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(54) Title: USE OF AN ADSORBENT FOR THE REMOVAL OF LIQUID, GASEOUS AND/OR DISSOLVED CONSTITUENTS FROM A PROCESS STREAM

(57) Abrégé/Abstract:

The invention pertains to a process for the removal of liquid, gaseous and/or dissolved constituents from a process stream comprising the steps of a) contacting a process stream with a porous material having pores with an average diameter of 0.01 to 50 µm wherein an extraction liquid is immobilized; and b) subsequently contacting the resulting process stream with an adsorbent.

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(54) **Title:** USE OF AN ADSORBENT FOR THE REMOVAL OF LIQUID, GASEOUS AND/OR DISSOLVED CONSTITUENTS FROM A PROCESS STREAM

(57) **Abstract:** The invention pertains to a process for the removal of liquid, gaseous and/or dissolved constituents from a process stream comprising the steps of a) contacting a process stream with a porous material having pores with an average diameter of 0.01 to 50 μm wherein an extraction liquid is immobilized; and b) subsequently contacting the resulting process stream with an adsorbent.

USE OF AN ADSORBENT FOR THE REMOVAL OF LIQUID, GASEOUS AND/ OR DISSOLVED CONSTITUENTS FROM A PROCESS STREAM

The invention pertains to a process for the removal of liquid, gaseous and/or dissolved constituents from a process stream.

Such a process is known from WO 94/03249, which discloses the use of porous polymers, the pores of which are filled with an extraction liquid immobilized therein, for removing hydrophobic constituents from an aqueous solution. The porous polymer contains pores having an average diameter of 0.1 μm or more. The porous materials described herein are very effective in the removal of organic constituents, such as benzene, toluene, ethyl benzene, xylene, and polycyclic aromatic hydrocarbons such as naphthalene and anthracene, which are poorly soluble or insoluble in the aqueous solution. These materials, however, are much less effective in the removal of more soluble organic constituents, such as phenol, dichloromethane, and methyl tert-butyl ether. The amount of porous material necessary to considerably reduce the concentration of these constituents in the aqueous process stream – for example a reduction by a factor of 1,000 in concentration in the effluent – is too high, and the dimensions of the cleaning unit containing the porous material will become too large.

The object of the present invention is to provide an improved process for the removal of constituents from a process stream which enables the removal of more soluble constituents more effectively.

This object is achieved by a process comprising the steps of
a) contacting a process stream with a porous material having pores with a diameter of 0.01 to 50 μm wherein an extraction liquid is immobilized; and
b) subsequently contacting the resulting process stream with an adsorbent.
The process of the invention enables effective removal of poorly soluble or insoluble constituents, such as benzene, toluene, and xylene, as well as of

more soluble constituents such as dichloromethane and methyl tert-butyl ether. A further advantage is that the dimensions of the cleaning unit comprising the porous material and the adsorbent can be reduced considerably, which is more attractive economically. The porous material will extract poorly soluble or insoluble constituents which would otherwise irreversibly adsorb onto the adsorbent, thereby ensuring that the lifespan of the adsorbent in the process is increased, or alternatively, that a smaller amount of adsorbent can be used. A longer lifespan or a smaller amount of adsorbent renders the process more attractive economically. A further advantage of the process of the invention is that the extracted constituents can be removed from the extraction liquid in the porous material by regeneration with steam.

In a preferred embodiment of the present invention, the size of the bed of porous material is chosen such that the poorly soluble or insoluble constituents are reduced by more than a factor 100, preferably by more than a factor 1,000, and most preferably by more than a factor 10,000. In this way, the adsorbent, which is also able to adsorb the poorly soluble or insoluble constituents, can be used almost exclusively for the removal of constituents not effectively removed by the porous material. This further enables the adsorbent to be used for an even longer period of time, rendering the process more attractive economically. It is noted that the determination of the size of the bed of porous material lies within the skill of the skilled person.

Alternatively, this effect can be achieved using a bed of the porous material of the invention having a size so as to reduce the concentration of the poorly soluble or insoluble organic constituents in the process stream to less than 5% of the solubility of the constituent having the highest solubility, preferably to less than 1%, more preferably to less than 0.5%, and most preferably to less than 0.05%. For the purposes of determining the solubility of the constituent having the highest solubility of the poorly soluble and insoluble organic constituents in the process stream, the constituent is preferably chosen from benzene, toluene, ethyl benzene, xylene, and polycyclic aromatic hydrocarbons such as naphthalene and anthracene.

The porous material of the invention can be a porous polymer. Examples of suitable polymers are low-pressure polyethene, high-pressure polyethene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene terpolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(4-methyl-pentene-1), and polybutene.
Optimum results have been attained using polyolefin-based polymers. In that case preference is given to the use of a porous material based on polypropylene.

The porous material can be used in the form of a fibre, film, granulate or powder, with preference being given to use in the form of a granulate or powder having an average particle diameter of 0.1 to 10 mm.

The porous material of the invention is at least partially filled with an extraction liquid, which is immobilized in the pores of the porous material. This “immobilization” can be achieved by using a porous material having an average pore diameter of between 0.01 and 50 μm, preferably an average pore diameter of between 0.1 and 30 μm, and most preferably an average pore diameter of 0.2-15 μm. Additionally, the extraction liquid generally is a liquid with minimal solubility in the medium to be extracted in order to minimize the loss of extraction liquid during the process of the invention, and it also helps to keep the liquid immobilized in the pores of the porous material. As a rule, the solubility of these liquids in the medium to be extracted is not more than 100 mg per 1,000 ml.

The extraction liquid suitable for the process of the invention is a liquid which has the highest possible affinity for the organic constituents to be extracted. Suitable examples of such extraction liquids are liquids in the form of a glycerol ester of one or more, preferably unsaturated fatty acids, and oils, such as palm oil, olive oil, peanut oil, paraffin oil, fish oil such as herring oil, linseed oil, soybean oil, and castor oil. A combination of two or more of these extraction liquids is also contemplated.

Preferably, at least 30 vol.% of the pores of the porous material is filled with extraction liquid. In a more preferred embodiment of the process of the invention, at least 50 vol.% of the pores of the porous material is filled with extraction liquid. It is most preferred to use a porous material at least 90 vol.% of the pores of which is filled with extraction liquid.

The adsorbent according to the invention may be any material, and in particular any porous material, suitable for adsorbing the constituents to be removed from the process stream, and in particular suitable for adsorbing the more soluble constituents. Suitable examples of adsorbents are activated carbon, carbon black, synthetic particles based on a wide range of polymers, porous inorganic materials modified with organic substituents or not, such as: porous silica or titania, zeolites such as molecular sieves, silica gels, and porous alumina including the activated types. So far, optimum results have been achieved using an adsorbent selected from the group of activated carbon, zeolites, carbonized sulphonated cross-linked polystyrene, and cross-linked polystyrene such as polystyrene cross-linked with divinyl benzene. Activated carbon is less preferred, as the constituents adsorbed thereon in the process of the invention are irreversibly adsorbed onto the adsorbent and cannot be sufficiently regenerated with, for instance, steam.

The porous material and the adsorbent are generally provided in separate beds inside a cleaning unit. The volume ratio of the porous material to the adsorbent depends on the types of constituents (poorly soluble/insoluble versus more soluble constituents) and the concentration of these constituents in the process stream. Generally, the volume ratio of porous material filled with extraction liquid to adsorbent is between 20:1 and 1:20, preferably between 10:1 and 1:10, and most preferably between 5:1 and 1:5.

In a preferred embodiment of the process of the invention, the porous material which is saturated with constituents extracted from the process stream is regenerated, preferably by being contacted with steam or hot air, or a solution of acid or base, depending on the nature of the extracted constituents. If the extracted constituents are predominantly organic, the porous material is preferably regenerated using steam or hot air.
Preferably, regeneration is performed such that the constituents that emerge from the porous material do not come into contact with the adsorbent, as they will irreversibly adsorb to the adsorbent, thereby reducing the lifespan of the adsorbent.

The invention further pertains to a cleaning unit for the removal of liquid, gaseous and/or dissolved constituents from a process stream comprising:

a) an inlet for introducing the process stream into the cleaning unit;
b) a first bed of porous material having pores with an average diameter of 0.01-50 mm wherein an extraction liquid is immobilized;
c) a second bed of an adsorbent;
d) an outlet for removing the process stream from the cleaning unit,

wherein the first bed is located in between the inlet and the second bed and the second bed is located in between the first bed and the outlet.
This cleaning unit is suitable for performing the process of the invention. The process stream containing the constituents to be removed is led into the cleaning unit via the inlet. The process stream is then contacted with the first bed of porous material filled with extraction liquid, where the concentration of poorly soluble or insoluble constituents is reduced by a factor of at least 100, preferably of at least 1,000, and most preferably of at least 10,000. Also more soluble constituents will be removed, but to a much lesser extent. The thus treated process stream is subsequently contacted with the second bed of

adsorbent, where the concentration of the more soluble constituents is reduced by a factor of at least 100, preferably of at least 1,000, and most preferably of at least 10,000. The cleaned process stream is subsequently led out of the cleaning unit via the outlet.

In one embodiment the first and second beds are positioned adjacent to each other in one column. This embodiment enables a reduction of the dimensions of the cleaning unit, rendering the cleaning unit simpler and more attractive economically.

In one embodiment of the cleaning unit, the first and second beds are located in two separate sub-units. These sub-units are interconnected via the outlet of the first sub-unit containing the first bed and the inlet of the second sub-unit containing the second bed, so that the process of the invention can be conducted therein.

It is also envisaged to use a third sub-unit containing a bed of porous material filled with extraction liquid, which is connected in parallel to the first sub-unit. With this configuration it is possible to lead the (untreated) process stream through the third sub-unit once the concentration of the constituents to be extracted increases to an unacceptable level beyond the first sub-unit. In the meantime, the porous material of the first bed, which is saturated with the extracted constituents, can be regenerated, e.g. by exposing it to steam or hot air.

The invention is illustrated by the following Examples.

Examples

Two glass columns both having a diameter of 5 cm were placed in series one after the other. In the first column a bed of MPP-10 (a porous polypropylene filled with castor oil as extraction liquid ex Akzo Nobel) was placed; the height of the bed being 5 cm. The second column was filled with a 10 cm high bed of

adsorbent XAD-4 (a porous polystyrene-vinylbenzene resin ex Rohm & Haas). The first and second columns were connected such that a water stream could be passed through the respective columns.
The water stream contained 575 ppm phenol and 285 ppm toluene. The flow rate of the water stream was 3.7 l/h.
The outlet concentrations of phenol and toluene were measured after the first column (comprising MPP-10) and after the second column (comprising XAD-4). The results are shown as a function of time in the Table below.

Table 1

	Outlet concentration after 1st column		Outlet concentration after 2nd column	
Time (min)	Phenol (ppm)	Toluene (ppm)	Phenol (ppm)	Toluene (ppm)
1	5	0	0	0
10	3	0	0	0
20	365	0	4	0
40	445	0	21	0
60	480	0	68	0
80	515	0	180	0
100	519	0	304	0
120	536	0	435	0

The Table demonstrates that toluene is extracted completely by the porous material in the first column, and that phenol breaks through the first bed of MPP-10 already within 20 minutes. The phenol concentration after the second column is considerably lower than the phenol concentration after the first column. This experiment illustrates that toluene can be removed completely by the porous material of the invention, while the second bed significantly extends the breakthrough time of phenol without being contaminated by toluene.

What is claimed is:

1. A process for the removal of liquid, gaseous and/or dissolved constituents from a process stream including the steps consisting of:
   a) an extraction step for extracting constituents chosen from the group consisting of benzene, toluene, ethyl benzene, xylene, and polycyclic aromatic hydrocarbons, comprising contacting a process stream with a first bed of porous material having pores with an average diameter of 0.01 to 50 μm wherein an extraction liquid is immobilized;
   b) an adsorption step for adsorbing constituents chosen in the group consisting of phenol, dicholoromethane, and methyl tertiary-butyl ether comprising contacting the process stream from said extraction step with a second bed of an adsorbent, said adsorbent being chosen from the group consisting of zeolites, carbonized sulphonated crosslinked polystyrene, and cross-linked polystyrene, said adsorption step being reversible, the first and the second beds being positioned adjacent to each other in one column; and
   c) a regeneration step of the porous material saturated with constituents extracted from the process stream wherein the regeneration is performed such that the constituents that emerge from the porous material do not come into contact with the adsorbent.

2. Process according to claim 1 wherein at least 30 vol.% of the pores of the porous material is filled with the extraction liquid.

3. Process according to claim 2 wherein at least 90 vol.% of the pores of the porous material is filled with the extraction liquid.