Abstract:

An adsorbent of an embodiment includes first particles and second particles different in contact angle.
Description

Title of Invention: ADSORBENT AND WASTEWATER TREATMENT METHOD

Technical Field

[0001] Embodiments described herein generally relate to an adsorbent.

Background Art

[0002] There has conventionally been a demand for the effective use of industrial wastewater and the like. The industrial wastewater unavoidably contains oil, and the separation/collection of the oil is now an issue of burning concern.

[0003] As one method for collecting oil in water, there has been considered a method of magnetically separating and collecting oil in oil-containing water by using magnetic particles. An example thereof is a method in which oil-adsorbing films are formed on fine particles of magnetic substances, the magnetic substances are scattered on a sea surface, and oil is collected by being attracted by a magnetic force (for example, Patent Literature 1).

[0004] However, what are formed on the magnetic substances are hydrophobic films of aliphatic acid such as stearic acid, and such magnetic substances are low in water dispersibility and hence tend to sink or float on the surface, which prevents efficient oil collection.

Citation List

Patent Literature


Summary of Invention

Technical Problem

[0006] It is an object of the present invention to efficiently collect oil in water and to provide an adsorbent excellent in dispersibility.

Solution to Problem

[0007] An adsorbent of an embodiment includes first particles and second particles different in contact angle.

Description of Embodiments

[0008] Hereinafter, an embodiment will be described.

[0009] (Adsorbent)

An adsorbent in this embodiment contains first particles and second particles different in contact angle. As will be described below, the first particles have high hydrophilicity due to their structural characteristic, and for example, their contact angle is
within a range of 0 degree to 90 degrees, and further, within a range of 0 degree to 40
degrees. However, in order for a lower limit value of the contact angle to set ap-
proximate 0 degree, optimum control of various parameters is necessary, and the
contact angle generally falls within a range of 30 degrees to 40 degrees.

[0010] The second particles exhibit hydrophobicity due to their structural characteristic, and
for example, their contact angle is within a range of 10 degrees to 100 degrees, and
further within a range of 50 degrees to 100 degrees. As will be detailed below, the
contact angle generally tends to be larger when a magnetic particle is covered by a hy-
drophobic polymer layer.

[0011] The first particles exhibit hydrophilicity as described above and hence contribute to
excellent dispersibility in wastewater when used as the adsorbent. On the other hand,
the second particles exhibit hydrophobicity and thus suppress aggregation of the
adsorbent in the wastewater when used as the adsorbent. Therefore, though the range
of the contact angle of the first particles and the range of the contact angle of the
second particles partly overlap with each other, the first particles and the second
particles that are to be used are selected so that their contact angles differ from each
other to ensure the aforesaid dispersibility and non-aggregation, whereby the function
as the adsorbent can be fully exhibited at the time of the adsorption of the oil in the
wastewater.

[0012] For example, in such a case where the second particles are large in the contact angle
and are hence excellent in hydrophobicity, it is possible to suppress the aggregation of
the adsorbent in the wastewater even if a content ratio of the second particles is
relatively small, necessarily resulting in a large content ratio of the first particles. On
the other hand, in such a case where the second particles are small in the contact angle
and are hence not very excellent in hydrophobicity, it is necessary to increase the
content ratio of the second particles, necessarily resulting in a small content ratio of the
first particles.

[0013] The contact angle can be found in the following manner: the particles are put in a
vessel, the surface is flattened, and a contact angle of water droplets formed on the
surface is measured. Concretely, a static contact angle of the water droplets on the
surface of the adsorbent was measured with a contact angle measuring device
(FAMAS manufactured by Kyowa Interface Science Co., Ltd.) by a theta
12 method.

[0014] Next, the first particles and the second particles included in the adsorbent will be
described.

[0015] <First Particles>
The first particles each can be formed so as to contain a magnetic particle and an
inorganic oxide layer formed on a surface of the magnetic particle and containing at
least one kind selected from the group consisting of silica, titania, alumina, zirconia, and zinc oxide produced through hydrolysis of metal alkoxide.

As the magnetic particles, ferromagnetic substances in general are usable. Examples thereof are iron, an iron-containing alloy, magnetic iron ore, ilmenite, pyrrhotite, magnesia ferrite, cobalt ferrite, nickel ferrite, barium ferrite, and the like. Among them, a ferritic compound excellent in stability in water is capable of attaining the present invention more effectively. For example, magnetite (Fe₃O₄) as magnetic iron ore is preferable because it not only is inexpensive but also is stable as the magnetic substance even in water and is safe as an element and thus can be easily used for water treatment.

The magnetic particles can take various shapes such as a sphere, a polyhedron, and an indeterminate shape, but preferably have a spherical structure or a polyhedral structure with rounded corners. Particles having acute corners are likely to damage the inorganic oxide layers when the inorganic oxide layers are formed and to impair the function of oil adsorption. Incidentally, the magnetic particles may be surface-treated for the purpose of corrosion prevention or the like, or may be Cu-plated, Ni-plated, or the like if necessary.

An average particle size of the magnetic particles is preferably within a range of 0.1 to 1000 micrometers, more preferably within a range of 10 to 500 micrometers. The average particle size less than 0.1 micrometer results in a small magnetic force and makes the collection by magnetism difficult, which is not preferable. Further, the average particle size over 1000 micrometers results in a small specific surface area and thus is likely to worsen a collection ratio of impurities, which is not very preferable.

The average particle size of the magnetic particles is measured by laser diffractometry. Concretely, a SALD-DS21 measurement unit (manufactured by Shimazu Corporation) is usable. Further, X-ray diffraction measurement and transmission electron microscope (TEM) measurement are also adoptable. Alternatively, a microscope is usable for defining the average particle size. The magnetic particle does not necessarily have to be entirely made of a magnetic substance. That is, the magnetic particle may contain very fine magnetic particles and a binder such as an organic oxide layer or resin binding the very fine magnetic particles.

The inorganic oxide layer preferably contains silica, titania, alumina, zirconia, and zinc oxide. This is because these materials are easily available and excellent in terms of easy control of reaction.

To form the inorganic oxide layer containing silica, a silicon compound or an organic silicon compound is used as a precursor.

As the silicon compound, usable are alkoxy silanes such as tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, and tetrabutoxysilane.
As the organic silicon compound, usable is an organic silicon compound represented by a general formula RaSi(OR’)4-a. In the general formula, R represents a vinyl group, an aryl group, an acryl group, an alkyl group with 1 to 18 carbon number, a hydrogen atom, or a halogen atom, and R’ represents a vinyl group, an aryl group, an acryl group, an alkyl group with 1 to 8 carbon number, or a hydrogen atom, a is preferably an integer from 0 to 3. Concretely, usable are generally-known compounds such as methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, methyltriisopropoxysilane, vinyltrimethoxysilane, phenyltrimethoxysilane, and dimethyldimethoxysilane. A silica layer having a functional group specified by R or R’ in the above general formula not only contributes to improvement in hydrophilicity and dispersibility of the adsorbent in water but also plays a role of adsorbing oil in water.

To form the inorganic oxide layer containing titania, an organic titanium compound such as titanium alkoxide is used.

As the organic titanium compound, a compound represented by a general formula RaTi(OR’)3-a is usable. In the general formula, R represents a vinyl group, an aryl group, an acryl group, an alkyl group with 1 to 18 carbon number, a hydrogen atom, or a halogen atom, R’ represents a vinyl group, an aryl group, an acryl group, an alkyl group with 1 to 8 carbon number, or a hydrogen atom, and a is an integer from 0 to 2. Concretely, for example, usable are: well-known titanium alkoxide compounds such as titanium trimethoxide, titanium triethoxide, titanium tri-n-propoxide, titanium tri-i-propoxide, titanium tri-n-butoxide, titanium tri-sec-butoxide, titanium tri-tert-butoxide, isopropoxy bis(ethylacetoacetate) titanium, and tetraalkoxide titanium compounds such as tetraisopropoxytitanium, tetra-n-butoxytitanium, and tetramethoxytitanium; a titanium xylate compound; a titanium acylate compound; and the like. A titania layer having a functional group specified by R or R’ in the above general formula not only contributes to improvement in hydrophilicity and dispersibility of the adsorbent in water but also plays a role of adsorbing oil in water.

As the inorganic compound layer containing alumina, an aluminum metal compound such as aluminum alkoxide is usable. Concrete examples are trialkoxy aluminum compounds and so on such as aluminum isopropinate, aluminum tri-sec-butoxide, and mono-sec-butoxy aluminum diisopropylate. Further, aluminum ethyl acetoacetate diisopropylate, aluminum tris(ethylacetoacetate), aluminum tris(acetylacetoacetate), and aluminum bis ethyl acetoacetate mono acetylacetone may be used.

As the inorganic oxide layer containing zirconia, a material such as zirconium alkoxide is usable. Concrete examples are diacetylacetone tributoxy zirconium, and a tetraalkoxy zirconium compound such as tetra-n-butoxy zirconium.

As the inorganic oxide layer containing zinc oxide, a zinc metal compound such as zinc alkoxide is usable. Concrete examples are dialk oxy zinc compounds and so on.
such as zinc isopropinate, zinc di-sec-butoxide, and mono-sec-toxy zinc diisopropylate. Further, zinc ethyl acetoacetate isopropylate, zinc di(ethylacetoacetate), zinc di(acetylacetate), and zinc bis ethyl acetoacetate mono acetylacetonate may be used.

[0029] As a precursor of the inorganic oxide layer, usable are, besides the above-described ones, alkoxide, halide, and the like forming cobalt trioxide (CoO₃), cobalt oxide (CoO), tungsten oxide (WO₃), molybdenum oxide (MoO₃), indium tin oxide (ITO), indium oxide (In₂O₃), lead oxide (PbO₂), PZT, niobium oxide (Nb₂O₅), thorium oxide (ThO₂), tantalum oxide (Ta₂O₅), calcium titanate (CaTiO₃), lanthanum cobaltate (LaCoO₃), rhenium trioxide (ReO₃), chromium oxide (Cr₂O₃), iron oxide (Fe₂O₃), lanthanum chromate (LaCrO₃), barium titanate (BaTiO₃), and the like.

[0030] Further, as the precursor, generally-known organic compounds or metal compounds such as alkoxide containing metal such as Si, Ti, Zr, Al, Zn, Sn, W, Mo, Co, In, Sb, As, Ti, Co, Al, Zr, Yb, Sr, Th, or Ta, a metal complex such as acetate or metal organic acid salt, metal salt, metal soup, and halide are usable independently or as a mixture.

[0031] The average particle size of the first particles preferably falls within a range of 5 to 100 micrometers. When the average particle size is over 100 micrometers, a particle size of an aggregate of these particles becomes too large, which sometimes deteriorates the dispersion into the wastewater to lower an adsorption degree of the oil. Further, when the average particle size is less than 5 micrometers, the surface area becomes too small, which sometimes lower the adsorption degree of the oil in the wastewater.

[0032] A specific gravity of the first particles is generally 2 g/cm³ or more, preferably 3 g/cm³ or more and 10 g/cm³ or less. When the specific gravity is too low, the first particles float on the water, which sometimes necessitates an energy to stir them and disperse them in the water. On the contrary, when the specific gravity is too high, the first particles sink, which some times necessitates an energy to stir them and disperse them in the water.

[0033] Since the first particles each have a hydroxyl group on its surface, the oil is adsorbed mainly via the hydroxyl group.

[0034] <Second Particles>

The second particles each contain a magnetic particle and an inorganic oxide layer formed on a surface of the magnetic particle and containing at least one kind selected from the group consisting of silica, titania, alumina, zirconia, and zinc oxide produced through hydrolysis of metal alkoxide, and can be obtained through the treatment of surfaces of the inorganic oxide layers with a silane coupling agent. That is, the second particles can be obtained through the treatment of the first particles obtained in the above-described manner with the silane coupling agent.

[0035] It is generally known that an alkyl group is formed on a surface of a particle treated with the silane coupling agent, and hence the particle surface is made hydrophobic.
Therefore, based on such a property of the silane coupling agent, the second particles are obtained through the treatment of the first particles with the silane coupling agent.

Examples of the silane coupling agent are: alkylsilane such as methyltrimethoxysilane, ethyltrimethoxysilane, hexyltrimethoxysilane, dodecamethoxysilane, octadecyltrimethoxysilane, and ethyltriethoxy silane; aromatic silane such as phenyltrimethoxysilane and naphthalenetrimethoxy silane; epoxysilane such as gamma-glycidoxypropyltrimethoxysilane, gamma- glycidoxypropylmethyldiethoxysilane, and beta-(3,4- epoxycyclohexyl)ethyltrimethoxysilane; vinylsilane such as vinyltriethoxysilane, vinyltrimethoxysilane, and gamma-methacryloxy methoxy silane; aminosilane such as gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, and N-phenyl-gamma-aminopropyltrimethoxysilane; mercaptosilane such as gamma-mercaptopropyltrimethoxysilane; and coupling agents such as titanate, Alumichelate, zirconaluminate.

The second particles each can be obtained so as to contain a magnetic particle and a hydrophobic polymer layer formed on a surface of the magnetic particle.

As the magnetic particles, the same magnetic particles as those forming the first particles are usable. The hydrophobic polymer layer can be formed from one not dissolving in a predetermined organic solvent in a later-described washing process. Concrete examples are polystyrene resin, hydrogenated polystyrene resin, butadiene resin, isoprene resin, acrylonitrile resin, cycloolefin resin, polyvinylpyridine resin, and polyvinyl butyral resin. More concrete examples are polystyrene, polyvinylpyridine, polycycloolefin (for example, ZEONEX 480 (trade name, manufactured by Zeon Corporation)), polyvinylbutyral, a polystyrene/polybutadiene block copolymer, polybutadiene, an acrylonitrile/butadiene copolymer, a polystyrene/polyisoprene copolymer, a hydrogenated polystyrene/butadiene copolymer, and the like.

Incidently, the second particles each can be formed as an aggregate containing a plurality of the aforesaid magnetic particles, with the aforesaid polymer layer functioning as a binder. In this case, many projections and depressions can be formed on the surface of the aggregate depending on an amount and a formation method of the polymer layer. Therefore, the second particles exhibit a high oil adsorbing property due to such a porous structure.

An average particle size of the second particles preferably falls within a range of 5 to 50 micrometers. When the average particle size of the second particles is over 50 micrometers, the dispersion of the second particles in the wastewater deteriorates, which sometimes lower the adsorption degree of the oil. Further, when the average particle size is less than 5 micrometers, a surface area of each of the second particles becomes too small, which sometimes lower the adsorption degree of oil in the wastewater.

A specific gravity of the second particles is generally 2 g/cm³ or more, preferably 3
g/cm$^3$ or more and 10 g/cm$^3$ or less. When the specific gravity is too low, the second particles float on the water, which sometimes necessitates an energy to stir them and disperse them in the water. On the contrary, when the specific gravity is too high, the second particles sink, which some times necessitates an energy to stir them and disperse them in the water.

[0042] Since the second particles each have the hydrophobic, that is, lipophilic polymer layer on its surface, the oil is adsorbed mainly via the polymer layer.

[0043] <Method of Producing First Particles>

First, washing with an organic solvent such as ethanol, UV washing, plasma processing, and so on are applied to the magnetic particles to form the hydroxyl groups on the surfaces of the magnetic particles.

[0044] Next, metal alkoxide is mixed in water to be hydrolized. The metal alkoxide is the precursor of the inorganic oxide layers formed on the surfaces of the magnetic particles as described in the structure of the first particles. A concentration of the metal alkoxide is 1 x 10$^5$ to 1 mol/L, and temperature (condition) at the time of the hydrolysis is from room temperature to 100 degrees Celsius or lower.

[0045] Next, the magnetic particles are put into the solution in which the metal alkoxide has already been hydrolyzed, whereby a slurry solution is prepared, the slurry solution is spray-dried by a spray-drying method, whereby an aggregate is obtained. This aggregate includes the magnetic particles covered by the inorganic oxide layers, and as a result, the first particles are obtained.

[0046] According to the spray-drying method, it is possible to adjust the average particle size by adjusting an environmental temperature, a spray velocity, and so on of the spray-drying, and in addition, holes are formed in the aggregate particles when the organic solvent is removed from between the aggregated particles, so that a porous structure suitable as the adsorbent can be easily formed.

[0047] The environmental temperature at the time of the spray-drying is preferably higher than a boiling point of water. The reason is that water can be easily evaporated quickly from the adsorbent and outer hulls can be formed before the inside water volatilizes, and a presence density difference can be formed between the inside and the outer hulls.

[0048] Further, a viscosity of the aforesaid slurry is 10 poises or lower, preferably 5.0 poises or lower. When the viscosity of the slurry is larger than 10 poises, there arises a problem such as the precipitation of the magnetic particles and metal alkoxide on a disk.

[0049] <Method of Producing Second Particles>

In the case where the second particles are obtained through the treatment of the first particles with the silane coupling agent, the first particles obtained in the above-described manner are treated with the silane coupling agent. The treatment with the
silane coupling agent may be either a wet method or a dry method.

In the case where the second particles are formed so as to contain the magnetic particles and the hydrophobic polymer layers formed on the surfaces of the magnetic particles, polymer such as the aforesaid polystyrene resin forming the polymer layers is dissolved in an organic solvent, and the magnetic particles are dispersed in the organic solvent to make a dispersion medium (slurry). This dispersion medium (slurry) is spray-dried by the spray-drying method. According to this method, by adjusting an environmental temperature, a spray velocity, and so on of the spray-drying, it is possible to obtain the second particles as secondary aggregates in which the magnetic particles are aggregated, with the aforesaid polymers functioning as a binder.

In this case, holes are formed in the thus obtained aggregated primary particles when the organic solvent is removed from between the aggregated primary particles, so that a suitable porous structure can be easily formed.

Industrially, the second particles can be also obtained in the following manner: a polymer solution in which polymer is dissolved in an organic solvent capable of dissolving the polymer is prepared. Then, the polymer solution is poured onto the surfaces of the magnetic particles put in a mold or the like, and the solidified solution from which the organic solvent is removed is crushed, or the magnetic particles are dispersed in the polymer solution, and the solidified dispersion medium (slurry) from which the inorganic solvent is removed is crushed. In this case as well, holes are formed in the solidified substance when the organic solvent is removed from the dispersion medium (slurry) and the holes remain also in the second particles, so that the porous structure can be realized.

An alternative method to produce the second particles is to drop a dispersion medium (slurry) in which polymer is dissolved in a solvent, onto a Henschel mixer, a ball mill, a granulator, or the like and dry the dispersion medium.

Next, an oil collection method using the adsorbent of this embodiment will be described. The oil collection is to separate oil from water that contains the oil. Here, the "oil" means, among organic substances mingled/dispersed in the water, an organic substance that is generally a liquid at room temperature, is hardly soluble in water, has a relatively high viscosity, and is lower in specific gravity than water. More concretely, it is animal plant fat and oil, hydrocarbon, essential oil, and the like. They are represented by aliphatic acid glyceride, petroleum, higher alcohol, and the like. These oils are characterized in a functional group that they each have, and therefore, a resin and a functional group forming the aforesaid adsorbent can be selected according to them.

First, the aforesaid adsorbent is immersed and dispersed in water containing the oil defined as described above. The adsorbent has functional groups (first particles) such
as hydroxyl groups and lipophilic groups (second particles) such as hydrocarbon, due
to the composition of the materials forming its cover layers and also has the porous
structure if necessary, so that the adsorbent has high affinity to oil. Therefore, a
relatively large amount of the oil is adsorbed by the adsorbent.

[0056] After the adsorbent adsorbs the oil, the adsorbent is separated from the water,
resulting in the separation and removal of the oil present in the water. The use of
magnetism enables the easy separation of the adsorbent because the first particles and
the second particles forming the adsorbent contain the magnetic particles.

[0057] It should be noted that water as a target of the oil collection is not particularly
limited. Concretely, the oil collection is usable for industrial wastewater, sewage,
household wastewater, and the like. A concentration of oil contained in water to be
treated is not particularly limited either.

[0058] (Recover of Adsorbent)

After the oil is adsorbed by the adsorbent to be removed from the water in the above-
described manner, the adsorbent is washed with a predetermined solvent, whereby the
adsorbed oil is removed. This solvent has to be one not dissolving the cover layers of
the adsorbent. Concretely, a solvent in which solubility of the cover layers is 10 mg/L
or less is used.

[0059] Examples of the aforesaid solvent are methanol, ethanol, n-propanol, isopropanol,
butanol, isobutanol, hexyl alcohol, cyclohexanol, acetone, methyl ethyl ketone, methyl
isobutyl ketone, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, diethyl
ether, isopropyl ether, dibutyl ether, tetrahydrofuran, dioxane, cyclohexane,
chloroform, dimethylaniline, fluorocarbon, n-hexane, cyclohexanon, toluene, xylene,
and so on.

[0060] Among them, a nonpolar solvent is especially preferable. The nonpolar solvent
exhibits hydrophobicity and has high affinity especially to oil, and thus is capable of
easily and efficiently wash the oil adsorbed by the adsorbent. "Hydrophobicity"
mentioned here is defined as a property having 10% water solubility or lower and a
property to separate from water. In particular, hexane is preferable because it has a
high oil-solvent power, its boiling point is about 70 degrees Celsius, and it is a liquid
constantly stable at room temperature and thus is easily handled.

[0061] Further, alcohol is also preferably used as the aforesaid solvent. In this case, the
solvent is easily substituted for water adhering or adsorbed on the surface of the
adsorbent, and easily removes impurities other than the oil. Among alcohols, methanol
and ethanol which are low in boiling point are especially preferable.

[0062] In this process, examples of the separation method are a method to fill the adsorbent
in, for example, a column and pass the solvent inside the column, and especially when
the adsorbent contains the magnetic substances, a method to put the adsorbent in a
washing tank, supply a large amount of the solvent into the washing tank, and use cyclone or a magnetic force for the separation.

[0063] Next, after the oil is removed from the adsorbent, the solvent used for the washing is dried if necessary. At this time, when the adsorbent is not deteriorated and is within the standard, it is possible to reuse the adsorbent again by completely removing the solvent.

[0064] A process of the drying is not particularly limited, and for example, drying in a well-ventilated place, drying under depressurized condition, or ventilation in a column is adopted for the removal of the solvent.

**Examples**

[0065] (Example 1)

Magnetic particles with a 1 micrometer average particle size were added to ethanol and were centrifuged at 5,000 rpm for three minutes. After a supernatant was removed, the magnetic particles were washed with ultrapure water three times in the same manner to wash the surfaces thereof, so that hydroxyl groups were formed on the surfaces of the magnetic particles.

[0066] The obtained magnetic particles were put in water, and acetic acid and vinyltrimethoxysilane were added, whereby a slurry was prepared. The slurry was sprayed by a spray dryer, whereby first particles with a 10 micrometers average particle size were obtained.

[0067] The first particles were put into toluene, methyltrimethoxysilane was added thereto, and the resultant was stirred. The above dispersion medium was filtrated and was further washed with ethanol, whereby second particles were obtained.

[0068] A dispersibility test of the adsorbent was conducted in the following manner. 40 ml of water was put into a 100 ml test tube, the first particles and the second particles were supplied in a ratio of 0.8 g for the former and 0.2 g for the latter into the test tube, and after the adsorbent was dispersed by violently shaking the test tube, the test tube was left standstill. Thereafter, it was confirmed that the adsorbent sunk on a bottom of the test tube. Further, the test tube was turned upside down, and a dispersion state of the adsorbent sinking on the bottom was checked. This operation was repeated, and it was observed how many times this operation had to be repeated until the adsorbent dispersed completely. As a result, a mixture of the first particles and the second particles completely dispersed at the second time.

[0069] Next, 50 ml of the aforesaid adsorbent was measured to be put into a colorimetric tube, 20 ml of water containing 100 micro liters straight aliphatic oil was added thereto, and the oil was adsorbed by the adsorbent by full stirring. Thereafter, after the adsorbent was taken out of the colorimetric tube by using a magnet, 10 ml of hexane
was added, followed by full stirring, and the oil in the water was extracted. When an amount of the oil contained in the hexane was analyzed by using a gas chromatography mass spectrometer and an amount of the oil adsorbed by the adsorbent was measured, it was found that 98.7 micro liters of the oil was adsorbed (a removal ratio 98.7%).

Further, when the resin mixture that was taken out was supplied into 10 ml of hexane to be fully stirred. When a resin complex was taken out from the hexane by using a magnet and the hexane was analyzed, it was found that a total amount of the oil was desorbed.

(Example 2)
A dispersibility test and an oil adsorbency test of the adsorbent were conducted in the same manner as in the example 1 except that used were second particles with a 10 micrometers average particle size and with polymer layers of polymethyl methacrylate formed on surfaces of their magnetic particles, which were formed by dissolving polymethyl methacrylate (manufactured by Sumitomo Chemical Co., Ltd., SUMIPEX) in acetone and adding the aforesaid magnetic particles to this to prepare a slurry, and spraying the slurry by a spray dryer. An amount of the first particles was 0.8 g and an amount of the second particles was 0.2 g.

As a result, a mixture of the first particles and the second particles completely dispersed at the second time. Further, the adsorbent obtained in this example adsorbed 98.7 micro liters of the oil and a total amount of the oil was desorbed.

(Example 3)
The tests were conducted in the same manner as in the example 1 except that butyltrimethoxysilane was used instead of methyltrimethoxysilane.

(Example 4)
The tests were conducted in the same manner as in the example 1 except that phenyltrimethoxysilane was used instead of methyltrimethoxysilane.

(Example 5)
The tests were conducted in the same manner as in the example 1 except that the amounts of the first and second particles used in the example 1 were 0.6 g and 0.4 g respectively.

(Example 6)
The tests were conducted in the same manner as in the example 1 except that the amounts of the first and second particles used in the example 2 were 0.6 g and 0.4 g respectively.

(Example 7)
The tests were conducted in the same manner as in the example 1 except that methyltrimethoxysilane was used instead of vinyltrimethoxysilane and butyltrimethoxysilane was used instead of trimethoxysilane.
The tests were conducted in the same manner as in the example 1 except that methyltrimethoxytitanium was used instead of vinyltrimethoxysilane.

(Example 9)

The tests were conducted in the same manner as in the example 1 except that ethyltrimethoxyzirconium was used instead of vinyltrimethoxysilane.

(Example 10)

The tests were conducted in the same manner as in the example 1 except that ethyltrimethoxyzinc was used instead of vinyltrimethoxysilane.

(Example 11)

The tests were conducted in the same manner as in the example 1 except that ethyltrimethoxymanganese was used instead of vinyltrimethoxysilane.

(Example 12)

The tests were conducted in the same manner as in the example 2 except that polystyrene was used instead of polymethyl methacrylate (manufactured by Sumitomo Chemical Co., Ltd., SUMIPEX).

(Comparative Example 1)

The tests were conducted in the same manner as in the example 1 except that the amount of the first particles in the example 1 was 1.0 g and the second particles were not used.

(Comparative Example 2)

The tests were conducted in the same manner as in the example 2 except that the amount of the second particles in the example 2 was 1.0 g and the first particles were not used.

(Comparative Example 3)

The tests were conducted in the same manner as in the example 1 except that the first particles obtained by using icosane trimethoxysilane instead of methyltrimethoxysilane were used in an amount of 1.0 g and the second particles were not used.
<table>
<thead>
<tr>
<th>Example</th>
<th>Contact Angle of First Particles (degree)</th>
<th>Contact Angle of Second Particles (degree)</th>
<th>Oil Adsorption Amount (%)</th>
<th>Number of Times Required for Dispersion (times)</th>
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<td>-</td>
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It has been found that the composition of any of the examples exhibits a high oil adsorption ratio of 97% or more and also has excellent dispersibility because the number of dispersion times is twice. In particular, the adsorbent using the first particles produced by using the silane coupling agent was more excellent.

While certain embodiments have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. Indeed, the novel methods described herein may be embodied in a variety of other forms; furthermore, various omissions, substitutions and changes in the form of the methods described herein may be made without departing from the spirit of the inventions. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the inventions.
Claims

[Claim 1] An adsorbent comprising: first particles and second particles different in contact angle.

[Claim 2] The adsorbent according to claim 1, wherein the first particles have hydrophilicity while the second particles have hydrophobicity so that a contact angle of the first particles is set larger than a contact angle of the second particles.

[Claim 3] The adsorbent according to claim 1, wherein the first particles each contain a magnetic particle and an inorganic oxide layer formed on a surface of the magnetic particle and containing at least one kind selected from a group consisting of silica, titania, alumina, zirconia, and zinc oxide produced through hydrolysis of metal alkoxide.

[Claim 4] The adsorbent according to claim 1, wherein the second particles each contain a magnetic particle and an inorganic oxide layer formed on a surface of the magnetic particle and containing at least one kind selected from a group consisting of silica, titania, alumina, zirconia, and zinc oxide produced through hydrolysis of metal alkoxide, and a surface of the inorganic oxide layer is treated with a silane coupling agent.

[Claim 5] The absorbent according to claim 1, wherein the second particles each contain a magnetic particle and a hydrophobic polymer layer formed on a surface of the magnetic particle.

[Claim 6] The adsorbent according to claim 1, wherein the second particles each contain a plurality of magnetic particles and a hydrophobic polymer layer, and the polymer layer covers surfaces of the plural magnetic particles and functions as a binder binding the plural magnetic particles with one another.

[Claim 7] The adsorbent according to claim 1, wherein an average particle size of the first particles falls within a range of 5 micrometers to 100 micrometers.

[Claim 8] The adsorbent according to claim 1, wherein an average particle size of the second particles falls within a range of 5 micrometers to 50 micrometers.

[Claim 9] A wastewater treatment method, comprising: a first step of dispersing the adsorbent according to claim 1 in wastewater containing oil and making the adsorbent adsorb the oil; and
a second step of separating the adsorbent from the wastewater by using a magnetic force.

[Claim 10] The method according to claim 9, wherein the wastewater is industrial wastewater.

[Claim 11] The wastewater treatment method according to claim 10, further comprising, after the second step, a third step of recovering the adsorbent by washing the oil adhering to the adsorbent with an organic solvent.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J20/28 B01J20/32 C02F1/00 C02F1/68 C02F1/28
B01J20/26 B01J20/06

ADD.

According to International Patent Classification (IPC) or both national classification and IPC

B. 

FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search

14 February 2012

Date of mailing of the international search report

22/02/2012

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Tel. (+31-70) 340-2040
Fax: (+31-70) 340-3016

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