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(54) Title: FLUID TREATMENT VESSEL

(57) Abstract: A fluid treatment apparatus comprising a tank containing a bed of at least one fluid treatment medium, a distributor plate separating the bed from an end portion of the tank, and an inert medium comprising amorphous particles having a harmonic mean diameter from 2.5 to 250 mm and a density from 0.57 to 0.998 cm<sup>3</sup>/g. The volume of the end portion containing inert medium is from 25 to 95% of the total volume of the end portion.



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## FLUID TREATMENT VESSEL

### Background

This invention relates generally to a method for reducing dilution effects in fluid treatment vessels.

5 Ion Exchange Resins are regenerated with a chemical solution once they are exhausted. The volume of regeneration liquid depends in part on the concentration of the liquid. Free water present in a vessel will negatively influence the effectiveness of the regeneration, leading to lower operating capacity, increased chemical consumption and more waste. For example, US2014/0263069 discloses the use of filler material in the end portions of the vessel, i.e., those  
10 portions not containing a fluid treatment medium. However, this reference does not disclose an efficient method.

### Statement of Invention

The present invention is directed to a fluid treatment apparatus comprising:

- 15 (a) a tank comprising a bed of at least one fluid treatment medium,  
(b) a distributor plate separating the bed from an end portion of the tank, and  
(c) at least one inert medium comprising amorphous particles having a harmonic mean diameter from 2.5 to 250  $\mu\text{m}$  and a density from 0.57 to 0.998  $\text{cm}^3/\text{g}$ ;  
wherein volume of the end portion containing inert medium is from 25 to 95% of total volume of  
20 the end portion.

Detailed Description

All percentages are weight percentages (wt%), and all temperatures are in °C, unless otherwise indicated. Averages are arithmetic averages unless indicated otherwise. All operations are performed at room temperature (18 and 25 °C) unless specified otherwise. Weight average molecular weights,  $M_w$ , are measured by gel permeation chromatography (GPC) using polyacrylic acid standards, as is known in the art. The techniques of GPC are discussed in detail in Modern Size Exclusion Chromatography, W. W. Yau, J. J. Kirkland, D. D. Bly; Wiley-Interscience, 1979, and in A Guide to Materials Characterization and Chemical Analysis, J. P. Sibilis; VCH, 1988, p. 81-84. The molecular weights reported herein are in units of daltons.

Percentages of monomer units in a polymer are based on total polymer weight (dry weight). The “harmonic mean diameter” (HMD) is defined by the following equation:

$$\text{HMD} = \frac{N}{\sum_{i=1}^N \left( \frac{1}{d_i} \right)}$$

where  $i$  is an index over the individual beads;  $d_i$  is the diameter of each individual particle; and  $N$  is the total number of beads. A particle that is not spherical is considered to have a diameter equal to the diameter of a sphere having the same volume as the particle. “Sphericity” ( $\Psi$ ) is the degree to which a particle is spherical and is characterized by using two of the three principal orthogonal axes of the object,  $a$  (longest),  $b$  (intermediate), and  $c$  (shortest), as follows:  $\Psi = c / a$ . “Roundness” ( $R$ ) is defined as the ratio of the average radius of curvature of the corners and edges of an object’s silhouette to the radius of the largest circle which can be inscribed within the silhouette. Sphericity and roundness are described in more detail in H. Waddell, *The Journal of Geology*, vol. 41, pp. 310-331 (1933).

The volume of the end portion containing inert medium is defined by the upper boundary of the inert medium when at rest. For example, if one defines a plane touching all of the uppermost particles of inert medium, i.e., a plane defining an upper surface of the inert medium, then the volume of the end portion below this plane is the volume of the end portion containing inert medium. For clarity, this is not the total volume of the particles themselves. Preferably, the volume of the lower end portion containing inert medium is at least 30% of the volume of the lower end portion, preferably at least 35%, preferably at least 40%, preferably at least 45%, preferably at least 50%; preferably no more than 90%, preferably no more than 85%.

Preferably, the amorphous particles have an average sphericity from 0.7 to 1.0 and an average roundness from 0.4 to 1.0. Preferably, average sphericity is at least 0.75, preferably at least 0.80; preferably no more than 0.95, preferably no more than 0.92, preferably no more than 0.90. Preferably, average roundness is at least 0.45, preferably at least 0.50, preferably at least 5 0.55; preferably no more than 0.95, preferably no more than 0.90, preferably no more than 0.85, preferably no more than 0.80, preferably no more than 0.75, preferably no more than 0.70. Preferably, the average sphericity and the average roundness are not both greater than 0.95, preferably 0.90.

Preferably, the amorphous particles have a harmonic mean diameter no greater than 150 10 mm, preferably no greater than 100 mm, preferably no greater than 50 mm, preferably no greater than 25 mm, preferably no greater than 10 mm, preferably no greater than 6 mm.

Preferably, the amorphous particles have a density of at least 0.60 cm<sup>3</sup>/g, preferably at least 0.65 cm<sup>3</sup>/g, preferably at least 0.70 cm<sup>3</sup>/g, preferably at least 0.75 cm<sup>3</sup>/g, preferably at least 0.80 cm<sup>3</sup>/g, preferably at least 0.85 cm<sup>3</sup>/g. Preferably, the amorphous particles have a density no 15 greater than 0.997 cm<sup>3</sup>/g, preferably no greater than 0.996 cm<sup>3</sup>/g.

Typical end portions (also known as dish heads) of tanks used for fluid treatment include, e.g., Klöpper heads, elliptical heads and spheroid heads. Typically, dish head water volume is 15 – 35% of the installed resin volume in the main portion of the tank and dish head water volume is 40 – 100% of the resin void water in the main compartment. Preferably, the main portion of the 20 tank is cylindrical.

Reduction of void water due to the presence of inert material in the end portions is calculated as follows for a spheroid end portion.

$V_s$  = spheroid compartment volume

$V_{sx}'$  = the spheroid remaining free water after (partial) filling of X ml IF62 (ml)

25  $S_x$  = the solid fill of the spheroid volume due to the X ml filling with IF62 (ml)

X = inert filling (ml)

$F_w$  = free water (%)

$$V_{sx}' = V_s - (X * F_w)$$

30 
$$S_x = V_s - V_{sx}'$$

Preferably, the fluid treatment medium in the main (center) compartment of the tank is an ion exchange resin, activated carbon, an adsorbent, a non functionalized co polymer or a zeolite. Preferably, the fluid treatment medium is an ion exchange resin, preferably in the form of spherical beads. Preferably, the beads are crosslinked polymer beads.

Depending in the technology applied:

Co-flow systems have 10 – 60 % filling

Countercurrent systems:

Packed beds: 85% - 97,5 % filling

Blocked beds 25 – 60% filling

Mixed beds 25 – 60% filling

Inert filling in the main compartment (cylinder) depends on the system technology and is either a fixed value ranging from 10-12 cm in an Amberpack/ Schwebebett or a range of heights depending on the vessel diameter. Typically <1000mm : 150 mm; <2500 : 200 mm and all other over 2500 : 300 mm

Or 15 – 25 cm as block layer in a blocked bed system with air hold down.

Examples

The equipment used in the present examples was as follows:

- 2 PVC columns in parallel for the comparison; Outer diameter 6 cm and column height 1000 mm

- Top and bottom compartments 160 mm wall height equipped with nozzle plates. The compartment represent the vessel spheroid dish head net volume  $V_s = 350$  ml; the compartment is physically separated from the resin column by a nozzle plates to retain the filling.

- Instrumentation: 8 rotameters,  
2 manometers

- Other equipment: 2 water tanks (1m<sup>3</sup>),  
2 chemical tanks (NaOH 30% HCl 37%),  
4 pumps (2 feed, 2 dosing)

- 2 conductivity meters

**[We should describe how the PE particles are made, since this is not a commercial product]**

<b>IWAKI Electromagnetic Metering pumps</b>		<b>Model</b>	<b>EWN-B16VCER</b>
<b>Capacity</b>	65 mL/min · 3.9 L/h · 0.09-0.18 mL/stroke	<b>Power supply</b>	100-240 VAC
<b>Disch. Press.</b>	7 bar	<b>Frequency</b>	50/60 Hz
<b>Pressure Max.</b>	8 bar	<b>Current (Input)</b>	0.8 A
<b>Stroke Length</b>	50-100% (0.5-1.0 mm)	<b>Power (Input)</b>	20 W
<b>Stroke Rate</b>	0.1-100 (1-360 spm)	<b>Materials</b>	PVC (head) PTFE +EPDM (diaphragm)

#### 5 **Example 1: Tests with Upper and/or Lower Compartments Filled**

##### **OPERATING CONDITIONS FOR THE TESTS**

<b>Configuration</b>	1 column
<b>Regen. technology</b>	UPCORE™
<b>Resins</b>	DOWEX™ MARATHON™ 1200H New commercial name Amberlite HPR1200 H DOWEX™ UPCORE™ IF-62 New commercial name Amberlite 62i
<b>Setups</b>	None compartment filled Bottom compartment filled Bottom + Top compartment filled
<b>Feed water</b>	Raw water after sand filter treatment
<b>Regenerant</b>	HCl 4.5%

**Cycles monitoring**

## Conductivity measurement

**DOWEX MARATHON™ 1200 – UPCORE™**

Floating inert	DOWEX™ UPCORE™ IF-62
Floating inert height <sup>(1)</sup> (mm)	85
Freeboard (mm)	50
Filling inert	DOWEX™ UPCORE™ IF-62
Volume of filling inert <sup>(2)</sup> (L)	0.350
Volume of resin in swollen form (L)	1.89
Resin height (mm)	865

**COMPACTION**

Direction	UPFLOW
Influent	Demineralized water
Flow rate (L/h)	60
Linear velocity (m/h)	30.6

**REGENERANT INJECTION**

Direction	UPFLOW
Regenerant	HCl 35% w/w %
Quantity (g/L <sub>R</sub> )	120
Regenerant solution concentration (w/w %)	4.5
Flow rate (L/h)	15.0
Specific flow rate (BV/h)	8.6
Duration (min)	18
Linear velocity (m/h)	7.6
Volume (L)	4.5

**REGENERANT DISPLACEMENT (SLOW RINSE)**

Direction	UPFLOW
Effluent	Demineralized water
Flow rate (L/h)	15.0
same as during regenerant injection	
Specific flow rate (BV/h)	8.6
End point	Conductivity <1000 µS/cm

**SETTLING**

Duration (min)	10
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**FAST RINSE (RINSE TO QUALITY)**

Direction	DOWNFLOW
Influent	Demineralized water

Flow rate (L/h)	55.0
same as loading cycle	
Specific flow rate (BV/h)	29.1
same as loading cycle	
End point	Conductivity after SBA < 10 $\mu$ S/cm
<b>LOADING CYCLE</b>	
Direction	<b>DOWNFLOW</b>
Influent	Water after sand filters
Flow rate (L/h)	55.0
Specific flow rate (BV/h)	29.1
Linear velocity (m/h)	28
End point	Conductivity after SBA > 2 $\mu$ S/cm



Results

	<b>Loading cycles</b>	<b>Regeneration cycles</b>		
	Op. Cap. (eq/L <sub>R</sub> )	BV for displacement	AVG BV for fast rinse to reach 10 μS/cm	
<b>No compartment filled</b>	1.34 ± 0.01	5.9 ± 0.2	2.06	Fr = 0%
<b>Bottom compartment filled</b>	1.47 ± 0.07	6.2 ± 0.3	1.58	Fr = 66,5%
<b>Bottom and Top compartment filled</b>	1.58 ± 0.03	6.2 ± 0.6	1.41	Fr =66,5%

- [Cations] (eq/liter) = Total cation concentration obtained from the feed water analysis.
- VT = Throughput (liter): Total amount of water treated at the resin breakthrough point.
- VR = The volume of resin loaded (liter)

$$\text{Op. Capacity} = \frac{VT \times [\text{Cations}]}{VR} \quad (\text{Eq/l}_{\text{resin}})$$

Compared to F<sub>wr</sub> = 0% (no filling), the resin operating capacity improves at 100% filling of V<sub>s</sub> at F<sub>wr</sub> = 66,5%

F<sub>wr</sub> = free water reduction in compartment  
 V<sub>s</sub> = spheroid compartment volume

The fast rinse volume to reach 10 μS/cm is improved from 2.06 to 1.41 bed volumes.

**Example 2: Tests with Gradual Filling of Lower Compartment**

The operating conditions and fill in the main compartment were the same as in Example 1.

ResultsOperating Capacity

<b>Cycles</b>	<b>% of Compartment Containing Filling</b>	<b>Op. Cap. (eq/L<sub>R</sub>)</b>	<b>Standard deviation</b>
inert filling 0 ml	0	1,31	0,06
inert filling 100 ml	28.6	1,44	0,06
Inert filling 200 ml	57.1	1,48	0,02
Inert filling 300 ml	85.7	1,48	0,01
Inert filling 350 ml	100	1,47	0,07

5 Displacement (BV)

<b>Cycles</b>	<b>% of Compartment Containing Filling</b>	<b>Displacement (BV)</b>	<b>St. Dev.</b>
Regen_0	0	5,8	0,3
Regen_100	28.6	6,2	0,4
Regen_200	57.1	6,9	0,3
Regen_300	85.7	6,3	0,2
Regen_350	100	6,2	0,3

10 Displacement performance is substantially independent of the percent of the compartment which contains fill.

15

Claims

1. A fluid treatment apparatus comprising:
- (a) a tank comprising a bed of at least one fluid treatment medium,
  - (b) a distributor plate separating the bed from an end portion of the tank, and
  - (c) at least one inert medium comprising amorphous particles having a harmonic mean diameter from 2.5 to 250 mm and a density from 0.57 to 0.998 cm<sup>3</sup>/g;
- wherein volume of the end portion containing inert medium is from 25 to 95% of total volume of the end portion.
2. The method of claim 1 in which the amorphous particles have an average sphericity from 0.7 to 1 and an average roundness from 0.4 to 1.
3. The method of claim 2 in which volume of the end portion containing inert medium is from 30 to 90% of volume of the end portion.
4. The method of claim 3 in which the harmonic mean diameter is from 2.5 to 100 mm.
5. The method of claim 4 in which the amorphous particles have an average sphericity from 0.7 to 0.95 and an average roundness from 0.45 to 0.95.
6. The method of claim 5 in which the fluid treatment medium is an ion exchange resin.
7. The method of claim 6 in which volume of a lower end portion containing inert medium is from 40 to 90% of volume of the lower end portion

INTERNATIONAL SEARCH REPORT

International application No  
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A. CLASSIFICATION OF SUBJECT MATTER  
 INV. B01J47/022 B01J49/60 B01J49/06 B01J49/05  
 ADD.  
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
 Minimum documentation searched (classification system followed by classification symbols)  
 B01J

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 practicable, search terms used)  
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 497 632 A1 (PERMUTIT CO LTD [GB]) 5 August 1992 (1992-08-05) figure 1 page 4, line 29 - page 5, line 37 page 3, line 37 - line 51 -----	1,6,7
X	EP 0 551 002 A1 (ROHM & HAAS [US]) 14 July 1993 (1993-07-14) claims 1-3,6,7,10 page 5, line 21 - line 33 page 5, line 28 - line 29 table 1 -----	1-7
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Kaluza, Nicoleta

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2019/062106

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>Anonymous: "Product Data Sheet AMBERLITE(TM) 14i Inert Resin Polypropylene, Inert Resin for Industrial Demineralization Applications",</p> <p>1 May 2018 (2018-05-01), pages 1-3, XP055670919, Retrieved from the Internet: URL:https://www.lenntech.com/Data-sheets/DOW-177-03819-14i-L.pdf [retrieved on 2020-02-21] page 1</p>	1-7
X	<p>RO 121 020 B1 (DOW DEUTSCHLAND INC [DE]; OBSESTVO S OGRANICENNOJ OTVETS [RU]) 30 November 2006 (2006-11-30) figures 1-4 claims 1-3 page 4, line 1 - line 24 page 4, line 45 - line 48</p>	1-7
X	<p>Anonymous: "Product Data Sheet AMBERLITE(TM) 62i Inert Resin Polyethylene, Inert Resin for Industrial Demineralization Applications",</p> <p>1 May 2018 (2018-05-01), pages 1-3, XP055670920, Retrieved from the Internet: URL:https://www.lenntech.com/Data-sheets/DOW-177-03820-62i-L.pdf [retrieved on 2020-02-21] page 1 - page 2</p>	1-7
X	<p>US 4 269 715 A (BARRAQUE CHRISTIAN ET AL) 26 May 1981 (1981-05-26) claims 10-12 figure 1 column 6, line 20 - line 35</p>	1-7
A	<p>WADDELL H: "VOLUME, SHAPE, AND ROUNDNESS OF ROCK PARTICLES", JOURNAL OF GEOLOGY, UNIVERSITY OF CHICAGO PRESS, CHICAGO, IL, US, vol. 40, 1 January 1932 (1932-01-01), pages 443-451, XP009050547, ISSN: 0022-1376 the whole document</p>	1-7

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2019/062106
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0497632	A1	05-08-1992	NONE
-----			
EP 0551002	A1	14-07-1993	AU 654224 B2 27-10-1994
			BR 9300049 A 24-08-1993
			CA 2086636 A1 11-07-1993
			CN 1074148 A 14-07-1993
			EP 0551002 A1 14-07-1993
			FI 930074 A 11-07-1993
			JP H05253497 A 05-10-1993
			NZ 245639 A 28-03-1995
			PL 297340 A1 20-09-1993
			SG 45313 A1 16-01-1998
			SI 9300012 A 30-09-1993
-----			
RO 121020	B1	30-11-2006	CZ 20004349 A3 12-09-2001
			EA 200000983 A2 22-10-2001
			HU 224645 B1 28-12-2005
			PL 344103 A1 04-06-2001
			RO 121020 B1 30-11-2006
			RU 2149685 C1 27-05-2000
			SK 17832000 A3 07-01-2002
			UA 66855 C2 17-09-2001
-----			
US 4269715	A	26-05-1981	CA 1141047 A 08-02-1983
			FR 2443283 A1 04-07-1980
			US 4269715 A 26-05-1981
-----			