic state, in the form of particles of dimensions 0.3-2 mm;
- of manganese dioxide grains having an apparent
10 density of the order of 2 and a hardness greater than 6 on Moh's scale.

2. Method according to claim 1, characterized in that the said iron-based divided material used is metallic iron.

15 3. Method according to claim 2, characterized in that the said iron-based divided material used is in the form of filings and/or chips and/or foils.

4. Method according to claim 1, characterized in that the iron-based divided material used is in the
20 hydroxide state.

5. Method according to claim 4, characterized in that the iron-based divided material used is in the form of grains of ferric and/or ferrous hydroxide .

6. Method according to any one of claims 1-5,
25 characterized in that the said association of iron-based divided material and of manganese dioxide is in the form of a mixture of iron-based divided material and manganese dioxide grains.

7. Method according to any one of claims 1-5, characterized in that the said association of iron-based divided material and manganese dioxide is present in the form of a superposition of layer(s) (3a, 3b) of iron-based divided material and of manganese dioxide grains.

8. Method according to claim 7, characterized in that the said association of iron-based divided materials and of manganese dioxide is present in the form of an upper layer (3a) of iron-based divided material and a lower layer (3b) of manganese dioxide grains.

9. Method according to claim 8, characterized in that the said association of iron-based divided material and manganese dioxide grains is present in the form of a superposition of an upper layer (3a) of ferric hydroxide grains and a lower layer (3b) of manganese dioxide grains.

10. Method according to claim 9, characterized in that the layer of ferric hydroxide grains has an apparent density of about 1.2-1.5.

11. Method of water treatment according to any one of claims 1-10, characterized in that it comprises, when necessary, a step of regeneration of the said filtering material (3), performed by simple washing by means of a stream of water and/or of a gaseous fluid such as air.

12. Method of water treatment according to claim 11, characterized in that the washing is performed counter-current to the flow of water to be treated within the said filter bed.

13. Method according to claim 11, characterized in that the said washing is performed co-current with the flow of water to be treated within the said filter bed.

14. Method of water treatment according to any one
5 of claims 1-13, characterized in that the iron and/or the manganese dioxide grains are associated with at least one other material chosen from among the following materials:

- sand,
- 10 - anthracite,
- grains of active carbon,
- neutralizing material.

15. Method of water treatment according to any one of claims 1-14, characterized in that it comprises a
15 preliminary step of crushing and screening of manganese dioxide in order to obtain a particle size of 0.3-1 mm.

16. Method of water treatment according to any one of claims 1-15, characterized in that the said association of iron-based divided material and
20 manganese dioxide grains comprises by volume 5% - 95% of iron-based divided material and 95% - 5% of manganese dioxide grains.

17. Method of water treatment according to claim 16, characterized in that the said association
25 comprises by volume about 70% of iron-based divided material and 30% of manganese dioxide grains.

18. Method of water treatment according to any one of claims 1-17, characterized in that it comprises a supplementary step of pH adjustment of the said waters,
30 by treatment with air, caustic soda, or lime water, upstream of the filtration step.

19. Method of water treatment according to any one of claims 1-18, characterized in that the said step of causing the water to pass over at least one bed of filtering material is performed at atmospheric
5 pressure.

20. Method of water treatment according to any one of claims 1-18, characterized in that the said step consisting of causing the said waters to pass over at least one bed of filtering material is performed under
10 pressure.

21. Method of water treatment according to any one of claims 1-20, characterized in that the said step consisting of causing the said waters to pass over at least one bed of filtering material is performed with a
15 contact time of 30 seconds - 10 minutes.