



(51) International Patent Classification:

C02F 1/28 (2006.01) *C07H 1/04* (2006.01)
B01D 39/00 (2006.01) *C08B 5/00* (2006.01)
B01J 20/22 (2006.01) *C02F 101/10* (2006.01)
B01J 20/24 (2006.01) *C02F 101/20* (2006.01)
C07H 1/02 (2006.01) *C02F 101/22* (2006.01)

(21) International Application Number:

PCT/AU2012/000083

(22) International Filing Date:

1 February 2012 (01.02.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2011900307 1 February 2011 (01.02.2011) AU

(71) Applicant (*for all designated States except US*): **AUS-
TRALIAN BIOREFINING PTY LTD** [AU/AU]; 1 Win-
jeel Road, Evans Head, New South Wales 2473 (AU).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **BLUNN, Adam Justin**
[AU/AU]; 94 Bank Street, Woodburn, New South Wales
2471 (AU).

(74) Agent: **IP LINK**; P.O. Box 1101, Wynnum, Queensland
4178 (AU).

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD,
SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: CELLULOSE PHOSPHATE POWDER PRODUCT AND PROCESS FOR MANUFACTURE THEREOF, AND AP-
PLICATION TO REMOVAL OF CONTAMINANTS FROM AQUEOUS SOLUTIONS

(57) Abstract: A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions comprising reacting one or more biomass based cellulose containing raw materials with dilute phos-
phoric acid where the reaction mixture containing said cellulose containing materials is heated to a reaction temperature and after
completion of the reaction time, separation of the dilute phosphoric acid solution from the remaining insoluble raw material, neutral-
isation of the solution by means of a suitable neutralising agent resulting in precipitation of the modified cellulose, and then separat-
ing, washing and removing excess water from the resultant precipitate.



**Cellulose phosphate powder product and process for manufacture thereof,
and application to removal of contaminants from aqueous solutions**

Field of the invention

5 This invention relates to a chemical process for synthesising a modified cellulose phosphate powder from biomass sources of cellulose including, but not limited to, algae, bagasse, and waste paper.

10 This invention further relates to the application of the cellulose phosphate powder for use in removal of various contaminants or chemical species from water, including but not limited to Mercury, Cadmium, Chromium, Copper, Zinc, Iron, Bismuth, Selenium, Tin, Cobalt, Nickel, Vanadium, Manganese, Uranium, Thorium, Arsenic, Lead and Ammonia.

Background of the invention

15 This invention has particular application in near neutral pH aqueous solutions that are contaminated with various water soluble species. Typical species include those containing transition metals, and also other contaminants containing ammonia, arsenic, and selenium. At low concentrations these contaminants are soluble in water and often have toxicological, clinical or environmental impacts. At low concentrations, many contaminants are difficult to
20 separate from water. The existing solutions for removal of trace level contaminants, particularly those utilized in industrial applications, include the use of ion exchange resins, activated carbon or alumina, or titanium dioxide, reverse osmosis, chemical precipitation, or biological filtration. Each of these works with only specific contaminants. However none of these options is satisfactory for all contaminants. Further, other limitations of these
25 processes include insufficient removal of particular contaminants, impractical application for large volumes, and high expense. Often a combination of two or more techniques is necessary, and creates process engineering difficulties.

Summary of the invention

30 The present invention involves creating a modified cellulose based powder by reacting a biomass based cellulosic raw material with dilute phosphoric acid at elevated temperature. The cellulosic raw material is partially dissolved and then the remaining insoluble raw material is separated from the dilute phosphoric acid solution. The clear

phosphoric acid solution is then neutralized with subsequent precipitation of the modified cellulose, followed by , separating, washing and removal of excess water prior to use. The resulting product is a sorbent powder. (Wherever the term "sorbent" is used in this specification, this shall be interpreted to mean adsorbent. However, it is to be understood
5 that the product may also have absorbent properties.) The sorbent product, which may be in the form of a powder or a slurry, is particularly useful for removal of low levels of contaminants from water and aqueous solutions. The solid residue resulting from extraction is then inert and non flammable, and the remaining filtrate is discarded, or may be processed for recovery of unreacted phosphoric acid.

10 As a sorbent for trace contaminants, the method of application includes but is not limited to contacting the sorbent product with the contaminated water or aqueous solution by mixing and then separating either by allowing the product to settle and decanting the supernatant treated water or solution, or by filtering, or some other method of solid liquid separation.

15 Additionally the sorbent product can be used as an active component in a filter or permeable reactive barrier

Detailed Description of the Preferred Embodiments

The synthesis of the sorbent powder is performed by utilizing a cellulosic feedstock.
20 This may include but is not limited to algae, bagasse, and favourably, waste paper. The cellulosic feedstock is then mixed with dilute phosphoric acid (typically in the concentration range from approximately 2g/l up to 40 g/l but may also be in the range 1g/l up to 80g/l), and heated to reaction temperature for at least 2 minutes, but more preferably at least 5 minutes, up to 4 hours. The heating may be performed by conventional means, but may also include
25 alternative heating technologies for water including microwave heating. The ratio of cellulosic feedstock to dilute phosphoric acid may typically be between a ratio of 1 part feedstock to 5 parts dilute phosphoric acid, up to 1 part feedstock to 40 parts of dilute phosphoric acid. However, this ratio may also foreseeably be in the range of 1 part feedstock to 2 parts dilute phosphoric acid , up to 1 part feedstock to 80 parts of dilute phosphoric acid. This is more of
30 a practical issue rather than a technical limit. The yield of sorbent from feedstock ranges from 4% by weight up to 40% by weight depending upon the feedstock used, the dilute acid concentration and volume, and the temperature and heating time of the synthesis.

Following reaction of the feedstock with dilute phosphoric acid, the remaining solids and the solution are separated by any suitable means. Simple filtering has been shown to be
35 effective. The solid residue consists of insoluble and unreactive cellulosic feedstock. This

residue is non flammable and, based upon this characteristic, may be useful as a fire retardant and in insulation products. Subsequent to the initial solid liquid separation, the filtrate or supernatant is neutralized to pH 7 with any suitable neutralizing agent but preferably caustic soda. As the neutralization is performed, a fine precipitate develops in solution which settles easily and filters easily. This precipitate is the object of the process and is recovered by filtering or other suitable solid liquid separation technique. The precipitate is then washed with water to remove any remaining salts, and excess water removed. Accordingly, the product may be a dried powder or may be in the form of a slurry.

The application of the sorbent product for treatment of low level water contaminants is performed by simple mixing of the sorbent product with water. Contact and mixing time may typically be between approximately 5 minutes and 2 hours. However, this range may be greater and foreseeably may be between approximately 2 minutes and 24 hours, with dose rate determined by total load of contaminants and capacity of the sorbent for a given contaminant. Following mixing of the sorbent and the water to be treated, solid liquid separation is performed by any suitable means including but not limited to filtering, centrifugation, and decanting. Additionally the sorbent can be utilized as a filter bed with the contaminated water passed through the filter bed with removal of various contaminants taking place within the filter bed.

The use of cellulose phosphate derivatives has been described in prior art patents DE19850286 (A1); DE19753196 (A1); DE19859746 (A1); US6579977 (B1); US6761272 (B1); US2007093654 (A1); GB1001803 (A). In these patents all cellulose feedstocks described are prepared via several steps which include caustic pulping, further pulp preparation, and derivatisation with complex and expensive phosphate reagents. In the above prior art documents, derivatisation is performed in organic solvents which increase the safety risks and expense of producing a cellulose phosphate derivative. Further, additional derivatisation is needed to achieve satisfactory performance for trace contaminant removal and this usually includes but is not limited to addition of amine or nitrogen species to effect an improved functionality of the cellulose derivative.

The present invention provides an alternative and more cost effective solution for the removal of the abovementioned contaminants from water. The cellulose phosphate product has different physical characteristics and improved performance as water treatment product, particularly for trace contaminants. In addition, the cellulose phosphate of the present invention has a Fourier Transformation Infrared spectrum that shows significant differences from conventional cellulose phosphate esters and ethers. The process described in the present invention utilizes a different method of synthesis to previously taught approaches and offers a number of advantages including greater simplicity, lower risk and production

costs. This results in a product with affinity for a range of contaminants (the affinity of which may vary according to the contaminant) without the need for further functionalization.

The following examples are provided in order to illustrate the process:

Example 1: 3.128 g of waste paper was reacted with 120 mls of 8% w/v phosphoric acid at 104 degrees C for 2 hours 43 minutes. The resultant mixture was cooled, separated by filtering and the residue washed and dried. 2.206 g of residue was recovered. The filtrate and washings were neutralized with 40 g/l caustic soda to a pH of 7.0, the resultant precipitated powder was filtered and washed and dried to give a final weight of 0.845 g of sorbent powder. 0.5g of this powder was added to a 1 litre water sample with 24 hours mixing and the resultant change in composition was:

Sample Analyte	Untreated Sample	Treated Sample
ARSENIC (mg/L)	0.130	0.078
COPPER (mg/L)	0.023	0.007
IRON (mg/L)	3.388	1.357
LEAD (mg/L)	0.159	0.001
SELENIUM (mg/L)	1.698	1.181
ZINC (mg/L)	0.042	0.023
MERCURY (mg/L)	0.009	<0.001
THALLIUM (mg/L)	0.0019	0.0011

Example 2: 2.003 g of bagasse was reacted with 100 mls of 8% w/v phosphoric acid at 100 degrees C for 3 hours and 15 minutes. The resultant mixture was cooled separated by filtering and the residue washed and dried. 1.782 g of residue was recovered. The filtrate and washings were neutralized with 40 g/l caustic soda to a pH of 7.0, the resultant precipitated powder was filtered and washed and dried to give a final weight of 0.241 g of sorbent powder.

Example 3: 1.030 g of dried filamentous algae was reacted with 100 mls of 8% w/v phosphoric acid at 100 degrees C for 3 hours and 15 minutes. The resultant mixture was cooled separated by filtering and the residue washed and dried. 0.962 g of residue was recovered. The filtrate and washings were neutralized with 40 g/l caustic soda to a pH of 7.0, the resultant precipitated powder was filtered and washed and dried to give a final weight of 0.073 g of sorbent powder.

Example 4: 1170 g of waste paper was boiled with 23.3 litres of 4.4% w/v phosphoric acid for 2 hours. The resultant mixture was cooled separated by decanting and then filtering and the

residue washed and dried. The filtrate and washings were neutralized with 80 g/l caustic soda to a pH of 6.5, the resultant precipitated powder was filtered and washed and dried to give a final weight of 221 g of sorbent powder. 339 mg of this powder was prepared as a column filter and 100 ml of contaminated water was passed through the filter. The resultant

5 change in water composition was:

Sample Analyte	Untreated Sample	Treated Sample
IRON (ug/L)	1620	5
COPPER (ug/L)	440	035
MANGANESE (ug/L)	3360	1480
LEAD (ug/L)	9	<0.5

The invention enables the reduction of a range of trace contaminants from contaminated water sources with near neutral pH, without any toxic or aesthetic reduction in water quality. This invention has particular application in dilute waste water treatment, or
10 environmental water treatment.

Accordingly the invention has both commercial and environmental advantages. It will of course be realised that while the foregoing has been given by way of illustrative example of this invention, all such and other modifications and variations thereto as would be apparent to persons skilled in the art are deemed to fall within the broad scope and ambit of
15 this invention as is herein set forth.

Claims

1. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions comprising reacting one or more biomass based cellulose containing raw materials with dilute phosphoric acid where the reaction mixture containing said cellulose containing materials is heated to a reaction temperature and after completion of the reaction time, separation of the dilute phosphoric acid solution from the remaining insoluble raw material, neutralisation of the solution by means of a suitable neutralising agent resulting in precipitation of the modified cellulose, and then separating, washing and removing excess water from the resultant precipitate.
2. A process for producing a cellulose based sorbent material comprising reacting one or more biomass based cellulose containing raw materials with dilute phosphoric acid where the reaction mixture containing said cellulose containing materials is heated to a reaction temperature and after completion of the reaction time, separation of the dilute phosphoric acid solution from the remaining insoluble raw material, neutralisation of the solution by means of a suitable neutralising agent resulting in precipitation of the modified cellulose, and then filtering, washing and drying the resultant precipitate.
3. A process for producing a cellulose based sorbent material in accordance with claim 1 or 2 in which the concentration of the phosphoric acid is in the range of approximately 1g/l to 80g/l.
4. A process for producing a cellulose based sorbent material in accordance with claim 1 or 2 in which the concentration of the phosphoric acid is in the range of approximately 2g/l to 40g/l.
5. A process for producing a cellulose based sorbent material in accordance with any one of claims 1 to 4 wherein the reaction mixture is heated to reaction temperature for at least 2 minutes.
6. A process for producing a cellulose based sorbent material in accordance with any one of claims 1 to 4 wherein the reaction mixture is heated to reaction temperature for at least 5 minutes.
7. A process for producing a cellulose based sorbent material in accordance with any one of claims 1 to 4 wherein the reaction mixture is heated to reaction temperature for at least 1 hour.
8. A process for producing a cellulose based sorbent material in accordance with any one of claims 1 to 4 wherein the reaction mixture is heated to reaction

temperature for up to 4 hours.

9. A process for producing a cellulose based sorbent material in accordance with any one of claims 1 to 8 in which the ratio of cellulosic feedstock to dilute phosphoric acid is in the range of part feedstock to 5 parts dilute phosphoric acid up to 1 part feedstock to 40 parts of dilute phosphoric acid.
10. A process for producing a cellulose based sorbent material in accordance with any one of claims 1 to 8 in which the ratio of cellulosic feedstock to dilute phosphoric acid is in the range of part feedstock to 2 parts dilute phosphoric acid up to 1 part feedstock to 80 parts of dilute phosphoric acid.
11. A process for producing a cellulose based sorbent material in accordance with any one of claims 1 to 10 wherein the neutralisation agent used to neutralize the solution is caustic soda.
12. A process for producing a cellulose based sorbent material in accordance with any one of claims 1 to 11 wherein the solution is neutralized to approximately pH 7.
13. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Mercury.
14. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Cadmium.
15. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Chromium.
16. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Copper.
17. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Zinc.
18. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in

- accordance with any one of claims 1 to 12 wherein at least one contaminant contains Iron.
19. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Bismuth.
 20. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Selenium.
 21. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Tin.
 22. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Cobalt.
 23. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Nickel.
 24. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Vanadium.
 25. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Manganese.
 26. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Uranium.
 27. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant

contains Thorium.

28. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Arsenic.
29. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Lead.
30. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions in accordance with any one of claims 1 to 12 wherein at least one contaminant contains Ammonia.
31. A process for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions substantially as hereinbefore described with reference to the examples.
32. A cellulose based sorbent product manufactured in accordance with the process in any one of claims 1 to 13.
33. A cellulose based sorbent product manufactured in accordance with the process in any one of claims 1 to 13 in which the product is in the form of a powder.
34. A cellulose based sorbent product manufactured in accordance with the process in any one of claims 1 to 13 in which the product is in the form of a slurry.
35. A method for the removal of water soluble contaminants from water and other aqueous solution by contacting a sorbent product manufactured in accordance with the process in any one of claims 1 to 13 with the contaminated water or aqueous solution by mixing and then separating the product and the treated water or aqueous solution.
36. A method in accordance with claim 17 in which separation is effected by allowing the product to settle and decanting the supernatant treated water or aqueous solution.
37. A method in accordance with claim 17 in which separation is effected by filtration.
38. A method in accordance with claim 17 in which separation is effected by some other method of solid liquid separation.
39. A method for the removal of water soluble contaminants from water and other aqueous solutions by utilising the sorbent product manufactured in accordance with the process in any one of claims 1 to 13 as an active component in a filter.
40. A method for the removal of water soluble contaminants from water and other

aqueous solutions by utilising the sorbent product manufactured in accordance with the process in any one of claims 1 to 13 as an active component in a permeable reactive barrier.

41. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Mercury.
42. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Cadmium.
43. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Chromium.
44. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Copper.
45. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Zinc.
46. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Iron.
47. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Bismuth.
48. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Selenium.
49. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Tin.
50. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Cobalt.
51. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Nickel.
52. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Vanadium.
53. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Manganese.
54. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Uranium.
55. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Thorium.
56. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Arsenic.
57. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Lead.

58. A method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Ammonia.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2012/000083

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C02F 1/28 (2006.01) *C07H 1/02* (2006.01) *C02F 101/20* (2006.01)
B01D 39/00 (2006.01) *C07H 1/04* (2006.01) *C02F 101/22* (2006.01)
B01J 20/22 (2006.01) *C08B 5/00* (2006.01)
B01J 20/24 (2006.01) *C02F 101/10* (2006.01)

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)

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)

WPI; EPODOC: (C02F 1/28, 101/20, 101/22, 101/10; B01J 20/22, 20/24; B01D 39/-; C07H 1/04; C08B 5/00, 3/00, 15/00) and
 +cellulos+, phosphoric acid, H3PO4, separate+, isolate+, precipitat+, phosphor+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/0175758 A1 (KORBER ET AL) 11 August 2005 Whole document	1, 2, 13-30, 35, 41-57
X	GB 1445754 A (ELEPON KAKOKI CO LTD) 11 August 1976 Page 1 lines 9- page 2 lines 46; claims	1, 2, 13-30, 41-57
X	GB 899284 A (UNITED KINGDOM ATOMIC ENERGY AUTHORITY) 20 June 1962 Page 1 lines 10-page 2 lines 23; page 2 lines 45-69; example	1, 2, 27, 55

☒ 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	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
15 May 2012

Date of mailing of the international search report
18 May 2012

Name and mailing address of the ISA/AU
 AUSTRALIAN PATENT OFFICE
 PO BOX 200, WODEN ACT 2606, AUSTRALIA
 E-mail address: pct@ipaustalia.gov.au
 Facsimile No. +61 2 6283 7999

Authorized officer
G DIVEN
 AUSTRALIAN PATENT OFFICE
 (ISO 9001 Quality Certified Service)
 Telephone No : +61 2 6283 2992

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/AU2012/000083

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/0252509 A1 (KIPERS) 7 October 2010 Abstract; paragraphs [0006]-[0008]; [0013]-[0015]; examples	1, 2
X	US 6579977 B1 (PIESCHEL ET AL) 17 June 2003 Whole document	1, 2, 14, 16, 29, 42, 44, 57
X	RU 2291113 C1 (UCHREZH DENIE OBRAZOVANIJA BRUS) 10 January 2007 Espace abstract	43
X	AU 2010295857 A1 (CONOCOPHILLIPS CO) 8 March 2012 Abstract	41
X	TW 200938494 A (APPLIED PROCESS TECHNOLOGY INC) 16 September 2009 Espace abstract	48
X	JP 2002-192186 A (FUJI PHOTO FILM CO LTD) 10 July 2002 Espace abstract	41-57
X	TW 1320029 B (BARRETT J. R. ET AL) 1 February 2010 Espace abstract	41-57
X	MX 2008012759 A (CT DE INVESTIGACION EN MATERIA) 5 April 2010 Espace abstract	43, 44, 45, 56, 57
X	GR 1006922 B (VAGENAS DIMITRIOS VASILEIOU) 30 July 2010 Espace abstract	46, 53, 58
X	CN 101508426 A (UNIV CENTRAL SOUTH) 19 August 2009 Espace abstract	44, 47, 49
X	CZ 9700211 A3 (ECO AGUA SERVIS PRAZAK MICHAL) 15 October 1997 Espace abstract	41-57
X	JP 58-161926 A (SUMITOMO CHEMICAL CO ET AL) 26 September 1983 Espace abstract	54

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2012/000083

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RU 2334802 C2 (OAO SOLIKAMSKIJ MAGNIEVYJ ZD) 27 September 2008 Espace abstract	55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2012/000083

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 31
because they relate to subject matter not required to be searched by this Authority, namely:

Claim 31 does not comply with Rule 6.2(a) because it relies on references to the description and/or drawings.
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

[See Supplemental Box A]

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Supplemental Box A

(To be used when the space in any of Boxes I to IV is not sufficient)

Continuation of Box No: III

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-30, 32-40 are directed to processes and methods for producing a cellulose based sorbent material for the removal of water soluble contaminants from water and other aqueous solutions comprising reacting one or more biomass based cellulose containing raw materials with dilute phosphoric acid where the reaction mixture containing said cellulose containing materials is heated to a reaction temperature and after completion of the reaction time the separation of the dilute phosphoric acid solution from the remaining insoluble raw material, neutralisation of the solution by means of a suitable neutralising agent resulting in precipitation of the modified cellulose, and then separating, washing and removing excess water from the resultant precipitate. The feature of a cellulose based sorbent materials is specific to this group of claims.
- Claim 41 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Mercury. The feature of Mercury removal from water is specific to this claim.
- Claim 42 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Cadmium. The feature of Cadmium removal from water is specific to this claim.
- Claim 43 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Chromium. The feature of Chromium removal from water is specific to this claim.
- Claim 44 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Copper. The feature of Copper removal from water is specific to this claim.
- Claim 45 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Zinc. The feature of Zinc removal from water is specific to this claim.
- Claim 46 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Iron. The feature of Iron removal from water is specific to this claim.
- Claim 47 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Bismuth. The feature of Bismuth removal from water is specific to this claim.
- Claim 48 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Selenium. The feature of Selenium removal from water is specific to this claim.

[See Supplemental Box B]

Supplemental Box B

(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: Supplemental Box A

- Claim 49 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Tin. The feature of Tin removal from water is specific to this claim.
- Claim 50 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Cobalt. The feature of Cobalt removal from water is specific to this claim.
- Claim 51 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Nickel. The feature of Nickel removal from water is specific to this claim.
- Claim 52 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Vanadium. The feature of Vanadium removal from water is specific to this claim.
- Claim 53 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Manganese. The feature of Manganese removal from water is specific to this claim.
- Claim 54 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Uranium. The feature of Uranium removal from water is specific to this claim.
- Claim 55 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Thorium. The feature of Thorium removal from water is specific to this claim.
- Claim 56 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Arsenic. The feature of Arsenic removal from water is specific to this claim.
- Claim 57 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Lead. The feature of Lead removal from water is specific to this claim.
- Claim 58 is directed to a method for the removal of water soluble contaminants from water and other aqueous solutions wherein at least one contaminant contains Ammonia. The feature of Ammonia removal from water is specific to this claim.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

[See Supplemental Box C]

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2012/000083

Supplemental Box C

(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: Supplemental Box B

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a priori*.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2012/000083

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
US	2005175758	AU	2003227575	CA	2482140	DE	10215642
		EP	1507921	WO	03085198		
GB	1445754	CA	997246	DE	2357696	FR	2206977
		JP	49073846				
GB	899284	NONE					
US	2010252509	WO	2010114990				
US	6579977	AU	18690/99	BR	9815130	CA	2312791
		DE	19753196	DE	19850286	EP	1036109
		NO	20002770	WO	9928372		
RU	2291113	NONE					
AU	2010295857	CA	2774488	US	2011068046	WO	2011034791
TW	200938494	US	2009152194	US	7815801	US	2011011798
		WO	2009078917				
JP	2002192186	NONE					
TW	1320029	NONE					
MX	2008012759	NONE					
GR	1006922	NONE					
CN	101508426	NONE					
CZ	9700211	NONE					
JP	58161926	NONE					
RU	2334802	RU	2006140732				
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							