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(54) **BIOREACTOR CARRIER, PROCESS FOR PRODUCING THE CARRIER AND METHOD FOR USING THE SAME**

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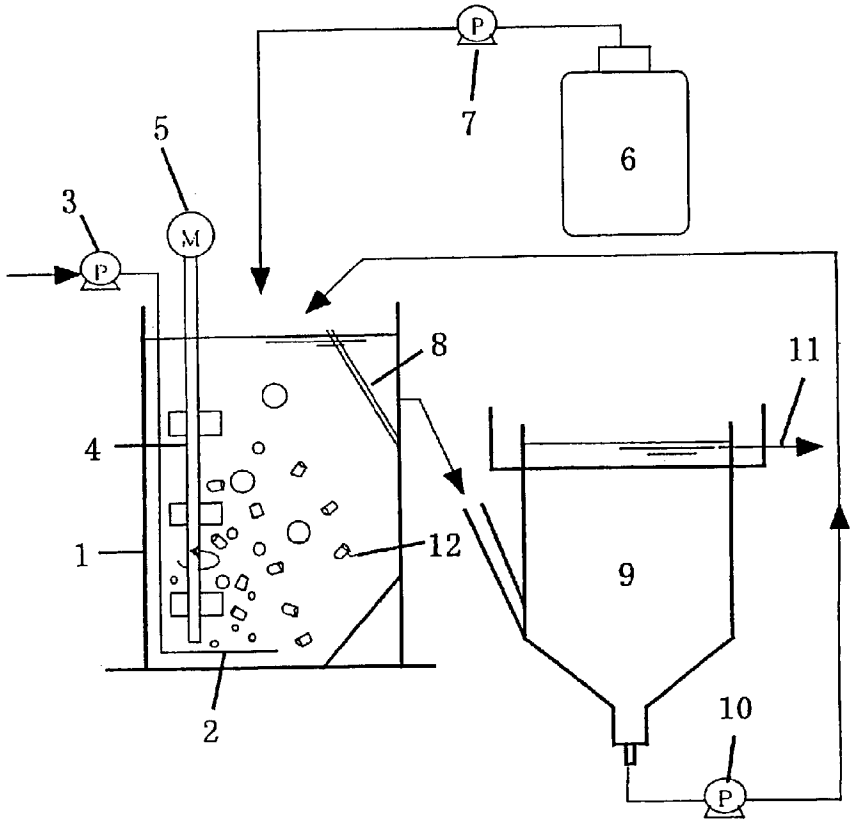
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(57) **ABSTRACT**

There are disclosed a bioreactor carrier comprising a (A) water swellable thermoplastic resin, preferably water swellable thermoplastic polyurethane resin and a (B) specific inorganic filler which is added thereto at the time of producing and/or molding said resin, characterized in that the specific gravity of the carrier on swelling in water is controlled within the range of 1.02 to 1.35; a process for producing the bioreactor carrier; and a process for denitrifying treatment of organic waste water which comprises nitrifying and denitrifying nitrogen components in the organic waste water with microbes by the use of the above bioreactor carrier. The bioreactor carrier has high physical strength, can be readily produced and uniformly fluidized in a reactor, and enables microbial and enzymatic reactions to be effectively performed.



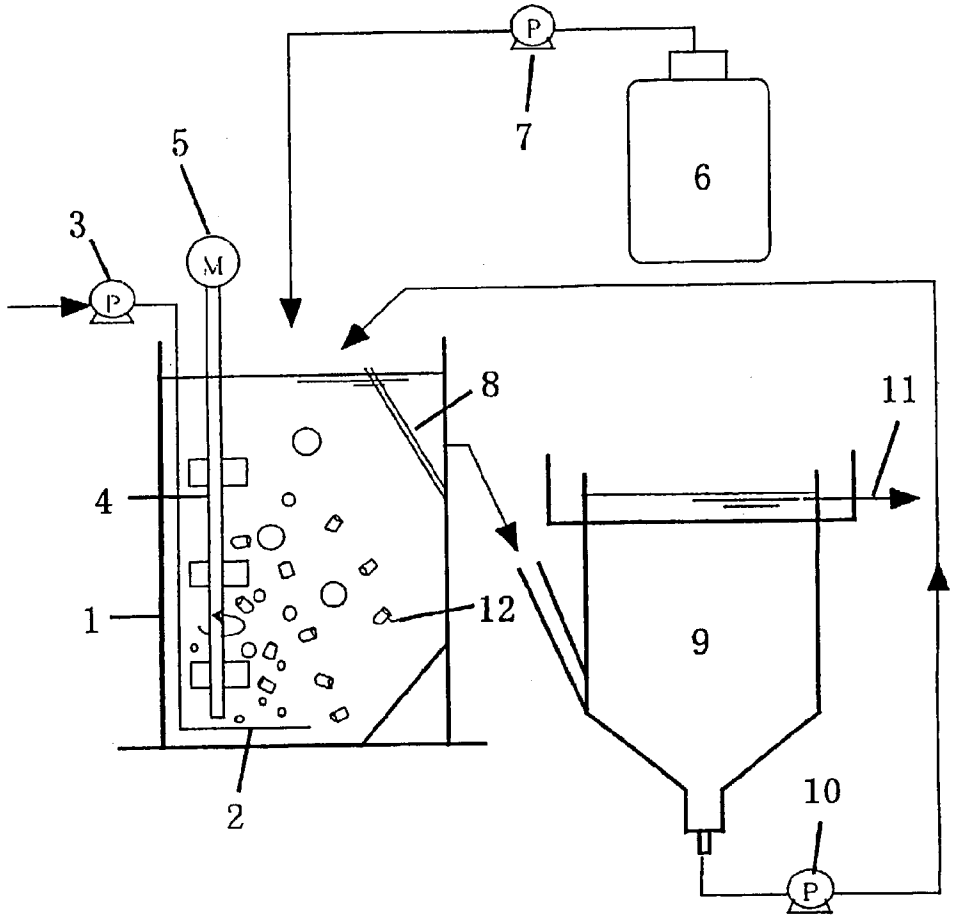


Fig. 1

BIOREACTOR CARRIER, PROCESS FOR PRODUCING THE CARRIER AND METHOD FOR USING THE SAME

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a bioreactor carrier, a process for producing the carrier and a method for using the same. More particularly, it pertains to a bioreactor carrier which is imparted with water swelling properties, a specific gravity controlled within a specific range, and high physical strength; enables microbial reactions and enzymatic reactions to be effectively performed; and moreover is readily producible, to a process for producing the carrier in high efficiency, and to a method for effectively carrying out denitrifying treatment for organic waste water with microbes by the use of the above-stated carrier.

[0003] 2. Description of the Related Arts

[0004] The carriers to be employed in bioreactors can be broadly classified into porous carriers and gel carriers. Examples of the porous carriers include those made of polyurethane, cellulose, polypropylene, polyvinyl formal, ceramic etc., respectively. Because of their being porous, the carriers have a large surface area and in the majority of cases, are employed in a state of binding immobilizing animal cells, plant cells, microbes and/or protozoans onto the porous surfaces thereof.

[0005] However, the above-mentioned porous carriers suffer from various disadvantages and drawbacks as described hereunder. Polyurethane and polypropylene porous bodies, because of their being hydrophobic, have inferior fluidity in water and in addition, make it difficult for animal cells, plant cells, microbes and/or protozoan to be bonded thereonto. Cellulose porous bodies are subject to attack by microbe, whereby their service life is unfavorably shortened. With regard to polyvinyl formal porous bodies, an industrial process for producing the same is not yet established. Ceramic porous bodies can not be fluidized in water due to their high specific gravity, thereby inevitably restricting the usage.

[0006] On the other hand, there are known as gel carriers, those made of polyacrylamide, polyethylene glycol, polyvinyl alcohol and alginic acid, thermoplastic water absorbing bodies, etc., respectively {refer to Japanese Patent Application Laid-Open No.136980/1998 (Heisei-10)}. It is a general practice to use these gel carriers by entrapping immobilizing animal cells, plant cells, microbes and/or protozoans at the inside of the gel, and alternatively it is possible to use the above-mentioned carriers by binding immobilizing animal cells, plant cells, microbes and/or protozoans onto the gel surfaces.

[0007] The aforesaid gel carriers, which highly contain water, generally have high affinity for living matters and at the same time, impart favorable habitat to animal cells, plant cells, microbes and/or protozoans. Nevertheless, the physical strength is not necessarily sufficient in such carriers as those made of polyacrylamide, polyethylene glycol, polyvinyl alcohol and alginic acid, which bring about a fear of wear and collapse in the course of service in a reaction tank. In addition, the gel carriers just mentioned, when once molded into a definite shape, can not be changed to an other shape by remelting. Thus, such carriers are generally cut into a required shape in the majority of cases. In fact, the gel carriers suffer from serious disadvantages in that the step of cutting the water-containing and swollen gel into several millimeter sized regular hexahedron requires tremendous labor and period of time with the result that the production thereof becomes extremely intricate and troublesome, thus necessitating markedly long time and high cost in production.

[0008] As opposed to the foregoing, thermoplastic water absorbing gel carriers that are typified by thermoplastic water absorbing polyurethane gel carriers are well suited for use as bioreactor carriers owing to such advantages as high physical strength, capability of industrial mass production, capability of adsorbing animal cells, plant cells, microbes and/or protozoans due to their hydrophilicity without deteriorating the physiological activity thereof, favorable resistance to attack by microbes and the like.

[0009] In this connection, utmost importance is attached to the specific gravity of the bioreactor carriers. For instance, the specific gravity thereof, when being close to that of water on attaining steady state of adhesion, bonding and immobilization of microbes in a reactor, gives rise to such a problem, in the case of fluidizing the liquid to be treated in a reactor for the purpose of reaction, that the microbes are apt to move upwards and difficult to be present in the lower portion, thus causing failure to assure uniform fluidity and deteriorating the efficiency of microbe reaction.

SUMMARY OF THE INVENTION

[0010] In such circumstances, an object of the present invention is to provide a bioreactor carrier which is imparted with water swelling properties, a specific gravity controlled within a specific range, and high physical strength; enables microbial reactions and enzymatic reactions to be effectively performed; and moreover is readily producible, to a process for producing the carrier, and to a method for using the same.

[0011] Other objects of the present invention will be obvious from the text of this specification hereinafter disclosed.

[0012] In order to achieve the above-mentioned objects, research and investigation were intensively and extensively accumulated by the present inventors. As a result, it has been found that a bioreactor carrier which conforms to its purpose of application is obtainable by adding a specific inorganic filler to a water swellable thermoplastic resin such as water swellable thermoplastic polyurethane resin at the time of producing the resin and/or molding the same; controlling the specific gravity within a specific range; and thereafter molding the mixed resin into a desirable form by means of an extruder, and at the same time that organic waste water can effectively be subjected to denitrification treatment by using the molding thus obtained as a carrier for immobilizing microbes in nitrifying and denitrifying nitrogenous components in the organic waste water. The present invention has been accomplished on the basis of such findings and information.

[0013] That is to say, the present invention provides:

[0014] (1) a bioreactor carrier comprising a (A) water swellable thermoplastic resin and (B) at least one inorganic filler which is added thereto at the time of

producing and/or molding said resin and which is selected from the group consisting of barium sulfate, silica, kaolin, quarts sand, diatomaceous earth, barite, talc, alumina, titanium dioxide and iron oxides, with the proviso that any of barium sulfate, kaolin, diatomaceous earth and talc, when being added thereto at the time of molding, is subjected to dehydrating treatment in advance, characterized in that the specific gravity of said carrier on swelling in water is controlled within the range of 1.02 to 1.35;

[0015] (2) a process for producing a bioreactor carrier the specific gravity of which on swelling in water is controlled within the range of 1.02 to 1.35, comprising the steps of blending at least one inorganic filler selected from the group consisting of barium sulfate, kaolin, diatomaceous earth, talc, each of which has been subjected to dehydrating treatment, silica, quarts sand, barite, alumina, titanium dioxide and iron oxides with a water swellable thermoplastic resin; thereafter heat melting the resultant blend; extruding the molten blend through an extruder into the form of strand; and continuously cutting the strand;

[0016] (3) a process for producing a bioreactor carrier the specific gravity of which on swelling in water is controlled within the range of 1.02 to 1.35, comprising the steps of blending at least one inorganic filler selected from the group consisting of barium sulfate, silica, kaolin, quarts sand, diatomaceous earth, barite, talc, alumina, titanium dioxide and iron oxides at the time of producing a water swellable thermoplastic resin from reactants of said resin; thereafter heat melting the resultant blend as such or after further blending of said at least one inorganic filler with the proviso that any of barium sulfate, kaolin, diatomaceous earth and talc, when being added thereto, is subjected to dehydrating treatment in advance; extruding the molten blend through an extruder into the form of strand, and continuously cutting the strand; and

[0017] (4) a process for denitrifying treatment of organic waste water which comprises nitrifying and denitrifying nitrogen components in the organic waste water with microbes by the use of the bioreactor carrier as set forth in the preceding item (1).

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] **FIG. 1** is a simplified process flow diagram showing one embodiment of a nitrifying denitrifying apparatus according to the present invention, wherein the symbols therein shall have the following designations:

[0019] **1**: biotreatment tank

[0020] **2**: air diffusion pipe

[0021] **3**: aeration pump

[0022] **4**: agitation impeller

[0023] **5**: agitation motor

[0024] **6**: raw water tank

[0025] **7**: liquid transfer pump

[0026] **8**: carrier separation screen

[0027] **9**: settling tank

[0028] **10**: sludge return pump

[0029] **11**: discharge line

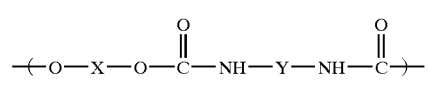
[0030] **12**: carrier

DESCRIPTION OF PREFERRED EMBODIMENTS

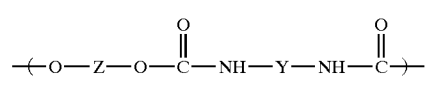
[0031] The bioreactor carrier according to the present invention comprises a (A) water swellable thermoplastic resin and a (B) inorganic filler. The aforesaid water swellable thermoplastic resin as the component (A) is exemplified by water swellable thermoplastic polyurethane resin, water swellable thermoplastic polyethylene glycol and the like, among which is particularly preferable water swellable thermoplastic polyurethane resin.

[0032] The water swellable thermoplastic polyurethane resin as mentioned above is the polyurethane copolymer comprising a soft segment which is randomly top-to-end bonded by urethane bond and a hard segment. The polyurethane copolymer is synthesized by reacting a bifunctional long chain diol compound, a bifunctional diisocyanate compound and a short chain diol compound.

[0033] The soft segment obtained by the reaction between the long chain diol compound and the diisocyanate compound is represented by the following general formula (I):



[0034] On the other hand, the hard segment obtained by the reaction between the short chain diol compound and the diisocyanate compound is represented by the following general formula (II):



[0035] wherein X in the above-mentioned general formulae (I) and (II) is the group which is generated by the reaction of the terminal hydroxy groups of the long chain diol compound with the diisocyanate, and from which the terminal hydroxy groups are removed. It is thought that the molecular weight of X in the formulae exerts a remarkable influence on the degree of swelling and the like of the resin. The molecular weight thereof is in the range of preferably 1,000 to 13,000, more preferably 4,000 to 8,000. The molecular weight of X, when being unreasonably low, causes decrease in the molecular weight of the soft segment and as a result, gives rise to the tendency that the degree of swelling thereof is lowered. On the other hand, the molecular weight of X, when being higher than 13,000, brings about such unfavorable problems as an increase in the viscosity of the reactants at the time of synthesis and a rise in melting temperature. As the long chain diol compound to be used in the present invention, there are preferably usable a water-soluble polyoxyalkylene diol (polyol), and particularly pref-

erably usable a water-soluble ethylene oxide-propylene oxide copolymer polyether-based diol having two terminal hydroxy groups in one molecule, or polyethylene glycol. In particular, the content of oxyethylene group is preferably at least 70% by weight, more preferably at least 85% by weight. The content of the oxyethylene group of less than 70% by weight sometimes leads to the resin lowered in the degree of swelling.

[0036] In addition, Y in the above-mentioned general formulae (I and (II) is the group which is generated by the reaction between the diisocyanate compound usually having a number average molecular weight in the range of 100 to 1000 and the hydroxy groups, and from which the isocyanate groups are removed. Specific examples of the diisocyanate compounds that are used in the present invention include tolylene diisocyanate, xylylene diisocyanate, naphthylene diisocyanate, diphenylmethane diisocyanate, biphenylene diisocyanate, diphenyl ether diisocyanate, tolidine diisocyanate, hexamethylene diisocyanate and isophorone diisocyanate.

[0037] On the other hand, Z in the foregoing general formula (II) is the group which is generated by the reaction of the terminal hydroxy groups of the short chain diol compound usually having a number average molecular weight in the range of 30 to 400 with the diisocyanate, and from which the terminal hydroxy groups are removed.

[0038] Examples of the short chain diol compound to be used in the present invention include ethylene glycol; 1, 2-propylene glycol; 1,3-propylene glycol; 1,3-butanediol; 2,3-butanediol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; 2,2-dimethyl-1,3-propanediol; diethylene glycol; dipropylene glycol; 1,4-cyclohaxane dimethanol; 1,4-bis-(β-hydroxyethoxy)benzene; p-xylilenediol; phenyldiethanolamine; methyldiethanolamine; 3,9-bis(2-hydoxy-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro-(5,5)-undecane; etc.

[0039] The ratio of the amount to be used of the long chain diol compound to that of the short chain diol compound can be varied according to the molecular weight of each, desirable physical properties of the resin and the like. Although depending upon the molecular weight of the long chain diol compound, the molar ratio of the long chain diol compound to the short chain diol compound is preferably in the range of 5:1 to 1:2. In the case where the long chain diol compound has a high molecular weight, since the viscosity at the time of synthesizing the thermoplastic resin is prone to become high, it is preferable to decrease the molar ratio of the short chain diol compound which forms the hard segment. However, in order to enhance the degree of volumetric swelling, while maintaining high physical strength it is preferable to increase the molar ratio thereof. Moreover, it is preferable that the ratio of the number of the isocyanate groups in the diisocyanate compound to the total number of the hydroxy groups in the long chain diol compound and the short chain diol compound (NCO/OH) be in the range of preferably 0.95 to 1.8, more preferably 1.0 to 1.6. It being so, there are usable in the present invention, not only polyurethane copolymer wherein the polymer synthesis reaction has been completed sufficiently, but also incomplete thermoplastic polyurethane, that is, polyurethane copolymers wherein part of active groups such as isocyanate groups remain unreacted, by causing the incomplete polyurethane to be cross-linked after molding.

[0040] As the method for producing the thermoplastic polyurethane to be used in the present invention, there are adoptable both a prepolymer method in which the long chain diol compound and diisocyanate compound are reacted in advance, and thereafter the reaction product is reacted with a short chain diol compound as a chain extender; and a one shot method in which all the starting reactants are simultaneously mixed.

[0041] On the other hand, regarding the inorganic filler as the component (B), there is properly and optionally selected for use at least one member from among barium sulfate, silica, kaolin, quarts sand, diatomaceous earth, barite, talc, alumina, titanium dioxide and iron oxides. In the present invention, the foregoing inorganic filler is used at the time of producing the water swellable thermoplastic resin as the component (A) and/or at the time of molding for producing the carrier. Among the foregoing inorganic filler, barium sulfate, kaolin, diatomaceous earth and talc, which usually contain moisture, need to be dehydrated in advance when being added at the time of molding, since the use thereof as such without dehydration causes a fear of the resin swelling. Conversely, there is no need to dehydrate any of the fillers just mentioned when it is added at the time of resin production.

[0042] It is advantageous to use the inorganic filler which has an average particle diameter in the range of preferably 0.1 to 50 μm, more preferably 0.5 to 30 μm, and which has a specific gravity (true specific gravity, and the same applies hereinafter) of preferably at least 1.5, more preferably in the range of 2.0 to 6.0. Examples of the specific gravity of the inorganic filler to be used in the present invention include 4.3 for barium sulfate; 2.2 for silica; 2.4 for kaolin; 2.56 for quarts sand; 2.15 to 2.31 for diatomaceous earth; 4.5 for barite; 2.6 to 2.8 for talc; 3.99 for alumina; 3.8 to 4.1 for titanium dioxide; and 5.2 for iron oxides.

[0043] The content of the aforesaid inorganic filler, although depending upon the desirable specific gravity of the carrier, the specific gravity of the inorganic filler and the like, is selected in the range of generally 1 to 250, preferably 10 to 200 parts by weight per 100 parts by weight of the component (A).

[0044] The specific gravity of the bioreactor carrier according to the present invention at the time of swelling in water is controlled within the range of 1.02 to 1.35, preferably 1.02 to 1.22 so as to enable the carrier to uniformly flow in a reactor when the adhesion and bonding immobilization of microbes onto the carrier reach a steady state in the reactor.

[0045] The specific gravity of the bioreactor carrier at the time of swelling in water is obtained from the weight and the volume of the carrier immersed in pure water at 25° C. by regarding the volume which does not change any longer as the volume on complete swelling in water.

[0046] The bioreactor carrier according to the present invention has a degree of volumetric swelling in water as represented by the formula (III) in the range of preferably 120 to 3000% particularly preferably 150 to 1000%:

$$\text{degree of volumetric swelling in water (\%)} = \{\text{volume upon complete swelling in water } (cm^3)/\text{volume on bone dryness } (cm^3)\} \times 100 \quad \text{(III)}$$

[0047] The degree of volumetric swelling in water as defined above, when being less than 120%, causes unrea-

sonably low water absorbability leading to a fear of deteriorating the adhesion of microbes, whereas the degree of volumetric swelling in water, when being more than 3000%, brings about a tendency to markedly decrease the physical strength of the carrier. In the present invention, the bone dryness is the dryness where the weight does not change any longer when dried at 100° C., and the volume upon complete swelling in water is the volume which does not change any longer when immersed in pure water at 25° C.

[0048] The size and shape of the bioreactor carrier in the present invention are not specifically limited, but the carrier is preferably in the form of regular hexahedron, column, sphere or chip having a uniform size. Specifically preferable forms are a regular hexahedron of 1 to 10 mm in side, a column of 1 to 10 mm in diameter and 1 to 10 mm in length and a sphere of 1 to 10 mm in diameter.

[0049] The bioreactor carrier according to the present invention can be efficiently produced by any of the processes according to the present invention as described in the following.

[0050] (1) a process wherein the inorganic filler is not added at the time of producing the water swellable thermoplastic resin, but is added at the time of melt molding; (2) a process wherein the inorganic filler is added at the time of producing the water swellable thermoplastic resin, followed by melt molding without adding the same; (3) a process wherein the inorganic filler is added at the time of producing the water swellable thermoplastic resin, and is also added at the time of melt molding.

[0051] The inorganic filler to be added at the time of producing and/or molding has already been described, respectively in the section of the component (B).

[0052] The melt molding is carried out by heat melting the mixture of the components (A) and (B) and extruding the same into the form of strand (string) by the use of an extruder, and thereafter cutting the resultant strand into a proper length. For the purpose of enhancing the adhesivity of animal cells, plant cells and microbes, the mixture of the components may be incorporated with inorganic powder such as activated carbon, carbon powder and zeolite in addition to the inorganic filler for modifying the specific gravity. It is also possible to adhere the aforestated inorganic powder to the surface of the strand extruded from the extruder, followed by cutting the same. The bioreactor carrier according to the present invention which is obtained by the foregoing manner has water swelling properties, high hydrophilicity, properties of accumulating a large quantity of water and high affinity for animal cells, plant cells, microbes and/or protozoans. The bioreactor carrier is used by adding itself in a culture solution and water to be treated in each of which animal cells, plant cells, microbes and/or protozoans are present. Owing to extremely high affinity for living matters the bioreactor carrier allows animal cells, plant cells, microbes and/or protozoans to adhere to the surfaces thereof and proliferate there. In particular, the carrier preferentially allows strongly tacky animal cells, plant cells, microbes and/or protozoans such as ammonium oxidizing bacteria, nitrite oxidizing bacteria, other bacteria for nitrifying ammonia, denitrifying bacteria and filamentous bacteria to adhere and to be bindingly immobilized onto the surfaces thereof.

[0053] The bioreactor carrier according to the present invention, which has high shearing resistance, enables efficient agitation by means of an impeller agitator or the like in a state that a large number of animal cells, plant cells, microbes and/or protozoans each serving as biological catalysts are densely immobilized onto the outside surface of the carrier.

[0054] In addition, the bioreactor carrier the specific gravity of which is controlled within a specific range enables uniform flow of liquid in a reactor and efficient proceeding of microbe reaction and the like.

[0055] In the following, some description will be given of a process for the denitrification treatment of organic waste water according to the present invention.

[0056] In a process for the denitrification treatment according to the present invention, use is made of the above-mentioned bioreactor carrier of the invention as a carrier for immobilizing microbes in the case of nitrifying and denitrifying nitrogenous components in organic waste water.

[0057] Ammonia nitrogen in waste water is converted to nitrate nitrogen by the nitrifying bacteria present in activated sludge, while the nitrate nitrogen is converted to gaseous nitrogen by the denitrifying bacteria so that the nitrogen is released into the atmosphere. Due to extremely low breeding rate, nitrifying bacteria are present at a relatively low concentration in suspended microbes group, namely activated sludge. Accordingly, it is impossible for conventional activated sludge process used for general waste water treatment to sufficiently treat ammonia nitrogen.

[0058] There exist in activated sludge, such bacteria as having a high breeding rate including BOD digesting bacteria. Thus it follows that BOD digesting bacteria predominantly proliferate to suppress the proliferation of the bacteria having a low breeding rate such as nitrifying bacteria. Consequently, concentration of nitrifying bacteria is low at all times. The bioreactor carrier according to the present invention, when applied to such a system, causes nitrifying bacteria to adhere to even smooth surfaces of the carrier because of their strong tackiness, but causes microbes that are devoid of strong tackiness such as BOD digesting bacteria to be less prone to adhere to smooth surfaces thereof. Consequently, it follows that nitrifying bacteria predominantly proliferate at a high concentration on the surface of the carrier, whereby the ammonia nitrogen is biological treated by the function of the nitrifying bacteria thus proliferated in an extremely efficient manner in a high rate.

[0059] It has been confirmed that the bioreactor carrier according to the present invention, which has physical strength and durability that can withstand a long-term mechanical agitation and besides, has a high molecular gel structure upon swelling by water absorption, is capable of firmly binding immobilizing denitrifying bacteria without installing an uneven portion. In addition, the carrier to be used in the present invention, which is usable in both nitrification step as an aerobic condition and denitrification step as an anaerobic condition, is applicable to a variety of denitrifying activated sludge process. In particular, as compared with various carrier addition/recycled nitrification/denitrification process in which different carriers are separately added to an anaerobic tank and an aerobic tank, respectively, and thus countercurrent carrier return is

needed, the process according to the present invention dispenses with the distinction between an anaerobic carrier and an aerobic carrier and can perform carrier return in the same manner as nitrifying liquid circulation. What is more, the present process is well suited for various intermittent aeration method and oxidation ditch method which have hitherto few examples of adding a carrier.

[0060] It is made possible in the process according to the present invention, for instance, to alternately and repeatedly make use of the same microbe carrier in both the nitrification condition and denitrification condition by a method comprising supplying waste water to be treated continuously or intermittently into a treatment tank, and alternately and repeatedly switching the treatment conditions between the nitrification condition and denitrification condition in a state that the bioreactor carrier is retained in a treatment tank. In this case there is no restriction on the number of cycles or one cycle time for aerobic and anaerobic cycles.

[0061] In an example of adding a microbe carrier to denitrifying activated sludge process unit, there exists the problem in that long-term acclimatization is necessary in the early stage of operation. A solution thereagainst has hitherto been contrived by the use of an entrappingly immobilized carrier. Nevertheless, by using the microbe carrier under both environments including aerobic and anaerobic conditions in the process according to the present invention, it is made possible not only to obtain the microbe carrier imparted with nitrification and denitrification performances, but also to accelerate the rise in an early stages of nitrification and denitrification as compared with the case of acclimatization under either condition only, thereby enabling to shorten the acclimatization term.

[0062] When the microbe carrier to be used in the present process is acclimatized in a coexistence of activated sludge under an aerobic condition wherein nitrifying bacteria are proliferated, the nitrifying bacteria are thickly grown on the surface of the carrier, and also protozoa such as ciliates are thickly grown thereon as if they cover the bacteria. It has been found by the present inventors that when the aerobic condition is switched to the anaerobic condition wherein denitrifying bacteria are proliferated, the denitrifying bacteria are adsorbed onto the carrier and thereby are firmly immobilized thereon. It has been confirmed that this phenomenon is not limited to one cycle only, and that both the rises of nitrification and denitrification performances are accelerated at every time the aerobic and anaerobic conditions are alternately repeated. It is considered to be related to cohesive force among the microbes themselves and the denitrifying bacteria being so-called anaerobic.

[0063] In the following, the present invention will be described more specifically with reference to the drawings.

[0064] **FIG. 1** is a simplified process flow diagram showing one embodiment of a nitrifying denitrifying apparatus according to the present invention. In **FIG. 1, a** biotreatment tank **1** is equipped inside with an air diffusion pipe **2**, an agitation impeller **4** and further a microbe carrier **12**. When the inside of the biotreatment tank **1** is brought to an aerobic condition, an aeration pump **3** is operated and air is blown therein through the air diffusion pipe **2** to carry out aeration.

[0065] When the inside thereof is brought to an anaerobic condition, an agitation motor **5** is operated to operate the agitation impeller **4** so as to mix raw water (waste water to be treated), activated sludge and the carrier **12** in the biotreatment tank **1**, while the raw water is allowed to flow into the biotreatment tank **1** from a raw water tank via a liquid transfer pump **7**. Irrespective of aerobic or anaerobic condition, organic matters in the raw water are decomposed by the activated sludge in the biotreatment tank **1** and the microbe which is immobilized on the carrier **12**, and simultaneously organonitrogen components are decomposed into ammonia nitrogen.

[0066] Subsequently upon becoming aerobic state, by the action of the nitrifying bacteria bonded to the carrier **12**, the ammonia nitrogen begins to be oxidized and converted to nitrate nitrogen and nitrite nitrogen. Subsequently upon becoming anaerobic state denitrifying bacteria predominate on the surface of the carrier **12**, so that the nitrate nitrogen and the nitrite nitrogen are finally decomposed into nitrogen gas by the action of the bacteria. The denitrifying treatment is put into practice by continuously or intermittently supplying the biotreatment tank **1** with raw water and alternately repeating the aerobic state and anaerobic state.

[0067] The treated waste water flows out through overflow from the biotreatment tank **1** to a settling tank **9**, while the carrier **12** is made to always stay in the biotreatment tank **1** by a carrier separation screen **8**, whereby the microbe concentration in the biotreatment tank **1** is maintained at a high level irrespective of the flow rate of the raw water. The activated sludge is separated from the treated waste water by gravity settling in the settling tank **9**, and thus only the treated waste water is discharged from a discharge line **11** to the outside of the treatment system. The activated sludge thus settled is returned to the biotreatment tank **1** via a sludge return pump **10** so as to maintain the MLSS concentration therein. The denitrifying bacteria and nitrifying bacteria having a low proliferating rate are maintained at high concentrations by the carrier **12**, whereby the sludge control in the present process is more easy than in conventional standard processes.

[0068] As described hereinbefore, the process according to the present invention enables nitrification and denitrification of carrier addition system by intermittent aeration without exchanging the microbe carrier. Without being confined to the intermittent aeration, the process is applicable to various recycled nitrification/denitrification process, oxidation ditch process and the like.

[0069] In summarizing the effect of the present invention, the bioreactor carrier is imparted with water swelling properties, a specific gravity controlled within a specific range and high physical strength; enables microbial reactions and enzymatic reactions to be effectively performed; and moreover is readily producible. The use of the bioreactor carrier as a microbe immobilizing carrier in the case of nitrifying and denitrifying nitrogenous components in organic waste water with microbes, enables to efficiently treat the waste water by denitrification.

[0070] In the following, the present invention will be described in more detail with reference to comparative examples and working examples, which however shall not limit the present invention thereto.

[0071] Measurements were made of the specific gravity of the carrier thus obtained upon swelling in water and the degree of volumetric swelling in water thereof in the following manner:

[0072] (1) Specific Gravity upon Swelling in Water

[0073] By regarding the volume which did not change any longer when a sample was immersed in pure water at 25° C. as the volume upon complete swelling in water, from which specific gravity thereupon was determined.

[0074] (2) Degree of Volumetric Swelling

[0075] Degree of volumetric swelling was determined from the foregoing formula (III)

[0076] With regard to the inorganic filler used therein, barium sulfate powder had a particle diameter of 0.1 to 15 μm, an average particle diameter of 9.0, m and a specific gravity of 4.3; and silica powder had a particle diameter of 7.0 to 40 μm, an average particle diameter of 15.0 μm and a specific gravity of 2.2.

REFERENCE EXAMPLE 1

[0077] In a reaction kettle equipped with an agitator was placed 100 parts by weight of polyethylene glycol having a number average molecular weight of 2000 as the long chain diol compound Then preliminary heating was carried out at 110° C. for one hour in an atmosphere of nitrogen so as to release the moisture in the polyethylene glycol, and thereafter the reaction kettle was set to a temperature of 130° C. Subsequently in the reaction kettle was added 25 parts by weight of 4,4'-diphenylmethane diisocyanate as the diisocyanate compound under stirring at 130° C. for 2 hours to prepare a prepolymer. Subsequently 1.19 part by weight of 1,4-butanediol as the chain length extender was added with stirring at 130° C. for one hour. After the completion of the reaction, the prepolymer was cast onto a vat which had been subjected to releasing treatment, followed by heating treatment at 100° C. for 4 hours to obtain water swellable thermoplastic polyurethane resin.

REFERENCE EXAMPLE 2

[0078] The thermoplastic polyurethane resin prepared in Reference Example 1 was allowed to cool, then crushed into small pieces, heat melted at 180 to 230° C. by the use of an heating extruder under shearing force applied thereto, and extruded through the nozzles of the extruder to prepare strands of 2.5 mm in diameter. The strands thus obtained were cut into columnar carrier of 2.5 mm in length. The resultant carrier had a specific gravity upon swelling in water of 1.012 and a degree of volumetric swelling of 850%.

EXAMPLE 1

[0079] The procedure in Reference Example 2 was repeated to prepare a carrier, except that 100 parts by weight of water swellable thermoplastic polyurethane resin which was crushed into small pieces was blended with 43 parts by weight of silica powder, and the resultant blend was heat melted in the same manner as therein. Thus measurements were made of the specific gravity upon swelling in water and degree of volumetric swelling in water each for he carrier thus obtained. The results are given in Table 1.

EXAMPLE 2

[0080] The procedure in Reference Example 2 was repeated to prepare a carrier, except that 100 parts by weight of water swellable thermoplastic polyurethane resin which was crushed into small pieces was blended with 86 parts by weight of silica powder, and the resultant blend was heat melted in the same manner as therein. Thus measurements were made of the specific gravity upon swelling in water and degree of volumetric swelling in water each for the carrier thus obtained. The results are given in Table 1.

EXAMPLE 3

[0081] The procedure in Reference Example 2 was repeated to prepare a carrier, except that 100 parts by weight of water swellable thermoplastic polyurethane resin which was crushed into small pieces was blended with 100 parts by weight of barium sulfate powder which had been subjected to dehydrating treatment in advance, and the resultant blend was heat melted in the same manner as therein. Thus measurements were made of the specific gravity upon swelling in water and degree of volumetric swelling in water each for the carrier thus obtained. The results are given in Table 1.

EXAMPLE 4

[0082] The procedure in Reference Example 1 was repeated to prepare a water swellable thermoplastic polyurethane resin, except that 100 parts by weight of barium sulfate powder was blended at the time of preliminary heating in preparing the prepolymer based on 100 parts by weight of polyurethane resin to be obtained by synthetic reaction and thereafter, the procedure in Reference Example 2 was repeated to prepare a carrier. Thus measurements were made of the specific gravity upon swelling in water and degree of volumetric swelling in water each for the carrier thus obtained. The results are given in Table 1.

TABLE 1

	at Resin Preparation Time		at Molding Time		Carrier	
	Inorganic filler		Inorganic filler		Specific gravity on swelling in water	Degree of volumetric swelling in water (%)
	Kind	Parts by wt	Kind	Parts by wt		
Example 1	—	—	silica	43	1.043	520
Example 2	—	—	silica	86	1.083	480
Example 3	—	—	$\underline{BaSO_4}$	100	1.082	650
Example 4	$BaSO_4$	100	—	—	1.082	590
Reference Example 2	—	—	—	—	1.012	710

{Remarks} Parts by wt: parts by weight per 100 parts by weight of resin, $BaSO_4$: barium sulfate, $\underline{BaSO_4}$: dehydrated barium sulfate

EXAMPLE 5

Nitrification Denitrification Test for Carrier

[0083] By the use of the carrier which had been obtained in Example 2 and the nitrification denitrification apparatus as illustrated in **FIG. 1**, the raw water having the following composition was subjected to intermittent aeration treatment under the following operation conditions:

Composition of raw water	Concentration (mg/L)
glucose	61.8
L-qlutamic acid	61.8
Ammonium chloride	93.2
KH_2PO_4	4.3
$CaCl_2.2H_2O$	46.3
$MgSO_4.7H_2O$	32.4
$ZnCl_2$	0.208
$FeSO_4.7H_2O$	1.0
EDTA.2Na	1.8
$CuSO_4.5H_2O$	0.51
$MnCl_2.4H_2O$	0.072
$Na_2MoO_4.2H_2O$	0.05
$CoCl_2.6H_2O$	0.008

Operation conditions

Volume of biotreatment tank:	20 liters
Carrier:	4 liters of carrier in Example 2
Aeration cycle:	one cycle was constituted of 3 hours of aerobic aeration at a dissolved oxygen concentration of 6 mg/L, and 3 hours of anaerobic aeration under agitation with an agitation impeller.
Raw water flow rate:	added at 6.67 L/hr (80 L/day) only during anaerobic aeration
Retention time:	6.0 hour
Nitrogen concentration in raw water:	30 mg-N/L
Nitrogen load:	0.12 kg-N/m^3-tank·day
Sludge return:	returned so as to attain MLSS concentration of 2000 mg/L
Water temperature:	regulated to 22° C.

[0084] In Table 2 are given the average water qualities of the treated water on and after 60th day from the start of the test.

TABLE 2

	Raw water	Treated water in Example 5	Treated water in Comp. Example 1
T-BOD (mg/L)	100	4.0	5.8
T-N (mg/L)	30	2.4	5.9
NH_4—N (mg/L)	24.4	<0.1	1.8
NO_3—N + NO_2—N (mg/L)	ND	1.0	3.9

COMPARATIVE EXAMPLE 1

Nitrification Denitrification Test Without the Use of a Carrier

[0085] The procedure in Example 5 was repeated to carry out the intermittent aeration test except that none of carrier was added to the biotreatment tank and the MLSS concentration was set to 3000 to 3500 mg/L. The average water qualities of the treated water on and after 60th day from the start of the test are given in Table 2.

[0086] In this test, sludge floatation was observed in the settling tank on and after 10th day from the start of the test, and the suspended sludge flowed out. The water qualities of the treated water in both the nitrification and the denitrification steps was not stable, showing a T-N removal rate of about 80%.

What is claimed is:

1. A process for producing a bioreactor carrier, the specific gravity of which on swelling in water is controlled within the range of 1.02 to 1.35, comprising:

blending at least one inorganic filler selected from the group consisting of barium sulfate, kaolin, diatomaceous earth, talc, each of which has been subjected to dehydrating treatment, silica, quartz sand, barite, alumina, titanium dioxide and iron oxides with a water-swellable thermoplastic resin, thereby forming a resultant blend;

thereafter heat-melting the resultant blend, thereby forming a molten blend;

extruding the molten blend through an extruder into the form of strand; and

continuously cutting the strand.

2. A process for producing a bioreactor carrier, the specific gravity of which on swelling in water is controlled within the range of 1.02 to 1.35, comprising:

blending at least one inorganic filler selected from the group consisting of barium sulfate, silica, kaolin, quartz sand, diatomaceous earth, barite, talc, alumina, titanium dioxide and iron oxides at the time of producing a water-swellable thermoplastic resin from reactants of said resin, thereby forming a resultant blend of the at least one inorganic filler and the water-swellable thermoplastic resin;

thereafter heat-melting the resultant blend, thereby forming a molten blend;

extruding the molten blend through an extruder into the form of strand; and

continuously cutting the strand.

3. A process for producing a bioreactor carrier, the specific gravity of which on swelling in water is controlled within the range of 1.02 to 1.35, comprising:

blending at least one inorganic filler selected from the group consisting of barium sulfate, silica, kaolin, quartz sand, diatomaceous earth, barite, talc, alumina, titanium dioxide and iron oxides at the time of producing a water-swellable thermoplastic resin from reactants of said resin, thereby forming a resultant blend of the at least one inorganic filler and the water-swellable thermoplastic resin;

further blending said at least one inorganic filler with the resultant blend with the proviso that any of barium sulfate, kaolin, diatomaceous earth and talc, when being added thereto, is subjected to dehydrating treatment in advance, thereby forming a further blend;

thereafter heat-melting the further blend, thereby forming a molten blend;

extruding the molten blend through an extruder into the form of strand; and

continuously cutting the strand.

* * * * *