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(54) **Process for the removal of heavy metals from liquids.**

(57) The present invention discloses a process for the removal of heavy metals from a liquid comprising heavy metals, wherein hydrochloric acid is added to the liquid, wherein the fluid is brought in contact with a mixture comprising between 30%vol. and 60%vol. of an activated carbon catalyst impregnated with sulfur, between 30%vol. and 60%vol. of an activated carbon catalyst impregnated with iron and between 5%vol. and 40%vol. of a filler material, the total of these three ingredients being 100%vol. The fluid is left in contact with the mixture, the heavy metals are absorbed onto the mixture to obtain a fluid with a depleted level of heavy metals, which fluid is then evacuated from the mixture.

PROCESS FOR THE REMOVAL OF HEAVY METALS FROM LIQUIDS

Technical field

[0001] The present invention generally relates to the removal of heavy metals from liquids and relates in particular to a process for the removal of heavy metals from liquids in a fixed bed reactor.

Background Art

[0002] Activated carbon catalysts are widely used for different applications including heavy metal removals from gas and liquids. It has been found however that the performance of the activated carbon catalysts could still be enhanced.

[0003] US 7,722,843 discloses a process for the removal of mercury from a combustion exhaust gas stream in a combustion exhaust gas purification scheme that includes a combustion exhaust scrubber system that uses an aqueous liquid to remove acid gases from the combustion exhaust gas. The process comprises providing a powdered mercury sorbent, introducing the powdered mercury sorbent into the aqueous liquid in the scrubber system, and after introduction of the mercury sorbent into the aqueous liquid, separating at least some of the mercury sorbent from the aqueous liquid.

Technical problem

[0004] It is an object of the present invention to provide an activated carbon catalyst composition having an improved activity as well as a more efficient process for the removal of heavy metals from a liquid.

[0005] This object is achieved by a process for the removal of heavy metals from a liquid comprising heavy metals as claimed in claim 1.

General Description of the Invention

[0006] The object of the invention is achieved by a process for the removal of heavy metals from a liquid comprising heavy metals, wherein hydrochloric acid is added to the liquid, wherein the liquid and the hydrochloric acid are brought in contact with a mixture comprising between 30 %vol. and 60 %vol. of an activated carbon catalyst impregnated with sulfur, between 30 %vol. and 60 %vol. of an

activated carbon catalyst impregnated with iron and between 5 %vol. and 40 %vol. of a filler material, the total of these three ingredients being 100%vol., leaving the liquid in contact with the mixture, absorption of the heavy metals onto the mixture to obtain a liquid with a depleted level of heavy metals, evacuation of the liquid with a depleted level of heavy metals from the mixture.

[0007] Surprisingly it has been found that the process for removal of heavy metals from a liquid is more efficient if a mixture of an activated carbon catalyst impregnated with sulfur and of an activated carbon catalyst impregnated with iron and of a filler material is used. It has also been found that the catalyst activity is more easily regenerated if between 5 and 40 %vol. of a filler material is used. As a demonstration example of this, a Kombisorbon® unit (using an activated carbon catalyst alone (i.e. without a filler material) is regenerated periodically (2-4 times a year) on an industrial site. The drying time period after this regeneration period is reduced by more than 40 % (28 instead of 48 hours) in case of a reactor bed with an activated carbon (80 %) / filler material (20 %) mixture compared to activated carbon alone.

[0008] Surprisingly, it has been found that the removal of heavy metals from a liquid is even more efficient if hydrochloric acid is added to the liquid before it is put in contact with the mixture comprising between 30 %vol. and 60 %vol. of an activated carbon catalyst impregnated with sulfur, between 30 %vol. and 60 %vol. of an activated carbon catalyst impregnated with iron and between 5 %vol. and 40 %vol. of a filler material.

[0009] The hydrochloric acid is added preferably under the form of an aqueous solution. The concentration of hydrochloric acid in this solution is preferably between 5 % and 38 % w/w.

[0010] Preferably between 15 ml/l to 60 ml/l liquid of hydrochloric acid solution are added.

[0011] The concentration of hydrochloric acid in the liquid is preferably between 1 and 10% w/w.

[0012] The liquid is preferably an aqueous liquid.

[0013] The liquid comprises preferably phosphoric acid. The concentration of phosphoric acid in the liquid is between preferably 10 w% and 90 w%; more preferably between 20% and 55% w/w. The concentration of hydrochloric acid in the liquid is preferably between 1/40 and 1/20 of the phosphoric acid in the liquid.

[0014] In general, the usual initial concentration of phosphoric acid solution is between 10 w% and 90 w%; whereas the final concentration (after addition of hydrochloric acid solution) of phosphoric acid solution is between 9 w% and 85 w% depending on the added volume of hydrochloric acid solution.

[0015] It has been found that this process is particularly well suited for the removal of heavy metals from phosphoric acid that is obtained during the production of fertilizers. Indeed, phosphate rock (PR) is used as a raw material in the manufacture of most commercial phosphate fertilizers on the market. A weak phosphoric acid (40-55%) is produced from the reaction of PR with sulfuric acid, using a wet process. The obtained phosphoric acid is then used in the production of a series of liquid or solid fertilizers. During the reaction of PR with sulfuric acid, heavy metals contained in the PR are dissolved and end up in the phosphoric acid.

[0016] It can also be used for the removal of heavy metals from industrial waste water from the cement industry, from petroleum refining, from chemical manufacturing, from metal finishing, from printed circuit manufacturing, from oil and gas extraction and from hazardous wastes.

[0017] The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). A toxic heavy metal is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts. The term has particular application to cadmium, mercury, lead and arsenic, all of which appear in the World Health Organisation's list of 10 chemicals of major public concern. Other examples include manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), selenium (Se), silver (Ag) and antimony (Sb).

[0018] According to various embodiments, the mixture comprises at least 30 %vol., 31%vol., 32%vol., 33%vol., 34%vol., 35%vol., 36%vol., 37%vol., 38%vol.,

39%vol., 40%vol., 41%vol., 42%vol., 43%vol., 44%vol., 45%vol., 46%vol., 47%vol., 48%vol., 49%vol., 50%vol., 51%vol., 52%vol., 53%vol., 54%vol., 55%vol., 56%vol., 57%vol., 58%vol. or 59%vol. of an activated carbon catalyst impregnated with sulfur.

[0019] According to various embodiments, the mixture comprises at most 60%vol., 59%vol., 58%vol., 57%vol., 56%vol., 55%vol., 54%vol., 53%vol., 52%vol., 51%vol., 50%vol., 49%vol., 48%vol., 47%vol., 46%vol., 45%vol., 44%vol., 43%vol., 42%vol., 41%vol., 40%vol., 39%vol., 38%vol., 37%vol., 36%vol., 35%vol., 34%vol., 33%vol., 32%vol., or 31%vol., of an activated carbon catalyst impregnated with sulfur.

[0020] In a preferred embodiment, the mixture comprises between 40 %vol. and 50 %vol. of activated carbon catalyst impregnated with sulfur.

[0021] Preferably, the activated carbon catalyst impregnated with sulfur comprises between 5 %weight and 20 %weight of sulfur.

[0022] According to various embodiments, the mixture comprises at least 30%vol., 31%vol., 32%vol., 33%vol., 34%vol., 35%vol., 36%vol., 37%vol., 38%vol., 39%vol., 40%vol., 41%vol., 42%vol., 43%vol., 44%vol., 45%vol., 46%vol., 47%vol., 48%vol., 49%vol., 50%vol., 51%vol., 52%vol., 53%vol., 54%vol., 55%vol., 56 %vol., 57%vol., 58%vol. or 59%vol. of an activated carbon catalyst impregnated with iron.

[0023] According to various embodiments, the mixture comprises at most 60%vol., 59%vol., 58%vol., 57%vol., 56%vol., 55%vol., 54%vol., 53%vol., 52%vol., 51%vol., 50%vol., 49%vol., 48%vol., 47%vol., 46%vol., 45%vol., 44%vol., 43%vol., 42%vol., 41%vol., 40%vol., 39%vol., 38%vol., 37%vol., 36%vol., 35%vol., 34%vol., 33%vol., 32%vol., or 31%vol. of an activated carbon catalyst impregnated with iron.

[0024] In a preferred embodiment, the mixture comprises between 40 %vol. and 50 %vol. of activated carbon catalyst impregnated with iron.

[0025] Preferably, the activated carbon catalyst impregnated with iron comprises between 10 %weight and 30 %weight of iron.

[0026] The activated carbon catalyst is preferably extruded and has a grain size of 0.80 - 130 mm. The activated carbon catalyst is preferably granulated and has a grain size: 0.30 to 4.75mm. The activated carbon catalyst is thus not under powder form.

[0027] In an embodiment the activated carbon catalyst is preferably a mixture of granulated and extruded catalyst.

[0028] The carbon catalyst may be produced from brown and bituminous coals, fruit pits, coconut shells, lignite, peat, wood, sawdust / saw chip, petroleum coke, bone and paper mill waste (lignin), synthetic polymers like PVC, rayon, viscose, polyacrylonitrile or phenols.

[0029] The carbon catalyst may be activated by :

- a physical treatment: heat, steam, oxygen, CO_2, air
- a chemical treatment: impregnation with acid, strong base or salts (e.g. sulfuric, chlorhydric or phosphoric acid, potassium or sodium hydroxide, calcium or zinc chloride)
- a combination of both a physical and a chemical treatment.

[0030] The activated carbon catalyst may have a specific surface area (BET) from 400 to 1800 m^2/g and an acid or alkaline pH.

[0031] According to various embodiments, the mixture comprises at least 5%vol., 6%vol., 7%vol., 8%vol., 9%vol., 10%vol., 11%vol., 12%vol., 13%vol., 14%vol., 15%vol., 16%vol., 17%vol., 18%vol., 19%vol., 20%vol., 21%vol., 22%vol., 23%vol., 24%vol., 25%vol., 26%vol., 27%vol., 28%vol., 29%vol., 30 %vol., 31%vol., 32%vol., 33%vol., 34%vol., 35%vol., 36%vol., 37%vol., 38%vol. or 39%vol., of filler material.

[0032] According to various embodiments, the mixture comprises at most 40%vol., 39%vol., 38%vol., 37%vol., 36%vol., 35%vol., 34%vol., 33%vol., 32%vol., 31%vol., 30%vol., 29%vol., 28%vol., 27%vol., 26%vol., 25%vol., 24%vol., 23%vol., 22%vol., 21%vol., 20%vol., 19%vol., 18%vol., 17%vol., 16%vol., 15%vol., 14%vol., 13%vol., 12%vol., 11%vol., 10%vol., 9%vol., 8%vol., 7%vol. or 6%vol. of filler material.

[0033] In a preferred embodiment, the filler materials are present in an amount from 5 to 15 %vol.

[0034] Preferably, the filler material comprises plastic, metals, alumina, ceramic materials or mixture thereof.

[0035] According to various embodiments, the filler material is a shape chosen among saddle shaped, ring shaped, ball shaped, torus shaped, prism shaped or irregular shaped.

[0036] In particular, filler materials made of ceramic material, having a free volume (i.e. the volume that is not occupied by the ceramic material) of 50-79% may be used:

i. Novalox® Saddle : 12.7-76.2 mm
ii. Berl saddle : 4-50 mm
iii. Cylindrical ring : 5-200 mm
iv. Pall® ring : 25-100 mm
v. Transitional grid lining
vi. Cylindrical ring with 1 bar or 1 cross : 80-200 mm
vii. Grid block : 215*145*90 mm

[0037] In particular, filler materials made of metal, having a free volume of 95-98% may be used:

i. Cylindrical ring . 15-50 mm
ii. Pall® ring : 15-90 mm
iii. VSP® : 25-50 mm
iv. Top-Pak® : 15 mm
v. Novalox®-M : 15-70 mm
vi. Twin-Pak® : 10-15 mm
vii. Interpak® : 10-20 mm

[0038] In particular, filler materials made of plastic, having a free volume of 87-97% may be used:

i. Novalox® saddle : 12.7 – 50.8 mm
ii. Pall® ring : 15-90 mm

iii. VSP® : 25-90 mm
iv. Igel® : 40 mm
v. Netball® : 45-90 mm

[0039] The filler material is thus made up of distinct, individual particles that are added to the activated carbon catalyst to improve, to enhance some properties of the mixtured material. The filler material particles generally have a mean particle size (based on the average largest dimension (by number) of the particle) of more than 4 mm. Usually their mean particle size (based on the average largest dimension (by number) of the particle) is less than 200 mm.

[0040] In an embodiment, the mixture of activated carbon catalyst impregnated with sulfur, activated carbon catalyst impregnated with iron and a filler material contains no other solid ingredients than the activated carbon catalysts and the filler material. The total of these three ingredients makes thus 100%vol. of the mixture. It goes without saying that the mixture is a heterogeneous mixture since the components have a different particles sizes, different densities etc. The mixture comprises preferably a mixture of separate, distinct particles of filler and separate, distinct particles of activated carbon catalyst. This makes it easy to separate the activated carbon catalyst from the filler when the activated carbon catalyst needs to be replaced.

[0041] Preferably, the liquid is left in contact with the catalyst composition for at least 1h, 2h, 3h or 10h. Preferably, the liquid is left in contact with the catalyst composition for less than 20h, 15h, 12h or 10h.

[0042] According to various embodiments, the liquid comprises at least 50 mg/l of heavy metals, preferably at least 45 mg/l, more preferably at least 40 mg/l of heavy metals.

Description of Preferred Embodiments

[0043] Further details and advantages of the present invention will be apparent from the following detailed description of several not limiting embodiments.

[0044] The presence of filler allowed a more efficient washing of the activated carbon with sulfates removal coming from the reaction between SOx and NOx with water vapors from inlet flue gas.

[0045] The presence of filler allowed a quicker drying step after regeneration with water flow.

[0046] Test 1 – Removal from Liquid - Laboratory scale – single pass (with filler and with HCl)

[0047] 500 cm^3 of a mixture of 45 % of activated carbon impregnated with sulfur, 45 % of activated carbon impregnated with iron supplied from Watch-Water, and 10 % of a plastic filler material was used during this test.

[0048] Prior to starting the test, a hydrochloric acid solution at 25 w% was added in a proportion corresponding to one thirtieth of the volume of the phosphoric acid solution with a concentration of 50 w%. After addition, the final concentration of phosphoric acid solution is 48 w%. The level of heavy metals in a phosphoric acid solution was reduced significantly. 90 % removal for cadmium and mercury and 75 % removal for arsenic. The initial concentrations were 39 ppm for cadmium, 0.1 ppm for mercury and 23 ppm for arsenic.

[0049] The presence of filler material allowed less clogging from silica coming from the phosphoric acid media inside the activated carbon bed.

[0050] The presence of filler material allowed a more efficient washing of the activated carbon with easier silica removal.

[0051] The presence of hydrochloric acid increased the removal efficiency of heavy metals.

[0052] Test 2b – Comparative Example: Removal from Liquid - Laboratory scale – single pass (with filler no HCl)

[0053] The same materials and conditions were used except that no hydrochloric acid was added.

[0054] The level of heavy metals in a phosphoric acid solution was reduced: 75 % removal for cadmium and mercury and 65 % removal for arsenic.

[0055] The addition of hydrochloric acid to the liquid containing heavy metals allows thus to increase the removal of heavy metals: 90% removal (instead of 75 % removal) for cadmium and mercury and 75 % removal (instead of 65 % removal) for arsenic.

[0056] Test 2c – Comparative example - Removal from Liquid - Laboratory scale – single pass (impregnated catalyst, no filler and no HCl)

[0057] 500 cm^3 of 100 % of activated carbon impregnated with sulfur supplied from Jacobi Carbons was used during this test.

[0058] The level of heavy metals in a phosphoric acid solution (As: 23 ppm, Hg: 0.1 ppm and Cd: 39 ppm) was reduced. Only a 20 % removal rate for cadmium and mercury and only 35 % removal rate for arsenic were achieved.

[0059] Test 2d – Comparative example - Removal from Liquid - Laboratory scale – single pass (impregnated catalyst, no filler and no HCl)

[0060] 500 cm^3 of 100 % of activated carbon catalyst impregnated with iron supplied from Watch-Water was used during this test.

[0061] The level of heavy metals in a phosphoric acid solution (As: 23 ppm, Hg: 0.1 ppm and Cd: 39 ppm) was reduced. Only a 50 % removal rate for cadmium and mercury and only a 15 % removal rate for arsenic were achieved.

[0062] Test 2e – Removal from Liquid - Laboratory scale – single pass (no filler and no HCl)

[0063] 500 cm^3 of an aqueous phosphoric acid solution having initial concentrations of 39 ppm for cadmium, 0.1 ppm for mercury and 23 ppm for arsenic.: 30 % of activated carbon catalyst impregnated with sulfur supplied from Jacobi Carbons, 30 % of activated carbon impregnated with iron supplied from Watch-Water, 40 % of a plastic filler material was used during this test.

[0064] The level of heavy metals in a phosphoric acid solution was reduced significantly. 20 % removal rate for cadmium and mercury and 35 % removal rate for arsenic.

[0065] The experiments described have been carried out with a solution of phosphoric acid of 50 w%.

[0066] The activated carbon used in the tests above had a specific high catalytic surface area (BET at least 700 m^2/g) with impregnation (like Br, Cu, Fe, S, OH ...).

[0067] The activated carbon was mixed with various types of filler materials of different shapes (cylinder, balls, "Sattelkörper", ...) and different material (plastic, alumina, ceramic, ..) in various ratios (1/5; 1/3; 1/10; ...). Different suppliers of activated carbon catalysts for companies like Jacobi, Cabot Carbon, Chemviron, Desotec, Carbotech and ATEC were tested.

[0068] It was found that the removal of heavy metals from an aqueous solution was increased significantly when the activated carbon catalyst was mixed with filler material as described above.

[0069] It was further found that the removal of heavy metals from an aqueous solution was increased even more when the activated carbon catalyst was mixed with filler material and when hydrochloric acid was added to the liquid before it was put in contact with the mixture of catalyst and the filler materials as described above.

[0070] It must be noted that the active carbon catalysts do not contain:

a. any iodine, bromine or a compound thereof,

b. any water repellent,

c. any catalytically active metals such as Platinum, Palladium, Rhodium etc. or,

d. any organic/ catalytically active metal complexes based on metals such as Platinum, Palladium, Rhodium etc.

[0071] The active carbon catalyst is not hydrophobized by means of hydrophobic polymer compounds such as polytetrafluoroethylene, polyisobutylene, polyethylene, polypropylene or polytrichlorfluorethylen.

[0072] Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

[0073] All the features disclosed in this specification (including any accompanying claims, abstract, and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

P-INTFIB-014/LU

REVENDICATIONS

1. Procédé pour l'élimination de métaux lourds à partir d'un liquide comprenant des métaux lourds, dans lequel de l'acide chlorhydrique est ajouté au liquide, dans lequel le liquide et l'acide chlorhydrique sont amenés en contact dans un adsorbeur à lit fixe avec un mélange comprenant entre 30 % en volume et 60 % en volume d'un catalyseur à base de charbon activé, imprégné avec du soufre, entre 30 % en volume et 60 % en volume d'un catalyseur à base de charbon activé, imprégné avec du fer, et entre 5 % en volume et 40 % en volume d'une matière de charge, le liquide est maintenu en contact avec le mélange, les métaux lourds sont absorbés sur le mélange pour obtenir un liquide possédant une teneur appauvrie en métaux lourds, le liquide est évacué du mélange avec une teneur appauvrie en métaux lourds.

2. Procédé selon la revendication 1, dans lequel l'acide chlorhydrique est ajouté sous la forme d'une solution.

3. Procédé selon la revendication 2, dans lequel la concentration de l'acide chlorhydrique dans la solution se situe entre 5 % et 38 % en poids/poids.

4. Procédé selon la revendication 2, dans lequel la concentration de l'acide chlorhydrique dans le liquide se situe entre 1 % et 10 % en poids/poids.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le liquide comprend de l'acide phosphorique.

6. Procédé selon la revendication 5, dans lequel la concentration de l'acide phosphorique dans le liquide se situe entre 20 % et 55 % en poids/poids.

7. Procédé selon la revendication 5 ou 6, dans lequel la concentration de l'acide chlorhydrique dans le liquide se situe entre 1/40 et 1/20 de l'acide phosphorique dans le liquide.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le liquide comprend au moins 40 mg/litre de métaux lourds.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange comprend entre 40 % en volume et 50 % en volume d'un catalyseur à base de charbon activé, imprégné avec du soufre.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur à base de charbon activé, imprégné avec du soufre comprend entre 5 % en poids du 20 % en poids de soufre.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange comprend entre 40 % en volume et 50 % en volume d'un catalyseur à base de charbon activé, imprégné avec du fer.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur à base de charbon activé, imprégné avec du fer comprend entre 10 % en poids et 30 % en poids de fer.

13. Procédé selon l'une quelconque des revendications précédentes, dans lequel la matière de charge comprend une matière plastique, une matière à base d'alumine ou une matière céramique ou encore leurs mélanges.

14. Procédé selon l'une quelconque des revendications précédentes, dans lequel la matière de charge comprend un volume libre de 50 % en volume et de 97 % en volume.

15. Procédé selon l'une quelconque des revendications précédentes, dans lequel les matières de charge sont présentes en une quantité de 5 à 15 % en volume.

16. Procédé selon l'une quelconque des revendications précédentes, dans lequel la matière de charge possède une configuration choisie parmi une configuration en forme de selle, une configuration de forme annulaire, une configuration en forme de bille, une configuration de forme torique, une configuration en forme de prisme ou une configuration de forme irrégulière.

Abstract

The present invention discloses a process for the removal of heavy metals from a liquid comprising heavy metals, wherein hydrochloric acid is added to the liquid, wherein the fluid is brought in contact with a mixture comprising between 30 %vol. and 60 %vol. of an activated carbon catalyst impregnated with sulfur, between 30 %vol. and 60 %vol. of an activated carbon catalyst impregnated with iron and between 5 %vol. and 40 %vol. of a filler material, the total of these three ingredients being 100%vol. The fluid is left in contact with the mixture, the heavy metals are absorbed onto the mixture to obtain a fluid with a depleted level of heavy metals, which fluid is then evacuated from the mixture

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DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

National Application Number

LO 1788
LU 100464

SEARCH REPORT

in accordance with Article 35.1 a)
of the Luxembourg law on patents
dated 20 July 1992

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
E	WO 2017/174365 A1 (CPPE CARBON PROCESS & PLANT ENG S A [LU]) 12 October 2017 (2017-10-12) * paragraph [0059] - paragraph [0063]; claims *	1-16	INV. C01B25/237 B01D15/00
A	EP 0 333 489 A2 (IMI TAMI INSTITUTE RESEARCH [IL]) 20 September 1989 (1989-09-20) * column 2, line 37 - line 63; claims 1-3 *	1-16	
A	EP 1 172 331 A1 (TOYO BOSEKI [JP]) 16 January 2002 (2002-01-16) * paragraph [0012] - paragraph [0014] * * paragraph [0028] - paragraph [0029] *	1-16	
A	N. Abdennebi ET AL: "Removal of aluminium and iron ions from phosphoric acid by precipitation of organo-metallic complex using organophosphorous reagent", Journal of materials and Environmental Sciences, vol. 8, no. 2 1 January 2017 (2017-01-01), pages 557-565, XP055475147, Retrieved from the Internet: URL:http://www.jmaterenvironsci.com/Document/vol8/vol8_N2/60-JMES-2614-Abdennabi.pdf [retrieved on 2018-05-15] * the whole document *	1-16	TECHNICAL FIELDS SEARCHED (IPC) C01B B01D C02F B01J
A	US 3 978 196 A (TOSHIMITSU ITARU ET AL) 31 August 1976 (1976-08-31) * column 2, line 24 - line 39 * * column 3, line 17 - line 36 *	1	

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The present search report has been drawn up for all claims

Date of completion of the search	Examiner
16 May 2018	Fourgeaud, Damien

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	JP 2003 292305 A (NIPPON MINING CO) 15 October 2003 (2003-10-15) * abstract * -----	1	

TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

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ANNEX TO THE SEARCH REPORT ON LUXEMBOURG PATENT APPLICATION NO.

LO 1788
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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16-05-2018

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017174365 A1	12-10-2017	UY 37173 A	30-06-2017
		WO 2017174365 A1	12-10-2017
EP 0333489 A2	20-09-1989	AT 107607 T	15-07-1994
		AU 3138289 A	21-09-1989
		DE 68916292 D1	28-07-1994
		EP 0333489 A2	20-09-1989
		IL 85751 A	15-12-1991
		JP H0214803 A	18-01-1990
		NO 891149 A	18-09-1989
		ZA 8901917 B	29-11-1989
EP 1172331 A1	16-01-2002	CN 1332698 A	23-01-2002
		DE 69932857 T2	01-03-2007
		EP 1172331 A1	16-01-2002
		JP 4362976 B2	11-11-2009
		JP 5332953 B2	06-11-2013
		JP 2009209041 A	17-09-2009
		US 6861039 B1	01-03-2005
		WO 0040507 A1	13-07-2000
US 3978196 A	31-08-1976	CA 1011084 A	31-05-1977
		JP S501994 A	10-01-1975
		JP S5651122 B2	03-12-1981
		US 3978196 A	31-08-1976
JP 2003292305 A	15-10-2003	JP 4113369 B2	09-07-2008
		JP 2003292305 A	15-10-2003

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
LO1788	29.09.2017		LU100464

International Patent Classification (IPC)
INV. C01B25/237 B01D15/00

Applicant
CPPE Carbon Process & Plant Engineering S.A.

This report contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☒ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the application
- ☒ Box No. VIII Certain observations on the application

Examiner
Fourgeaud, Damien

Application No.
LU100464

WRITTEN OPINION

Box No. I Basis of the opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	1-16
	No:	Claims	
Inventive step	Yes:	Claims	1-16
	No:	Claims	
Industrial applicability	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations

see separate sheet

Application No.
LU100464

WRITTEN OPINION

Box No. VI Certain documents cited

☒ Certain published documents

see the Search Report

☐ Non-written disclosures

Box No. VIII Certain observations on the application

see separate sheet

Re Item VIII

Certain observations on the application

1.1. The claims appear to be broader than justified by the description, contrary to the requirements of the clarity criteria, the reasons being as follows: Claim 1 is directed to a method of removing heavy metals from a liquid. The disclosure of the description is however much more restrictive, and only deals with the removal of heavy metals from a phosphoric acid solution. There is no hint or suggestion informing the skilled reader that the disclosed process could equally remove heavy metals from a hydrocarbon liquid, from a molasse or from a leachate liquid. The statement in [0016] is not supported by any experimental result, thus, in view of the differences in chemical compositions of the liquids cited before, it cannot be easily expected that the claimed process would be equally efficient with anyone of such liquids. On the contrary, it seems that the claimed composition has been specifically designed for the purpose of removing heavy metals from a phosphoric acid solution only: This is supported by the fact that the process of claim 1 requires the addition of hydrochloric to the liquid i.e. the combination of HCl addition and the absorbent mixture is specifically designed for the treatment of phosphoric acid solutions.

Finally, in the examples too, the removal of the heavy metals is only shown for phosphoric acid solutions. It must thus be concluded that the scope of protection sought is not supported by the description.

1.2. In addition, the mixture used to remove the heavy metals comprises activated carbon impregnated with sulfur, activated carbon impregnated with iron and a filler. It is thus let open that other products are present in said mixture. The description again is more restrictive and indeed discloses that the mixture used consists in the three products only (see [0040] and [0070]).

2. The term "catalyst" used in the claims appears to be misleading, since the application does not give any information about a catalytic reaction. The claimed mixture appears to be an absorbent composition. Clarification may be needed.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

3. The following documents are cited in the search report:

D2 EP 0 333 489 A2 (IMI TAMI INSTITUTE RESEARCH [IL]) 20 September 1989 (1989-09-20)

D3 EP 1 172 331 A1 (TOYO BOSEKI [JP]) 16 January 2002 (2002-01-16)

D4 N. Abdennebi ET AL: "Removal of aluminium and iron ions from phosphoric acid by precipitation of organo-metallic complex using organophosphorous reagent",
Journal of materials and Environmental Sciences,
vol. 8, no. 2 1 January 2017 (2017-01-01), pages 557-565,
XP055475147,
Retrieved from the Internet:
URL:http://www.jmaterenvironsci.com/Document/vol8/vol8_N2/60-JMES-2614-Abdennabi.pdf
[retrieved on 2018-05-15]

D5 US 3 978 196 A (TOSHIMITSU ITARU ET AL) 31 August 1976 (1976-08-31)

D6 JP 2003 292305 A (NIPPON MINING CO) 15 October 2003 (2003-10-15)

4.1. Each of D2, D3 and D4 can be considered as the closest prior art to the subject-matter of claim 1 of the present application, since each of these documents deals with the removal of heavy metals from a phosphoric acid solution.

D2 discloses to add a reducing agent and a thio-organophosphene reagent to the solution, and to adsorb the metals on an adsorbent, possibly activated carbon (claims 1-3).

In D3, the phosphoric acid solution is brought into contact with a hydrogen halide to remove arsenic.

D4 discloses the removal of metals by precipitation using an organophosphorous reagent.

4.2. None of these documents discloses an adsorption method of heavy metals contained in a phosphoric acid solution using a mixture comprising activated carbon impregnated with sulfur, activated carbon impregnated with iron and a filler. The subject-matter of claim 1 is therefore novel.

4.3. The examples of the present application show very good results for the removal of cadmium, mercury and arsenic when additionally hydrochloric acid is added to the liquid to be treated. Accordingly, the present application solves the problem of proposing an alternative method of removal of the heavy metals, using adsorption.

There is no hint in the available prior art suggesting the proposed absorbing composition combined with the addition of HCl. Accordingly it is concluded that the solution is non-obvious and involves an inventive step.

4.4. Claims 2-16 depend directly on claim 1 and thus also comply with the requirements of novelty and inventive step.

4.5. The industrial applicability is obvious.

Re Item VI

Certain documents cited

Application No Patent No	Publication date *(day/month/year)*	Filing date *(day/month/year)*	Priority date *(valid claim)* *(day/month/year)*
D1: WO 2017/174365 A1 (CPPE CARBON PROCESS & PLANT ENG S A [LU])	12.10.2017	25.03.2017	04.04.2016

In case of entry of the present application in the European phase in front of the European Patent Office, the content of D1 might be considered relevant.