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(54) **FIXED BED DECOLORIZATION PROCESS FOR POLYUNSATURATED FATTY ACID**

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(57) **ABSTRACT**

The present invention relates to a fixed bed decolorization process for an polyunsaturated fatty acid, comprising a polyunsaturated fatty acid or a polyunsaturated fatty acid solution is either passed directly through a filler of the fixed bed or recycled in a filler of the fixed bed, a colorless or light-colored polyunsaturated fatty acid product is ultimately produced, at the same time, other than the color, other qualities of the polyunsaturated fatty acid remain unaffected. The decolorization process allows continuous operation or intermittent operation. The filler of the fixed bed comprises one or a mixture of activated carbon, diatomite, carclazyte, silicone and an ion-exchange resin. An upper or a middle or a bottom or a combination thereof is employed to feed a polyunsaturated fatty acid feedstock or a polyunsaturated fatty acid solution. The filler in the fixed bed can be used repeatedly. The filler can be reused after being washed when decolorization effects thereof become deteriorated or ineffective.

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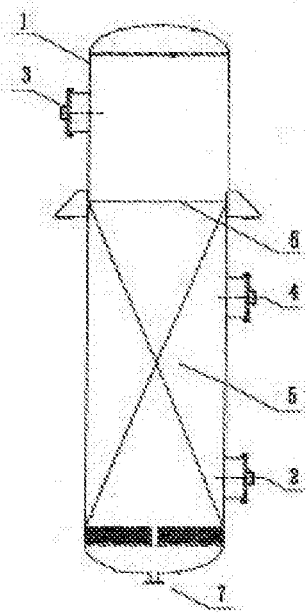


Figure 1

FIXED BED DECOLORIZATION PROCESS FOR POLYUNSATURATED FATTY ACID

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a national stage application of the PCT international application number PCT/CN2015/000637 titled "FIXED BED DECOLORIZATION PROCESS FOR UNSATURATED FATTY ACID", filed in the State Intellectual Property Office of the People's Republic of China on Sep. 9, 2015, which claims priority to and the benefit of Chinese patent application number 201410456702.0, filed in the State Intellectual Property Office of the People's Republic of China on Sep. 10, 2014. The specifications of the above referenced patent applications are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a fixed bed decolorization process for polyunsaturated fatty acid, in particular, relates to a polyunsaturated fatty acid feedstock or a polyunsaturated fatty acid solution is either passed directly through a fixed bed filler or recycled in the fixed bed filler, a colorless or light-colored polyunsaturated fatty acid product is ultimately produced. In the process, other than the color, other qualities of the polyunsaturated fatty acid remain unaffected. The process is suitable for decolorization application of one or mixture of polyunsaturated fatty acid such as fish oil (ω -3 polyunsaturated fatty acid by extraction

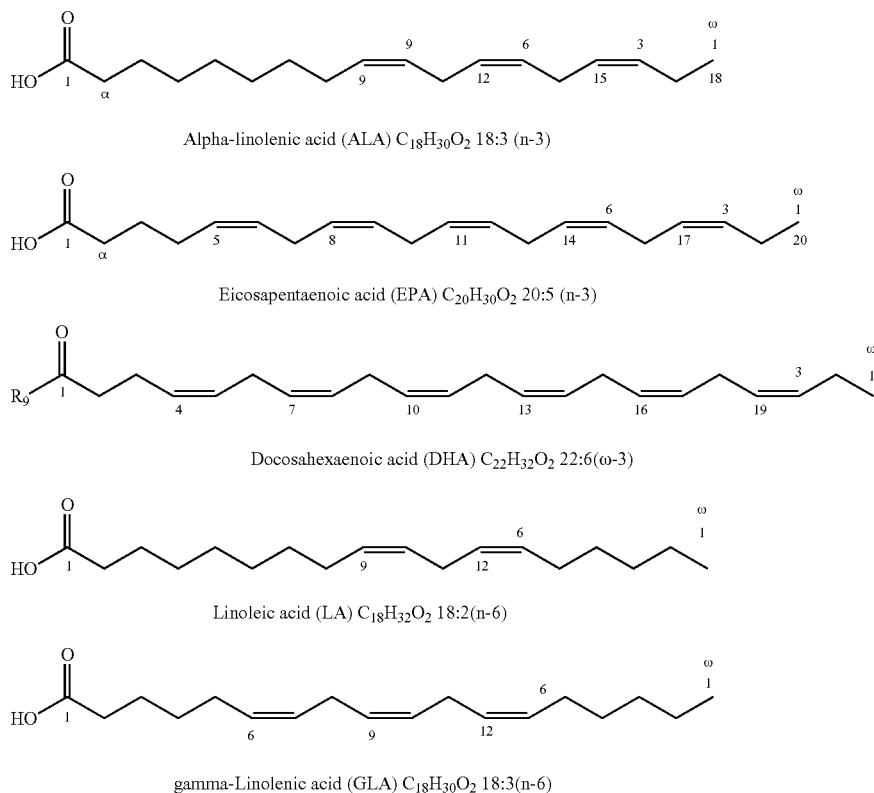
directly), algal oil (ω -3 polyunsaturated fatty acid by fermentation), linoleic acid, conjugated linoleic acid, linolenic acid, arachidonic acid etc.

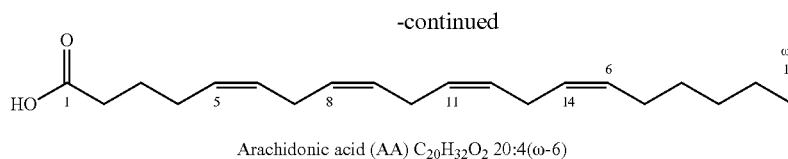
BACKGROUND OF THE INVENTION

[0003] As people pay more and more attention to their health, people starts with ingesting more and more nutritional and healthy dietary supplements, polyunsaturated fatty acid (PUFA) product plays an important role in dietary supplement.

[0004] PUFA is an important basic substance for body metabolism, especially for infant brain development. PUFA is a component of cell membrane. PUFA has mainly physiological functions such as maintaining cell membrane fluidity, promoting cholesterol esterification, reducing cholesterol and triglycerides levels, decreasing blood viscosity, and improving blood circulation and so on. Furthermore, PUFA can also have functions such as improving human thinking and enhancing memory. However, PUFA cannot be synthesized by human body itself. PUFA must be obtained from diet.

[0005] There are various kinds of PUFA including ω -3 PUFA, ω -6 PUFA, ω -9 PUFA, and other kinds of conjugated linoleic acid, such as α -Linolenic acid (ALA), eicosapentaenoic ester (EPA), docosahexaenoic acid (DHA), docosapentaenoic acid (DPA), linoleic acid (LA), conjugated linoleic acid (CLA), γ -linolenic acid (GLA), arachidonic acid (AA) and so on. Wherein EPA and DHA representing ω -3 PUFA are known and acceptable to the public. and obviously improve human thinking and enhance memory. Their molecular structures of polyunsaturated fatty acids are as follows.





[0006] Polyunsaturated fatty acid mainly derives from algae extract and marine oil, one of important sources comes from fish oil. Due to PUFA feedstock derives from extract, it contains colored impurity such as pigment. Some impurities are harmful to human body. Product standard of PUFA is colorless or light yellow transparent liquid. Therefore, industrial preparation process of polyunsaturated fatty acid contains a decolorization process.

[0007] At present, a decolorization process in industry use decolorizers including activated carbon, diatomite, carclazyte, silica gel or ion exchange resin etc. A kettle type mixing decoloring process is widely used. That is, PUFA and decolorizer are mixed together under certain condition, and then directly filtered and recovered after mixing to finally obtain PUFA product. The process has the following disadvantages: 1) feedstocks or intermediates easily contact with air or oxygen due to open operation of partial process, and then it would result in product oxidized and would reduce product quality; 2) industrial design and large-scale production have some difficulty because of intermittent operation; 3) decolorizer is difficult to be recovered; 4) decolorizer is difficult to be treated; 5) decolorize along with some PUFA is difficult to recycle and produce high loss and lower yield; 6) operation process is complex; 7) process would bring about a serious of environmental pollution and safety problems.

[0008] Currently some prior documents such as Chinese Patent No. CN102994236, CN1101935, CN103525564, CN1283392, CN103540415 disclose a decolorization process of polyunsaturated fatty acid by using 0.1~5% activated carclazyte as decolorizer. Chinese Patent No. CN103725403, CN1263145, CN101940240 disclose a decolorization process of polyunsaturated fatty acid by using active carbon as decolorizer. Chinese Patent No. CN1769409 uses diatomite as decolorizer. Chinese Patent No. CN101297708 uses an ion exchange resin as decolorizer. Wherein decolorization process is conducted by kettle type mixing under certain condition, and then directly filter after decolorization to obtain PUFA. These processes have some effects on decolorization. However, it would be difficult to transfer and feed because the filtered carclazyte, activated carbon and diatomite have some viscosity, and then cannot recycle directly. Besides, cleaning operation is too complex. Thus, decolorizer is generally directly discarded rather than recycled.

[0009] Due to intermittent caldron type mixing operation and partial opening operation of the above mentioned processes, polyunsaturated fatty acids easily contact with air or oxygen and make product oxidized and consequently reduce product quality. In the meanwhile, intermittent caldron type mixing operation would influence industrial scale production, and operation process would relatively complex. It also would not be convenient to monitor quality of product.

[0010] Moreover, decolorizers would absorb a certain amount of polyunsaturated fatty acid after using up decolorizers in intermittent caldron type mixing process. It would

make polyunsaturated fatty acid difficult recovery. Consequently it would result in loss of polyunsaturated fatty acid and influence yield of product.

[0011] Besides, these decolorizers in opening operation process may cause serious of environmental pollution, and activated carbon in opening operation process is flammable, and then would produce big security risks.

[0012] In general, the above mentioned processes have serious of disadvantages difficult to overcome, and consequently these processes could not be used for large-scale production.

[0013] How to choose proper implement method in decolorization process is also studying besides choosing decolorizers. Currently most of processes use intermittent caldron type mixing operation to carry out decoloring. But it could not overcome or improve the above mentioned deficiencies. A fixed bed technology has been used in other industrial applications such as used in the field of production separation, a good separation would be achieved comparing with traditional technology.

[0014] A fixed bed device is to fix some special fillers in fixed bed device, for example, liquid and gas may directly pass through fillers or circulate in fillers of fixed bed device, and make materials absorbed or separated. These processes have advantages of high efficiency, less environmental pollution and saving energy etc.

SUMMARY OF THE INVENTION

[0015] The present invention relates to a decolorization process, in particular, relates to use a filler of a fixed bed to decolorate for polyunsaturated fatty acid feedstock or a polyunsaturated fatty acid solution, that is, a polyunsaturated fatty acid feedstock or a polyunsaturated fatty acid solution is either passed directly through a fixed bed filler or recycled in the fixed bed filler, to achieve purposes of decolorization and then obtain a colorless or light-colored polyunsaturated fatty acid product.

[0016] According to the fixed bed decolorization process of the present invention, the fixed bed decolorization process comprising: 1) filling a fixed-bed filler in a decolorization fixed bed, and rinsing the decolorization fixed bed with a dissolving solvent; and then rinsing the decolorization fixed bed with a polyunsaturated fatty acid feedstock or a polyunsaturated fatty acid solution for 1~2 times to obtain a stable decolorization fixed bed; wherein the polyunsaturated fatty acid solution includes the polyunsaturated fatty acid feedstock and the dissolving solvent; 2) mixing the polyunsaturated fatty acid feedstock or the polyunsaturated fatty acid solution and the dissolving solvent together to obtain a mixture; and 3) passing the mixture through an inlet of the decolorization fixed bed to feed, passing the mixture through an outlet of the decolorization fixed bed to discharge, a temperature of the decolorization fixed-bed is 0° C.~150° C., to obtain a decolorized solution; and then recycle solvent from the decolorized solution under reduced pressures or

normal pressures, to obtain a decolorized polyunsaturated fatty acid product; wherein, the polyunsaturated fatty acid feedstock is selected from the group consisting of free radical type polyunsaturated fatty acid, methyl ester type polyunsaturated fatty acid, ethyl ester type polyunsaturated fatty acid and glyceride type unsaturated fatty acid; the fixed-bed filler is selected from the group consisting of activated carbon, diatomite, carclazyte, silica gel, and ion exchange resin; the dissolving solvent is selected from the group consisting of alkane solvent, esters solvent, alcohols solvent, ethers solvent, ketones solvent.

[0017] The polyunsaturated fatty acid feedstock of the present invention comprises free radical type polyunsaturated fatty acid, methyl ester type polyunsaturated fatty acid, ethyl ester type polyunsaturated fatty acid and glyceride type unsaturated fatty acid. Wherein the total content of the polyunsaturated fatty acid in the polyunsaturated fatty acid feedstock is 10~100% by weight.

[0018] The polyunsaturated fatty acid of the present invention comprises one or more types of fish oil (ω -3 polyunsaturated fatty acid by extraction directly), algal oil (ω -3 polyunsaturated fatty acid by fermentation), linoleic acid, conjugated linoleic acid, linolenic acid, and arachidonic acid or a mixture thereof.

[0019] The activated carbon in the fixed bed filler of the present invention comprises one or more kinds of powder-type activated carbon, granular-type activated carbon, amorphous particle-type activated carbon, cylinder-shaped activated carbon, and spherical-shaped activated carbon or a mixture thereof. The diatomite is various of diatomite. The carclazyte is various of carclazyte. The silica gel comprises one or more kinds of macroporous silica gel, silochrom, B-type silica gel, and pore silica gel or a mixture thereof. The ion exchange resin comprises one or more kinds of neutral ion exchange resin, weak acid ion exchange resin, and weak basic ion exchange resins or a mixture thereof.

[0020] The feeding way of the polyunsaturated fatty acid feedstock in the decolorization fixed bed of the present invention includes upper feeding, middle feeding and bottom feeding; and the discharging way of the polyunsaturated fatty acid feedstock in the decolorization fixed bed includes upper discharging, middle discharging and bottom discharging. Wherein the diameter ratio of the decolorization fixed bed is 1:1~1:20.

[0021] The dissolving solvent of the polyunsaturated fatty acid solution comprises one or more kinds of alkanes solvent, esters solvent, alcohols solvent, ethers solvent, ketones solvent. Wherein the alkanes solvent comprises one or more kinds of n-hexane, cyclohexane, n-heptane, octane, nonane, decane, 2,2-dimethyl butane, 2,3-dimethyl butane, 2-methyl pentane, 3-methyl pentane, 2,2,4-trimethyl pentane, 2,3,4-trimethyl pentane, 2,2,3-trimethyl pentane, 2,2,5-trimethyl pentane, isohepane or a mixture thereof. The esters solvent comprises one or more kinds of methyl formate, ethyl formate, propyl formate, isopropyl formate, butyl formate, isobutyl formate, amyl formate, isoamyl formate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, amyl acetate, isoamyl acetate, methyl propionate, ethyl propionate, propyl propionate, butyl propionate, Isobutyl propionate, amyl propionate, isoamyl propionate, methyl butyrate, ethyl butyrate, propyl butyrate, butyl butyrate, isobutyl butyrate, amyl butyrate, isoamyl butyrate, methyl isobutyrate, ethyl isobutyrate, propyl isobutyrate, butyl isobutyrate, isobutyl isobutyrate, amyl

isobutyrate, isoamyl isobutyrate, methyl valerate, ethyl valerate, propyl valerate, butyl valerate, isobutyl valerate, amyl valerate, isoamyl valerate, methyl isovalerate, ethyl isovalerate, propyl isovalerate, butyl isovalerate, isobutyl isovalerate, amyl isovalerate, isoamyl isovalerate or a mixture thereof. The ethers solvent comprises one or more kinds of diethyl ether, propyl ether, isopropyl ether, butyl ether, amyl ether, isoamyl ether, methyl ethyl ether, methyl propyl ether, methyl-n-butylether, ethyl butyl ether, methyl tert-butyl ether, ethyl tert-butyl ether, anisole, phenetole, butyl phenyl ether, and amyl phenyl ether or a mixture thereof. The ketones solvent comprises one or more kinds of acetone, butanone, methyl acetone, 2-pentanone, 3-pentanone, 3-methylbutanone or a mixture thereof. The alcohols solvent comprises one or more kinds of methanol, alcohol, propyl alcohol, isopropanol, butanol, isobutanol, sec-butyl alcohol, tertiary butanol, pentanol, 2-methyl-1-butanol, isopentyl alcohol, sec-amyl alcohol, 3-pentanol, tert-amyl alcohol, 3-methyl-2-butanol, neopentyl alcohol or a mixture thereof.

[0022] The present invention can be decolorized by using a solution. On the one hand, it would reduce damage as oxidation by diluting related concentration of the polyunsaturated fatty acid feedstock. On the other hand, it would be benefit for improving velocity and uniform distribution of the fixed bed filler and controlling the process.

[0023] The weight of the dissolving solvent in the polyunsaturated fatty acid solution of the present invention is 0.1~10 times as large as the weight of the polyunsaturated fatty acid feedstock.

[0024] The controlling temperature of the process of the present invention is 0~150° C. It not only can improve the process conditions to obtain the best decolorizing effects but also improve viscosity of the filler and flow velocity of the filler in the fixed bed.

[0025] The fixed-bed filler of the present invention can be repeatedly used. namely the decolorizing process can be carried out repeatedly, and has less influence on the decolorizing effect.

[0026] After decolorizing getting worse or finishing decolorizing of the present invention, the fixed-bed can be rinsed with rinsing solvent and then is repeatedly used. The rinsing method may use the same direction or the opposite direction as the flow direction of the filler of the decolorization process, in order to achieve the best rinsing effect.

[0027] The rinsing solvent of the fixed bed filler of the present invention may use one or more kinds of solvents. The rinsing solvent may be water or the rinsing solvent of dissolving the polyunsaturated fatty acid of the decolorization process. The rinsing solvent includes water or the dissolving solvent. The dissolving solvent of the polyunsaturated fatty acid solution comprises one or more kinds of alkanes solvent, esters solvent, alcohols solvent, ethers solvent, ketones solvent. Wherein the alkanes solvent comprises one or more kinds of n-hexane, cyclohexane, n-heptane, octane, nonane, decane, 2,2-dimethyl butane, 2,3-dimethyl butane, 2-methyl pentane, 3-methyl pentane, 2,2,4-trimethyl pentane, 2,3,4-trimethyl pentane, 2,2,3-trimethyl pentane, 2,2,5-trimethyl pentane, isohepane or a mixture thereof. The esters solvent comprises one or more kinds of methyl formate, ethyl formate, propyl formate, isopropyl formate, butyl formate, isobutyl formate, amyl formate, isoamyl formate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, amyl acetate, isoamyl acetate, methyl propionate, ethyl propionate, propyl

propionate, butyl propionate, Isobutyl propionate, amyl propionate, isoamyl propionate, methyl butyrate, ethyl butyrate, propyl butyrate, butyl butyrate, isobutyl butyrate, amyl butyrate, isoamyl butyrate, methyl isobutyrate, ethyl isobutyrate, propyl isobutyrate, butyl isobutyrate, isobutyl isobutyrate, amyl isobutyrate, isoamyl isobutyrate, methyl valerate, ethyl valerate, propyl valerate, butyl valerate, isobutyl valerate, amyl valerate, isoamyl valerate, methyl isovalerate, ethyl isovalerate, propyl isovalerate, butyl isovalerate, isobutyl isovalerate, amyl isovalerate, isoamyl isovalerate or a mixture thereof. The ethers solvent comprises one or more kinds of diethyl ether, propyl ether, isopropyl ether, butyl ether, amyl ether, isoamyl ether, methyl ethyl ether, methyl propyl ether, methyl-n-butylether, ethyl butyl ether, methyl tert-butyl ether, ethyl tert-butyl ether, anisole, phenetole, butyl phenyl ether, and amyl phenyl ether or a mixture thereof. The ketones solvent comprises one or more kinds of acetone, butanone, methyl acetone, 2-pentanone, 3-pentanone, 3-Methylbutanone or a mixture thereof. The alcohols solvent comprises one or more kinds of methanol, alcohol, propyl alcohol, isopropanol, butanol, isobutanol, sec-butyl alcohol, tertiary butanol, pentanol, 2-methyl-1-butanol, isopentyl alcohol, sec-amyl alcohol, 3-Pentanol, tert-amyl alcohol, 3-methyl-2-butanol, neopentyl alcohol or a mixture thereof.

[0028] After appropriate treating decolorization product, a colorless or light yellow polyunsaturated fatty acid product is obtained. Other than the color, other qualities of the polyunsaturated fatty acid remain unaffected. Especially, the process can also remove heavy metals, dioxin, benzopyrene and other trace species in the product.

[0029] Solvent may be recovered under reduced pressure or normal pressure in the fixed bed decolorization process of the present invention to obtain reused solvents and the polyunsaturated fatty acid, after decolorization of the polyunsaturated fatty acid solution.

[0030] The process of the present invention ensures product quality, because the process uses totally enclosed operation, no fillers contact with air or oxygen and no product oxidation is occurred, and only need controlling velocity of the filler and monitoring the product quality in the process.

[0031] Less waste is finally produced in the process. And no environmental pollution and security risk is occurred So the process is suitable for larger scale production.

[0032] The decolorizers used in the fixed-bed for the polyunsaturated fatty acid of the present invention adopt a fixed bed mode, the mode has the following advantages:

[0033] 1) The decolorization process allows continuous operation or intermittent operation. It could simplify the decolorization process and the decolorization process could be very stable.

[0034] 2) The decolorization process eliminates air or oxygen influences on products because the decolorization process uses continuous enclosed operation. It could improve quality of product to a certain degree. And the decolorization process overcomes disadvantages of the decolorizers attached in the product in the kettle type mixing intermittent operation because the decolorization process uses continuous enclosed operation. The decolorization process could reduce or eliminats loss of the product and increase yield of the product.

[0035] 3)The polyunsaturated fatty acid raw material or polyunsaturated fatty acid solution directly passes through the fixed bed or circulate in the fixed bed, wherein the

feeding way includes upper feeding, middle feeding, bottom feeding or combined feeding, and the discharging way includes upper discharging, middle discharging and bottom discharging. It could make polyunsaturated fatty acid or its solution greatly and uniformly contact with the decolorizer, to obtain the best decolorization effects.

[0036] 4) The decolorizer in the enclosed fixed bed could be used circularly. It could eliminate environment pollution and security risk.

[0037] 5) In comparison with the kettle type intermittent decolorizing operation, the decolorizer of the present invention could increase usage amount for each time. So the quality of the obtained product could improved highly.

[0038] 6) The fixed bed decolorization process of the present invention could be monitored and detected online at any time. The operation is very simple and convenient. The process could ensure the stability of product quality.

[0039] 7) When the effect of decolorization is degraded or lost, the decolorizer could be eluted with eluents. The eluting operation is substantially the same as that of the decolorization process, that is using downstream flow or upstream flow. The procedure is very simple, the decolorizer can be used immediately after eluting.

[0040] The present invention provides a fixed bed decolorization process for an polyunsaturated fatty acid by using a decolorizer as fillers. A polyunsaturated fatty acid or a polyunsaturated fatty acid solution is either passed directly through a fixed bed filler or recycled in fillers of the fixed bed, in order to achieve the purpose of decolorization. The decolorization process allows continuous operation or intermittent operation. It could simplify the decolorization process and the decolorization process could be very stable. It could improve product quality to a certain degree. The decolorization process could reduce or eliminate loss of product and increase yield of product. Using a simple or combination feeding mode could make polyunsaturated fatty acid or its solution greatly and uniformly contact with the decolorizer, to achieve the best decolorization effects. It could eliminate environmental pollution and security risk. When decolorization effect of decolorizer is degraded or lost, the decolorizer could be washed with eluents. The eluting operation is very simple and convenient, the decolorizer can immediately be used after eluting.

BRIEF DESCRIPTION OF FIGURES

[0041] FIG. 1 shows a fixed bed decolorization process for polyunsaturated fatty acid.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS THEREOF

[0042] Hereafter, the present invention will be described specifically with reference to the examples. The examples are given only for illustration of the technical solution of the present invention and should not be construed to limit the present invention.

EXAMPLE 1

[0043] To select a decolorization fixed bed 1, wherein the diameter of the decolorization fixed-bed is 0.1 m, the height is 0.5 m (the ratio of diameter to height of the decolorization fixed bed is 1:5). To fill a powder type activated carbon in the decolorization fixed-bed, and firstly rinse the decolorization fixed bed with n-hexane, and then rinse the decol-

orization fixed bed with a free type fish oil feedstock once or twice, to obtain a stable decolorization fixed-bed device, as shown in FIG. 1.

[0044] To mix 500 g of a free type fish oil feedstock (EPA 17.6%, DHA 11.7%, the total content of a free type polyunsaturated fatty acid is 42.1%, with orange-red color) with 500 g of n-hexane, to obtain an homogenous solution with light orange-red color.

[0045] The homogenous solution including a free type fish oil feedstock and n-hexane for decolorization passes through an upper feeding inlet 3 into a bottom discharging outlet 2 (upper-lower path) in the fixed bed. These feedstock directly passes through the fixed-bed without circulation, the temperature of the fixed-bed is at 30° C., the decolorizing time is 0.5 h. After decolorizing, a free type fish oil and n-hexane solution with light yellow color is recovered under reduced pressure, to obtain 496 g of free type fish oil product with light yellow color.

[0046] After finishing the decolorization, all of feedstocks are released from a bottom drain hole 7. And then a rinsing solvent n-hexane passes through a bottom inlet 2, middle inlet 5, and then passes through a partition 6, to discharge from a upper outlet 3. Rinsing a filler 5 of the fixed bed and then all of solvents are released from a bottom drain hole 7.

[0047] Determination of a free type fish oil product: EPA 17.3%, DHA 11.5%, the total content of a free type polyunsaturated fatty acid is 42.0% with light yellow color, the yield is 99.0%.

COMPARSION EXAMPLE 2

[0048] To mix 500 g of a free type fish oil feedstock (EPA17.6%, DHA11.7%, the total content of a free type polyunsaturated fatty acid is 42.1% with orange-red color) with 500 g of n-hexane in a reaction flask, to obtain a homogenous solution with light orange-red color.

[0049] To add 25 g of powder type activated carbon to the reaction flask, and then is decolorized under stirring at 30° C. for 1.0 h; afterwards, to filtrate and remove the activated carbon after finishing decolorization, to obtain a free type fish oil and n-hexane solution with light yellow color, and

then remove solvent under reduced pressure to obtain 459 g of product of free type fish oil with light yellow color.

[0050] Determination of a free type fish oil product: EPA17.1%, DHA 11.6%, the total content of the free type polyunsaturated fatty acid is 41.8% with light yellow color, the yield is 91.1%.

[0051] It could be shown from a comparison between the Example 1 of the present invention and the Comparison Example 2 that the Example 1 of the present invention uses an activated carbon as a filler of the fixed bed for decolorization at 30° C. by a solution including n-hexane and a free type fish oil containing polyunsaturated fatty acid, to obtain a free type fish oil product with quite light color. It could also be shown the decolorization process of the present invention has better decolorization effects, the yield is 99.0%. Other than the color, other qualities of the polyunsaturated fatty acid remain unaffected, and at the same time, the activated carbon can be directly reused.

[0052] The Comparison Example 2 uses a common kettle type mixing for decolorization under the same process condition, in particular, uses 5% activated carbon at 30° C. for decolorization by a solution including n-hexane and a free type fish oil containing polyunsaturated fatty acid, to obtain a free type fish oil product with light color. It could also be shown the decolorization process of the Comparison Example 2 has bad effects, the yield is 91.1%. Besides it would be difficult to obtain activated carbon to be reused because of high stickiness of received activated carbon.

[0053] In comparison with the decolorization process and experimental result of the present invention and the Comparison Example, it could be seen from it that the decolorization process of the present invention has many advantages such as simple process, better decolorizing effects, higher yield, lower cost and no environmental pollution, and consequently the decolorization process of present invention has feasibility for industrial scale production.

EXAMPLES 3~15

[0054] Please refer to various of implement objects and their parameters of Table 1 of Examples 3~15 as follows.

TABLE 1

exam- ples	State of fixed-bed		State of feedstock/solution				Feed-in Path			Product		
	ratio of diameter to height	filler	type of poly- unsaturated T/ ° C. feedstock	total content of poly- unsaturated fatty acid %	color	solvent g/g	feed-in path	decolor- izing way	color	total content of poly- unsaturated fatty acid %	yield/ %	
	3	1:1	Powder type activated carbon	0	glyceride type fish oil	59.8	orange- red	—	upper- lower path	directly pass	Light yellow	59.4
4	1:1	Particle type activated carbon	20	Ethyl ester linoleic acid	78.3	Light orange- red	n-hexane 0.5:1	lower- upper path	cycle	Light yellow	78.2	99.2
5	1:2	Amorphous particle type activated carbon	30	Ethyl ester conjugated linoleic acid	46.7	orange- red	Ethanol 4:1	upper/ middle- lower path	cycle	Light yellow	46.5	98.8

TABLE 1-continued

exam- ples	State of fixed-bed		State of feedstock/solution					Product				
	ratio of diameter to height	filler	type of poly- unsaturated fatty acid T/ ° C. feedstock	total content		solvent g/g	Feed-in Path		total content			
				of poly- unsaturated fatty acid %	color		feed-in path	decolor- izing way	color	of poly- unsaturated fatty acid %	yield/ %	
6	1:4	cylinder-shaped activated carbon	30	Ethyl ester fish oil	46.9	Light orange-red	—	lower-upper path	cycle	Light yellow	46.7	98.7
7	1:6	Spherical-shaped activated carbon	30	Free type algal oil	42.1	orange-red	—	upper-lower path	cycle	Light yellow	42.2	99.1
8	1:8	Activated diatomite	40	glyceride type algal oil	92.4	Light orange-red	Ethyl formate 2:1	middle/lower-upper path	directly pass	Light yellow	92.6	98.7
9	1:10	Activated carclazyte	50	Methyl ester linoleic acid	11.2	orange-red	Propyl formate 8:1	lower-upper path	directly pass	Light yellow	11.6	99.2
10	1:20	Macroporous silica gel	150	Free type conjugated linoleic acid	27.8	Light orange-red	Butyl isovalerate 6:1	upper-lower path	cycle	Light yellow	27.9	99.1
11	1:5	silochrom	100	Free type arachidonic acid	53.6	Light orange-red	Isobutyl acetate 1:1	upper/middle-lower path	cycle	Light yellow	53.8	98.8
12	1:4	pore silica gel	70	Free type linolenic acid	68.5	orange-red	Ethyl acetate 10:1	lower-upper path	cycle	Light yellow	68.4	99.2
13	1:5	Weak acidic ion exchange resin	30	glyceride type linolenic acid	68.2	Light orange-red	Methanol 3:1	middle/lower-upper path	cycle	Light yellow	68.0	99.1
14	1:8	Neutral ion exchange resin	60	Ethyl ester linolenic acid	36.7	orange-red	ether 6:1	middle/lower-upper path	cycle	Light yellow	36.5	98.7
15	1:9	Weak basic ion exchange resin	20	Ethyl ester arachidonic acid	46.7	Light orange-red	Butanone 5:1	lower-upper path	cycle	Light yellow	46.4	99.0

EXAMPLE 16~20

Example of Reused Decolorizer

[0055] To select the fix bed of Example 1 (wherein the diameter of the fix bed is 0.1 meter, the heigh is 0.5 m, the

ratio of diameter to heigh is 1:5, a powdered type activated carbon filler and 30° C. of temperature), the fix bed is reused for decolorization, as shown in Table 2. Some implement objects and their parameters of Examples 16~20 are listed in Table 2.

TABLE 2

Exam- ples	State of feedstock/solution					Product			
	Type of poly- unsaturated fatty acid feedstock	Total content of poly- unsaturated fatty acid %	Color	Solvent	Feed-in path	Feed-in path		Total content of poly-	
						Decolor- izing way	Color	unsaturated fatty acid %	Yield/ %
16	glyceride type fish oil	59.8	orange red	—	upper-lower path	directly pass	light yellow	59.7	99.2
17	ethyl ester linoleic acid	78.3	orange red	n-hexane 3:1	upper-lower path	directly pass	light yellow	78.2	99.0
18	ethyl ester conjugated linoleic acid	46.7	orange red	ethanol 4:1	upper/middle-lower path	directly pass	light yellow	46.6	98.9
19	free type algal oil	42.1	orange red	butanone 6:1	upper-lower path	directly pass	light yellow	41.7	98.6
20	glyceride type linolenic acid	68.2	orange red	ether 4:1	upper-lower path	directly pass	light yellow	68.2	98.5

EXAMPLE 21~22

Example of Reused Fixed Bed After Rinsing

[0056] To select the fix bed of Examples 21~22 (wherein the diameter of the fix bed is 0.1 meter, the height is 0.5 m, the ratio of diameter to height is 1:5, the filler is powdered type activated carbon and the temperature is 30° C.). After the fix bed is reused for decolorization, n-hexane is used for rinsing the fixed bed. After finishing rinsing, the fixed bed is reused for decolorization. Some implement objects and their parameters of Examples 3~15 are listed in Tables 3.

TABLE 3

Exam- ples	State of feedstock/solution				Product					
	Type of poly- unsaturated fatty acid feedstock	Total content of poly- unsaturated fatty acid %	Color	Solvent	Feed-in path		Decolor- izing way	color	Total content of poly- unsaturated fatty acid %	yield %
					Feed-in path	Decolor- izing way				
21	ethyl ester fish oil	46.9	orange red	n-hexane 3:1	upper-lower path	directly pass	light yellow	46.7	98.8	
22	Cylglycerol linolenic acid	68.2	orange red	n-hexane 2:1	upper-lower path	directly pass	light yellow	68.1	99.1	

[0057] Although the present invention has been described in connection with the above embodiments, it should be understood that the present invention is not limited to such preferred embodiments and procedures set forth above. The embodiments and procedures were chosen and described in order to best explain the principles of the invention and its practical application, to thereby enable others skilled in the art to best utilize the invention. It will be apparent to those skilled in the art that various substitution, modifications and changes may be thereto without departing from the scope and spirit of the invention. Therefore, the intention is intended to cover all alternative constructions and equivalents falling within the spirit and scope of the invention as defined only by the appended claims and equivalents thereto.

1. A fixed bed decolorization process for polyunsaturated fatty acid, the fixed bed decolorization process comprising:

- 1) filling a fixed-bed filler in a decolorization fixed bed, and rinsing the decolorization fixed bed with a dissolving solvent; and then rinsing the decolorization fixed bed with a polyunsaturated fatty acid feedstock or a polyunsaturated fatty acid solution for 1~2 times to obtain a stable decolorization fixed bed; wherein the polyunsaturated fatty acid solution includes the polyunsaturated fatty acid feedstock and the dissolving solvent;
- 2) mixing the polyunsaturated fatty acid feedstock or the polyunsaturated fatty acid solution with the dissolving solvent together to obtain a mixture; and
- 3) passing the mixture through an inlet of the decolorization fixed bed to feed, passing the mixture through an outlet of the decolorization fixed bed to discharge, a temperature of the decolorization fixed-bed is 0° C.~150° C., to obtain a decolorized solution; and then recycle solvent from the decolorized solution under reduced pressures or normal pressures, to obtain a decolorized polyunsaturated fatty acid product;

wherein the polyunsaturated fatty acid feedstock is selected from the group consisting of free type polyunsaturated fatty acid, methyl ester type polyunsaturated fatty acid, ethyl ester type polyunsaturated fatty acid and glyceride type unsaturated fatty acid;

the fixed-bed filler is selected from the group consisting of activated carbon, diatomite, carclazyte, silica gel and ion exchange resin;

the dissolving solvent is selected from the group consisting of alkanes solvent, esters solvent, alcohols solvent, ethers solvent and ketones solvent.

2. The fixed bed decolorization process according to claim 1, wherein the polyunsaturated fatty acid is selected from the group consisting of fish oil, algal oil, linoleic acid, conjugated linoleic acid, linolenic acid and arachidonic acid.

3. The fixed bed decolorization process according to claim 2, wherein the total content of the polyunsaturated fatty acid in the polyunsaturated fatty acid feedstock is 10~100% by weight.

4. The fixed bed decolorization process according to claim 1, wherein the activated carbon is selected from the group consisting of powder-type activated carbon, granular-type activated carbon, amorphous particle-type activated carbon, cylinder-shaped activated carbon, and spherical-shaped activated carbon.

5. The fixed bed decolorization process according to claim 1, wherein the silica gel is selected from the group consisting of macroporous silica gel, silochrom, B-type silica gel and pore silica gel.

6. The fixed bed decolorization process according to claim 1, wherein the ion exchange resin is selected from the group consisting of neutral ion exchange resin, weak acid ion exchange resin and weak basic ion exchange resins.

7. The fixed bed decolorization process according to claim 1, wherein the feeding way of the polyunsaturated fatty acid feedstock in the decolorization fixed bed includes upper feeding, middle feeding and bottom feeding; and the discharging way of the polyunsaturated fatty acid feedstock in the decolorization fixed bed includes upper discharging, middle discharging and bottom discharging.

8. The fixed bed decolorization process according to claim 7, wherein a ratio of diameter to height of the decolorization fixed bed is 1:1~1:20.

9. The fixed bed decolorization process according to claim 1, wherein the alkanes solvent is selected from the group consisting of n-hexane, cyclohexane, n-heptane, octane, nonane, decane, 2,2-dimethyl butane, 2,3-dimethyl butane, 2-methyl pentane, 3-methyl pentane, 2,2,4-trimethyl pentane, 2,3,4-trimethyl pentane, 2,2,3-trimethyl pentane, 2,2,

5-trimethyl pentane, isohepane; the esters solvent is selected from the group consisting of methyl formate, ethyl formate, propyl formate, isopropyl formate, butyl formate, isobutyl formate, amyl formate, isoamyl formate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, amyl acetate, isoamyl acetate, methyl propionate, ethyl propionate, propyl propionate, butyl propionate, isobutyl propionate, amyl propionate, isoamyl propionate, methyl butyrate, ethyl butyrate, propyl butyrate, butyl butyrate, isobutyl butyrate, amyl butyrate, isoamyl butyrate, methyl isobutyrate, ethyl isobutyrate, propyl isobutyrate, butyl isobutyrate, isobutyl isobutyrate, amyl isobutyrate, isoamyl isobutyrate, methyl valerate, ethyl valerate, propyl valerate, butyl valerate, isobutyl valerate, amyl valerate, isoamyl valerate, methyl isovalerate, ethyl isovalerate, propyl isovalerate, butyl isovalerate, isobutyl isovalerate, amyl isovalerate, isoamyl isovalerate; the ethers solvent is selected from the group consisting of diethyl ether, propyl ether, isopropyl ether, butyl ether, amyl ether, isoamyl ether, methyl ethyl ether, methyl propyl ether, methyl-n-butylether, ethyl butyl ether, methyl tert-butyl ether, ethyl tert-butyl ether, anisole, phenetole, butyl phenyl ether, and amyl phenyl ether; the ketones solvent is selected from the group consisting of acetone, butanone, methyl acetone, 2-pentanone, 3-pentanone, 3-methylbutanone; the alcohols solvent is selected from the group consisting of methanol, alcohol, propyl alcohol, isopropanol, butanol, isobutanol, sec-butyl alcohol,

tertiary butanol, pentanol, 2-methyl-1-butanol, isopentyl alcohol, sec-amyl alcohol, 3-Pentanol, tert-amyl alcohol, 3-methyl-2-butanol, neopentyl alcohol.

10. The fixed bed decolorization process according to claim 1, wherein the weight of the dissolving solvent in the polyunsaturated fatty acid solution is 0.1~10 times as large as the weight of the polyunsaturated fatty acid feedstock.

11. The fixed bed decolorization process according to claim 1, wherein the filler of the decolorization fixed-bed can be repeatedly used; the decolorization fixed-bed can be rinsed and then is repeatedly used after decolorizing getting worse or finishing decolorizing.

12. The fixed bed decolorization process according to claim 1, wherein the fixed-bed filler can be repeatedly used; after decolorizing getting worse or finishing decolorizing, the fixed-bed can be rinsed with a rinsing solvent and then is repeatedly used.

13. The fixed bed decolorization process according to claim 12, wherein the rinsing solvent is water and the dissolving solvent.

14. The fixed bed decolorization process according to claim 1, wherein recovering solvent under reduced pressure or normal pressure to obtain reused solvent and the polyunsaturated fatty acid, after decolorization of the polyunsaturated fatty acid solution.

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