

DescriptionProcessing of water by microorganisms

5 [0001] The present invention relates to a method of
microbiological processing of water, in particular
waste waters from semiconductor production, and
microorganisms which are suitable for use in such a
method. In addition, the invention relates to a
10 bioreactor, and also to a water processing plant having
such microorganisms.

[0002] Semiconductor production sites globally are
among the largest industrial water consumers. The
highest requirements are made of the quality of the
15 water required in the semiconductor industry. For
instance, the water must be essentially completely free
of particles and dissolved inorganic and organic
components. In recent years, attempts have increasingly
been made to reprocess waste waters from semiconductor
20 production (hereinafter also called reclaim water) and
to establish a circulation procedure in order to
minimize consumption of fresh water. Such a procedure
offers advantages in many aspects:

25 ➤ Waste waters from semiconductor production
generally have a better defined composition than
fresh water, and therefore they may be treated
more specifically.

30 ➤ Waste waters from semiconductor production do not
contain any significant amounts of inorganic
components and hardness-forming agents (calcium or
magnesium) and/or carbonates.

[0003] However, a problem for reprocessing is the
rather high fractions of organic components with which

waste waters from the semiconductor industry are generally admixed. Such waste waters customarily have a total organic carbon (TOC) content in the range between 500 ppb and 3000 ppb. The organic components are
5 predominantly residues of synthetic organic solvents. Compared with natural organic water components such as humic acids or biopolymers, these have a lower molar mass. In addition, they are polar and virtually indisociable. As an example thereof 2-propanol may be
10 mentioned, which frequently makes up the largest fraction of the impurities.

[0004] Therefore, if the production of ultrapure water for the semiconductor industry starts from reclaim water (and/or from a mixture of fresh water and reclaim
15 water), then special measures must be taken in order to remove said organic components from the water which is to be processed.

[0005] Some procedures are known from the prior art which are devoted to this special problem. For
20 instance, biological method stages started to be integrated a relatively long time ago in the process of ultrapure water processing (Golsham M. and Schmitt S.: Water reuse and reclaim operations at Hyundai semiconductor America, Ultrapure Water 05, 2001, 34-38;
25 JP 61111198; JP 2002-2336886). According to the procedures described there, microorganisms are either directly suspended in the process water or applied to solid support materials which are subsequently brought into contact with the process water. The microorganisms
30 take up organic compounds and also oxygen, nutrients and dissolved minerals from the waste water and convert these impurities to inert or easily removable compounds. Organic carbon is preferably mineralized in this case. Sewage sludge is generally used as a source
35 of the microorganisms, with which sewage sludge

suitable reactors in the ultrapure water processing process are inoculated.

[0006] In fact, a treatment with microorganisms can lead to a sometimes very significant reduction of the fraction of organic components. However, it has been observed that efficiency and reliability of such measures are frequently subject to large fluctuations. The results obtained have not always been reproducible. Furthermore, in many cases there is also the risk that the water treatment plants are microbially inoculated in an uncontrolled manner, in particular also with pathogenic microorganisms.

[0007] The object of the present invention is to provide a technical solution for the abovementioned problem. The solution should efficiently and reproducibly enable, in particular, the purification of waste waters from the semiconductor industry having a high fraction of low-molecular-weight organic impurities such as 2-propanol and acetone. In this case they should be configured simply and inexpensively.

[0008] This object is achieved by the method having the features of Claim 1, the bioreactor having the features of Claim 11 and also the microorganisms having the features of Claims 16 to 18. Preferred embodiments of the method according to the invention are described in dependent Claims 2 to 10. Preferred embodiments of the bioreactor according to the invention and of the microorganisms according to the invention are found in dependent Claims 12 to 14 and also 19 and 20. In addition, a water processing plant having the features of Claim 15 and also the use having the features of Claim 21 are also subject matter of the present invention. The wording of all claims is hereby incorporated in this description by reference.

[0009] A method according to the invention serves for the microbiological processing of water, in particular waste waters from semiconductor production. It comprises the water which is to be processed being
5 treated in a bioreactor with microorganisms. Particularly preferably, according to the invention, the water which is to be processed is treated with microorganisms of which at least 70% can break down 2-propanol and/or acetone. The microorganisms are
10 therefore specialized in the breakdown of said compounds and certainly not completely undefined.

[0010] The microorganisms can in principle here be not only a single bacterial strain but also bacterial cultures which comprise a plurality of bacterial
15 strains or even strains from different bacterial genera. The critical factor is that the fraction of microorganisms which break down 2-propanol and/or acetone does not fall below said limit. Preferably, the fraction of microorganisms breaking down 2-propanol
20 and/or acetone is greater than 80%, in particular greater than 90%, particularly preferably virtually 100%.

[0011] As mentioned at the outset, it is known to use microorganisms from sewage sludge for breaking down
25 low-molecular-weight organic compounds. However, this is in no way a targeted selection of microorganisms. The fraction of microorganisms which break down specifically determined impurities, is in all procedures known to date rather determined by chance.

30 [0012] In contrast, as per the process according to the invention, preferably microorganisms are used in a targeted manner, which microorganisms have growth and breakdown kinetics matched to specific impurities, namely to 2-propanol and/or acetone. By this measure,
35 organic carbon contained in reclaim water was

reproducibly and extremely efficiently removed. Generally - starting from reclaim water having a TOC value between 500 ppb and 3000 ppb - breakdown rates of 80% or more were always observed. Such a reliable
5 solution for removing organic carbon contained in reclaim water is to date not known from the prior art.

[0013] In the preparatory work for the present invention, diverse bacterial strains of different genera were investigated for their suitability in a method
10 according to the invention. Particularly suitable microorganisms were identified within the bacterial genus *Xanthobacter*. Correspondingly, in the context of a method according to the invention, the water which is to be processed is treated particularly preferably with
15 at least one bacterial strain of the bacterial genus *Xanthobacter* and/or a mutant thereof.

[0014] The strain which was deposited under the number DSM No. 19987 at the deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ [German
20 Collection of Microorganisms and Cell Cultures]) has proved to be particularly suitable.

[0015] On standard media, this strain generally formed transparent whiteish matt colonies having a smooth rim, round growth, homogeneous structure and flat profile.
25 Diplococci having coccoid cell shape and rounded corners, a width of approximately 0.8 μm and a length of approximately 1.2 μm were observed.

[0016] Precise phylogenetic assignment was made by determining the nucleic acid sequence by means of
30 direct sequencing of the PCR-amplified 16S rRNA. Thereafter the sequence data were compared with the known sequences of representatives of the genus *Xanthobacter*. The highest sequence agreement of 99.5% was found with *Xanthobacter flavus* (DSM 338).

[0017] In addition, the water which is to be processed can, according to the present invention, also be treated with at least one bacterial strain of the bacterial genus *Rhodococcus* and/or a mutant thereof.

5 Such bacterial strains have also proved to be very suitable for use in a method according to the invention.

[0018] In particular, the strain which was deposited at the deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ) under the DSM No. 19985 was
10 identified as particularly suitable.

[0019] For this strain also, the nucleic acid sequence was determined by means of direct sequencing of the PCR-amplified 16S rRNA. By comparing the sequence data
15 with the sequences of known representatives of the genus *Rhodococcus*, the strain was identified as a representative of suborder *Rhodococcus ruber*.

[0020] Bacterial strains of the bacterial genus *Paracoccus* and/or mutants thereof are likewise highly
20 suitable for use in a method according to the invention. In particular, very good results were achieved using the bacterial strain which was deposited under the DSM No. 19986 at the deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ).

25 [0021] The above bacterial strains identified as preferred can be used not only individually but also in combination in a method according to the invention. They can also be present in mixed cultures with one or more other bacterial strains which, if appropriate, are
30 not able to break down 2-propanol and/or acetone.

[0022] Preferably, the fraction of microorganisms which break down 2-propanol and/or acetone is then always above said preferred limit values. In preferred

embodiments of the method according to the invention, the microorganisms used are exclusively one or more of the strains identified as preferred.

5 [0023] The abovementioned bioreactor shall be taken to mean in the present context in the simplest case a container in which the water which is to be treated is brought into contact with the microorganisms, for example by suspending the microorganisms in the water which is to be processed.

10 [0024] However, particularly preferably the bioreactor used is an aerated or non-aerated filtration unit which in preferred embodiments has a particulate filter material. Equipped in such a manner, the bioreactor can fulfil simultaneously a plurality of functions.
15 Firstly, low-molecular-weight organic components such as 2-propanol and/or acetone can be broken down in it, secondly, it can act as a filter in order to remove particles from the water which is to be processed.

[0025] Particulate filter materials, owing to their
20 large surface area, offer good conditions for colonization by microorganisms. Particularly preferably, the microorganisms which are used in a method according to the invention are immobilized on the filter material in a bioreactor constructed as a
25 filtration unit. The microorganisms can form a continuous film on the particles and/or in pores of the filter material.

[0026] In the literature, generally a flow path from bottom to top is reported as a preferred mode of
30 operation of biofilters (see, e.g., EP 585036, JP 7284799, JP 6063592 and JP 62065792). When the flow passes through a biofilter from bottom to top, however, microorganisms can easily be washed out with the process water. Consequently, process stages downstream

can be microbially inoculated. Bioreactors known from the prior art, for this reason, are frequently combined with additional filtration stages which are connected downstream of the biofilter (see, e.g., JP 63185494, JP 8197094 and JP 9155371). However, such solutions are
5 complex in terms of equipment and expensive.

[0027] According to the invention it is preferred that the water which is to be processed is passed as waste stream through such a bioreactor which is constructed
10 as a filtration unit. In this manner it was ensured that elevated concentrations of microorganisms did not exit from the filtration unit. Reclaim water, for example, downstream of the biological treatment can be introduced directly into the filtrate water tank of a
15 water processing plant.

[0028] A bioreactor according to the invention serves specifically for water processing, in particular for processing waste water from the semiconductor industry, and is suitable, in particular, for use in a method
20 according to the invention. It has microorganisms which can break down 2-propanol and/or acetone.

[0029] In preferred embodiments it has microorganisms of which at least 70%, preferably more than 80%, in particular more than 90%, particularly preferably
25 virtually 100%, can break down 2-propanol and/or acetone.

[0030] As mentioned above, bacterial strains of the bacterial genus *Xanthobacter* and/or *Rhodococcus* and/or *Paracoccus* or mutants thereof are particularly suitable
30 as microorganisms. The above description of microorganisms which can preferably be used is hereby explicitly incorporated herein by reference.

[0031] According to the above embodiments, a bioreactor according to the invention, in preferred embodiments, is constructed as an aerated or non-aerated filtration unit, wherein the filtration unit
5 has a particulate filter material on which the microorganisms are immobilized. The advantageous bifunctionality of such a bioreactor has already been considered above.

[0032] The particulate filter material is particularly
10 preferably activated carbon. However, other materials, for example structured or irregular packings of plastics such as polystyrene, sand, expanded clay or anthracite, can also be very highly suitable. In preferred embodiments, the particulate filter material
15 can be porous, in particular have pores having a size which exceeds the size of the microorganisms at least by a factor of 10.

[0033] Activated carbon has a significant adsorption capacity for organic solvents, in particular for
20 2-propanol and acetone. By loading the filter material with these solvents, a reservoir of substrate is formed to which the microbiological culture is specifically adapted. In operation, fluctuations in rate and composition of the waste water to be treated can be
25 compensated for.

[0034] The present invention further comprises a water processing plant which is characterized in that it has a bioreactor according to the invention. Water processing plants of the type in question for producing
30 ultrapure water, in particular for purposes of the semiconductor industry, are sufficiently known from the prior art and therefore do not need to be described in detail in the context of this application.

[0035] The abovementioned microorganisms which are particularly suitable for use in a method according to the invention or in a bioreactor according to the invention are also comprised by the present invention.

5 [0036] In agreement with the above details, a microorganism according to the invention is distinguished in particular in that it is a bacterial strain of the bacterial genus *Xanthobacter* having the DSM No. 19987 or a mutant thereof. A further
10 microorganism according to the invention is distinguished in that it is a bacterial strain of the bacterial genus *Rhodococcus* having the DSM No. 19985 or a mutant thereof. A third microorganism according to the invention belongs to the genus *Paracoccus* and was
15 deposited at the DSMZ under the DSM No. 19986.

[0037] In preferred embodiments, microorganisms according to the invention can be immobilized on a support material such as activated carbon. Further suitable supports have been mentioned above as filter
20 materials.

[0038] In addition, it can be preferred that microorganisms according to the invention are present packed in a water-tight, air-permeable container. This is because, surprisingly, it is proved that
25 microorganisms according to the invention which are immobilized in particular on activated carbon can be preserved even over relatively long time periods, provided they are packed in containers which ensure sufficient oxygen supply to the microorganisms. Such
30 containers are, for example, flat bags made of plastic film, preferably polyethylene, in particular having a film thickness of approximately 0.05 mm. These have sufficient air permeability in order to ensure the oxygen supply of enclosed microorganisms over
35 relatively long time periods of up to several weeks.

The nutrient requirement of the microorganisms in this time period can be covered, for example, by 2-propanol stored by adsorption on the support material.

[0039] The bags can be closed in a sterile and water-tight manner. In this manner the immobilized microorganisms can be stored over relatively long time periods and transported over large distances to the site of use. At the site of use, e.g., the fixed bed of a filtration unit, for example a fixed bed of activated carbon, can very simply be inoculated with the immobilized microorganisms (conversion of a simple filtration unit into a bioreactor according to the invention). Addition of one part by volume of activated carbon having microorganisms immobilized thereon to generally 50 to 10 000 parts by volume of fixed bed is generally sufficient.

[0040] An important condition for the rapid multiplication of microorganisms in the bioreactor is the addition of nutrient salts to the reactor feed. The nutrient salts are preferably added until the bioreactor has reached its full output. The nutrient salts preferably contain the required macro elements (in particular N, P, S, Na, Ca and Mg) and also trace elements (in particular Fe, Cu, Cr, Co and Zn). The addition of nutrient salts is adjusted, in particular, in such a manner that in the reactor feed the mole-based concentrations of the elements C, N and P are in the ratio C:N:P = 100:10:1 to one another.

[0041] Several advantages result from the availability of the microorganisms according to the invention:

- The availability at short notice of microorganisms, e.g. for inoculating activated carbon fixed beds, is ensured at all times.

- The microorganisms can be provided in a constant and controlled quality.
- The above-described microorganisms are not pathogenic, and their use is therefore risk-free.
- 5 - The requirements of the biomatter regulation are complied with in full.
- The bioreactors can be activated by personnel who are not specially trained.
- Installation and operation of separate
10 fermentation plants at the site of the bioreactor are avoided.
- The bioreactor can be very rapidly put into operation, its start up-time is greatly shortened.

[0042] The use of one or more of said microorganisms
15 according to the invention for processing water, in particular in a method according to the invention or in a bioreactor according to the invention, is subject matter of the present invention. Preferred embodiments of the uses according to the invention result from the
20 above descriptions and need not be presented separately again.

[0043] Details on the features described and also other features of the invention result from the following description of preferred embodiments in
25 combination with the drawing and the subclaims. In this case the individual features of the invention can be effected each alone or in combination with one another.

[0044] **Fig. 1** shows a flow chart of an embodiment of a subsection of a water processing plant according to the
30 invention for treating reclaim water.

[0045] The figure shows the water tank 2 having the feed 11 for reclaim water. The water tank 2 has a means for controlling the pH of the reclaim water which is contained. Preferably, the pH in the water tank is set

to values between 4 and 9, in particular between 7 and 8. From the water tank 2, a line 12 leads to the bioreactor 1, in which there is situated a fixed bed of activated carbon, the surface of which is colonized by microorganisms of the strain having the DSM No. 19985. Before the reclaim water is introduced into the bioreactor 1, the reclaim water can be admixed, if needed, with electrolyte from the reservoir tank 3 via the line 16. This is necessary, if appropriate, since the reclaim water must not be completely salt free in order to ensure in the long term the survival of the microorganisms in the bioreactor. In the reservoir tanks 4 and 5 there are situated 2-propanol and nutrient salts. From these, substrate (e.g. 2-propanol) and nutrients can be added to the reclaim water via lines 17 and 18, which can, if appropriate, be necessary in the activation phase or for compensating for concentration variations in operation. If required, the water which is to be processed can be circulated and also aerated. The latter can be necessary during start-up of the biological activation. The valves 6a and 6b serve for switching over between production operation, circulation and backwash. The latter can be necessary, e.g., when the fixed bed of the bioreactor is blocked by dirt particles from the water which is to be processed. Furthermore, the water processing plant has a circulation pump 7 for circulation operation and also a shut-off valve 8 for the circulated stream. The outlet for water which is treated in the bioreactor in the production mode and also the feed of the backwash stream are indicated by the reference signs 13 and 14.

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Claims

1. Method for the microbiological processing of water, in particular waste waters from semiconductor
5 production, wherein the water which is to be processed is treated in a bioreactor with microorganisms, characterized in that at least 70% of the microorganisms can break down 2-propanol and/or acetone.
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2. Method according to Claim 1 or the preamble of Claim 1, characterized in that the water which is to be processed is treated with a bacterial strain of the bacterial genus *Xanthobacter* and/or a mutant thereof.
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3. Method according to Claim 2, characterized in that the bacterial strain is a representative of the species *Xanthobacter flavus*, in particular the strain having the DSM No. 19987.
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4. Method according to one of the preceding claims or the preamble of Claim 1, characterized in that the water which is to be processed is treated with a bacterial strain of the bacterial genus *Rhodococcus*
25 and/or a mutant thereof.
5. Method according to Claim 4, characterized in that the bacterial strain is a representative of the species *Rhodococcus ruber*, in particular the strain having the
30 DMS No. 19985.
6. Method according to one of the preceding claims or the preamble of Claim 1, characterized in that the water which is to be processed is treated with a
35 bacterial strain of the bacterial genus *Paracoccus* and/or a mutant thereof.

7. Method according to Claim 6, characterized in that the bacterial strain is the strain having the DMS No. 19986.

5 8. Method according to one of the preceding claims, characterized in that, as bioreactor, use is made of a filtration unit which in preferred embodiments has a particulate filter material.

10 9. Method according to Claim 8, characterized in that the microorganisms are immobilized on the filter material.

10. Method according to one of Claims 8 or 9, characterized in that the water which is to be processed is passed as waste stream through the filtration unit for treatment.

11. Bioreactor for water processing, in particular for use in a method according to one of the preceding claims, characterized in that it has microorganisms of which at least 70% can break down 2-propanol and/or acetone.

12. Bioreactor according to Claim 11 or the preamble of Claim 11, characterized in that it has at least one bacterial strain of the bacterial genera *Xanthobacter* and/or *Rhodococcus* and/or *Paracoccus* and/or at least one mutant thereof.

13. Bioreactor according to Claim 11 or Claim 12, characterized in that it is constructed as a filtration unit, wherein the filtration unit preferably has a particulate filter material on which the microorganisms are immobilized.

14. Bioreactor according to Claim 13, characterized in that the particulate filter material is activated carbon.
- 5 15. Water processing plant, characterized by a bioreactor according to one of Claims 11 to 14.
- 10 16. Microorganism, in particular for use in a method, a bioreactor, or in a water processing plant according to one of Claims 1 to 15, characterized in that it is a bacterial strain of the bacterial genus *Xanthobacter* having the DSM No. 19987 or a mutant thereof.
- 15 17. Microorganism, in particular for use in a method, a bioreactor, or in a water processing plant according to one of Claims 1 to 15, characterized in that it is a bacterial strain of the bacterial genus *Rhodococcus* having the DSM No. 19985 or a mutant thereof.
- 20 18. Microorganism, in particular for use in a method, a bioreactor, or in a water processing plant according to one of Claims 1 to 15, characterized in that it is a bacterial strain of the bacterial genus *Paracoccus* having the DSM No. 19986 or a mutant thereof.
- 25 19. Microorganism according to one of Claims 16 to 18, characterized in that it is immobilized on a support such as activated carbon.
- 30 20. Microorganism according to one of Claims 16 to 19, characterized in that it is packed in a water-tight, air-permeable container.
- 35 21. Use of a microorganism according to one of Claims 16 to 20 for processing water, in particular in a method, a bioreactor, or in a water processing plant according to one of Claims 1 to 15.