

Use of Oil-in-Water Emulsions in Aerobic Biological Sewage Treatment Plants

The present invention relates to the use of oil-in-water emulsions for reducing the air and/or oxygen demand of aerobic, biological sewage treatment plants. The present invention also relates to the use of oil-in-water emulsions for improving denitrification in aerobic, biological sewage treatment plants.

Sewage treatment plants are used in the purification of municipal and/or industrial waste waters to remove coarse dirt particles and biologically degradable substances from the waste water. As a rule, sewage treatment plants are comprised of a mechanical waste water purification, wherein coarse dirt particles and primary sludge are removed, and a biological waste water purification.

The first section of a biological waste water purification is the so-called aeration tank. The aeration tank contains the activated sludge which in its outer zone consists of microorganisms inducing flocculation. The waste water to be purified is introduced into the aeration tank and mixed with the activated sludge so as to form a suspension of water and microorganisms. Enzymes continuously formed by the microorganisms catalyze the oxidation of organic and NH_4 -containing waste water components to yield CO_2 and H_2O , and NO_2 and H_2O , respectively. The oxidation of the waste water components and the respiration of the microorganisms require oxygen and therefore, the suspension has to be aerated. As a rule, such aeration is effected using air, oxygen-enriched air, or pure oxygen, where an oxygen concentration of 1-3 mg/l in the suspension must be ensured. Following a certain residence time of the waste water in the aeration tank, virtually all of the biologically degradable waste water components have been oxidized, and the suspen-

sion is pumped into a secondary sedimentation tank wherein the purified water is separated from the microorganisms, mostly by sedimentation. The microorganisms are pumped back into the aeration tank, while the purified water exits the sewage treatment plant.

The aeration tank is supplied with oxygen by means of aeration systems dispersing the air and/or oxygen in the aeration tank, mostly in the form of fine bubbles. Indeed, such aeration systems have been optimized over many years, but even today, supplying oxygen is highly energy-consuming and thus, costly, because the aeration systems normally involve a high pressure loss.

It was therefore the object of the invention to provide materials or compositions that would reduce the oxygen demand and thus, the energy costs in aerobic, biological sewage treatment plants.

According to the invention, said object is accomplished by using oil-in-water emulsions for reducing the air and/or oxygen demand of aerobic biological sewage treatment plants, said oil-in-water emulsions containing in their oil phase at least one compound of the following classes of compounds or a mixture of members of the following classes of compounds:

- saturated or unsaturated, open-chain or cyclic, normal or isomeric hydrocarbons with 8-30 carbon atoms;
- saturated or unsaturated fatty alcohols, saturated or unsaturated fatty acids, fatty acid monoalkyl esters, fatty acid amides, or fatty acid monoalkylamides of saturated or unsaturated fatty acids, the fatty alcohols, fatty acids and fatty acid esters of the mentioned compounds having 8-30 carbon atoms;

- monoesters or polyesters of a saturated or unsaturated carboxylic acid or dicarboxylic acid having 4-30 carbon atoms with a monoalcohol and/or a polyol;
- polyamides of saturated or unsaturated fatty acids having 8-30 carbon atoms with aliphatic polyamines having 2-6 nitrogen atoms;
- acyclic, preferably monocyclic and/or bicyclic terpenes, particularly terpene hydrocarbons and/or terpene alcohols; and/or
- polyoxyalkylene compounds based on alkylene oxides and alkylene oxides with fatty alcohols and/or C₁₂-C₁₈ fatty acids and/or fatty acid glycerides of C₁₂-C₁₈ fatty acids.

The above-described oil-in-water emulsions are familiar from various fields. However, it was surprising to find that these emulsions have the property of reducing the oxygen demand of aerobic biological sewage treatment plants.

In the meaning of the invention, an aerobic biological sewage treatment plant is any municipal and/or industrial sewage treatment plant known to those skilled in the art, wherein the biologically degradable waste water components are eliminated from the waste water by oxidation. For example, such sewage treatment plants have been described in Taschenbuch der Stadtentwässerung, R. Oldenburg Verlag, Munich, Vienna, 1990, pp. 81-333; Ullmann's Encyclopedia of Industrial Chemistry, VCH-Verlagsgesellschaft, 1995, chapter 2.1, which hereby are incorporated by reference and thus deemed part of the disclosure.

Such aerobic, biological sewage treatment plants preferably have aeration tanks wherein the microorganisms are either



suspended or immobilized, with suspended microorganisms being preferred. Oxygen is introduced in the aeration tanks in such an amount that the oxygen concentration in the liquid surrounding the microorganisms preferably is 1-3 mg/l. The oxygen can be introduced in the aeration tank in the form of atmospheric oxygen and/or pure oxygen.

The production of the emulsions to be used according to the invention, particularly of stable oil-in-water emulsions, is well-known. To this end, the oil component is emulsified in water using suitable, well-known oil-in-water emulsifiers. Predominantly, the hydrophobic phase represents the active substance.

The hydrophobic oil component may be exemplified by the following:

- saturated hydrocarbons such as octane, tetradecane, octadecane, eisodecane; decene, hexadecene, and technical α -olefins;
- fatty alcohols such as octanol, dodecanol, tridecanol, hexadecanol, octadecanol, behenyl alcohol;
- fatty acids such as capric acid, stearic acid, melissic acid, oleic acid, and linolenic acid;
- fatty acid esters such as methyl stearate, octadecyl palmitate, octyl oleate, glycerol mono- and trioleate, ethylene glycol dilaurate, sorbitan stearates and oleates, and/or dibutyl adipate;
- fatty acid amides such as stearamide, coconut fatty acid butylamide, acetic acid oleylamide, and ethylene-bisstearamide;
- terpenes such as menthol or orange terpene (Weißmer Baltische HG, Hamburg).

Other suitable commercially available hydrocarbons or hydrocarbon mixtures are paraffin oil or mineral oil.

In addition, fats and oils on native basis are suitable, particularly vegetable oils and preferably rape oil.

The saturated or unsaturated fatty alcohols which, according to the invention, may be used as emulsion components, can be obtained according to well-known methods, e.g. in the oxo process as oxoalcohols or, according to the Guerbet reaction, as Guerbet alcohols.

As polyoxyalkylene compounds on the basis of alkylene oxides and/or fatty acid glycerides of C_{12} - C_{18} fatty acids, those described in, *inter alia*, DE-AS 12 70 542 and EP 0,247,509 B1 are used.

When using terpenes, they are preferably used in admixture with a saturated or unsaturated fatty alcohol.

The oil phase ratio in the oil-in-water emulsion is from 1 to 90% by weight, preferably from 1 to 50% by weight, and more preferably from 5 to 30% by weight of the overall emulsion.

The oil-in-water emulsions to be used according to the invention are employed as such or diluted with water, or water and/or mixtures containing solvents. The emulsion to be used according to the invention can be added at any point upstream of or in the aeration tank, with addition to the waste water to be purified immediately before its entry into the aeration tank being preferred.

The added amount preferably is from 0.1 to 1000 ppm, more preferably from 0.5 to 200 ppm, and even more preferably from 1.0 to 50 ppm, relative to the waste water to be purified.

By virtue of the emulsions to be used according to the invention, the amount of oxygen that has to be introduced into the aeration tank in order to oxidize the waste water components can be reduced by up to 60%. The emulsions to be used according to the invention have no or merely low toxicity and may be rated as water-polluting class 1; they are biologically degradable.

The invention will be illustrated with reference to an Example. These illustrations are given merely by way of example and do not limit the general idea of the invention.

Example 1

The pilot plant used in accordance with the Examples is illustrated in Figure 1 and operates according to the upstream denitrification principle. The plant is comprised of a receiver tank 1 and one tank 2, 3 each time for performing the denitrification and nitrification, with tank 3 being the so-called aeration tank. Each tank 2, 3 has a volume of 90 l. The receiver tank 1 is used to compensate fluctuations in the waste water composition and is dimensioned to be of such a size that the waste water composition remains constant for about 10 days. In addition, the pilot plant includes a secondary sedimentation 4.

Waste water at 5 l/h is pumped from the receiver tank 1 into the denitrification tank 2. The waste water has been taken from the inflow of the Neuss-Süd sewage treatment plant in Neuss-Weckhoven, Germany, but has been subjected to a previous mechanical purification. 70% of the waste water is of municipal origin and 30% of industrial origin. After the waste water has passed the denitrification 2 wherein NO_2 is reduced to yield N_2 , the waste water components are oxidized in aeration tank 3. Thereafter, the

waste water passes into the secondary sedimentation 4 wherein the sewage sludge is separated from the purified waste water. An internal recirculation stream between denitrification 2 and aeration tank 3 is maintained in order to preserve the biological equilibrium.

The bottom of aeration tank 2 has an aeration system which is used to disperse the air in the form of fine bubbles. The amount of air introduced into aeration tank 2 is regulated in such a way that an oxygen concentration in the aeration tank of 2 mg/l is maintained in the liquid. The amount of air fed into the aeration tank 2 is measured using a rotameter. The oxygen concentration in the liquid is measured using an electrode from WTW Company.

An oil-in-water emulsion is added continuously to the inflow section, optionally using a metering pump 5. This emulsion consisted of 14 kg of terpene, 1.0 kg of hexadecanol, 7 kg of a 75% paraffinsulfonate, and 2.1 kg of water, and was fused homogeneously and subsequently poured with stirring into a 60°C warm solution of 74.5 kg of water and 1.4 kg of an oleyl alcohol reacted with 20 moles of ethylene oxide. An oil-in-water emulsion including about 2.5% solids had formed.

Initially, the pilot plant was operated for several days with no addition of the above emulsion until constant conditions were present in the pilot plant. *Inter alia*, the introduced amount of air and the elimination performance with respect to COD (chemical oxygen demand) and nitrogen were measured continuously during this period. The amount of introduced air was 2 l/min on an average during this period.

After the pilot plant had been operated for several days under these constant conditions, the oil-in-water emulsion according to the invention was metered into the inflow of

tank 2 in such an amount that its concentration in the inflow of tank 2 was 2 ppm. Similarly, the amount of introduced air and the elimination performance of the pilot plant were measured in this test. Following an adaptation phase of about 3 days, the amount of introduced air was not more than 1.2 l/min on an average at otherwise unchanged conditions, so that the amount of introduced air and thus, the amount of energy required for this purpose had been reduced by about 40%. The COD and/or nitrogen elimination performance of the pilot plant were not impaired by metering the emulsion of the invention.

Likewise, the sedimentation behavior of the microorganisms had not been changed by adding the emulsion of the invention.

The present invention is also directed to the use of the above-specified oil-in-water emulsions for improving denitrification in aerobic biological sewage treatment plants, said oil-in-water emulsions, as previously mentioned, containing in their oil phase at least one compound of the following classes of compounds or a mixture of members of the following classes of compounds:

- saturated or unsaturated, open-chain or cyclic, normal or isomeric hydrocarbons with 8-30 carbon atoms;
- saturated or unsaturated fatty alcohols, saturated or unsaturated fatty acids, fatty acid monoalkyl esters, fatty acid amides, or fatty acid monoalkylamides of saturated or unsaturated fatty acids, the fatty alcohols, fatty acids and fatty acid esters of the mentioned compounds having 8-30 carbon atoms;
- monoesters or polyesters of a saturated or unsaturated carboxylic acid or dicarboxylic acid having 4-30 carbon atoms with a monoalcohol and/or a polyol;

- polyamides of saturated or unsaturated fatty acids having 8-30 carbon atoms with aliphatic polyamines having 2-6 nitrogen atoms;
- acyclic, preferably monocyclic and/or bicyclic terpenes, particularly terpene hydrocarbons and/or terpene alcohols; and/or
- polyoxyalkylene compounds based on alkylene oxides and alkylene oxides with fatty alcohols and/or C_{12} - C_{18} fatty acids and/or fatty acid glycerides of C_{12} - C_{18} fatty acids.

The above-described oil-in-water emulsions are familiar from various fields. However, it was surprising to find that these emulsions improve the denitrification in aerobic sewage treatment plants.

In the meaning of the invention, an aerobic biological sewage treatment plant is any municipal and/or industrial sewage treatment plant known to those skilled in the art, wherein the biologically degradable waste water components are eliminated from the waste water by oxidation, and which has at least one denitrification stage. In said denitrification stage, NO_3^- is reduced to yield N_2 . The denitrification stage can be arranged upstream or downstream of the so-called aeration tank. Preferably, the waste water to be treated passes through the denitrification stage prior to being treated in the so-called aeration tank.

The production of the emulsions to be used according to the invention, particularly of stable oil-in-water emulsions, is well-known. To this end, the oil component is emulsified in water using suitable, well-known oil-in-water emulsifiers. Predominantly, the hydrophobic phase represents the active substance.



The hydrophobic oil component may be exemplified by the following:

- saturated hydrocarbons such as octane, tetradecane, octadecane, eisodecane; decene, hexadecene, and technical α -olefins;
- fatty alcohols such as octanol, dodecanol, tridecanol, hexadecanol, octadecanol, behenyl alcohol;
- fatty acids such as capric acid, stearic acid, melissic acid, oleic acid, and linolenic acid;
- fatty acid esters such as methyl stearate, octadecyl palmitate, octyl oleate, glycerol mono- and trioleate, ethylene glycol dilaurate, sorbitan stearamides and oleates, and/or dibutyl adipate;
- fatty acid amides such as stearamide, coconut fatty acid butylamide, acetic acid oleylamide, and ethylene-bisstearamide;
- terpenes such as menthol or orange terpene (Weißmer Baltische HG, Hamburg).

Other suitable commercially available hydrocarbons or hydrocarbon mixtures are paraffin oil or mineral oil.

In addition, fats and oils on native basis are suitable, particularly vegetable oils and preferably rape oil.

The saturated or unsaturated fatty alcohols which, according to the invention, may be used as emulsion components, can be obtained according to well-known methods, e.g. in the oxo process as oxoalcohols or, according to the Guerbet reaction, as Guerbet alcohols.

As polyoxyalkylene compounds on the basis of alkylene oxides and/or fatty acid glycerides of C_{12} - C_{18} fatty acids, those described in, *inter alia*, DE-AS 12 70 542 and EP 0,247,509 B1 are used.

When using terpenes, they are preferably used in admixture with a saturated or unsaturated fatty alcohol.

The oil phase ratio in the oil-in-water emulsion is from 1 to 90% by weight, preferably from 1 to 50% by weight, and more preferably from 5 to 30% by weight of the overall emulsion.

The oil-in-water emulsions to be used according to the invention are employed as such or diluted with water, or water and/or mixtures containing solvents. The emulsion to be used according to the invention can be added at any point upstream of or in the aeration tank, with addition to the waste water to be purified immediately before its entry into the aeration tank being preferred.

The added amount preferably is from 0.1 to 1000 ppm, more preferably from 0.5 to 200 ppm, and even more preferably from 1.0 to 50 ppm, relative to the waste water to be purified.

By virtue of the emulsions to be used according to the invention, the denitrification can be improved by up to 50%. The emulsions to be used according to the invention have no or merely low toxicity and may be rated as water-polluting class 1; they are biologically degradable.

The invention will be illustrated with reference to an Example. These illustrations are given merely by way of example and do not limit the general idea of the invention.

Example 2

The tests used to demonstrate the improved denitrification were carried out in a municipal biological sewage treatment plant. This sewage treatment plant is of a two-line design

and operates according to the upstream denitrification principle. Each line has a denitrification, an aeration tank, and a secondary sedimentation, through which the waste water flows in this order. Both lines are identical in design, the lower line additionally having a metering station for the continuous addition of oil-in-water emulsion. This emulsion consisted of 14 kg of terpene, 1.0 kg of hexadecanol, 7 kg of a 75% paraffinsulfonate, and 2.1 kg of water, and was fused homogeneously and subsequently poured with stirring into a 60°C warm solution of 74.5 kg of water and 1.4 kg of an oleyl alcohol reacted with 20 moles of ethylene oxide.

Both lines were operated with the same waste water and an identical amount of waste water, and the waste water treated in the lower line was added with oil-in-water emulsion in such an amount that the concentration was 2 ppm.

The tests were performed over a period of two months. The NO_3^- concentration in the outflow of the denitrification stage operated with 2 ppm of oil-in-water emulsion had a value about 50% lower than the NO_3^- concentration in the outflow of the denitrification stage operated with no oil-in-water emulsion.



Claims:

1. Use of oil-in-water emulsions for reducing the air and/or oxygen demand of aerobic biological sewage treatment plants, characterized in that the emulsions in their oil phase include at least one compound of the following classes of compounds or a mixture of members of the following classes of compounds:
 - saturated or unsaturated, open-chain or cyclic, normal or isomeric hydrocarbons with 8-30 carbon atoms;
 - saturated or unsaturated fatty alcohols, saturated or unsaturated fatty acids, fatty acid monoalkyl esters, fatty acid amides, or fatty acid monoalkylamides of saturated or unsaturated fatty acids, the fatty alcohols, fatty acids and fatty acid esters of the mentioned compounds having 8-30 carbon atoms;
 - monoesters or polyesters of a saturated or unsaturated carboxylic acid or dicarboxylic acid with 4-30 carbon atoms with a monoalcohol and/or a polyol;
 - polyamides of saturated or unsaturated fatty acids having 8-30 carbon atoms with aliphatic polyamines having 2-6 nitrogen atoms;
 - acyclic, preferably monocyclic and/or bicyclic terpenes, particularly terpene hydrocarbons and/or terpene alcohols; and/or
 - polyoxyalkylene compounds based on alkylene oxides and alkylene oxides with fatty alcohols and/or C₁₂-C₁₈ fatty acids and/or fatty acid glycerides of C₁₂-C₁₈ fatty acids.



2. The use of oil-in-water emulsions according to claim 1, characterized in that the emulsions include octane, tetraoctane, octadecane as saturated hydrocarbon, and/or decene, hexadecene, and/or technical α -olefins as unsaturated hydrocarbon.
3. The use of oil-in-water emulsions according to claim 1, characterized in that the emulsions include octanol, dodecanol, tridecanol, octadecanol and/or behenyl alcohol as fatty alcohols.
4. The use of oil-in-water emulsions according to any of claims 1 to 3, characterized in that the emulsions include capric acid, stearic acid, melissic acid, oleic acid and/or linolenic acid as fatty acids.
5. The use of oil-in-water emulsions according to any of claims 1 to 4, characterized in that the emulsions include methyl stearate, octadecyl palmitate, octyl oleate, glycerol mono- and/or trioleate, ethylene glycol dilaurate, sorbitan stearate and/or oleate, and/or dibutyl adipate as fatty acid esters.
6. The use of oil-in-water emulsions according to any of claims 1 to 5, characterized in that the emulsions include stearamide, coconut fatty acid butylamide, acetic acid oleylamide, and/or ethylenebisstearamide as fatty acid amides.
7. The use of oil-in-water emulsions according to any of claims 1 to 6, characterized in that the emulsions include poly(ethylene oxide) and/or poly(propylene oxide) as polyoxyalkylene compounds.

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8. The use of oil-in-water emulsions according to any of claims 1 to 7, characterized in that the emulsions include rape oil as natural oil.
9. The use of oil-in-water emulsions according to any of claims 1 to 8, characterized in that the emulsions include an oil phase ratio of from 1 to 90% by weight, preferably from 1 to 50% by weight, and more preferably from 5 to 30% by weight, relative to the emulsion, and that the emulsions are added to the aerobic biological waste water purifications in amounts of from 0.1 to 1000 ppm, preferably from 0.5 to 200 ppm, and more preferably from 1.0 to 50 ppm, relative to the waste water to be purified.
10. The use of oil-in-water emulsions according to any of claims 1 to 9, characterized in that the sewage treatment plant is a municipal and/or industrial sewage treatment plant.
11. Use of oil-in-water emulsions for improving the denitrification in aerobic biological sewage treatment plants, characterized in that the emulsions in their oil phase include at least one compound of the following classes of compounds or a mixture of members of the following classes of compounds:
 - saturated or unsaturated, open-chain or cyclic, normal or isomeric hydrocarbons with 8-30 carbon atoms;
 - saturated or unsaturated fatty alcohols, saturated or unsaturated fatty acids, fatty acid monoalkyl esters, fatty acid amides, or fatty acid monoalkylamides of saturated or unsaturated fatty acids, the fatty alcohols, fatty acids and fatty acid esters of the mentioned compounds having 8-30 carbon atoms;



- monoesters or polyesters of a saturated or unsaturated carboxylic acid or dicarboxylic acid with 4-30 carbon atoms with a monoalcohol and/or a polyol;
 - polyamides of saturated or unsaturated fatty acids having 8-30 carbon atoms with aliphatic polyamines having 2-6 nitrogen atoms;
 - acyclic, preferably monocyclic and/or bicyclic terpenes, particularly terpene hydrocarbons and/or terpene alcohols; and/or
 - polyoxyalkylene compounds based on alkylene oxides and alkylene oxides with fatty alcohols and/or C₁₂-C₁₈ fatty acids and/or fatty acid glycerides of C₁₂-C₁₈ fatty acids.
12. The use of oil-in-water emulsions according to claim 11, characterized in that the emulsions include octane, tetraoctane, octadecane as saturated hydrocarbon, and/or decene, hexadecene, and/or technical α -olefins as unsaturated hydrocarbon.
13. The use of oil-in-water emulsions according to claim 11, characterized in that the emulsions include octanol, dodecanol, tridecanol, octadecanol and/or behenyl alcohol as fatty alcohols.
14. The use of oil-in-water emulsions according to any of claims 11 to 13, characterized in that the emulsions include capric acid, stearic acid, melissic acid, oleic acid and/or linolenic acid as fatty acids.
15. The use of oil-in-water emulsions according to any of claims 11 to 14, characterized in that the emulsions include methyl stearate, octadecyl palmitate, octyl oleate, glycerol mono- and trioleate, ethylene glycol

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dilaurate, sorbitan stearate and/or oleate, and/or di-butyl adipate as fatty acid esters.

16. The use of oil-in-water emulsions according to any of claims 11 to 15, characterized in that the emulsions include stearamide, coconut fatty acid butylamide, acetic acid oleylamide, and/or ethylenebisstearamide as fatty acid amides.
17. The use of oil-in-water emulsions according to any of claims 11 to 16, characterized in that the emulsions include poly(ethylene oxide) and/or poly(propylene oxide) as polyoxyalkylene compounds.
18. The use of oil-in-water emulsions according to any of claims 11 to 17, characterized in that the emulsions include rape oil as natural oil.
19. The use of oil-in-water emulsions according to any of claims 11 to 18, characterized in that the emulsions include an oil phase ratio of from 1 to 90% by weight, preferably from 1 to 50% by weight, and more preferably from 5 to 30% by weight, relative to the emulsion, and that the emulsions are added to the aerobic biological waste water purifications in amounts of from 0.1 to 1000 ppm, preferably from 0.5 to 200 ppm, and more preferably from 1.0 to 50 ppm, relative to the waste water to be purified.
20. The use of oil-in-water emulsions according to any of claims 11 to 19, characterized in that the sewage treatment plant is a municipal and/or industrial sewage treatment plant.