

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

20 August 2020 (20.08.2020)



(10) International Publication Number

WO 2020/167375 A1

(51) International Patent Classification:

B01D 15/00 (2006.01)

C02F 1/28 (2006.01)

B01J 20/22 (2006.01)

Published:

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

(21) International Application Number:

PCT/US2019/066641

(22) International Filing Date:

16 December 2019 (16.12.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/805,846

14 February 2019 (14.02.2019) US

(71) Applicants: CORNELL UNIVERSITY [US/US]; Center for Technology Licensing at Cornell University, 395 Pine Tree Road, Suite 310, Ithaca, NY 14850 (US). NORTHWESTERN UNIVERSITY [US/US]; Innovation and New Ventures Office, 1800 Sherman Avenue, Suite 504, Evanston, IL 60201 (US).

(72) Inventors: HELBLING, Damian; 11 Knoll Tree Road, Ithaca, NY 14850 (US). LING, Yuhang; 998 Church Street, Glenview, Illinois 60025 (US). CHING, Casey; 427 North Geneva Street, Apartment 1, Ithaca, NY 14850 (US). DICHTTEL, William, R.; 208 Golf Terrace, Wilmette, IL 60091 (US). KLEMES, Max; 1500 Avenue, Apartment 211, Chicago, IL 60201 (US).

(74) Agent: DIMAIO, John, T. M. et al.; HODGSON RUSS LLP, The Guaranty Building, 140 Pearl Street, Suite 100, Buffalo, NY 14202-4040 (US).

(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, KM, ML, MR, NE, SN, TD, TG).

(54) Title: POST-SYNTHETICALLY MODIFIED CYCLODEXTRIN POLYMERIC MATERIALS AND METHODS OF MAKING AND USING SAME

(57) Abstract: The present disclosure relates to mesoporous polymeric materials bearing pendant amine groups and methods of their use for purifying fluid samples from micropollutants, such as anion micropollutants.



**POST-SYNTHETICALLY MODIFIED CYCLODEXTRIN POLYMERIC
MATERIALS AND METHODS OF MAKING AND USING SAME**

Cross-Reference to Related Applications

[0001] This application claims priority to U.S. provisional patent application no.
5 62/805,846, filed February 14, 2019, the disclosure of which is incorporated herein by
reference.

Statement Regarding Federally Funded Research

[0002] This invention was made with government support awarded by Grant No.
CHE-1413862, awarded by the National Science Foundation, Grant No. ER18-1026, awarded
10 by the Strategic Environmental Research and Development Program, and Grant No. CHE-
1541820, awarded by the National Science Foundation. The government has certain rights in
this invention.

Background

[0003] Organic micropollutants (MPs) are chemicals present in water resources at ng
15 L⁻¹ to µg L⁻¹ concentrations as a consequence of human activities.^{1,2} Concerns about their
negative effects on human health³⁻⁷ and the environment⁸⁻¹⁰ motivate the development of
technologies that remove MPs more effectively.¹¹⁻¹⁶ MPs span a wide variety of
physiochemical properties including surface charge, size, and chemical functionality.
Charged MPs can be cationic, anionic, or zwitterionic and are typically difficult to remove in
20 the presence of complex matrix constituents like natural organic matter (NOM) using
conventional adsorption materials like activated carbon. Anionic PFASs present a particular
environmental problem because of their resistance to biodegradation or chemical
transformation and correlation to negative health effects. PFASs have been used in the
formulations of thousands of consumer goods¹ and are present in aqueous film-forming foam
25 (AFFF) formulations used to suppress aviation fires in training scenarios.^{18,19} As a result, they
have contaminated surface and ground waters near thousands of airports and military
installations.²⁰ In 2018, the Environmental Working Group reported that over 110 million
people in the United states were exposed to drinking water with PFAS concentrations above
2.5 ng L⁻¹.²⁴ PFASs have been linked to cancers,³ liver damage,⁴ thyroid disease⁵ and other
30 health problems.⁶

[0004] Contaminated water systems are typically remediated with granular activated
carbon (GAC), but its modest affinity for PFASs, particularly short chain derivatives, makes
it an expensive and stop-gap solution.^{23,24} In recent reports,^{14,15} it was discovered that

noncovalent interactions and the electrostatics of functional groups influence PFAS affinity to adsorbents. For example, the incorporation of more heavily fluorinated crosslinkers, as well as a lower incorporation of anionic functional groups in decafluorobiphenyl-linked CDPs were attributed to its promising perfluorooctanoic acid (PFOA) and

perfluorooctanesulfonic acid (PFOS) removal from water. In contrast, CDPs cross-linked by epichlorohydrin exhibited inferior PFAS removal.²⁵

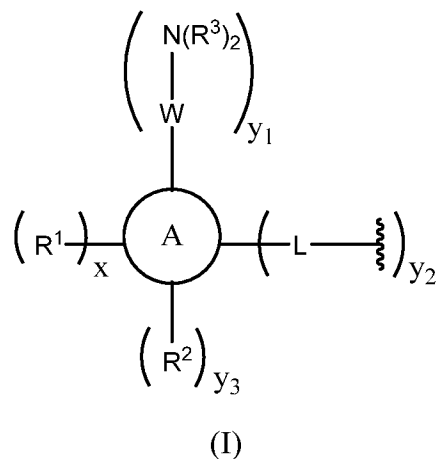
[0005] Adsorption processes can be employed to remove specific contaminants or contaminant classes from fluids like air and water. Activated carbons (ACs) are the most widespread sorbents used to remove organic pollutants, and their efficacy derives primarily from their high surface areas, nanostructured pores, and hydrophobicity. However, no single type of AC removes all contaminants well, particularly anionic MPs. Because of their poorly defined structure and binding site variation, optimal adsorption selectivities require empirical screening at new installations, precluding rational design and improvement. Furthermore, regenerating spent AC is energy intensive (heating to 500-900 °C, or other energy intensive procedures) and does not restore full performance. AC also has a slow pollutant uptake rate, achieving its uptake equilibrium in hours to days, such that more rapid contaminant removal requires excess sorbent. Finally, AC can perform poorly for many emerging contaminants, particularly those that are relatively hydrophilic.

[0006] An alternative adsorbent material can be made from polymeric cyclodextrin materials produced from insoluble polymers of β -cyclodextrin (β -CD), which are toroidal macrocycles comprised of seven glucose units whose internal cavities are capable of binding organic compounds. β -CD is an inexpensive and sustainably produced monomer derived from cornstarch that is used extensively to formulate and stabilize pharmaceuticals, flavorants, and fragrances, as well as within chiral chromatography stationary phases. Insoluble β -CD polymers have been formed by crosslinking with epichlorohydrin and other reactive compounds, and feature well defined binding sites and high association constants. Insoluble β -CD polymers crosslinked with epichlorohydrin have been investigated as alternatives to AC for water purification, but their low surface areas result in inferior sorbent performance relative to ACs.

[0007] Thus there is a need for new sorbents that address the deficiencies of AC and the like and which will provide more effective sorption and/or sequestration properties for MPs (such as anionic MPs). There is a need for an adsorbent that provides rapid anionic MP extraction, high total uptake, and facile regeneration and reuse procedures. This invention meets those needs.

Summary

[0008] In some embodiments, the present disclosure provides a mesoporous polymeric material comprising a plurality of cyclodextrins with a plurality of crosslinks comprising formula (I):



wherein

A is an aryl or heteroaryl moiety;

each R^1 is independently selected from the group consisting of $-\text{CF}_3$, $-\text{SO}_3\text{H}$, $-\text{CN}$, $-\text{C(O)}-\text{NH}_2$, $-\text{N}_2^+$, $-\text{NO}_2$, $-\text{NO}$, $-\text{NH-OH}$, $-\text{N-C(O)-alkyl}$, $-\text{halogen}$, $-\text{N}_3$, $-\text{CH}_2\text{-OH}$, $-\text{CH}_2\text{-N}_3$, $-\text{HC=O}$, $-\text{C-NH-C(O)C-NH-}$, $-\text{C-halogen}$, $-\text{C-NH-C(O)-CO-alkyl}$, $-\text{C-NH-C(O)-CO-aryl}$, $-\text{C-NH-(SO}_2\text{)-aryl}$, $-\text{C-NH-(SO}_2\text{)-alkyl}$, $-\text{C=N-OH}$, $-\text{C-NHC(O)-alkyl}$, and $-\text{NH-C(O)-NH}_2$;

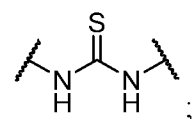
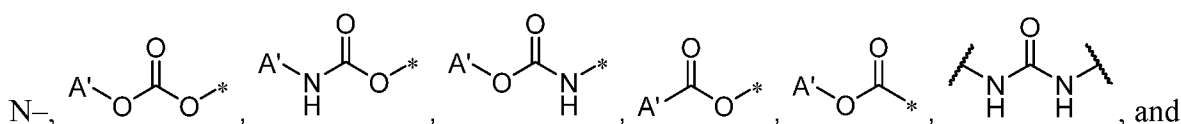
each R^2 is independently $-\text{OH}$, $-\text{O-metal cation}$, alkyl , $-\text{SH}$, $-\text{S-metal cation}$, $-\text{S-alkyl}$;

each R^3 is independently $-\text{H}$, $\text{C}_1\text{-C}_6$ alkyl , $\text{C}_1\text{-C}_3$ haloalkyl , aryl , $-\text{C(O)N(R}^a\text{)(R}^b\text{)}$, $-\text{C(O)R}^a$, $-\text{CO}_2\text{R}^a$, $-\text{SO}_2\text{N(R}^a\text{)(R}^b\text{)}$, or $-\text{SOR}^a$;

each R^a and R^b is independently H , or $\text{C}_1\text{-C}_6$ alkyl ;

each W is independently a bond an alkylene group, or $-(\text{O-CH}_2\text{-CH}_2)_x-$ wherein x is 1-100;

each L is independently a linking moiety selected from the group consisting of $-\text{O}-$, $-\text{S}-$, $-\text{N}-$,



A' is a covalent bond to A;

* is a covalent bond to ~~~~;

~~~~ is a point of attachment to the plurality of cyclodextrin carbon atoms;

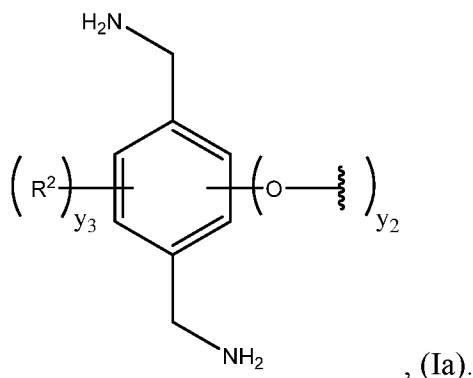
x is 0-8;

y<sub>1</sub> is 1-4;

y<sub>2</sub> is at least 2; and

y<sub>3</sub> is 0-4. In some embodiments, a plurality of cyclodextrins comprising the mesoporous

5 polymeric material of the present disclosure have a plurality of crosslinks of formula (Ia):



wherein R<sup>2</sup>, y<sub>2</sub> and y<sub>3</sub> are as defined above.

**[0009]** In some embodiments, the present disclosure provides a supported porous polymeric material comprising porous particles affixed to a solid substrate, wherein said  
10 porous particles comprise a plurality of cyclodextrin moieties crosslinked with a plurality of linking groups comprising formula (I) or formula (Ia).

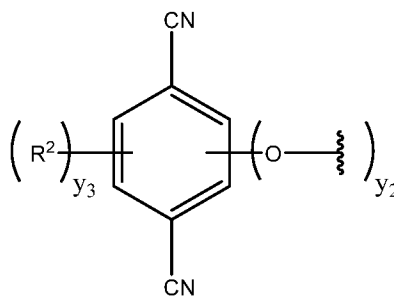
**[0010]** In some embodiments, the present disclosure provides a method of purifying a fluid sample comprising one or more pollutants, the method comprising contacting the fluid sample with the mesoporous polymeric material or the supported porous polymeric material  
15 of the present disclosure whereby at least 50 wt. % of the total amount of the one or more pollutants in the fluid sample is adsorbed by the mesoporous polymeric material.

**[0011]** In some embodiments, the present disclosure provides a method of removing one or more compounds from a fluid sample or determining the presence or absence of one or more compounds in a fluid sample comprising: a) contacting the sample with the mesoporous  
20 polymeric material or the supported porous polymeric material of the present disclosure for an incubation period; b) separating the mesoporous polymeric material or supported porous polymeric material after the incubation period from the sample; and c) heating the mesoporous polymeric material or supported porous polymeric material separated in step b), or contacting the mesoporous polymeric material or supported porous polymeric material  
25 separated in step b) with a solvent, thereby releasing at least a portion of the compounds from the mesoporous polymeric material or supported porous polymeric material; and d1) optionally isolating at least a portion of the compounds released in step c); or d2) determining

the presence or absence of the compounds released in step c), wherein the presence of one or more compounds correlates to the presence of the one or more compounds in the sample.

**[0012]** In some embodiments, the present disclosure provides an article of manufacture comprising the mesoporous polymeric material or the supported porous polymeric material of the present disclosure.

**[0013]** In some embodiments, the present disclosure provides a method of preparing a mesoporous polymeric material having a plurality of crosslinks of formula (Ia) comprising crosslinking a plurality of cyclodextrins with a crosslinking agent having one or more groups capable of reacting with the cyclodextrins, and one or more nitrile groups, thereby forming the mesoporous polymeric material comprising a plurality of crosslinks of formula (II), then reducing at least a portion of the nitrile groups with a suitable reducing agent to form a plurality of amine groups



(II).

### **Brief Description of the Drawings**

**[0014]** Fig. 1 shows post-polymerization reduction of **1** with borane-dimethylsulfide yields amine functionalized **2**. This modification renders the material able to remove anionic MPs from contaminated water.

**[0015]** Fig. 2 shows a) FT-IR spectra of polymers **1** and **2**. In the spectra of **2**, there is a significant reduction in the nitrile stretch at  $2240\text{ cm}^{-1}$  and appearance of an N-H bend at  $1580\text{ cm}^{-1}$  b) Chloranil test of **1** and **2**. Left two vials contain polymers **1** and **2** suspended in DMF and acetaldehyde (5%) and the right two vials contain polymers **1** and **2** suspended in DMF, acetaldehyde (5%), and chloranil (5%). The chloranil test turns blue-green in the presence of **2**, indicated the presence of amines.

**[0016]** Fig. 3 shows the affinity of 91 organic micropollutants to **2** and **1**. Data show that **2** has higher affinity for PFAS and anionic organic micropollutants and **1** has higher

affinity for cationic and zwitterionic organic micropollutants. **1** and **2** exhibit similar affinity for neutral organic micropollutants ( $25 \text{ mg L}^{-1}$  polymer,  $2 \text{ } \mu\text{g L}^{-1}$  MPs).

[0017] Fig. 4 shows a) removal of PFOA (middle dotted line) PFOS (lower dotted line) and the combination of PFOA and PFOS (highest dotted line) as a function of time showing that the combined concentration of PFOA + PFOS can be brought from  $2000 \text{ ng L}^{-1}$  to below the 2016 EPA advisory limit of  $70 \text{ ng L}^{-1}$  in 30 min and  $[\text{PFAS}]_0 = 1 \text{ } \mu\text{g L}^{-1}$ ;  $[\text{CDP}] = 10 \text{ mg L}^{-1}$ . b) PFAS removal by **2** with 30 minutes of contact time;  $[\text{PFAS}]_0 = 1 \text{ } \mu\text{g L}^{-1}$ ;  $[\text{CDP}] = 10 \text{ mg L}^{-1}$ .

[0018] Fig. 5 is a CP-MAS  $^{13}\text{C}$  NMR spectral comparison of **1** and of **2**.

[0019] Fig. 6 shows a comparison between the FT-IR of **1** (top) and **2** (bottom).

[0020] Fig. 7 shows 10 PFAS panel with **2** (left bar), PAC (middle bar), and GAC (right bar) for each PFAS after a) 30 min and b) 8 h of contact time. ( $500 \text{ ng L}^{-1}$  PFAS,  $10 \text{ mg L}^{-1}$  **2**,  $10\text{--}60 \text{ mg L}^{-1}$  PAC/GAC).

[0021] Fig. 8 shows  $\text{N}_2$  absorption isotherm of **2**. Brunauer–Emmet–Teller surface area of  $142 \text{ m}^2 \text{ g}^{-1}$ .

### Detailed Description

[0022] All documents cited herein are incorporated by reference in their entirety for all purposes to the same extent as if each individual document was specifically and individually indicated to be incorporated by reference.

[0023] As used above, and throughout this disclosure, the following terms, unless otherwise indicated, shall be understood to have the following meanings. If a term is missing, the conventional term as known to one skilled in the art controls.

[0024] As used herein, the terms “including,” “containing,” and “comprising” are used in their open, non-limiting sense.

[0025] The articles “a” and “an” are used in this disclosure to refer to one or more than one (*i.e.*, to at least one) of the grammatical object of the article. By way of example, “an element” means one element or more than one element.

[0026] The term “and/or” is used in this disclosure to mean either “and” or “or” unless indicated otherwise.

[0027] To provide a more concise description, some of the quantitative expressions given herein are not qualified with the term “about”. It is understood that, whether the term “about” is used explicitly or not, every quantity given herein is meant to refer to the actual

given value, and it is also meant to refer to the approximation to such given value that would reasonably be inferred based on the ordinary skill in the art, including equivalents and approximations due to the experimental and/or measurement conditions for such given value. Whenever a yield is given as a percentage, such yield refers to a mass of the entity for which the yield is given with respect to the maximum amount of the same entity that could be obtained under the particular stoichiometric conditions. Concentrations that are given as percentages refer to mass ratios, unless indicated differently.

**[0028]** The term adsorbent or adsorb is used to refer to compositions or methods of the present disclosure to refer to solid materials as described herein which remove contaminants or pollutants, typically but not exclusively organic molecules, from a fluid medium such as a liquid (e.g., water) or a gas (e.g., air or other commercially useful gases such as nitrogen, argon, helium, carbon dioxide, anesthesia gases, etc.). Such terms do not imply any specific physical mechanism (e.g., adsorption vs. absorption).

**[0029]** The term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in donut-shaped rings. The specific coupling and conformation of the glucose units give the cyclodextrins rigid, conical molecular structures with hollow interiors of specific volumes. The "lining" of each internal cavity is formed by hydrogen atoms and glycosidic bridging oxygen atoms; therefore, this surface is fairly hydrophobic. The unique shape and physical-chemical properties of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes with) organic molecules or parts of organic molecules which can fit into the cavity.

**[0030]** Unless otherwise stated, the terms "crosslinker" or "crosslink" or "linker" refer to a monomer capable of forming a covalent linkage between one or more cyclodextrins or polymers. For example, if the crosslinker reacts at the end of the polymer it may covalently react with one cyclodextrin moiety of the polymer (e.g., via the glycosidic oxygen of the cyclodextrin). The crosslinker may or may not further react with other monomers or cyclodextrin units or polymers. For example the crosslinker may be bound to 1, 2, 3, or 4+ monomers or cyclodextrin units or polymers.

**[0031]** As used herein, "alkyl" means a straight chain or branched saturated chain having from 1 to 10 carbon atoms. Representative saturated alkyl groups include, but are not

limited to, methyl, ethyl, n-propyl, isopropyl, 2-methyl-1-propyl, 2-methyl-2-propyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2-methyl-3-butyl, 2,2-dimethyl-1-propyl, 2-methyl-1-pentyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2,2-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, butyl, isobutyl, t-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl and the like, and longer alkyl groups, such as heptyl, and octyl and the like. An alkyl group can be unsubstituted or substituted. Alkyl groups containing three or more carbon atoms may be straight or branched. As used herein, "lower alkyl" means an alkyl having from 1 to 6 carbon atoms.

**[0032]** The term "alkylene" refers to straight- and branched-chain alkylene groups.

Typical alkylene groups include, for example, methylene ( $-\text{CH}_2-$ ), ethylene ( $-\text{CH}_2\text{CH}_2-$ ), propylene ( $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), isopropylene ( $-\text{CH}(\text{CH}_3)\text{CH}_2-$ ), n-butylene ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ), sec-butylene ( $-\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-$ ) and the like.

**[0033]** The term "hydroxyl" or "hydroxy" means an OH group.

**[0034]** It should also be noted that any carbon as well as heteroatom with unsatisfied valences in the text, schemes, examples and Tables herein is assumed to have the sufficient number of hydrogen atom(s) to satisfy the valences.

**[0035]** The term "halo" or "halogen" refers to fluorine, chlorine, bromine, or iodine.

**[0036]** The term "cyano" as used herein means a substituent having a carbon atom joined to a nitrogen atom by a triple bond, i.e.,  $\text{C}\equiv\text{N}$ .

**[0037]** The term "amine" or "amino" as used herein means a substituent containing at least one nitrogen atom. Specifically,  $-\text{NH}_2$ ,  $-\text{NH}(\text{alkyl})$  or alkylamino,  $-\text{N}(\text{alkyl})_2$  or dialkylamino, amide, carboxamide, urea, and sulfamide substituents are included in the term "amino".

**[0038]** Unless otherwise specifically defined, the term "aryl" refers to cyclic, aromatic hydrocarbon groups that have 1 to 3 aromatic rings, including monocyclic or bicyclic groups such as phenyl, biphenyl or naphthyl. Where containing two aromatic rings (bicyclic, etc.), the aromatic rings of the aryl group may be joined at a single point (e.g., biphenyl), or fused (e.g., naphthyl). The aryl group may be optionally substituted by one or more substituents, e.g., 1 to 5 substituents, at any point of attachment. The substituents can themselves be optionally substituted. Furthermore when containing two fused rings the aryl groups herein defined may have an unsaturated or partially saturated ring fused with a fully saturated ring. Exemplary ring systems of these aryl groups include, but are not limited to, phenyl, biphenyl, naphthyl, anthracenyl, phenalenyl, phenanthrenyl, indanyl, indenyl, tetrahydronaphthalenyl, tetrahydrobenzoannulenyl, and the like.

**[0039]** Unless otherwise specifically defined, "heteroaryl" means a monovalent monocyclic or polycyclic aromatic radical of 5 to 18 ring atoms or a polycyclic aromatic radical, containing one or more ring heteroatoms selected from N, O, or S, the remaining ring atoms being C. Heteroaryl as herein defined also means a polycyclic (e.g., bicyclic)

heteroaromatic group wherein the heteroatom is selected from N, O, or S. The aromatic radical is optionally substituted independently with one or more substituents described herein. The substituents can themselves be optionally substituted. Examples include, but are not limited to, benzothiophene, furyl, thienyl, pyrrolyl, pyridyl, pyrazinyl, pyrazolyl, pyridazinyl, pyrimidinyl, imidazolyl, isoxazolyl, oxazolyl, oxadiazolyl, pyrazinyl, indolyl, thiophen-2-yl, quinolyl, benzopyranyl, isothiazolyl, thiazolyl, thiadiazolyl, thieno[3,2-b]thiophene, triazolyl, triazinyl, imidazo[1,2-b]pyrazolyl, furo[2,3-c]pyridinyl, imidazo[1,2-a]pyridinyl, indazolyl, pyrrolo[2,3-c]pyridinyl, pyrrolo[3,2-c]pyridinyl, pyrazolo[3,4-c]pyridinyl, benzoimidazolyl, thieno[3,2-c]pyridinyl, thieno[2,3-c]pyridinyl, thieno[2,3-b]pyridinyl, benzothiazolyl, indolyl, indolinyl, indolinonyl, dihydrobenzothiophenyl, dihydrobenzofuranyl, benzofuran, chromanyl, thiochromanyl, tetrahydroquinoliny, dihydrobenzothiazine, dihydrobenzoxanyl, quinoliny, isoquinoliny, 1,6-naphthyridiny, benzo[de]isoquinoliny, pyrido[4,3-b][1,6]naphthyridiny, thieno[2,3-b]pyrazinyl, quinazoliny, tetrazolo[1,5-a]pyridiny, [1,2,4]triazolo[4,3-a]pyridiny, isoindolyl, pyrrolo[2,3-b]pyridiny, pyrrolo[3,4-b]pyridiny, pyrrolo[3,2-b]pyridiny, imidazo[5,4-b]pyridiny, pyrrolo[1,2-a]pyrimidinyl, tetrahydropyrrolo[1,2-a]pyrimidinyl, 3,4-dihydro-2H-1 $\lambda$ <sup>2</sup>-pyrrolo[2,1-b]pyrimidine, dibenzo[b,d]thiophene, pyridin-2-one, furo[3,2-c]pyridiny, furo[2,3-c]pyridiny, 1H-pyrido[3,4-b][1,4]thiazinyl, benzooxazolyl, benzoisoxazolyl, furo[2,3-b]pyridiny, benzothiophenyl, 1,5-naphthyridiny, furo[3,2-b]pyridine, [1,2,4]triazolo[1,5-a]pyridiny, benzo [1,2,3]triazolyl, imidazo[1,2-a]pyrimidinyl, [1,2,4]triazolo[4,3-b]pyridazinyl, benzo[c][1,2,5]thiadiazolyl, benzo[c][1,2,5]oxadiazole, 1,3-dihydro-2H-benzo[d]imidazol-2-one, 3,4-dihydro-2H-pyrazolo[1,5-b][1,2]oxazinyl, 4,5,6,7-tetrahydropyrazolo[1,5-a]pyridiny, thiazolo[5,4-d]thiazolyl, imidazo[2,1-b][1,3,4]thiadiazolyl, thieno[2,3-b]pyrrolyl, 3H-indolyl, and derivatives thereof. Furthermore when containing two fused rings the heteroaryl groups herein defined may have an unsaturated or partially saturated ring fused with a fully saturated ring.

**[0040]** Numerical ranges, as used herein, are intended to include sequential integers unless indicated otherwise. For example, a range expressed as "from 0 to 5" would include 0, 1, 2, 3, 4 and 5.

Mesoporous Polymeric Materials

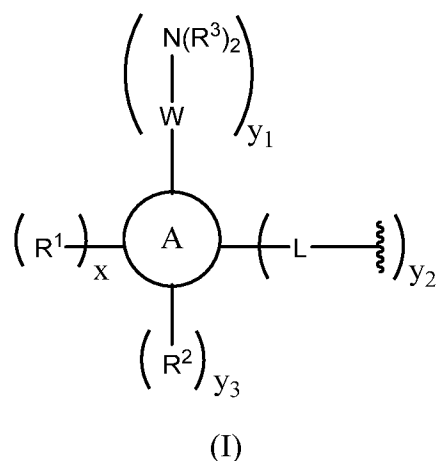
**[0041]** The present disclosure provides porous (e.g. mesoporous), typically high surface area cyclodextrin polymeric materials (P-CDPs), as well as methods of making and using these materials. The P-CDPs are comprised of insoluble polymers of cyclodextrin, which is an inexpensive, sustainably produced macrocycle of glucose. The cyclodextrin polymers are crosslinked with linking groups as described herein. The polymers of cyclodextrin are comprised of cyclodextrin moieties that are derived from cyclodextrins. The cyclodextrin moiety(s) can be derived from naturally occurring cyclodextrins (e.g.,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -, comprising 6, 7, and 8 glucose units, respectively) or synthetic cyclodextrins. The cyclodextrin moiety has at least one —O— bond derived from an —OH group on the cyclodextrin from which it is derived. The cyclodextrin moieties can comprise 3-20 glucose units, including 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20 glucose units, inclusive of all ranges therebetween. In many embodiments, the cyclodextrin moieties are derived from starch, and comprise 6-9 glucose units. The polymeric materials may comprise two or more different cyclodextrin moieties. In particular embodiments, the P-CDP is comprised of insoluble polymers of  $\beta$ -cyclodextrin ( $\beta$ -CD).

**[0042]** The P-CDP can also comprise cyclodextrin derivatives or modified cyclodextrins. The derivatives of cyclodextrin consist mainly of molecules wherein some of the OH groups are converted to OR groups. The cyclodextrin derivatives can, for example, have one or more additional moieties that provide additional functionality, such as desirable solubility behavior and affinity characteristics. Examples of suitable cyclodextrin derivative materials include methylated cyclodextrins (e.g., RAMEB, randomly methylated  $\beta$ -cyclodextrins), hydroxyalkylated cyclodextrins (e.g., hydroxypropyl- $\beta$ -cyclodextrin and hydroxypropyl- $\gamma$ -cyclodextrin), acetylated cyclodextrins (e.g., acetyl- $\gamma$ -cyclodextrin), reactive cyclodextrins (e.g., chlorotriazinyl- $\beta$ -CD), branched cyclodextrins (e.g., glucosyl- $\beta$ -cyclodextrin and maltosyl- $\beta$ -cyclodextrin), sulfobutyl- $\beta$ -cyclodextrin, and sulfated cyclodextrins. For example, the cyclodextrin moiety further comprises a moiety that binds (e.g., with specificity) a metal such as arsenic, cadmium, copper, or lead.

**[0043]** The P-CDP can also comprise cyclodextrin derivatives as disclosed in U.S. Pat. No. 6,881,712 including, e.g., cyclodextrin derivatives with short chain alkyl groups such as methylated cyclodextrins, and ethylated cyclodextrins, wherein R is a methyl or an ethyl group; those with hydroxyalkyl substituted groups, such as hydroxypropyl cyclodextrins and/or hydroxyethyl cyclodextrins, wherein R is a —CH<sub>2</sub>—CH(OH)—CH<sub>3</sub> or a —CH<sub>2</sub>CH<sub>2</sub>—OH group; branched cyclodextrins such as maltose-bonded cyclodextrins; cationic

cyclodextrins such as those containing 2-hydroxy-3-(dimethylamino)propyl ether, wherein R is  $\text{CH}_2\text{—CH(OH)—CH}_2\text{—N(CH}_3)_2$  which is cationic at low pH; quaternary ammonium, e.g., 2-hydroxy-3-(trimethylammonio)propyl ether chloride groups, wherein R is  $\text{CH}_2\text{—CH(OH)—CH}_2\text{—N}^+(\text{CH}_3)_3\text{Cl}^-$ ; anionic cyclodextrins such as carboxymethyl cyclodextrins, cyclodextrin sulfates, and cyclodextrin succinylates; amphoteric cyclodextrins such as carboxymethyl/quaternary ammonium cyclodextrins; cyclodextrins wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure, e.g., the mono-3-6-anhydrocyclodextrins, as disclosed in “Optimal Performances with Minimal Chemical Modification of Cyclodextrins”, F. Diedaini-Pilard and B. Perly, The 7th International Cyclodextrin Symposium Abstracts, April 1994, p. 49 said references being incorporated herein by reference; and mixtures thereof. Other cyclodextrin derivatives are disclosed in U.S. Pat. No. 3,426,011, Parmerter et al., issued Feb. 4, 1969; U.S. Pat. Nos. 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued Jul. 1, 1969; U.S. Pat. No. 3,459,731, Gramera et al., issued Aug. 5, 1969; U.S. Pat. No. 3,553,191, Parmerter et al., issued Jan. 5, 1971; U.S. Pat. No. 3,565,887, Parmerter et al., issued Feb. 23, 1971; U.S. Pat. No. 4,535,152, Szejtli et al., issued Aug. 13, 1985; U.S. Pat. No. 4,616,008, Hirai et al., issued Oct. 7, 1986; U.S. Pat. No. 4,678,598, Ogino et al., issued Jul. 7, 1987; U.S. Pat. No. 4,638,058, Brandt et al., issued Jan. 20, 1987; and U.S. Pat. No. 4,746,734, Tsuchiyama et al., issued May 24, 1988; all of said patents being incorporated herein by reference.

**[0044]** In some embodiments, the present disclosure provides a mesoporous polymeric material comprising a plurality of cyclodextrins crosslinked with a plurality of linking groups comprising a moiety of formula (I):



wherein

A is an aryl or heteroaryl moiety;

each  $R^1$  is independently selected from the group consisting of  $-\text{CF}_3$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{CN}$ ,  $-\text{C}(\text{O})-\text{NH}_2$ ,

$-\text{N}_2^+$ ,  $-\text{NO}_2$ ,  $-\text{NO}$ ,  $-\text{NH}-\text{OH}$ ,  $-\text{N}-\text{C}(\text{O})-\text{alkyl}$ ,  $-\text{halogen}$ ,  $-\text{N}_3$ ,  $-\text{CH}_2-\text{OH}$ ,  $-\text{CH}_2-\text{N}_3$ ,  $-\text{HC}=\text{O}$ ,  
 $-\text{C}-\text{NH}-\text{C}(\text{O})-\text{NH}-$ ,  $-\text{C}-\text{halogen}$ ,  $-\text{C}-\text{NH}-\text{C}(\text{O})-\text{CO}-\text{alkyl}$ ,  $-\text{C}-\text{NH}-\text{C}(\text{O})-\text{CO}-\text{aryl}$ ,  $-\text{C}-\text{NH}-$

5  $(\text{SO}_2)-\text{aryl}$ ,  $-\text{C}-\text{NH}-(\text{SO}_2)-\text{alkyl}$ ,  $-\text{C}=\text{N}-\text{OH}$ ,  $-\text{C}-\text{NHC}(\text{O})-\text{alkyl}$ , and  $-\text{NH}-\text{C}(\text{O})-\text{NH}_2$ ;

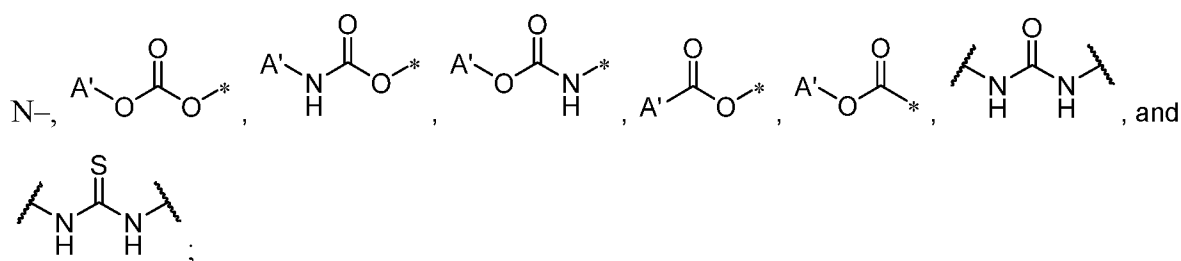
each  $R^2$  is independently  $-\text{OH}$ ,  $-\text{O}-\text{metal cation}$ ,  $\text{alkyl}$ ,  $-\text{SH}$ ,  $-\text{S}-\text{metal cation}$ ,  $-\text{S}-\text{alkyl}$ ;

each  $R^3$  is independently  $-\text{H}$ ,  $\text{C}_1-\text{C}_6$   $\text{alkyl}$ ,  $\text{C}_1-\text{C}_3$   $\text{haloalkyl}$ ,  $\text{aryl}$ ,  $-\text{C}(\text{O})\text{N}(\text{R}^a)(\text{R}^b)$ ,  $-\text{C}(\text{O})\text{R}^a$ ,  
 $-\text{CO}_2\text{R}^a$ ,  $-\text{SO}_2\text{N}(\text{R}^a)(\text{R}^b)$ , or  $-\text{SOR}^a$ ;

each  $\text{R}^a$  and  $\text{R}^b$  is independently  $\text{H}$ , or  $\text{C}_1-\text{C}_6$   $\text{alkyl}$ ;

10 each  $\text{W}$  is independently a bond an alkylene group, or  $-(\text{O}-\text{CH}_2-\text{CH}_2)_x-$  wherein  $x$  is 1-100;

each  $\text{L}$  is independently a linking moiety selected from the group consisting of  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{N}-$ ,



$\text{A}'$  is a covalent bond to  $\text{A}$ ;

15  $*$  is a covalent bond to  $\text{C}$ ;

$\text{C}$  is a point of attachment to the plurality of cyclodextrin carbon atoms;

$x$  is 0-8;

$y_1$  is 1-4;

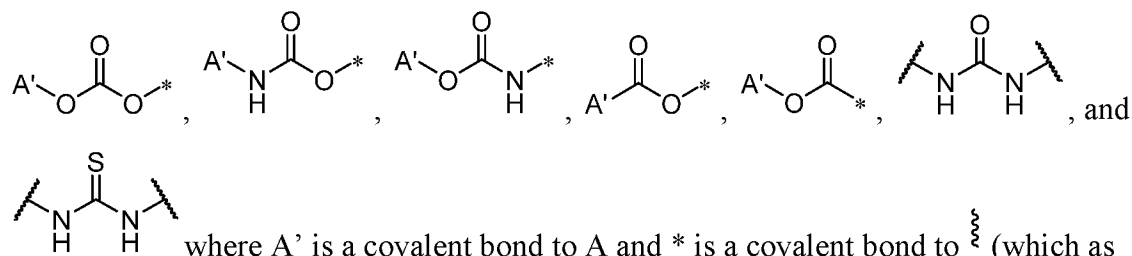
$y_2$  is at least 2; and

20  $y_3$  is 0-4.

**[0045]** In accordance with certain embodiments of the present disclosure,  $\text{W}$  is independently a bond, an alkylene group, or  $-(\text{O}-\text{CH}_2-\text{CH}_2)_x-$  wherein  $x$  is 1-100. Thus in some embodiments, each  $\text{W}$  is a bond (i.e., a covalent bond). In other embodiments, each  $\text{W}$  is an alkylene group. For example, each  $\text{W}$  may be, methylene ( $-\text{CH}_2-$ ), ethylene ( $-\text{CH}_2\text{CH}_2-$ ), propylene ( $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), isopropylene ( $-\text{CH}(\text{CH}_3)\text{CH}_2-$ ), n-butylene ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ), sec-butylene ( $-\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2-$ ) and the like. In some embodiments, each  $\text{W}$  is methylene ( $-\text{CH}_2-$ ). In some embodiments,  $\text{W}$  is  $-(\text{O}-\text{CH}_2-\text{CH}_2)_x-$ .

**[0046]** In some embodiments, each  $\text{L}$  is a linking moiety. In some embodiments, each  $\text{L}$  is independently a linking moiety selected from the group consisting of each  $\text{L}$  is

independently a linking moiety selected from the group consisting of  $-O-$ ,  $-S-$ ,  $-N-$ ,



described herein represents a point of attachment to the plurality of cyclodextrin carbon

atoms). In some embodiments, each L is independently  $-O-$ . In certain embodiments, when

each L is independently  $\text{A}'\text{-O-C(=O)-O-}^*$ ,  $\text{A}'\text{-NH-C(=O)-O-}^*$ ,  $\text{A}'\text{-C(=O)-O-}^*$  or  $-O-$ , the oxygen atom may be a glycosidic oxygen from the plurality of cyclodextrins of the mesoporous polymeric material of the present disclosure. For example, in some embodiments, when each L is independently  $-O-$ , the oxygen atom is a glycosidic oxygen atom from the plurality of cyclodextrins of the mesoporous polymeric material of the present disclosure.

**[0047]** In some embodiments, A is an aryl or heteroaryl moiety. In some embodiments, A is an aryl moiety. For example, A may be phenyl, biphenyl, naphthyl, anthracenyl, phenalenyl, phenanthrenyl, indanyl, indenyl, tetrahydronaphthalenyl, or tetrahydrobenzoannulenyl. In some embodiments, A is a heteroaryl moiety. For example, A may be benzothiophene, furyl, thienyl, pyrrolyl, pyridyl, pyrazinyl, pyrazolyl, pyridazinyl, pyrimidinyl, imidazolyl, isoxazolyl, oxazolyl, oxadiazolyl, pyrazinyl, indolyl, thiophen-2-yl, quinolyl, benzopyranyl, isothiazolyl, thiazolyl, thiadiazolyl, thieno[3,2-b]thiophene, triazolyl, triazinyl, imidazo[1,2-b]pyrazolyl, furo[2,3-c]pyridinyl, imidazo[1,2-a]pyridinyl, indazolyl, pyrrolo[2,3-c]pyridinyl, pyrrolo[3,2-c]pyridinyl, pyrazolo[3,4-c]pyridinyl, benzoimidazolyl, thieno[3,2-c]pyridinyl, thieno[2,3-c]pyridinyl, thieno[2,3-b]pyridinyl, benzothiazolyl, indolyl, indolinyl, indolinonyl, dihydrobenzothiophenyl, dihydrobenzofuranyl, benzofuran, chromanyl, thiochromanyl, tetrahydroquinoliny, dihydrobenzothiazine, dihydrobenzoxanyl, quinoliny, isoquinoliny, 1,6-naphthyridiny, benzo[de]isoquinoliny, pyrido[4,3-b][1,6]naphthyridiny, thieno[2,3-b]pyrazinyl, quinazoliny, tetrazolo[1,5-a]pyridiny, [1,2,4]triazolo[4,3-a]pyridiny, isoindolyl, pyrrolo[2,3-b]pyridiny, pyrrolo[3,4-b]pyridiny, pyrrolo[3,2-b]pyridiny, imidazo[5,4-b]pyridiny, pyrrolo[1,2-a]pyrimidinyl, tetrahydropyrrolo[1,2-a]pyrimidinyl, 3,4-dihydro-2H-1 $\lambda^2$ -pyrrolo[2,1-b]pyrimidine, dibenzo[b,d]thiophene, pyridin-2-one, furo[3,2-c]pyridiny, furo[2,3-c]pyridiny, 1H-pyrido[3,4-b][1,4]thiazinyl, benzooxazolyl, benzoisoxazolyl, furo[2,3-b]pyridiny,

benzothiophenyl, 1,5-naphthyridinyl, furo[3,2-b]pyridine, [1,2,4]triazolo[1,5-a]pyridinyl, benzo [1,2,3]triazolyl, imidazo[1,2-a]pyrimidinyl, [1,2,4]triazolo[4,3-b]pyridazinyl, benzo[c][1,2,5]thiadiazolyl, benzo[c][1,2,5]oxadiazole, 1,3-dihydro-2H-benzo[d]imidazol-2-one, 3,4-dihydro-2H-pyrazolo[1,5-b][1,2]oxazinyl, 4,5,6,7-tetrahydropyrazolo[1,5-a]pyridinyl, thiazolo[5,4-d]thiazolyl, imidazo[2,1-b][1,3,4]thiadiazolyl, thieno[2,3-b]pyrrolyl, or 3H-indolyl. In some embodiments, A is selected from the group consisting of phenyl, naphthyl, pyridyl, benzofuranyl, pyrazinyl, pyridazinyl, pyrimidinyl, triazinyl, quinoline, benzoxazole, benzothiazole, 1H-benzimidazole, isoquinoline, quinazoline, quinoxaline, pyrrole, indole, biphenyl, pyrenyl, and anthracenyl. In some embodiments, A is phenyl. In some embodiments, A is an aryl or heteroaryl ring system as described in U.S. Patent No. 9,855,545, which is hereby incorporated by reference in its entirety.

**[0048]** The mesoporous polymeric material of the present disclosure comprises a plurality of cyclodextrins with a plurality of crosslinks comprising formula (I). The plurality of cyclodextrins of the present disclosure may be any cyclodextrin containing from six to twelve glucose units. For example, in some embodiments, the plurality of cyclodextrins of the present disclosure are selected from the group consisting of  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin,  $\gamma$ -cyclodextrin, and combinations thereof. In some embodiments, each cyclodextrin is a  $\beta$ -cyclodextrin.

**[0049]** The  $R^1$  groups of the plurality of crosslinks comprising formula (I) are independently selected from the group consisting of  $-CF_3$ ,  $-SO_3H$ ,  $-CN$ ,  $-C(O)-NH_2$ ,  $-N_2^+$ ,  $-NO_2$ ,  $-NO$ ,  $-NH-OH$ ,  $-N-C(O)-alkyl$ ,  $-halogen$ ,  $-N_3$ ,  $-CH_2-OH$ ,  $-CH_2-N_3$ ,  $-HC=O$ ,  $-C-NH-C(O)C-NH-$ ,  $-C-halogen$ ,  $-C-NH-C(O)-CO-alkyl$ ,  $-C-NH-C(O)-CO-aryl$ ,  $-C-NH-(SO_2)-aryl$ ,  $-C-NH-(SO_2)-alkyl$ ,  $-C=N-OH$ ,  $-C-NHC(O)-alkyl$ , and  $-NH-C(O)-NH_2$ . In certain embodiments, 0-8  $R^1$  groups are present on the plurality of crosslinks comprising formula (I). For example, 0, 1, 2, 3, 4, 5, 6, 7, or 8  $R^1$  groups are present on each of the individual crosslinks comprising formula (I). It is understood that any positions of A not substituted with  $R^1$ ,  $R^2$ ,  $-W-N(R^3)_2$  or  $-L-$  will be unsubstituted or have one or more H atoms as required to satisfy the valency of that position. As will be appreciated by a skilled artisan, the number of  $R^1$  groups on each of the individual crosslinks of formula (I) may vary throughout the mesoporous polymeric material of the present disclosure. For example, when  $R^1$  is  $-CN$  and the polymerized mesoporous material of the present invention is exposed to reducing conditions (as described herein), the  $-CN$  groups on some crosslinks will be reduced to  $-CH_2NH_2$ , whereas in other crosslinks, the  $-CN$  groups may be effectively shielded from the

reducing conditions and thus not react. Accordingly, a mesoporous polymeric material of the present disclosure may have multiple linking groups of formula (I) present, and each individual linking group may independently have 0-8 (e.g. 1, 2, or 3)  $R^1$  groups.

**[0050]** In some embodiments, the mesoporous polymeric material of the present disclosure may be characterized as having, on average, a fractional number of  $R^1$ ,  $R^2$ ,  $-W-N(R^3)_2$  or  $-L-$  groups in each crosslinking group. This fractional number of substituents can be calculated by dividing the total number of such groups by the total number of crosslinks in the mesoporous polymeric material. For example, if half of the crosslinking groups are functionalized with a  $-CH_2NH_2$  group (e.g., where W is a  $-CH_2-$  and  $N(R^3)_2$  is  $-NH_2$ ), then the average number (or fraction) of  $-CH_2NH_2$  groups corresponding to  $-W-N(R^3)_2$  per crosslinking group is 0.5. For  $R^1$ , the fractional number of such groups includes values of about 0, about 0.1, about 0.2, about 0.3, about 0.4, about 0.5, about 0.6, about 0.7, about 0.8, about 0.9, about 1.0, about 1.1, about 1.2, about 1.3, about 1.4, about 1.5, about 1.6, about 1.7, about 1.8, about 1.9, about 2.0, about 2.1, about 2.2, about 2.3, about 2.4, about 2.5, about 2.6, about 2.7, about 2.8, about 2.9, about 3.0, about 3.1, about 3.2, about 3.3, about 3.4, about 3.5, about 3.6, about 3.7, about 3.8, about 3.9, about 4.0, about 4.1, about 4.2, about 4.3, about 4.4, about 4.5, about 4.6, about 4.7, about 4.8, about 4.9, about 5.0, about 5.1, about 5.2, about 5.3, about 5.4, about 5.5, about 5.6, about 5.7, about 5.8, about 5.9, about 6.0, about 6.1, about 6.2, about 6.3, about 6.4, about 6.5, about 6.6, about 6.7, about 6.8, about 6.9, about 7.0, about 7.1, about 7.2, about 7.3, about 7.4, about 7.5, about 7.6, about 7.7, about 7.8, about 7.9, or about 8.0, inclusive of all ranges between any of these values. For  $R^2$ , the fractional number of such groups includes values of about 0, about 0.1, about 0.2, about 0.3, about 0.4, about 0.5, about 0.6, about 0.7, about 0.8, about 0.9, about 1.0, about 1.1, about 1.2, about 1.3, about 1.4, about 1.5, about 1.6, about 1.7, about 1.8, about 1.9, about 2.0, about 2.1, about 2.2, about 2.3, about 2.4, about 2.5, about 2.6, about 2.7, about 2.8, about 2.9, about 3.0, about 3.1, about 3.2, about 3.3, about 3.4, about 3.5, about 3.6, about 3.7, about 3.8, about 3.9, or about 4.0, inclusive of all ranges between any of these values. For  $-W-N(R^3)_2$ , the fractional number of such groups includes values of about 0.1, about 0.2, about 0.3, about 0.4, about 0.5, about 0.6, about 0.7, about 0.8, about 0.9, about 1.0, about 1.1, about 1.2, about 1.3, about 1.4, about 1.5, about 1.6, about 1.7, about 1.8, about 1.9, about 2.0, about 2.1, about 2.2, about 2.3, about 2.4, about 2.5, about 2.6, about 2.7, about 2.8, about 2.9, about 3.0, about 3.1, about 3.2, about 3.3, about 3.4, about 3.5, about 3.6, about 3.7, about 3.8, about 3.9, or about 4.0, inclusive of all ranges between any of these values. For  $-L-$ , the fractional number of such groups includes values of about

2.0, about 2.1, about 2.2, about 2.3, about 2.4, about 2.5, about 2.5, about 2.7, about 2.8, about 2.9, about 3.0, about 3.1, about 3.2, about 3.3, about 3.4, about 3.5, about 3.6, about 3.7, about 3.8, about 3.9, or about 4.0, inclusive of all ranges between any of these values.

**[0051]** Without being bound by any particular theory, in certain embodiments, the presence of  $R^1$  groups on the plurality of crosslinks comprising formula (I) are the result of incomplete reaction, such as the conversion of  $R^1$  to  $-W-NH_2$  (e.g. unreduced  $-CN$ ). Thus, the present disclosure provides mesoporous polymeric materials comprising a plurality of cyclodextrins with a plurality of cyclodextrins comprising formula (I), where the plurality of crosslinks comprising formula (I) have no  $R^1$  groups and the plurality of crosslinks comprising formula (I) have at least one  $R^1$  group. In certain embodiments,  $R^1$  is  $-CN$ .

**[0052]** The  $R^2$  groups are independently  $-OH$ ,  $-O$ -metal cation, alkyl,  $-SH$ ,  $-S$ -metal cation, or  $-S$ -alkyl. In some embodiments, each  $R^2$  is  $-OH$ . In some embodiments, each  $R^2$  is  $-O$ -metal cation. In some embodiments, each  $R^2$  is alkyl. In some embodiments, each  $R^2$  is  $-SH$ . In some embodiments, each  $R^2$  is  $-S$ -metal cation. In some embodiments, each  $R^2$  is  $-S$ -alkyl. In accordance with embodiments of the present disclosure, there may be 1, 2, 3, or 4  $R^2$  groups. For example, 0, 1, 2, 3, or 4  $R^2$  groups are present on the plurality of crosslinks comprising formula (I). As will be appreciated by a skilled artisan, the number of  $R^2$  groups on each of the individual plurality of linking groups comprising formula (I) may vary by each individual linking group throughout the mesoporous polymeric material of the present disclosure. Accordingly, a mesoporous polymeric material of the present disclosure may have multiple linking groups of formula (I) present, and each individual linking group may independently have e.g., 0, 1, 2, 3, or 4  $R^2$  groups. When there are more than one  $R^2$  groups on the plurality of linking groups of formula (I), the  $R^2$  groups may be the same or different. For example, in some embodiments, one or more  $R^2$  group is  $-O$ -metal cation and one or more  $R^2$  group is  $-OH$ .

**[0053]** Each  $R^3$  is independently  $-H$ ,  $C_1$ - $C_6$  alkyl,  $C_1$ - $C_3$  haloalkyl, aryl,  $-C(O)N(R^a)(R^b)$ ,  $-C(O)R^a$ ,  $-CO_2R^a$ ,  $-SO_2N(R^a)(R^b)$ , or  $-SOR^a$ , wherein each  $R^a$  and  $R^b$  is independently  $H$ , or  $C_1$ - $C_6$  alkyl. In some embodiments, each  $R^3$  is  $H$ .

**[0054]** In some embodiments, one or more of the  $-W-N(R^3)_2$  groups may exist as an ammonium salt (e.g.  $-W-NH(R^3)_2^+$ ), for example by addition of an acid addition salt or upon contact with an aqueous solution having an acidic pH. In some embodiments, one or more of the  $-W-N(R^3)_2$  groups, taken as a whole are  $-CH_2-NH_2$ . In some embodiments, one or more of the  $-W-N(R^3)_2$  groups, taken as a whole are  $-CH_2-NH_3^+$ .

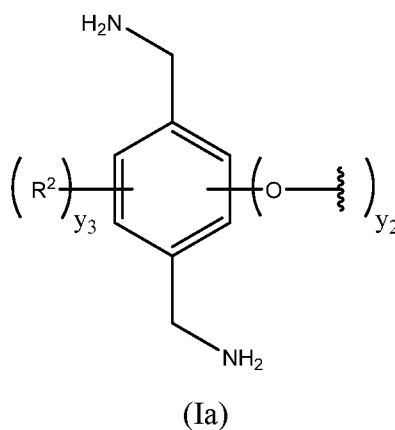
[0055] In certain embodiments, x is 0-3. For example, x may be 0, 1, 2, or 3. In some embodiments, x is 1 and R<sup>1</sup> is –CN.

[0056] In certain embodiments, y<sub>1</sub> is 1-4. For example, y<sub>1</sub> may be 1, 2, 3, or 4. In some embodiments, y<sub>1</sub> is 1-2.

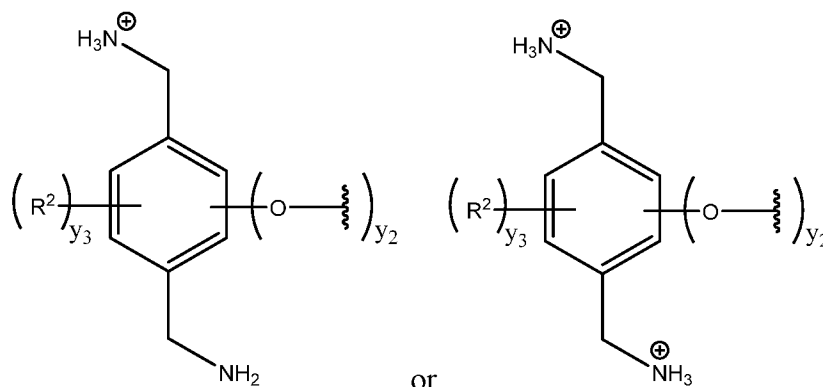
5 [0057] In certain embodiments, y<sub>2</sub> is at least 2. For example, y<sub>2</sub> may be 2, 3, or 4. In some embodiments, y<sub>2</sub> is 2-3.

[0058] In certain embodiments, y<sub>3</sub> is 1-4. For example, y<sub>3</sub> may be 1, 2, 3, or 4. In some embodiments, y<sub>3</sub> is 1-2.

[0059] In certain embodiments, the present disclosure provides a mesoporous  
10 polymeric material comprising a plurality of cyclodextrins crosslinked with a plurality of linking groups of formula (Ia):



15 wherein the plurality of cyclodextrins and the plurality of linking groups of formula (Ia) are present in approximately equimolar amounts. In some embodiments, one or both of the –CH<sub>2</sub>–NH<sub>2</sub> moieties on linking groups of formula (Ia) may exist as an ammonium salt (i.e. –CH<sub>2</sub>–NH<sub>3</sub><sup>+</sup>), for example by addition of an acid addition salt or upon contact with an aqueous solution having an acidic pH. Accordingly, the linking group of formula (Ia) may have one



of the following structures

20 [0060] In certain embodiments, the mesoporous polymeric material comprises a plurality of cyclodextrins crosslinked with a plurality of linking groups of formula (Ia), the

plurality of cyclodextrins and crosslinking groups of formula (Ia) are present in approximately equimolar amounts, and  $y_2$  and  $y_3$  are each about 2. In certain embodiments,  $R^1$  is fluoro. In certain embodiments, each cyclodextrin is  $\beta$ -cyclodextrin.

**[0061]** In certain embodiments, the molar ratio of cyclodextrin to linking groups of formula (I) or formula (Ia) ranges from about 1:1 to about 1:X, wherein X is three times the average number of glucose subunits in the cyclodextrin. In certain embodiments, the molar ratio of cyclodextrin to linking groups of formula (I) or formula (Ia) is about 1:6. In certain embodiments, the molar ratio of cyclodextrin to linking groups of formula (I) or formula (Ia) is about 1:5. In certain embodiments, the molar ratio of cyclodextrin to linking groups of formula (I) or formula (Ia) is about 1:4. In certain embodiments, the molar ratio of cyclodextrin to linking groups of formula (I) or formula (Ia) is about 1:3. In certain embodiments, the molar ratio of cyclodextrin to linking groups of formula (I) or formula (Ia) is about 1:2. In various embodiments, the molar ratio of cyclodextrin moieties to aryl crosslinking moieties is about 1:1 to about 1:24, including about 1:1, about 1:1.5, about 1:2, about 1:2.5, about 1:3, about 1:3.5, about 1:4, about 1:4.5, about 1:5, about 1:5.5, about 1:6, about 1:6.5, about 1:7, about 1:7.5, about 1:8, about 1:8.5, about 1:9, about 1:9.5, about 1:10, about 1:10.5, about 1:11, about 1:11.5, about 1:12, about 1:12.5, about 1:13, about 1:13.5, about 1:14, about 1:14.5, about 1:15, about 1:15.5, about 1:16, about 1:16.5, about 1:17, about 1:17.5, about 1:18, about 1:18.5, about 1:19, about 1:19.5, about 1:20, about 1:20.5, about 1:21, about 1:21.5, about 1:22, about 1:22.5, about 1:23, about 1:23.5, or about 1:24, including all ranges of ratios therebetween. In an embodiment, the molar ratio of cyclodextrin moieties to aryl crosslinking moieties is about 1:2.5 to about 1:10.

**[0062]** In any of the embodiments of the present disclosure, the mesoporous polymeric material comprising a plurality of cyclodextrins crosslinked with a plurality of linking groups comprising formula (I) or formula (Ia) may have a net cationic charge. For example, the mesoporous polymeric material comprising a plurality of cyclodextrins crosslinked with a plurality of linking groups comprising formula (I) or formula (Ia) may e.g. be reacted with an acid addition salt, such that at least one of the amines of the linking groups of formula (I) or formula (Ia) form a quaternary ammonium salt. For example, the mesoporous polymeric material comprising a plurality of cyclodextrins crosslinked with a plurality of linking groups comprising formula (I) or formula (Ia) may e.g. be added to a water source having an acidic pH, such that at least one of the amines of the linking groups of formula (I) or formula (Ia) form a quaternary ammonium salt. Without being bound by any particular theory, the mesoporous polymeric materials having a net cationic charge (e.g.

via one or more quaternary ammonium salts) will display a higher affinity for anionic micropollutants.

### Supported Materials

**[0063]** In some embodiments, a composition according to the present disclosure

5 comprises one or more porous polymeric material and one or more support materials, where the porous polymeric material is bound (e.g., covalently, adhesively, or mechanically bonded as described herein) to the support material. Examples of support materials include cellulose (e.g., cellulose fibers), carbon-based materials such as activated carbon, graphene oxide, and oxidized carbon materials, silica, alumina, natural or synthetic polymers, and natural or  
10 synthetic polymers modified to include surface hydroxyl groups. One of skill in the art will recognize that any material with mechanical or other properties suitable to act as a support, which can covalently bond to the porous polymeric material, or can serve as a suitable support material if the porous polymeric material is adhesively bonded to the support via a suitable binder material. In an embodiment, the composition is in the form a membrane or a  
15 column packing material. In an embodiment, the support is a fiber (e.g., a cellulose, nylon, polyolefin or polyester fiber). In an embodiment, the support is a porous particulate material (e.g., porous silica and porous alumina). In an embodiment, the support is a woven or non-woven fabric. In an embodiment, the support is a garment (such as a protective garment) or a surgical or medical drape, dressing, or sanitary article.

20 **[0064]** In some embodiments, the P-CDP may be grafted or bonded (e.g., chemically or mechanically bonded) onto a support to provide an adsorbent where the particle size and morphology are well-controlled to give ideal flow characteristics. The term "mechanical bond" refers to a bond formed between two materials by pressure, ultrasonic attachment, and/or other mechanical bonding process without the intentional application of heat, such as  
25 mechanical entanglement. The physical entanglement and wrapping of microfibrils to hold in place micron-sized particulate matter is a prime example of a mechanical bond. The term mechanical bond does not comprise a bond formed using an adhesive or chemical grafting. In some embodiments, the P-CDP may be grafted or bonded (e.g., chemically or mechanically bonded) onto a support to provide an adsorbent where the particle size and  
30 morphology are further engineered (e.g., by granulation or milling) to provide particles with a well-controlled size and morphology to give ideal flow characteristics.

**[0065]** The P-CDP-support complex may be prepared by a variety of methods, including conventional grafting methods. As used herein, the term "grafting" refers to

covalently attaching P-CDPs to a substrate surface through coupling reactions between one or more functional groups on the P-CDP and one or more functional groups on the substrate. In some embodiments, grafting includes an “in situ” process as described herein in which cyclodextrins, linking groups of the present disclosure, and a substrate having surface bound nucleophiles (e.g., hydroxyls) are reacted together such that the linking groups of the present disclosure reacts with the hydroxyl groups of the cyclodextrins and the surface nucleophiles of the substrate, forming a P-CDP which is partially bonded via one or more linking groups of the present disclosure to the substrate. The substrate having surface bound nucleophiles include, but are not limited to hydroxyls (such as microcrystalline cellulose), amines, phosphines, and thiols.

**[0066]** In some embodiments, “grafted” P-CDP-support complexes are prepared by first synthesizing the P-CDPs in a dedicated chemical reactor with adequate control of the reaction conditions and material purification to produce optimized P-CDP particles. The P-CDPs are then chemically reacted with a suitably functionalized substrate. For example, a substrate functionalized with carboxylic acid groups (or activated forms thereof such as acid halides, anhydrides, etc. known in the art) can react with one of more hydroxyls on the P-CDP to form an ester bond with the substrate. Alternatively, the P-CDP can be appropriately functionalized (e.g., by selection of a functionalized cyclodextrin as described herein) or by a subsequent modification of the P-CDP such that it can react with suitable functional groups on the substrate. Any suitable reaction chemistries can be contemplated, such as reactions between carboxylic acids (and derivatives thereof) and hydroxyls to form ester bonds, reactions between carboxylic acids (and derivatives thereof) and amine groups to form amide bonds, reactions between isocyanates and alcohols to make urethanes, reactions between isocyanates and amines to make ureas, reactions between cyclic carbonates and amines to make urethanes, reactions between thiols and alkenes or alkynes to make thioethers, reactions between epoxides and amine groups, photochemical reactions between acrylates, methacrylates, thiols etc. and olefins, and so forth. The reactive functional groups described herein can be on either of the P-CDP or substrate provided the reaction forms a covalent bond between the substrate and the P-CDP. For example, of the reactive functional groups are hydroxyls and carboxylic acids (forming an ester bond after reaction), the hydroxyl groups can be present on the P-CDP and the carboxyl groups on the substrate or vice-versa.

**[0067]** In other embodiments, the substrate can be coated with a “primer” having reactive functional groups as described above. The primer adheres to the surface of the

substrate, and under suitable conditions can react with a suitably functionalized P-CDP to form a covalent bond between the P-CDP and the primer.

**[0068]** The P-CDP particles may be engineered to achieve specific particle sizes. In some embodiments, the P-CDP is produced in the form of crosslinked particles which may require further reduction in size (e.g., for the purposes of forming stable dispersions or slurries, or in providing optimal flow characteristics). A variety of means that are readily apparent to a skilled artisan can be employed to reduce the particle size of the P-CDP such as grinding or milling. Grinding and milling can be employed to create smaller particles with sizes less than 1 micron. Typical milling operations can be used by a skilled artisan and include both wet and dry milling. Milling can be employed through a variety of methods including, but not limited to: ball mill, autogeneous mill, SAG mill, pebble mill, rod mill, Buhrstone mill, tower mill, vertical shaft impactor mill, and the like. Milling media includes, but is not limited to: metals, silicates, and other inorganic materials in various form factors including, rods, balls, and irregular shapes. In some embodiments, the milling is performed on dry P-CDP powder material in a dry process to produce a finer dry powder or on wet aqueous slurries of the P-CDP powder with or without emulsifying agents to produce a finer particulate dispersion. Emulsifying agents may be used and are readily apparent to a skilled artisan, including, but not limited to: small molecule and polymeric surfactant compounds with nonionic, anionic, or cationic character. A skilled artisan will appreciate that using fine particulate form factors will enable a variety of benefits, such as (1) more stable aqueous dispersions that remain homogeneous over time by resisting separation, (2) enable a high loading of material by weight in the dispersion with values of 50% by weight or higher, (3) produce particulate matter that can be evenly coated or applied to various substrates, surfaces, fibers, yarns, fabrics and the like to produce a finished material with minimal perceptible changes in “hand,” and (4) produce dispersions that are stable to dilution and blending with other emulsions or solutions such as binders, surfactants, wetting agents, or softeners. In some embodiments, the final particle diameter includes <1 micron, 1-5 micron, 5-10 micron, 10-15 micron, and 15-20 micron, or ranges therebetween.

**[0069]** If larger particle sizes are desired, the composition may be granulated to form agglomerates of larger particle size. Thus, in some embodiments, granules (e.g., self-supporting granules) are produced from P-CDP particle powders of various sizes. Broadly, this process will transform P-CDP particle powders in the size regimes ranging from 1-30 microns to granules in excess of 100 microns, 200 microns, 300 microns, and larger. This process may be achieved via granulation techniques common to the pharmaceutical industry

(*Handbook of Granulation Technology*, Ed. Parikh, D. M., 2005, Taylor & Francis Group) in which the powders are bound together via physical and/or chemical means in batch or continuous modes. In the simplest form, particles of the P-CDP are blended mechanically with a fluid (e.g., aqueous) mixture containing an adhesive binder – typically a synthetic, semi-synthetic, or natural polymer. Suitable semi-synthetic polymers that can be used include cellulose ethers, specifically ethylcellulose, methylcellulose, hydroxypropylcellulose, carboxymethylcellulose, starch and starch derivatives, and others. Suitable fully synthetic polymers such as polyvinylpyrrolidone or polyethylene glycol can be used. Other suitable binders include sizes and other coatings used in the textile industry and paper industries including polyamide amine epichlorohydrin (PAE) or polymeric glyoxal crosslinkers, polyvinylalcohol, and starch-based sizes. In order to create robust granules which are resistant to dissolution in water or other solvents, further covalent crosslinking may be facilitated via the addition of small molecule crosslinkers such as glyoxal, formaldehyde, diisocyanate, and/or diepoxide functionalities. In addition to covalent crosslinking, electrostatic agglomeration of polyelectrolytes can also be utilized as a binding motif in which cationic polyelectrolytes form suitable adhesive properties when blended with anionic polyelectrolytes in the presence of P-CDP powders and/or support structures. Polycations can comprise those commonly used for flocculation including, but not limited to polydiallyldimethylammonium chloride (polyDADMAC), acidic polyethyleneimine, and polyacrylamides. Polyanions can comprise those commonly used for flocculation including, but not limited to sodium polyacrylate, sodium polystyrene sulfonate, and polyvinylsulfonate.

**[0070]** Mechanical blending during the granulation may be achieved via low shear processes such as rotary drum mixing or overhead mechanical stirring. As will be readily apparent to a skilled artisan, the stirring rate and total length of stirring time effects the granule size. Granulation may also be conducted in fluidized beds or via spray drying techniques. In each case, the P-CDP particle are combined with the aqueous or solvent borne mixture containing the binder compounds and the mechanical or physical agitation is conducted at a specified shear for a determined number of cycles. The resultant particles will display a step growth change in their average diameters and can also display a changed polydispersity. The physical properties of these granules depend on the binder selected, the crosslinking chemistry, and the physical process used in their granulation. These larger granular particles will be suitable for packed bed column filtration commonly employed for water filtration and industrial separations.

**[0071]** In some embodiments, the present disclosure provides a stable aqueous dispersion comprising P-CDP particles. In some embodiments, the P-CDP particles of the present disclosure, which can be used in such stable aqueous dispersions are from about 1  $\mu\text{m}$  to about 150  $\mu\text{m}$ . For example, the P-CDP particles are from about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, to about 150  $\mu\text{m}$ . A stable aqueous dispersion may be used in “grafting” applications. For example, the stable aqueous dispersion may be used in applications with chemical binders or fibrillating fibers for mechanical loading and binding, and incorporation into thermally-bonded particulate pressed forms and into solution processed polymer form factors.

**[0072]** The P-CDP materials of the present disclosure can also be prepared on a support material (alternatively termed a “substrate”), for example covalently bonded, adhesively bonded, or mechanically attached to a support such as a fibrous substrate. The support material can be any material that has one or more groups (e.g., hydroxyl or amino, thiol, or phosphine, or other group as described herein) that can form an interaction (e.g., a covalent or mechanical bond) with a crosslinking agent or cyclodextrin. For example, one end of a crosslinking agent (e.g., the linking groups of Formulas (I), (Ia), or (II)) is covalently bound to the substrate material and another end of the crosslinking agent is covalently bound to a cyclodextrin glucose unit or a reactive center on modified cyclodextrin (such as an acid halide or activated ester bound to the cyclodextrin). It is desirable that the support material not dissolve (e.g., to an observable extent by, for example, visual inspection, gravimetric methods, or spectroscopic methods) under use conditions, for example in aqueous media. Examples of support materials include, but are not limited to, microcrystalline cellulose, cellulose nanocrystals, polymer materials (e.g., acrylate materials, methacrylate materials, styrenic materials (e.g., polystyrene), polyester materials, nylon materials, and combinations thereof or inorganic materials (e.g., silicates, silicones, metal oxides such as alumina, titania, zirconia, and hafnia, and combinations thereof). In various examples, the polymer materials are homopolymers, copolymers, or resins (e.g., resins comprising polymeric materials). The support material may be hydroxyl or amino containing polymer beads or irregular particles.

The support material can be in the form a fiber (e.g., pulps, short cut, staple fibers, and continuous filaments), fiber bundles (e.g., yarn – both spun and continuous filament), fiber mats (e.g., nonwovens – both staple and continuous filament), fabrics (e.g., knits, woven, nonwovens), membranes (e.g., films, spiral wound, and hollow fibers, cloth, particulate (e.g., a powder), or a solid surface. In some embodiments, the fibrous substrate is a cellulosic substrate. Cellulosic substrates can comprise any suitable form of cellulose, such as cellulose derived from plant sources such as wood pulp (e.g., paper or paper fibers), cotton, regenerated cellulose, modified cellulose esters and/or ethers, and the like, starch, polyvinylalcohols and derivatives thereof. The cellulosic substrate can be in the form of a fabric, such as a woven or nonwoven fabric, or as fibers, films, or any other suitable shape, particularly shapes that provide high surface area or porosity. In a particular embodiment, the P-CDP materials of the present disclosure are bonded to fibers, for example, a cellulosic fiber or a fabric, such as cotton.

**[0073]** In addition to the substrates listed in the preceding paragraph, the substrate may include any of the following: polyvinylamine, polyethylenimine, proteins, protein-based fibers (e.g., wool), chitosan and amine-bearing cellulose derivatives, polyamide, vinyl chloride, vinyl acetate, polyurethane, melamine, polyimide, polystyrene, polyacryl, polyamide, acrylate butadiene styrene (ABS), Barnox, PVC, nylon, EVA, PET, cellulose nitrate, cellulose acetate, mixed cellulose ester, polysulfone, polyether sulfone, polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PFTE or Teflon R.), polyethylene, polypropylene, polycarbonate, phosphine or thiol functional materials, and silicone or combinations thereof. The substrate may also consist of silicon or silicon oxide, or glass (e.g. as microfibrils). Suitable materials further include textiles or synthetic or natural fiber-based materials. The material may exhibit any form or shape and may for instance be in the form of a sheet, bead, granule, rod, fiber, foam or tube, and may be rigid, flexible or elastic.

**[0074]** If necessary, the material surface may be activated by any method known in the art, such as known surface activation techniques, including for instance corona treatment, oxygen plasma, argon plasma, selective plasma bromination, chemical grafting, allyl chemistry, chemical vapour deposition (CVD) of reactive groups, plasma activation, sputter coating, etching, or any other known technique. For instance in the case of a glass surface, such an activation is usually not required as such a surface is herein considered already activated. The purpose of the activation of the surface is to provide for a surface suitable for the covalent attachment of a surface-modifying functionality or (directly) of a primer

polymer. Following its optional activation, the surface may be further functionalized. The purpose of the functionalization of the surface is to provide for functional group suitable for the covalent attachment of a pre-coat polymer.

[0075] The skilled artisan is well aware of the various possibilities of attaching polymers to optionally activated surfaces. These techniques generally involve the introduction of amino-, silane-, thiol-, hydroxyl- and/or epoxy-functionalities to the surface, and the subsequent attachment thereto of the polymer.

[0076] The functionalization may also comprise the introduction of spacers or linker to the surface for the attachment of the primer polymer to the surface at a predetermined distance. A suitable spacer is for instance an alkylation by reacting the surface with for instance aminoalkylsilane.

[0077] The P-CDP may be bound to the substrate via the linking groups of the present disclosure (e.g. via an amino group of the linking group). A “linker moiety” refers to the intervening atoms between the P-CDP and substrate. The terms “linker” and “linking moiety” herein refer to any moiety that connects the substrate and P-CDP to one another. The linking moiety can be a covalent bond or a chemical functional group that directly connects the P-CDP to the substrate. The linking moiety can contain a series of covalently bonded atoms and their substituents which are collectively referred to as a linking group. In some embodiments, linking moieties are characterized by a first covalent bond or a chemical functional group that bonds the P-CDP to a first end of the linker group and a second covalent bond or chemical functional group that bonds the second end of the linker group to the substrate. The first and second functionality, which independently may or may not be present, and the linker group are collectively referred to as the linker moiety. The linker moiety is defined by the linking group, the first functionality if present and the second functionality if present. In certain embodiments, the linker moiety contains atoms interposed between the P-CDP and substrate, independent of the source of these atoms and the reaction sequence used to synthesize the conjugate. In some embodiments, the linker moiety is an aryl moiety as described herein. In some embodiments, the linker has one or more of the following functionalities:

multifunctional isocyanate (e.g., a diisocyanate), epoxy, carboxylic acid, ester, activated ester, cyanuric chloride, cyanuric acid, acid chloride, halogen, hydroxyl, amino, thiol, and phosphine.

[0078] In some embodiments, the P-CDP is grafted or bonded onto microcrystalline cellulose (CMC). CMC is available in a variety of median particles sizes from about 10 – about 500  $\mu\text{m}$  including about 10  $\mu\text{m}$ , 20  $\mu\text{m}$ , 45  $\mu\text{m}$ , 50  $\mu\text{m}$ , 65  $\mu\text{m}$ , 75  $\mu\text{m}$ , 100  $\mu\text{m}$ , 150

μm, 180 μm, 190 μm, 200 μm, 225 μm, 250 μm, 275 μm, 300 μm, 325 μm, 350 μm, 375 μm, 400 μm, 425 μm, 450 μm, 475 μm, and about 500 μm and all particle sizes

therebetween. In some embodiments, P-CDP is grafted or bonded onto CMC having a median particle size of about 50 μm. In one example, CMC is commercialized as Avicel™.

- 5 In other embodiments, the P-CDP is grafted or bonded onto a polymeric substrate other than cellulose, as described herein, in which the surface is treated to produce surface functional groups as disclosed herein, such as hydroxyl groups.

**[0079]** In some embodiments, the P-CDP-substrate complex (e.g., a P-CDP crosslinked with an aryl linker of formula (Ia)-CMC substrate complex) has a polymer thickness (i.e., the thickness of the porous P-CDP particles on the surface of the substrate) of between about 1 nm to about 2000 nm. For example, P-CDP-substrate complex has a polymer thickness of about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350, 1400, 1450, 1500, 1550, 1600, 1650, 1700, 1750, 1800, 1850, 1900, 1950, to about 2000 nm. In some embodiments, P-CDP-substrate complex has a polymer thickness of less than 1000 nm. In some embodiments, P-CDP-substrate complex as a polymer thickness of about 800 nm. As will be readily apparent to a skilled artisan, a having a lower thickness (e.g., less than 1000 nm) will allow for faster kinetics to absorb contaminants, for example aqueous contaminants.

20 **[0080]** In some embodiments, the P-CDP-substrate complex (e.g., a P-CDP crosslinked with an aryl linker of formula (Ia)-CMC substrate complex) has a contaminant adsorption capacity of up to 500 mg contaminant/g CD. For example, the adsorption capacity may be up to about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 25 175, 180, 185, 190, 195, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, to about 500 mg contaminant/g CD. In some embodiments, the adsorption capacity is up to about 200 mg contaminant/g CD. In some embodiments, the contaminant is an anionic micropollutant (e.g. PFASs). In some embodiments, the cyclodextrin is β-cyclodextrin. In some embodiments, the linking groups are the linking groups of Formulas (I), (Ia), or (II).

30 **[0081]** In some embodiments, the P-CDP-substrate complex (e.g., a P-CDP crosslinked with an aryl linker of formula (Ia)-CMC substrate complex) has an equilibrium contaminant adsorption capacity of up to 500 mg contaminant/g CD. For example, the

equilibrium adsorption capacity may be up to about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, to about 500 mg contaminant/g CD. In some embodiments, the equilibrium adsorption capacity is up to about 200 mg contaminant/g CD. In some embodiments, the contaminant is an anionic micropollutant (e.g. PFASs). In some embodiments, the cyclodextrin is  $\beta$ -cyclodextrin. In some embodiments, the linking groups are the linking groups of Formulas (I), (Ia), or (II).

**[0082]** In some embodiments, the P-CDP-substrate complex (e.g., a P-CDP crosslinked with an aryl linker of formula (Ia)-CMC substrate complex) has a relaxation time of less than 2 minutes. In some embodiments, the P-CDP-substrate complex has a relaxation time of about  $0.99 \pm 0.03$  s. As will be appreciated by a skilled artisan, where processes with high relaxation times slowly reach equilibrium, while processes with small relaxation times adapt to equilibrium quickly. In some embodiments, the contaminant is an anionic micropollutant (e.g. PFASs). In some embodiments, the cyclodextrin is  $\beta$ -cyclodextrin. In some embodiments, the linking groups are the linking groups of Formulas (I), (Ia), or (II).

#### Microcrystalline Cellulose Supports

**[0083]** In some embodiments, any of the P-CDP materials disclosed herein are grafted or bonded onto CMC directly or via a linker group as defined herein. In some embodiments, the P-CDP is homogeneously distributed on the CMC surface. In some embodiments, the aryl linker is an aryl linker of formula (Ia). In some embodiments, the aryl linker is a linking groups of Formula (II), and the nitrile groups are either partially or fully converted to amines (e.g. via a reduction) to yield a linking group of Formula (I) or Formula (Ia). In some embodiments, the median particle size is about 50  $\mu\text{m}$ . In other embodiments, the median particle size is from about 1 – about 250  $\mu\text{m}$ .

**[0084]** CMC can also be distinguished by a particle shape known to impact flow characteristics among other things. A non-limiting list of particle shapes includes spherical (round-shaped), rod-shaped, and needle-like. Particles can also be described as flat, flat and elongated, or be characterized by their aspect ratio. In some embodiments, the CMC has a spherical particle shape. In some embodiments, the CMC is present in the form of agglomerates of smaller CMC particles. Such CMC agglomerates can have particle sizes in the range of 200  $\mu\text{m}$  up to about 2 mm. For example, the particle sizes of CMC agglomerates

can be about 200  $\mu\text{m}$ , about 300  $\mu\text{m}$ , about 400  $\mu\text{m}$ , about 500  $\mu\text{m}$ , about 600  $\mu\text{m}$ , about 700  $\mu\text{m}$ , about 800  $\mu\text{m}$ , about 900  $\mu\text{m}$ , about 1 mm, about 1.2 mm, about 1.3 mm, about 1.4 mm, about 1.5 mm, about 1.6 mm, about 1.7 mm, about 1.8 mm, about 1.9 mm, or about 2 mm, inclusive of all ranges therebetween.

5 **[0085]** In some embodiments, the P-CDP is grafted or bonded onto CMC via a linking groups of Formula (I). In some embodiments, the P-CDP is grafted or bonded onto CMC via a linking groups of Formula (Ia). In some embodiments, the P-CDP is grafted or bonded onto CMC via a linking groups of Formula (II), and the nitrile groups are either partially or fully converted to amines (e.g. via a reduction) to yield a linking group of  
10 Formula (I) or Formula (Ia).

**[0086]** In some embodiments, P-CDP of the present disclosure is grafted or bonded onto CMC via an aryl linker, and the aryl linker is homogenously distributed on the CMC crystal. In some embodiments, the aryl linker is TFN and the nitrile groups are either partially or fully converted to amines (e.g. via a reduction) to yield a linking group of  
15 Formula (I) or Formula (Ia). In some embodiments, the median particle size is about 100 nm.

**[0087]** In addition to the use of CMC as illustrated herein, examples of other potential support materials include those materials described above, such as activated carbon, graphene oxide, as well as silica and alumina.

**[0088]** In some embodiments, it is desirable that the supported P-CDP materials  
20 disclosed herein (e.g., a P-CDP crosslinked with an aryl linker of formula (Ia)-CMC substrate complex) are in the form of particles having a narrow dispersity of particle sizes. In some embodiments, the particle size distribution has a low relative span of about 5 or less, where relative span is defined by the ratio  $(D_{90}-D_{10})/D_{50}$ , where  $D_{90}$ ,  $D_{50}$ , and  $D_{10}$  are, respectively the diameters at which 90%, 50%, and 10% of the particles in the distribution have a smaller  
25 diameter. Suitable spans are no more than 5, 4.5, 4, 3.5, 3, 2.5, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1, including all ranges therebetween.

#### Cellulose Nanocrystal Substrates

**[0089]** In other various embodiments, the P-CDP may be grafted or bonded onto  
30 cellulose nanocrystals (CNCs). CNCs are the crystalline regions of cellulose microfibrils obtained after mechanical, chemical, and enzyme treatments. Depending on the source and preparation method, CNCs are available with lengths ranging from about 1-1000 nm and widths ranging from about 3-50 nm, inclusive of all values therebetween. For example, the

CNCs have a length of about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, to about 1000 nm. The CNCs have a width of about 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, or about 50. In some embodiments, the P-CDP-CNC substrates may be 2-3 times the size (length and width) as the unbound CNCs. The CNCs are further characterized by aspect ratio values (L/D) ranging from about 2-100 (George, J., et al., Cellulose nanocrystals: synthesis, functional properties, and applications. *Nanotechnology, Science and Applications*. 2015;8:45-54). For example, the CNCs have an aspect ratio of about 2, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, or 100.

**[0090]** In some embodiments, the P-CDP is grafted or bonded onto CNC via the linking groups are the linking groups of Formulas (I), (Ia), or (II) as described herein. In some embodiments, the P-CDP is grafted or bonded onto CMC via a linking groups of Formula (I). In some embodiments, the P-CDP is grafted or bonded onto CMC via a linking groups of Formula (Ia). In some embodiments, the P-CDP is grafted or bonded onto CMC via a linking groups of Formula (II), and the nitrile groups are either partially or fully converted to amines (e.g. via a reduction) to yield a linking group of Formula (I) or Formula (Ia).

**[0091]** In some embodiments, P-CDP is grafted or bonded onto CNC via a linker, and the linker is homogenously distributed on the CNC crystal. In some embodiments, the linker is TFN. In some embodiments, the linker is TFN and the TFN nitriles are subsequently reduced (partially or fully) to their corresponding amines (e.g. via a borane reduction). In some embodiments, the median particle size is about 100 nm.

**[0092]** CNC can also be distinguished by particle shape known to impact flow characteristics among other things. A non-limiting list of particle shapes includes spherical (round-shaped), rod-shaped, and needle-like. Particles can also be described as flat, flat and elongated, or be characterized by their aspect ratio. In some embodiments, the CNC has an aspect ratio of between about 5 to about 100. For examples, the aspect ratio may be about 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 to about 100. In some embodiments, the CNC aspect ratio is about 20-25. In some embodiments, the CNCs are needle-like. In some embodiments, the CNC is present in the form of agglomerates of smaller CNC particles. Such CNC agglomerates can have particle sizes which are 5-100

times larger than the sizes of the individual particles, depending on the sizes and number of the particles constituting the aggregates.

#### Fabric and Fiber Substrates

5   **[0093]**        In some embodiments, the substrate is a fabric or fiber. Thus, in some embodiments, the present disclosure provides a composition comprising a P-CDP grafted or bonded (e.g., chemically or mechanically) to a fiber. In some embodiments, the P-CDP is grafted or bonded onto a fiber via the linker of formulas (I), (Ia), or (II), as described herein. In some embodiments, the fiber is a nonwoven fiber. In some embodiments, the present  
10    disclosure provides a composition comprising a P-CDP grafted or bonded (e.g., chemically, adhesively, or mechanically) to a fabric. In some embodiments, the P-CDP is grafted or bonded onto a fabric via the linker of formulas (I), (Ia), or (II).

**[0094]**        Fibers suitable for use include, but are not limited to fibers comprising any of the polymers disclosed herein, for example fibers made from highly oriented polymers, such  
15    as gel-spun ultrahigh molecular weight polyethylene fibers (e.g., SPECTRA® fibers from Honeywell Advanced Fibers of Morristown, N.J. and DYNEMA® fibers from DSM High Performance Fibers Co. of the Netherlands), melt-spun polyethylene fibers (e.g., CERTRAN® fibers from Celanese Fibers of Charlotte, N.C.), melt-spun nylon fibers (e.g., high tenacity type nylon 6,6 fibers from Invista of Wichita, Kans.), melt-spun polyester fibers  
20    (e.g., high tenacity type polyethylene terephthalate fibers from Invista of Wichita, Kans.), and sintered polyethylene fibers (e.g., TENSYLON® fibers from ITS of Charlotte, N.C.). Suitable fibers also include those made from rigid-rod polymers, such as lyotropic rigid-rod polymers, heterocyclic rigid-rod polymers, and thermotropic liquid-crystalline polymers. Suitable fibers also include those made from regenerated cellulose including reactive wet  
25    spun viscose rayon (Viscose from Birla of India or Lenzing of Austria), cuproammonium based rayon (Cupro® Bemberg from Asahi Kasei of Japan), or air gap spun from NMMO solvent (Tencel® from Lenzing of Austria). Suitable fibers made from lyotropic rigid-rod polymers include aramid fibers, such as poly(p-phenyleneterephthalamide) fibers (e.g., KEVLAR® fibers from DuPont of Wilmington, Del. and TWARON® fibers from Teijin of  
30    Japan) and fibers made from a 1:1 copolyterephthalamide of 3,4'-diaminodiphenylether and p-phenylenediamine (e.g., TECHNORA® fibers from Teijin of Japan). Suitable fibers made from heterocyclic rigid-rod polymers, such as p-phenylene heterocyclics, include poly(p-phenylene-2,6-benzobisoxazole) fibers (PBO fibers) (e.g., ZYLON® fibers from Toyobo of

Japan), poly(p-phenylene-2,6-benzobisthiazole) fibers (PBZT fibers), and poly[2,6-diimidazo[4,5-b:4',5'-e]pyridinylene-1,4-(2,5-dihydroxy)phenylene] fibers (PIPD fibers) (e.g., M5® fibers from DuPont of Wilmington, Del.). Suitable fibers made from thermotropic liquid-crystalline polymers include poly(6-hydroxy-2-naphthoic acid-co-4-hydroxybenzoic acid) fibers (e.g., VECTRAN® fibers from Celanese of Charlotte, N.C.). Suitable fibers also include carbon fibers, such as those made from the high temperature pyrolysis of rayon, polyacrylonitrile (e.g., OPF® fibers from Dow of Midland, Mich.), and mesomorphic hydrocarbon tar (e.g., THORNEL® fibers from Cytec of Greenville, S.C.). In certain possibly preferred embodiments, the yarns or fibers of the textile layers comprise fibers selected from the group consisting of gel-spun ultrahigh molecular weight polyethylene fibers, melt-spun polyethylene fibers, melt-spun nylon fibers, melt-spun polyester fibers, sintered polyethylene fibers, aramid fibers, PBO fibers, PBZT fibers, PIPD fibers, poly(6-hydroxy-2-naphthoic acid-co-4-hydroxybenzoic acid) fibers, carbon fibers, and combinations thereof.

**[0095]** The P-CDP materials of the present disclosure can be adhered to such fibers by means of a suitable binder polymer as described herein, or chemically bonded to such fibers by functionalizing the surface of the fibers as described herein (e.g., surface oxidation to produce surface hydroxyl groups) and either forming the P-CDP in situ on the fiber surface, or by reacting a suitably functionalized P-CDP directly with the functionalized fiber surface, or indirectly via a linker moiety as described herein.

**[0096]** The fibers may be converted to nonwovens (either before or after attachment of the P-CDP) by different bonding methods. Continuous fibers can be formed into a web using industry standard spunbond type technologies while staple fibers can be formed into a web using industry standard carding, airlaid, or wetlaid technologies. Typical bonding methods include: calendar (pressure and heat), thru-air heat, mechanical entanglement, hydrodynamic entanglement, needle punching, and chemical bonding and/or resin bonding. The calendar, thru-air heat, and chemical bonding are the preferred bonding methods for the starch polymer fibers. Thermally bondable fibers are required for the pressurized heat and thru-air heat bonding methods.

**[0097]** The fibers of the present invention may also be bonded or combined with other synthetic or natural fibers to make nonwoven articles. The synthetic or natural fibers may be blended together in the forming process or used in discrete layers. Suitable synthetic fibers include fibers made from polypropylene, polyethylene, polyester, polyacrylates, and copolymers thereof and mixtures thereof. Natural fibers include cellulosic fibers and

derivatives thereof. Suitable cellulosic fibers include those derived from any tree or vegetation, including hardwood fibers, softwood fibers, hemp, and cotton. Also included are fibers made from processed natural cellulosic resources such as rayon.

**[0098]** The fibers of the present invention may be used to make nonwovens, among other suitable articles. Nonwoven articles are defined as articles that contains greater than 15% of a plurality of fibers that are continuous or non-continuous and physically and/or chemically attached to one another. The nonwoven may be combined with additional nonwovens or films to produce a layered product used either by itself or as a component in a complex combination of other materials. Preferred articles are disposable, nonwoven articles. The resultant products may find use in filters for air, oil and water; textile fabrics such as micro fiber or breathable fabrics having improved moisture and odor absorption and softness of wear; electrostatically charged, structured webs for collecting and removing dust and pollutants; medical textiles such as surgical drapes, wound dressing, bandages, dermal patches; textiles for absorbing water and oil for use in oil or water spill clean-up, etc.. The articles of the present invention may also include disposable nonwovens for hygiene and medical applications to absorb off-odors. Hygiene applications include such items as wipes; diapers, particularly the top sheet or back sheet; and feminine pads or products, particularly the top sheet.

**[0099]** The yarns or fibers of the textile layers can have any suitable weight per unit length (e.g., denier). Typically, the fibers have a weight per unit length of about 1 to about 50 denier per filament (1 to about 50 g per 9000 meters). The yarns contain a plurality of filaments from 10 to about 5000.

**[0100]** In some embodiments, the P-CDP is adhesively bound to a substrate such as a fiber or fabric via a binder. In some embodiments, the P-CDP is coated on a substrate such as a fiber or fabric via a binder. In some embodiments, the P-CDP is bound to or coated on a substrate such as a fiber or fabric via a binder by introducing the surface to stable aqueous dispersions of the P-CDP particles in conjunction with binders. The P-CDP particle dispersion may be 1-50% by weight and a polymeric binder material may be present in an emulsion or solution in 1-50% by weight. For example, the P-CDP particle dispersion may be present at about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, or about 50% by weight. The polymeric binder material may be present in an emulsion or solution at about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48,

49, or about 50 % by weight. Additional auxiliary agents can be used as minor components by weight to control the wetting by the substrate (wetting agent), solution foaming or de-foaming, softening agent for substrate hand, and/or catalyst for binder curing.

**[0101]** A variety of coating techniques known in the art can be applied, such as: dip and squeeze, solution casting, foam coating, or spraying of the formulated solution onto the substrate of interest. Substrates include, but are not limited to: woven, knit or nonwoven fabrics, continuous filament yarns, spun yarns, spun fibers, wood surfaces, and thermoplastic surfaces. In some embodiments, upon application of the formulated solution to the substrate, the combined system will be dried to remove the water solvent at which time an even film of P-CDP particles mixed with polymeric binder will be present. During the drying process, the binder material present as an emulsified polymer will flow together and become a continuous phase. Depending on the choice of binder, the P-CDP particles may be held in place through mechanical means or adhesion to the binder continuous phase only, or additional covalent linkages could be present if a cure-able binder is selected. Such covalent linkages could extend the underlying substrate which would further increase the durability of the P-CDP particle coating.

**[0102]** As will be readily apparent to a skilled artisan, the resultant P-CDP particle film conforms to the underlying substrate and is durable to physical abrasion, and washing such that the article can be deployed. Furthermore, if the P-CDP particles have access to the aqueous or vapor phase within the coating, they will demonstrate the same selective and high affinity small molecule adsorption characteristics as the monolithic particles. Such form factors can be converted into filter cartridges, pleated filters, nonwoven needlepunched filters, hygienic nonwovens, and apparel.

**[0103]** A variety of binders known to a skilled artisan may be used in the context of the present disclosure, such as any of those disclosed in US Patent Publication No. 2014/0178457 A1, which is hereby incorporated by reference in its entirety. Suitable binders include, but are not limited to, latex binders, isocyanate binders (e.g., blocked isocyanate binders), acrylic binders (e.g., nonionic acrylic binders), polyurethane binders (e.g., aliphatic polyurethane binders and polyether based polyurethane binders), epoxy binders, urea/formaldehyde resins, melamine/formaldehyde resins, polyvinylalcohol (PvOH) resins (disclosed in US Patent No. 5,496,649, which is hereby incorporated by reference in its entirety) and crosslinked forms thereof, poly-ethylenevinylalcohol (EvOH) and crosslinked forms thereof, poly-ethylenevinylacetate (EVA), starch and starch derivatives, cellulose ether derivatives, and cellulose ester derivatives. Small molecule, polymeric or inorganic

crosslinking agents could be used additionally including formaldehyde, glyoxal, diisocyanates, diepoxides, and/or sodium tetraborate, and combinations thereof.

#### Fibrillating Fiber Substrates

5    **[0104]**       In some embodiments, the P-CDP particles are mechanically bound to a surface, such as a fibrillating fiber. Fibrillating fibers are used to create high surface area, extended networks which can wrap around and entrap particulate matter. Fibers such as fibrillating polyolefin (such as Mitsui Fybrel®), fibrillating regenerated cellulose (such as Lenzing Tencel™) or fibrillating acrylic (such as Sterling Fibers CFF™) are deployed in wet  
10   laid processes to create specialty papers which excellent mechanical properties, good wet strength, and the ability to hold particulate matter (US Patent No. 4,565,727, which is hereby incorporated by reference in its entirety), Onxy Specialty Papers, Helsa Corporation, and others. In particular, powdered activated carbon particles with diameters greater than 5 microns have been loaded into specialty carbon papers that are deployed in liquid and vapor  
15   filtration applications such as point of use water filters or cabin air filters.

**[0105]**       In the paper making process, an aqueous dispersion or slurry blend of short cut fibers (such as wood pulp, polyester, nylon, or polyolefin), fibrillating fibers (such as Fybrel®, Tencel™, or CFF™), and particle powder material are mixed (e.g., under high shear). This mixture can then be rapidly passed through a nonwoven mesh or screen to  
20   deposit a wet laid nonwoven web. This web is dried (e.g., in hot air oven or on heated rolls) to remove the water carrier. Further bonding may be achieved through cold or hot calendaring either in flat format or with a patterned roll to produce the bonded specialty paper. The particulate powder used can be a dispersion of P-CDP particulates of defined particle size. Particulate size can be set via grinding and milling techniques as defined  
25   previously. The particulate loading in the finished nonwoven can be as high as 60% by weight. The particulate can be used alone or blended with other particulate such as powdered activated carbon. Additional chemical binders, such as those described herein, may be used to alter or enhance the properties of the paper and will be applied as one skilled in the art.

**[0106]**       The resultant powder loaded papers are amenable to a high loading of P-CDP  
30   adsorbent particles in a convenient paper filter form factor for water and/or air filtration. The paper can be used in the flat form, cut into a variety of shapes, or pleated and bonded into a filter media cartridge.

**[0107]**       In some embodiments, the P-CDP particles are mechanically entangled in yarn (e.g., continuous filament yarn). In some embodiments, the P-CDP particles are

mechanically entangled in continuous filament yarn. As will be readily apparent to a skilled artisan, a special subset of yarn finishing enables the mechanical binding of particulate matter within a continuous filament yarn in some circumstances. When a yarn (e.g., continuous filament) comprised of multiple filaments of a typical synthetic polymer such as polyethyleneterephthalate (PET) or polyamide (nylon 6 or nylon 6,6) that bears microfibrillating tendencies on each filament surface, there exists the possibility to incorporate particulate within the yarn bundles. The P-CDP particles of the present disclosure can be incorporated into the yarn in a variety of ways. One non-limiting example is to apply a dispersion of the P-CDP particles of interest via dip coating or oil roll application onto a moving yarn bundle during the false twist texturing process. In this process, the filaments are mechanically separated via twisting, first in one direction followed by the opposite direction. After the first twisting, the filaments are individualized and void space is presented within the yarn bundle. The dispersion solution is applied at this point within the process after which the bundles are twisted back to the standard orientation and the yarn heated to dry the solution. This process enables the application of dispersion particles within the yarn bundles that are held in place by the continuous filaments and microfibrils emanating from the continuous filament surface. Such approaches have been used to apply various micron sized particles to continuous filament yarns, including microcapsules (US Patent Publication No. 2005/0262646 A1, which is hereby incorporated by reference in its entirety), metallic silver microparticles (US Patent Publication No. 2015/0361595 A1, which is hereby incorporated by reference in its entirety), and (US Patent Publication No. 2006/0067965 A1, which is hereby incorporated by reference in its entirety) other functional particles to synthetic fiber yarn bundles. These textured and particle loaded yarns may then be processed through typical means to create knit and woven fabrics for use in apparel, upholstery, medical, displays, or other uses.

**[0108]** In some embodiments, the P-CDP particles are incorporated into thermally-bonded, particulate pressed forms. A common form factor for powdered absorbent material is in thermally-bonded pressed forms. Such form factors can contain as high as 95% by weight P-CDP particles, with the addition of fibrillating fibers (Fybrel®, Tencel™, or CFF™), sometimes inorganic materials such as attapulgite clays, and finally an organic binder material (most typically cellulose esters and similar derivatives) to create a porous composite structure with adequate mechanical strength and particulate holding efficiency for medium pressure filtration applications such as faucet filters and refrigerator filters (US

Patent Nos. 5,488,021 and 8,167,141, both of which are hereby incorporated by reference in their entireties).

**[0109]** P-CDP dry particles or dispersion can be used in place of or blended with other adsorbent materials to form such a composite adsorbent P-CDP particulate-containing forms as described above. In such embodiments, the solid dry components may be dry blended, optionally including dry P-CDP particles and organic binder powder with or without inorganic clays and/or fibrillating fibers. If an aqueous dispersion of P-CDP particles is used, they may be diluted with water and added to the mixture. Water is added (e.g., in 80-150 wt%) and the mixture is blended (e.g., under high shear) to create a plastic material. This material may be formed into the desired form factor, dried and cured at temperatures ranging from 125 to 250 °C. This final form factor presents the P-CDP adsorbent particles in a form factor common to and useful for point of use water filters.

**[0110]** In some embodiments, the P-CDP particles are incorporation into solution processed polymer form factors. A variety of means are available to produce filter membrane materials. For example, via solution cast films or extrude hollow fibers of membrane polymers where controlled coagulation creates a condensed film of controlled pore size. In some embodiments, a polymer such as cellulose acetate dissolved in a water miscible organic solvent such as NMP, DMSO, or THF is used. This solution can be cast as a film into a water bath which causes rapid coagulation of the cellulose acetate polymer and densification of the film. These films may be processed on roll to roll equipment and many layers are wrapped to create a spiral wound membrane filter for use in micro-filtration, ultra-filtration, gas filtration, or reverse osmosis applications. In place of cellulose acetate, common polymers used include polyamides, polyolefins, polysulfones, polyethersulfones, polyvinylidene fluoride, and similar engineered thermoplastics. It is also possible to extrude hollow fibers into the aqueous solution to create membrane fibers through the phase inversion process that are known as hollow-fiber membranes commonly used for dialysis, reverse osmosis, and desalination applications.

**[0111]** In some embodiments, the P-CDP particle matter is incorporated into membrane material to enhance the performance of the membrane materials. For example, it is possible to have present in the aqueous coagulation bath a small quantity of P-CDP particle dispersion that will become incorporated into the dense portions or porous portions of the membrane during the phase inversion process. A second manner to incorporate the P-CDP particles into the membrane is the incorporation of a small amount of well-dispersed particles

into the organic solution of the membrane polymer that become encapsulated in the membrane following coagulation. Through each of these methods, the production of P-CDP loaded polymer forms may be enabled. In various embodiments, such as micro-filtration, ultra-filtration, and reverse osmosis, the P-CDP particle incorporation acts to enhance the micropollutant removal of the membrane system.

[0112] In some embodiments, the P-CDP particles are incorporated into melt extruded thermoplastics (e.g., fibers and molded parts). Having access to small diameter dry powder P-CDP particle material of low polydispersity enables its incorporation into melt processed polymer forms including fibers and molded parts. Typical thermoplastics of use include polyethyleneterephthalate, co-polyesters, polyolefins, and polyamides. Typical extrusion temperatures are between 250-300 °C and therefore P-CDP particle stability to those temperatures either under air (most preferred) or inert atmosphere is required. Single or twin-screw extrusion is used to blend and mix the powdered material at elevated temperatures under shear with the thermoplastic in up to five weight percent. Once adequately mixed, the blended components can be extruded through small round or otherwise shaped orifices and drawn to produce fibers bearing the particulate matter linear densities ranging from 1 to 20 denier per filament. A common particle added to most thermoplastic fibers is titanium dioxide added to whiten and deluster the fiber. The P-CDP particles will be added in a similar fashion. In the most ideal embodiment, the P-CDP particles will migrate to the surface of the fibers and bloom due to their higher surface energy such that a portion of the particles are present and accessible by the vapor or liquid phase. In other embodiments, instead of extruding the polymer melt through small orifices, it can be blow molded or otherwise melt processed to produce a plastic part. This plastic part will also bear the P-CDP particles that bloom to the surface and become active for the removal of small molecule micropollutants (e.g. anionic MPs) from the vapor and liquid phase.

### Performance

[0113] While it is not unknown to provide adsorbents in a supported form, it is important that the methods used to affix the adsorbent to the substrate or support are sufficiently robust so as to withstand the use conditions. Further, the means of attachment to the substrate should not interfere with or block the adsorption mechanism of the adsorbent. The adsorbents disclosed herein can be attached to supports, as described herein, so that the resulting performance characteristics are only minimally affected by the attachment method.

In various embodiments, the supported polymeric materials of the present invention provide performance characteristics which are at least 50% of the same performance characteristic which would be provided by the same composition of adsorbent prepared without a support material (based on equivalent amounts of the adsorbent) when measured under identical conditions. So for example a porous material grafted to microcrystalline cellulose (e.g., a P-CDP crosslinked with an aryl linker of formula (Ia)-CMC substrate complex) may have at least 50% of one or more of a particular performance characteristic found in unsupported porous material tested under the same conditions.

[0114] In some embodiments, the performance characteristic can be the amount of uptake (adsorption capacity) of a particular pollutant, measured as the milligrams of pollutant adsorbed per gram P-CDP particle under particular conditions. In other embodiments, the performance characteristic can be the equilibrium adsorption capacity ( $q_e$ ), defined as discussed herein as:

$$q_e = q_{max} \frac{C_e K_L}{C_e K_L + 1}$$

wherein  $q_{max}$  (mg pollutant/g adsorbent) is the maximum adsorption capacity of the sorbent for a particular pollutant at equilibrium,  $K_L$  ( $\text{mol}^{-1}$ ) is the equilibrium constant and  $C_e$  (mM) is the pollutant concentration at equilibrium.

[0115] In still other embodiments, the performance characteristic is the rate at which equilibrium adsorption of a pollutant is reached (rate of equilibrium adsorption for a particular adsorbent. This rate can be expressed as the time required for a supported or unsupported P-CDP of the present disclosure to reach equilibrium for a particular adsorbed species (or pollutant).

[0116] In still other embodiments, the performance characteristic is the rate at which competing adsorbents sequester pollutants. Competing adsorbents may be unsupported P-CDPs as described herein, or other agents, such as activated carbons (powdered or granular), ion-exchange resins, and specialized resins used for solid-phase microextraction (e.g., HLB).

[0117] For any of these performance characteristics disclosed above, the performance of the supported P-CDP of the present disclosure is at least about 50%, 60%, 70%, 80%, 90%, 100%, 120%, 140%, 160%, 180%, 200%, 220%, 240%, 260%, 280%, 300%, 350%, 400%, 450%, 500% or greater, inclusive of all values, ranges, and subranges therebetween compared to unsupported P-CDP of the same composition, tested under essentially the same conditions, e.g., with the same pollutant, temperature, pressure, exposure time, etc.

[0118] The performance characteristics of the present disclosure can be measured, for example based on bisphenol A or PFASs or another suitable specie as disclosed herein, by a variety of methods which will be readily apparent to a skilled artisan. For example, the contaminant may be measured at initial concentrations of BPA or another suitable specie ranging from 1 ppb (or 1 microgram/L or 5 nM) to 1 ppt (or 1 g/L or 5 mM) in any aqueous sample, including but not limited to drinking water, wastewater, ground water, aqueous extracts from contaminated soils, landfill leachates, purified water, or other waters containing salts, or other organic matter. The pH may be range from 0-14. For example, the pH may be 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, or 14, inclusive of all ranges therebetween. The performance characteristics may be measured substantially as described herein (e.g., in Examples 1 and 2), with routine modifications (such as temperature and pressure) also being envisioned.

#### Articles of Manufacture

[0119] In some embodiments, the present disclosure provides an article of manufacture comprising one or more P-CDPs or one or more P-CDP-substrate complexes of the present disclosure.

[0120] In an embodiment, the article of manufacture is protective equipment. In an embodiment, the article of manufacture is clothing. For example, the article of manufacture is clothing comprising one or more P-CDPs or one or more P-CDP-substrate complexes of the present disclosure (e.g., clothing such as a uniform at least partially coated with the porous polymeric material or composition). In another example, the article is filtration medium comprising one or more P-CDPs or one or more P-CDP-substrate complexes of the present disclosure. The filtration medium can be used as a gas mask filter. In an embodiment, the article is a gas mask comprising the filtration medium. In some embodiments, the article is an extraction device.

[0121] In another embodiment, the article is a solid phase microphase (SPME) extraction device comprising one or more P-CDPs or one or more P-CDP-substrate complexes of the present disclosure, where the P-CDPs or P-CDP-substrate complexes is the extracting phase the device.

[0122] In another embodiment, the article is a device for a solid-phase extraction of polar and semi-polar organic molecules. The device comprises one or more P-CDPs or one or more P-CDP-substrate complexes of the present disclosure instead of HLB media

(hydrophilic/lipophilic balanced). The article with the one or more P-CDPs or one or more P-CDP-substrate complexes outperforms the HLB media.

**[0123]** In another embodiment, the article is a device for liquid filtration of polar and semi-polar organic molecules. The device comprises one or more P-CDPs or one or more P-CDP-substrate complexes of the present disclosure adhered within a fibrous web (as disclosed in U.S. Patent No. 7,655,112, which is hereby incorporated by reference in its entirety). Other embodiments include the device comprising P-CDP powders fused via thermoplastic binder polymer to create porous monolithic filtration media (as disclosed in U.S. Patent No. 4,753,728, which is hereby incorporated by reference in its entirety).

### Methods

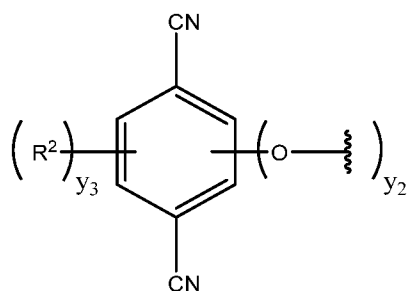
**[0124]** In some embodiments, the present disclosure provides methods of making the porous polymeric materials. In an embodiment, the porous polymeric material is made by a method disclosed herein.

**[0125]** The P-CDPs of the present disclosure comprise cyclodextrin moieties crosslinked with a suitable crosslinking agent that provides a porous, relatively high surface area polymeric material as described herein. Suitable crosslinking agents can include any, at least difunctional compound capable of reaction with any of the cyclodextrins disclosed herein to form a crosslinked network of cyclodextrin moieties. In order to provide the desired porosity and surface area for the polymeric material, in various embodiments the crosslinking agent should be relatively rigid and inflexible, such as the crosslinkers disclosed herein. For example, in some embodiments, crosslinkers which form crosslinks with no more than about 6 "rotatable" bonds (e.g., 2, 3, 4, 5, or 6 rotatable bonds) may be suitable. The term rotatable refers to bonds in the crosslink having a calculated rotational barrier which is no more than about 80 kJ/mol (298 K), for example in the range of about 10-30 kJ/mol. Such crosslinks have limited mobility, which is believed to aid in the formation of high porosity and surface area materials.

**[0126]** In an embodiment, a method of making a porous polymeric material comprises contacting a cyclodextrin with a crosslinking agent, such as an aryl or heteroaryl compound such that the crosslinking agent (e.g., aryl compound) crosslinks at least two cyclodextrin moieties. The crosslinking agent comprises at least two groups (e.g., halide groups, anhydrides, acid chlorides, esters, sulfonic esters, ureas, isocyanates, etc.) that can react with a cyclodextrin or appropriately functionalized cyclodextrin to form covalent (e.g., aryl ether

bonds). Without intending to be bound by any particular theory, it is considered that the reaction between a cyclodextrin and an aryl halide compound is a nucleophilic aromatic substitution reaction. In accordance with embodiments of the present disclosure, the resultant porous polymeric material will have appropriate functional groups present on the linking groups, which are subsequently converted to amines (e.g. nitriles, amides, nitro groups, etc. can be reduced to amines under appropriate conditions). In some embodiments, a  $-\text{CN}$  can be converted to  $-\text{CH}_2\text{-NH}_2$  via a reduction (e.g. a borane reduction).

**[0127]** In some embodiments, the present disclosure provides a method of making a mesoporous polymeric material, wherein the plurality of cyclodextrins are crosslinked with at least an equimolar amount of an appropriate linking group to form a plurality of crosslinks of formula (Ia), the method comprising reducing one or more of the nitrile groups of a linking group of formula (II) with a suitable reducing agent



(II).

A variety of suitable reducing agents are well known to a person having ordinary skill in the art. In some embodiments, the suitable reducing agent is selected from the group consisting of  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , diborane, DIBAL-H,  $\text{BH}_3\text{-THF}$ ,  $\text{BH}_3\text{-SMe}_2$ ,  $\text{H}_2$  + Raney Ni, and  $\text{H}_2$  + Pd/C. In some embodiments, the suitable reducing agent is  $\text{BH}_3\text{-SMe}_2$ .

**[0128]** In some embodiments, a method of making a P-CDP-substrate complex is provided, comprising contacting P-CDPs with one or more substrates, under conditions sufficient to bond or graft the P-CDPs to the one or more substrates (e.g., covalently, adhesively, or mechanically), for example by any of the methods described herein. In some embodiments, the P-CDPs have free amines prior to complexation with one or more substrates, for example via conversion of the amine masking group or alkyl amine masking group of the linking groups of the present disclosure. In some embodiments, the P-CDP-substrate complex has masked amines prior to complexation with one or more substrates, and subsequently undergoes conversion of the amine masking group or alkyl amine masking group to the corresponding amine or alkyl amine.

[0129] In some embodiments, the present disclosure provides a method of removing one or more compounds (e.g. anionic MPs) from a fluid sample or determining the presence or absence of one or more compounds in a fluid sample comprising: a) contacting the sample with the mesoporous polymeric material of the present disclosure or the supported porous polymeric material of the present disclosure for an incubation period; b) separating the mesoporous polymeric material or supported porous polymeric material after the incubation period from the sample; and c) heating the mesoporous polymeric material or supported porous polymeric material separated in step b), or contacting the mesoporous polymeric material or supported porous polymeric material separated in step b) with a solvent, thereby releasing at least a portion of the compounds from the mesoporous polymeric material or supported porous polymeric material; and d1) optionally isolating at least a portion of the compounds released in step c); or d2) determining the presence or absence of the compounds released in step c), wherein the presence of one or more compounds correlates to the presence of the one or more compounds in the sample. In some embodiments, the one or more cyclodextrin moieties are  $\beta$ -cyclodextrin moieties. In some embodiments, said determining is carried out by gas chromatography, liquid chromatography, supercritical fluid chromatography, or mass spectrometry. In some embodiments, said contacting is by flowing the aqueous phase across, over, around, or through the supported porous polymeric material. In some embodiments, the aqueous sample is contacted with the P-CDP-substrate complex under static conditions for an incubation period and after the incubation period the aqueous sample is separated from the porous polymeric material. In some embodiments, the sample is a food and the compounds are volatile organic compounds. In some embodiments, the aqueous sample is drinking water, wastewater, ground water, aqueous extracts from contaminated soils, or landfill leachates. In some embodiments, the sample is a perfume or fragrance and the compounds are volatile organic compounds. In some embodiments, the compounds are anionic micropollutants, heavy metals, and/or dyes. In some embodiments the compounds are anionic MPs, such as PFASs.

[0130] In an embodiment, a method of purifying an aqueous sample comprising one or more organic compounds is provided, the method comprising contacting the aqueous sample with the mesoporous polymeric material of the present disclosure or the supported porous polymeric material of the present disclosure such that, for example, at least 50% to at least 99% of the one or more pollutants is bound to one or more of the cyclodextrin (e.g.,  $\beta$ -cyclodextrin) moieties of the porous polymeric material. For example, the aqueous sample is flowed across, around, or through the porous polymeric material. In another example, the

aqueous sample contacted with the mesoporous polymeric material or the supported porous polymeric material under static conditions for an incubation period and after the incubation period the aqueous sample is separated (e.g., by filtration) from the porous polymeric material. The method can be used to purify aqueous samples such as drinking water, wastewater, ground water, aqueous extracts from contaminated soils, and landfill leachates. In some embodiments, the organic compounds are anionic MPs, such as PFASs.

**[0131]** In an embodiment, a method of determining the presence or absence of compounds (e.g., anionic MPs) in a sample comprises: a) contacting the sample with the mesoporous polymeric material of the present disclosure or the supported porous polymeric material of the present disclosure for an incubation period (e.g., 1 minute or less, 5 minutes or less, or 10 minutes or less); b) isolating the complex from a) from the sample; and c) heating the complex material from b) or contacting the complex from b) with a solvent (e.g., methanol) such that at least part of the compounds are then released by the mesoporous material; and d) determining the presence or absence of any compounds, wherein the presence of one or more compounds correlates to the presence of the one or more compounds in the sample, or isolating (e.g., by filtration) the compounds. For example, the determining (e.g., analysis) is carried out by gas chromatography or mass spectrometry. For example, the sample is a food or beverage (e.g., milk, wine, fruit juice (e.g., orange juice, apple juice, and grape juice), or an alcoholic beverage (e.g., beer and spirits)) and the compounds are volatile organic compounds. The mesoporous polymeric material or supported porous polymeric material can be the extracting phase in a solid phase microextraction (SPME) device. In some embodiments, the organic compounds are anionic MPs, such as PFASs.

**[0132]** In an embodiment, a method for removing compounds (e.g., organic compounds) from a sample comprises: a) contacting the sample with the mesoporous polymeric material of the present disclosure or the supported porous polymeric material of the present disclosure for an incubation period such that at least some of the compounds are sequestered in the polymer; b) isolating complex from a) from the sample; c) heating the complex from b) or contacting the complex from b) with a solvent (e.g., methanol) such that at least part of the compounds are released by the porous polymeric material; and d) optionally, isolating at least a portion of the compounds. In some embodiments, the compounds are anionic MPs, such as PFASs.

**[0133]** A variety of compounds can be involved (e.g., sequestered, detected, and/or isolated) in the methods. The compounds can be organic compounds. The compounds can be desirable compounds such as flavorants (e.g., compounds that impact the palatability of

foods) or pharmaceutical compounds (or pharmaceutical intermediates), contaminants (e.g., PCBs, PBAs, etc.), and/or adulterants. In some embodiments, the compounds are anionic MPs, such as PFASs. In some embodiments, the compounds are anionic MPs selected from the group consisting of gemfibrozil, oxybenzone, diclofenac, ioxynil, ketoprofen, naproxen, sulfamethoxazole, warfarin, 2,4-dichlorophenoxyacetic acid, clofibric acid, ibuprofen, 2-methyl-4-chlorophenoxyacetic acid, mecoprop, valsartan, perfluorobutanoic acid, perfluorobutane sulfonic acid, perfluoropentanoic acid, perfluoropentane sulfonic acid, perfluorohexanoic acid, perfluorohexane sulfonic acid, perfluoroheptanoic acid, perfluoroheptane sulfonic acid, perfluorooctanoic acid, perfluorooctane sulfonic acid, perfluorononanoic acid, perfluorononane sulfonic acid, perfluorodecanoic acid, perfluorodecane sulfonic acid, perfluoroundecanoic acid, perfluorododecanoic acid, perfluorotridecanoic acid, perfluorotetradecanoic acid, 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate, and combinations thereof.

**[0134]** The cyclodextrins are chiral. In an embodiment, a chiral compound is sequestered, detected, and/or isolated. In an embodiment, a chiral column (e.g., a preparative-scale or analytical-scale column is packed with a chiral porous polymeric material or composition comprising chiral porous polymeric material) is used to separate and detect or isolate (or at least significantly enrich the sample in one enantiomer) a single enantiomer of a compound.

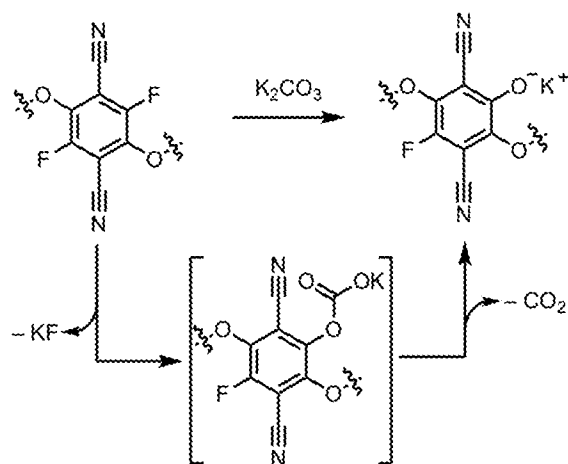
**[0135]** In the methods, the mesoporous polymeric material or the supported porous polymeric material can be regenerated (e.g., for reuse in the methods). For, example, the porous polymeric material is regenerated by heating and/or exposure to solvent (e.g., alcohols such as methanol or ethanol, and aqueous mixtures thereof).

**[0136]** The following examples are provided to illustrate the present disclosure, and should not be construed as limiting thereof.

**[0137] Example 1: Post-Synthetically Modified Cyclodextrin Polymer for Removal of PFAS and other anionic organic micropollutants**

**[0138]** A variety of polymers were previously synthesized to combat the problems of MPs in water with a group of  $\beta$ -cyclodextrin ( $\beta$ -CD) base polymers (CDPs) synthesized (i.e. using nucleophilic aromatic substitution ( $S_NAr$ )) with aryl-fluoride containing crosslinkers. See, for example, U.S. Patent Nos. 9,624,314, 9,855,545, and 10,086,360, which are hereby incorporated by reference in their entireties. For example, a CDP crosslinked by

tetrafluoroterephthalonitrile (TFN), was formed as a permanently porous network (**1**, Fig 1) that rapidly removes many MPs from water,<sup>11</sup> resists fouling by natural organic matter,<sup>13,14</sup> and can be regenerated.<sup>17</sup> A study of the binding of 83 MPs under environmentally relevant concentrations revealed that **1** rapidly removes many cationic and neutral MPs, but removal of anionic MPs was variable and relatively low.<sup>13</sup> This selectivity for cations was attributed to anionic phenolate groups introduced to the TFN crosslinkers during the polymerization (see Scheme 1 below).<sup>16</sup> However, the inability of this **1** to bind anionic micropollutants, including anionic perfluorinated alkyl substances (PFASs),<sup>13,16</sup> is a major limitation to its broad utility and technological promise.



**Scheme 1.** During the polymerization of **1** phenolation is a side reaction that incorporates phenolates into the polymer.

**[0139]** Polymers crosslinked with decafluorobiphenyl were also synthesized and found to have a high affinity for the PFAS perfluorooctanoic acid (PFOA) possibly due to a fluorophilic interaction. Unfortunately, decafluorobiphenyl is too expensive to make the resulting polymer commercially viable.

**[0140]** Based on a hypothesis that cationic CDPs would show selectivity for anionic substances and PFASs relative to our previous adsorbents, we reduced the nitriles of CDP **1** to primary amines rendering the resulting polymer cationic. CDP **2** was synthesized from **1** (Fig 1), and this simple post-polymerization reduction transformed a polymer with low affinity to anionic MPs to a material with a high affinity for many anionic MPs, including ten anionic PFASs tested at environmentally relevant concentrations. It was hypothesized that post-synthetically modifications (e.g. by reducing one or more of the nitriles of **1** to primary amines) would render the resulting polymer cationic and could be a cost-effective adsorbent for targeting PFASs. To this end, **2** was synthesized from **1** using a BH<sub>3</sub>•S(CH<sub>3</sub>)<sub>2</sub> reduction

(Fig. 1). This polymer has complementary and opposite MP affinity when compared to its parent polymer **1** and unlike polymer **1** has broad spectrum PFAS removal. This work uses a simple post-synthetic modification to render an anionic polymer cationic which provides a cost-effective and broad spectrum adsorbent for PFASs and other anionic MPs.

## 5 [0141] Results and Discussion

[0142] The nitriles of a commercial sample of **1** were reduced to primary amines using excess  $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$  in THF at reflux for 40 hours, using conditions adapted from Mason *et al.* (Fig 1) for TFN-containing linear polymers.<sup>26</sup> After reduction, insoluble polymer **2** was subjected to an acidic workup followed by treatment with base. The reduction was characterized by FT-IR, cross-polarized magic angle spinning (CP-MAS) solid-state  $^{13}\text{C}$  NMR, a chloranil test for amines, combustion analysis, and zeta potential measurements. FT-IR was consistent with partial reduction of the nitriles, as the spectrum of **2** shows a strongly attenuated nitrile stretch at  $2238\text{ cm}^{-1}$  relative to that of **1** when each spectrum was normalized at the C-O stretch at  $1020\text{ cm}^{-1}$ . The spectrum of **2** also shows an N-H bending signal at  $1580\text{ cm}^{-1}$  (Fig 2a). In the CP-MAS  $^{13}\text{C}$ -NMR, the nitrile carbons of **1** resonate at 94.44 ppm. This signal is attenuated in the spectrum of **2**, and a new peak is observed at 36.73 ppm (Fig 5), consistent with that of a benzylic amine carbon. The presence of amines in **2** was also verified by a positive chloranil test (Fig 2b), which is commonly used to qualitatively monitor the deprotection, capping, or coupling of amine groups in solid-phase peptide synthesis.<sup>29,30</sup> In a chloranil test, acetaldehyde reacts with a primary or secondary amine forming an enamine, which then reacts with chloranil to yield a dark blue aminovinyl-quinone chromophore.<sup>31</sup> In the presence of acetaldehyde and chloranil, the suspension of polymer **1** is light yellow-green, indicating the absence of amines, while the polymer **2** suspension is a dark blue-green, indicating the presence of amines (Fig 2b). Because the elemental composition of **1** and **2** in its free base form are too similar to differentiate by combustion analysis, the conversion of nitriles to amines was estimated by comparing the chloride content of each polymer following treatment with aqueous HCl. Treatment of **2** with HCl protonates its amines to the corresponding hydrochloride salts ( $2 \cdot \text{HCl}$ ), whereas polymer **1** does not contain functional groups that are easily protonated. The conversion of nitriles to amines was estimated from the N:Cl molar ratio in  $2 \cdot \text{HCl}$  of 0.72, corresponding to approximately 72% conversion of the nitrile reduction. As a control, **1** was treated with HCl as above and virtually no chloride was detected by the elemental analysis. Surface charges of the two polymers in neutral water were probed by zeta potential measurements. Aqueous suspensions of **1** at neutral pH have a zeta potential of  $-28.9 \pm 0.7\text{ mV}$ , suggesting an

anionic surface charge. Aqueous suspensions of **2** at neutral pH show a zeta potential of +1.7 +/- 0.8 mV, suggesting a cationic surface charge. **2** also exhibits modest porosity with average Brunauer–Emmet–Teller surface areas of 135 m<sup>2</sup> g<sup>-1</sup>.

**[0143]** As a consequence of its transformed crosslinkers, **2** has a relatively high

5 affinity for anionic MPs, including anionic PFASs, which is the opposite trend observed for **1**. The adsorption distribution coefficients (log K<sub>D</sub> values) of 91 structurally diverse MPs for **1** and **2** ([MP]<sub>0</sub> = 2 µg L<sup>-1</sup>; [CDP] = 25 mg L<sup>-1</sup>) were measured. **1** exhibited relatively high log K<sub>D</sub> values for cationic MPs, along with neutral compounds that bind to CDs well, which is consistent with a previous report<sup>16</sup> and observations (Fig 3).<sup>13,17</sup> All 18 cationic substances  
10 exhibited log K<sub>D</sub> values greater than 2 on polymer **1**. In contrast, 21 of 25 anionic substances and all 10 anionic PFASs exhibited relatively low log K<sub>D</sub> values between -0.5 and 1.0 on polymer **1**. These low affinities make polymer **1** an ineffective adsorbent for most anionic MPs at environmentally relevant concentrations and economically reasonable doses of **1**. In contrast, polymer **2** strongly binds anionic substances, with 21 of 25 exhibiting log K<sub>D</sub> values  
15 >2.6 and all ten anionic PFASs exhibiting log K<sub>D</sub> values between 2.8-4.0. However, polymer **2** binds cationic MPs more weakly with log K<sub>D</sub> values for 16 of 18 cationic MPs between 0-1.5. These findings demonstrate that crosslinker chemistry plays a major role in the selectivity of CD-based adsorbents and that strategies to incorporate charged groups, either during the polymerization (phenolates),<sup>16,27</sup> or by post-polymerization modification (amines),  
20 are powerful techniques to completely change the removal profiles of materials derived from a single crosslinker.

**[0144]** Based on the high affinity of polymer **2** for anionic PFASs, removal and uptake kinetics were also measured at environmentally relevant concentrations ([PFAS]<sub>0</sub> = 1 µg L<sup>-1</sup>; [CDP] = 10 mg L<sup>-1</sup>). Polymer **2** removes PFOA and PFOS rapidly, as the combined  
25 residual PFOA + PFOS concentration was 58 ng L<sup>-1</sup> after 30 minutes (below the 2016 EPA health advisory level of 70 ng L<sup>-1</sup> for PFOA and PFOS co-contamination) and reached an equilibrium aqueous phase concentration of approximately 25 ng L<sup>-1</sup> after 9 h (Fig 4a).

Broad-spectrum PFAS removal was also evaluated across a range of PFAS chain lengths and anionic head groups (carboxylic and sulfonic acids) after 30 min of contact time ([PFAS]<sub>0</sub> = 1  
30 µg L<sup>-1</sup>; [CDP] = 10 mg L<sup>-1</sup>). Under these conditions, 8 of 10 PFASs were removed to at least 95%, with the short, four carbon perfluorobutanoic acid (PFBA) and branched 2,3,3,3,-tetrafluoro-2-(heptafluoropropoxy) propanoate (GenX) removed to at least 80%. These two PFASs are likely to have lower affinity for β-CD binding such that their removal may rely more heavily (or even exclusively) on interactions with amine/ammonium groups in polymer

**2** (Fig 4b). Benchmarking **2** against powdered activated carbon (PAC, 200-950 Mesh, 10-75  $\mu\text{m}$ ) and GAC (20-40 Mesh, 425-850  $\mu\text{m}$ ) shows that **2** performs similarly to PAC and is superior to GAC at environmentally relevant conditions after 30 min (Fig 7), and outperforms PAC and GAC after 8 h of contact time. Specifically, these data also show that **2** outperforms  
5 PAC at removing PFBA, which is difficult to remove by current commercial methods. These overall findings demonstrate the promise of using polymer **2** as an adsorbent to remove anionic PFASs in contaminated ground and surface waters.

**[0145] Conclusion**

**[0146]** The MP selectivity of a porous CDP was reversed from strongly binding  
10 cationic substances to strongly binding anionic substances through a post-polymerization reduction of its nitrile groups. The conversion of nitriles to primary amines was confirmed by spectroscopy, combustion analysis, and changes in the zeta potential. This effect likely arises from both the presence of amine groups that are partially protonated at pH 7 in water, as well as the increased  $\text{pK}_a$  of phenolates found on the crosslinkers upon reduction of the strongly  
15 electron withdrawing nitrile groups. The reduced polymer binds many anionic MPs strongly and is particularly effective at binding PFASs. A relatively low adsorbent loading ( $10 \text{ mg L}^{-1}$ ) removed a wide range of PFASs at environmentally relevant concentrations, outperforming granular activated carbon at 30 minutes of contact time and also powdered activated carbon at 8 hours of contact time. This affinity for PFASs may arise from localizing amine groups near  
20 the CD binding sites within the network. Characterizing this effect and the nature of PFAS-polymer interactions is an important next step. More broadly, these findings demonstrate the broad tunability of CD-based adsorbents available from a single polymerization as well as the continued promise of novel adsorbents constructed from molecular receptors.

**[0147] Example 2: Materials and Methods**

**[0148]** Materials: 1 ‘Dexsorb MP’ was obtained from CycloPure, Inc (Skokie, IL). Borane dimethyl sulfide complex solution (5 M in dimethyl ether), hydrochloric acid (ACS reagent, 37%), sodium hydroxide (Fisher, >97.0%) and tetrahydrofuran (THF, anhydrous,  $\geq 99.9\%$ , inhibitor-free) was purchased from Sigma Aldrich and used without further  
25 purification. The selected 91 MPs, that are representative of a broad range of  
30 physicochemical properties, were purchased from a variety of suppliers including Aldrich, USP, Cerilliant, and Acros Organics. The detailed information of each MP can be found in the SI of a previous study.<sup>1,2</sup> Commercially available AquaCarb 1230C activated carbon was selected for our experiments (Westates Carbon, Siemens, Roseville, MN). To generate granular activated carbon (GAC) and powdered activated carbon (PAC), the AquaCarb

1230C was pulverized with a mortar and pestle and collected on a series of sieves. The size range for the GAC was 425-850  $\mu\text{m}$  (20-40 Mesh) and the size range for the PAC was 10-75  $\mu\text{m}$  (200-950 Mesh).

**[0149] Instrumentation:** Surface area measurements were conducted on a

5 Micromeritics ASAP-2420 Accelerated Surface Area and Porosimetry Analyzer. Each sample (20-50 mg) was degassed at 90 °C for until off gas was less than 0.2  $\mu\text{mHg min}^{-1}$ ) and then backfilled with  $\text{N}_2$ .  $\text{N}_2$  isotherms were generated by incremental exposure to ultra high purity nitrogen up to 1 atm in a liquid nitrogen (77 K) bath, and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics  
10 ASAP-2420 V4.00).

**[0150]** Infrared spectra were recorded using a Nicolet iS10 FT-IR spectrometer equipped with a diamond ATR.

**[0151]** Elemental analysis was performed by Robertson Microlit Laboratories.

Carbon, hydrogen, and nitrogen elemental analysis was performed by combustion analysis,

15 Fluorine elemental analysis was done by ion-selective electrode methodology, and Chlorine elemental analysis we done by a titration method.

**[0152]** The quantification of analytes from affinity experiments of 91 MPs were performed by HPLC-MS/MS (QExactive, ThermoFisher Scientific) with a previously described analytical method. Analytical details used for the detection and quantification of  
20 each analyte are provided in previous reports.<sup>1,2</sup>

**[0153]** CP-MAS  $^{13}\text{C}$  NMR was taken on a Bruker Advance III HD 400 MHz solid NMR system.

**[0154]** The zeta potentials of  $\beta$ -CD polymers at pH 7.5 were determined with 100 mg  $\text{L}^{-1}$  polymer in 9 mM phosphate buffer at 25 °C. Zeta potential measurements were  
25 performed on a Nano Zetasizer (Malvern Instruments Ltd.) with a He-Ne laser (633 nm, Max 5 mW).

**[0155] Synthetic Procedures: Synthesis of 2: 1** (6.0 g) was ground to a fine powder using a mortar and pestle and dried under vacuum for 20 h at 80 °C. The anhydrous powder was then transferred into an oven dried three-neck 1 L RBF equipped with a condenser, a 300  
30 mL addition funnel, and magnetic stir bar. Then the atmosphere was carefully replaced with  $\text{N}_2$ . The flask was charged with anhydrous THF (420 mL) and was cooled with an ice water bath. Borane dimethylsulfide (5 M in ether, 120 mL, 301.8 mmol) was added dropwise over 30 min to the solution with stirring. The ice bath was removed, the reaction warmed to room temp for 3 h, and then the suspension was refluxed for 40 h. The suspension was then cooled

to room temp and transferred to a 2 L Erlenmeyer flask cooled with an ice water bath.

Ethanol (~240 mL) was added dropwise to the flask for 1 h to quench excess borane (caution H<sub>2</sub> bubbling) with stirring. When the suspension stopped bubbling and additional ethanol did not produce bubbling, the suspension was filtered and washed with methanol (~100 mL). The

5 powder was then suspended for 1 h in methanol spiked with concentrated HCl (1 M, 400 mL MeOH / 25 mL conc. HCl) with stirring. The suspension was filtered and washed with

methanol (~100 mL) and water (~100 mL). The powder was then suspended for 1 h in aqueous NaOH (5%, 600 mL) with stirring. The suspension was then filtered, washed with

10 water (~200 mL) and methanol (~200 mL), then resuspended for 1 h in methanol (~100 mL)

and with stirring. The suspension was then filtered and transferred still wet into 3 teabags.

Each teabag was placed into another teabag, sealed with staples, and these were soaked in

methanol. The methanol-soaked teabags were dried by supercritical CO<sub>2</sub> (99 exchange

cycles, ~12 h) to yield a gray-white powder (5.703 g, 95 %). IR (solid, attenuated total

15 reflectance, ATR) 3,030-3650 (-OH), 2,920, 1580 (N-H), 1,471, 1,367, 1,301, 1,256, 1,161,

1,020 cm<sup>-1</sup> (C-O). Elemental Analysis: C, 50.51 H, 4.58; N, 5.79; F, 3.83; Cl; 2.04.

**[0156]      Synthesis of 2•HCl:** **2** (0.5 g) was suspended in HCl (1 M, 20 mL) for 1h.

This was then filtered, washed with MilliQ water (100 mL) and transferred into a vacuum oven at 80 °C for 24 h. Elemental Analysis: C, 45.04 H, 4.25; N, 5.88; F, 2.80; Cl; 10.68.

N:Cl molar ratio 0.72.

20 **[0157]      Polymer 1: 1** was donated by CycloPure Inc. IR (solid, attenuated total reflectance, ATR) 3,030-3650 (-OH), 2,928, 2,238 (-CN) 1,686, 1,618, 1,471, 1,369, 1,265, 1,020 cm<sup>-1</sup> (C-O). Elemental Analysis: C, 51.48 H, 3.13; N, 6.92; F, 4.12; Cl; 0.21.

Elemental Analysis after HCl treatment (same procedure as **2•HCl** where **2** is replaced by **1**): C, 51.24 H, 3.50; N, 6.64; F, 3.62; Cl; 0.16. N:Cl molar ratio 0.01.

25 **[0158]      Affinity experiments:** Experiments to estimate affinity (*K<sub>D</sub>*) of each MP and PFAS were performed in 125mL glass (MPs) or polypropylene (PFASs) Erlenmeyer flasks with magnetic stir bars on a multi-position stirrer (VWR) with a stirring rate of 400

revolutions per minute (rpm) at 23 °C. Experiments were performed at adsorbent doses of 25 mg L<sup>-1</sup>. The MPs and PFASs were spiked to generate an initial concentration of each

30 adsorbate of 2 µg L<sup>-1</sup>. Samples were collected in 8 mL volumes at 1 hour and filtered through a 0.22 µm PVDF (MPs) or cellulose acetate (PFAS) syringe filter (Restek). Control

experiments to account for other MP losses were performed under the same conditions with

no addition of adsorbent. All experiments (including controls) were performed with triplicates.

**[0159] PFAS kinetics experiments:** The kinetics experiments at  $1 \mu\text{g L}^{-1}$  of PFASs were performed in 125 mL polypropylene flasks with magnetic stir bars. The experiments were conducted at  $23^\circ\text{C}$  on a stirring plate with the stirring rate at 500 revolutions per minute (rpm). The adsorbent dose was  $10 \text{ mg L}^{-1}$  and the PFAS mixture solution was spiked to generate an initial concentration of each PFAS at  $1 \mu\text{g L}^{-1}$ . The matrix was nanopure water. Prior to experiments, vacuum-dried adsorbents were rehydrated. Samples were collected in 8 mL volumes at 30 minutes, 9 hours, and 48 hours and filtered with a  $0.45 \mu\text{m}$  cellulose acetate filter (Restek), spiked with isotope labelled internal standards ( $^{13}\text{C}_8$ -PFOA and  $^{13}\text{C}_8$ -PFOS), and measured by means of LC-MS as described elsewhere.<sup>2</sup> Control experiments to account for PFAS losses were performed at the same condition except for the addition of adsorbents. All batch experiments were performed with triplicates.

**[0160] PFAS benchmarking with PAC and GAC:** The experiments with powdered activated carbon (PAC) and granular activated carbon (GAC) were conducted at  $500 \text{ ng L}^{-1}$  of PFASs in 15 mL Falcon tubes on a rotary tumbler at  $23^\circ\text{C}$ . The PAC was sieved to  $10\text{-}75 \mu\text{m}$  and the GAC was sieved to  $425\text{-}850 \mu\text{m}$ . The PAC and GAC dose was approximately  $10\text{-}60 \text{ mg L}^{-1}$  and complementary experiments with polymer **2** were conducted at a dose of approximately  $10 \text{ mg L}^{-1}$ . Each experiment was conducted in 10 mL of nanopure water, and triplicate experiments with each adsorbent were sacrificed at 30 minutes and 8 hours, filtered with a  $0.45 \mu\text{m}$  cellulose acetate filter (Restek), spiked with isotope labelled internal standards ( $^{13}\text{C}_8$ -PFOA and  $^{13}\text{C}_8$ -PFOS), and measured by means of LC-MS as described elsewhere.<sup>2</sup> Control experiments to account for PFAS losses were performed at the same condition except for the addition of adsorbents. All experiments were performed with triplicates.

**[0161]** Table 1: List of micropollutants, affinities, and charge in water at pH 7.

| Component Name | Charge  | Affinity for 1 (log $K_D$ ) | Affinity for 2 (log $K_D$ ) |
|----------------|---------|-----------------------------|-----------------------------|
| 2,4-D          | Anionic | 0.33                        | 3.25                        |
| Clofibric Acid | Anionic | 0.24                        | 3.09                        |
| Diclofenac     | Anionic | 1.13                        | 2.65                        |
| Gemfibrozil    | Anionic | 1.69                        | 2.08                        |
| Ibuprofen      | Anionic | 0.95                        | 1.85                        |
| Ioxynil        | Anionic | 0.61                        | 3.74                        |
| Ketoprofen     | Anionic | 0.88                        | 3.06                        |
| MCPA           | Anionic | 0.21                        | 3.16                        |

| Component Name          | Charge   | Affinity for 1 (log K <sub>D</sub> ) | Affinity for 2 (log K <sub>D</sub> ) |
|-------------------------|----------|--------------------------------------|--------------------------------------|
| Mecoprop                | Anionic  | 0.36                                 | 3.15                                 |
| Methomyl                | Anionic  | 0.00                                 | 0.53                                 |
| Naproxen                | Anionic  | 1.30                                 | 2.83                                 |
| Sulfamethoxazole        | Anionic  | 0.90                                 | 1.91                                 |
| Sulfathiazole           | Anionic  | 0.77                                 | 1.57                                 |
| Valsartan               | Anionic  | 0.25                                 | 2.87                                 |
| Warfarin                | Anionic  | 1.23                                 | 3.12                                 |
| Acebutolol              | Cationic | 2.58                                 | 1.35                                 |
| Albuterol               | Cationic | 2.02                                 | 0.60                                 |
| Amphetamine             | Cationic | 2.09                                 | 0.58                                 |
| Atenolol                | Cationic | 2.19                                 | 0.36                                 |
| Bupropion               | Cationic | 2.39                                 | 1.11                                 |
| Cimetidine              | Cationic | 2.24                                 | 0.87                                 |
| Codeine                 | Cationic | 2.25                                 | 0.87                                 |
| Erythromycin            | Cationic | 3.39                                 | 2.20                                 |
| Famotidine              | Cationic | 2.30                                 | 1.07                                 |
| Fluoxetine              | Cationic | 2.55                                 | 4.12                                 |
| Hydrocodone             | Cationic | 2.25                                 | 0.76                                 |
| Metoprolol              | Cationic | 2.46                                 | 0.83                                 |
| Morphine                | Cationic | 2.11                                 | 0.88                                 |
| Nadolol                 | Cationic | 2.18                                 | 0.58                                 |
| Sitagliptin             | Cationic | 2.51                                 | 1.01                                 |
| Tramadol                | Cationic | 2.27                                 | 0.62                                 |
| Trimethoprim            | Cationic | 2.48                                 | 1.01                                 |
| Venlafaxine             | Cationic | 2.32                                 | 1.00                                 |
| Abacavir                | Neutral  | 2.24                                 | 0.45                                 |
| Acetaminophen           | Neutral  | 1.36                                 | 0.02                                 |
| Acetochlor              | Neutral  | 1.30                                 | 0.10                                 |
| Allopurinol             | Neutral  | 1.33                                 | 1.21                                 |
| Atrazine                | Neutral  | 1.01                                 | 0.32                                 |
| Benzotriazole-methyl-1H | Neutral  | 1.10                                 | 1.30                                 |
| Bromacil                | Neutral  | 0.71                                 | 0.74                                 |
| Caffeine                | Neutral  | 1.28                                 | 0.38                                 |
| Carbamazepine           | Neutral  | 0.91                                 | 0.56                                 |
| Carbaryl                | Neutral  | 1.06                                 | 0.72                                 |
| Carbofuran              | Neutral  | 0.32                                 | 0.53                                 |
| Chloridazon             | Neutral  | 0.93                                 | 0.37                                 |
| Chloroxylenol           | Neutral  | 0.57                                 | 2.63                                 |
| Cotinine                | Neutral  | 0.75                                 | 1.13                                 |
| DEET                    | Neutral  | 0.64                                 | 0.21                                 |

| Component Name     | Charge         | Affinity for 1 (log K <sub>D</sub> ) | Affinity for 2 (log K <sub>D</sub> ) |
|--------------------|----------------|--------------------------------------|--------------------------------------|
| Diazinon           | Neutral        | 2.10                                 | 0.81                                 |
| Dimethoate         | Neutral        | 0.40                                 | 0.70                                 |
| Diuron             | Neutral        | 2.00                                 | 1.70                                 |
| Efavirenz          | Neutral        | 1.69                                 | 1.23                                 |
| Estrone            | Neutral        | 1.77                                 | 1.6                                  |
| Fluconazole        | Neutral        | 0.59                                 | 0.26                                 |
| Iopromid           | Neutral        | 0.62                                 | 1.69                                 |
| Isoproturon        | Neutral        | 1.58                                 | 1.02                                 |
| Linuron            | Neutral        | 2.08                                 | 1.71                                 |
| Malaoxon           | Neutral        | 0.71                                 | 0.42                                 |
| Meprobamate        | Neutral        | 0.17                                 | 0.66                                 |
| Metolachlor        | Neutral        | 1.40                                 | 0.47                                 |
| Metribuzin         | Neutral        | 0.93                                 | 0.34                                 |
| Molinate           | Neutral        | 1.16                                 | 0.60                                 |
| Oxcarbazepine      | Neutral        | 0.78                                 | 0.73                                 |
| Oxybenzone         | Neutral        | 2.29                                 | 2.20                                 |
| Paraxanthine       | Neutral        | 0.49                                 | 0.82                                 |
| Penciclovir        | Neutral        | 2.31                                 | 0.66                                 |
| Pentoxifylline     | Neutral        | 1.02                                 | 0.17                                 |
| Phenytoin          | Neutral        | 1.06                                 | 1.25                                 |
| Progesterone       | Neutral        | 2.19                                 | 2.39                                 |
| Prometon           | Neutral        | 1.87                                 | 0.66                                 |
| Propachlor         | Neutral        | 0.57                                 | 0.58                                 |
| Siduron            | Neutral        | 1.58                                 | 1.25                                 |
| Simazine           | Neutral        | 1.06                                 | 0.73                                 |
| Sucralose          | Neutral        | 0.47                                 | 0.47                                 |
| TCEP               | Neutral        | 0.62                                 | 0.40                                 |
| Testosterone       | Neutral        | 1.80                                 | 1.88                                 |
| Tributyl phosphate | Neutral        | 1.15                                 | 0.40                                 |
| Triclosan          | Neutral        | 2.32                                 | 2.40                                 |
| Atenolol Acid      | Zwitter        | 1.81                                 | 0.50                                 |
| Imidacloprid       | Zwitter        | 1.06                                 | 0.42                                 |
| Ranitidine         | Zwitter        | 2.33                                 | 1.17                                 |
| PFBA               | PFAS (anionic) | -0.28                                | 2.90                                 |
| PFHxA              | PFAS (anionic) | 0.16                                 | 3.57                                 |
| PFHpA              | PFAS (anionic) | 0.29                                 | 3.67                                 |
| PFOA               | PFAS (anionic) | 0.39                                 | 3.66                                 |
| PFNA               | PFAS (anionic) | 0.20                                 | 3.69                                 |
| PFDA               | PFAS (anionic) | 0.63                                 | 3.77                                 |
| PFBS               | PFAS (anionic) | 0.64                                 | 3.74                                 |
| PFHxS              | PFAS (anionic) | 0.69                                 | 3.80                                 |

| Component Name | Charge         | Affinity for 1 (log K <sub>D</sub> ) | Affinity for 2 (log K <sub>D</sub> ) |
|----------------|----------------|--------------------------------------|--------------------------------------|
| PFOS           | PFAS (anionic) | 0.80                                 | 3.84                                 |
| GenX           | PFAS (anionic) | 0.10                                 | 3.22                                 |

## References

- (1) Richardson, S. D.; Ternes, T. A. *Anal. Chem.* **2018**, *90*, 398–428.
- (2) Carpenter, C. M. G.; Helbling, D. E. *Environ. Sci. Technol.* **2018**, *52*, 6187–6196.
- 5 (3) Barry, V. Winquist, A. Steenland, K. *Environ. Health Perspect.* **2013**, *121*, 1313–1318.
- (4) Gallo, V.; Leonardi, G.; Genser, B.; Lopez-Espinosa, M.-J.; Frisbee, S. J.; Karlsson, L.; Ducatman, A. M.; Fletcher, T. *Environ. Health Perspect.* **2012**, *120*, 655–660.
- (5) Melzer, D.; Rice, N.; Depledge, M. H.; Henley, W. E.; Galloway, T. S. *Environ. Health Perspect.* **2010**, *118*, 686–692.
- 10 (6) DeWitt, J. Dietert, R. R., Ed.; *Molecular and Integrative Toxicology*; Springer International Publishing: Springer Cham Heidelberg New York Dordrecht London, 2015.
- (7) Diamanti-Kandarakis, E.; Bourguignon, J.-P.; Giudice, L. C.; Hauser, R.; Prins, G. S.; Soto, A. M.; Zoeller, R. T.; Gore, A. C. *Endocr. Rev.* **2009**, *30*, 293–342.
- 15 (8) Vajda, A. M.; Barber, L. B.; Gray, J. L.; Lopez, E. M.; Woodling, J. D.; Norris, D. O. *Environ. Sci. Technol.* **2008**, *42*, 3407–3414.
- (9) Tetreault, G. R.; Bennett, C. J.; Shires, K.; Knight, B.; Servos, M. R.; McMaster, M. E. *Aquat. Toxicol.* **2011**, *104*, 278–290.
- 20 (10) Gagné, F.; Bouchard, B.; André, C.; Farcy, E.; Fournier, M. *Comp. Biochem. Physiol. - C Toxicol. Pharmacol.* **2011**, *153*, 99–106.
- (11) Alsbaiee, A.; Smith, B. J.; Xiao, L.; Ling, Y.; Helbling, D. E.; Dichtel, W. R. *Nature* **2016**, *529*, 190–194.
- (12) Alzate-Sánchez, D. M.; Smith, B. J.; Alsbaiee, A.; Hinestroza, J. P.; Dichtel, W. R. *Chem. Mater.* **2016**, *28*, 8340–8346.
- 25 (13) Ling, Y.; Klemes, M. J.; Xiao, L.; Alsbaiee, A.; Dichtel, W. R.; Helbling, D. E. *Environ. Sci. Technol.* **2017**, *51*, 7590–7598.
- (14) Xiao, L.; Ling, Y.; Alsbaiee, A.; Li, C.; Helbling, D. E.; Dichtel, W. R. *J. Am. Chem. Soc.* **2017**, *139*, 7689–7692.
- 30 (15) Ji, W.; Xiao, L.; Ling, Y.; Ching, C.; Matsumoto, M.; Bisbey, R. P.; Helbling, D. E.; Dichtel, W. R. *J. Am. Chem. Soc.* **2018**, *140*, 12677–12681.
- (16) Klemes, M. J.; Ling, Y.; Chiapasco, M.; Alsbaiee, A.; Helbling, D. E.; Dichtel, W. *Chem. Sci.* **2018**, *9*, 8883–8889.

- (17) Li, C.; Klemes, M. J.; Dichtel, W. R.; Helbling, D. E. *J. Chromatogr. A* **2018**, *1541*, 52–56.
- (18) Ahrens, L.; Bundschuh, M. *Environ. Toxicol. Chem.* **2014**, *33*, 1921–1929.
- 5 (19) Wang, Z.; Dewitt, J. C.; Higgins, C. P.; Cousins, I. T. *Environ. Sci. Technol.* **2017**, *51*, 2508–2518.
- (20) D’Agostino, L. A.; Mabury, S. A. *Environ. Sci. Technol.* **2017**, *51*, 13603–13613.
- (21) Barzen-Hanson, K. A.; Roberts, S. C.; Choyke, S.; Oetjen, K.; McAlees, A.; Riddell, N.; McCrindle, R.; Ferguson, P. L.; Higgins, C. P.; Field, J. A. *Environ. Sci. Technol.* **2017**, *51*, 2047–2057.
- 10 (22) Breysse, P. N. *U.S. Department of Health and Human Services: Agency for Toxic Substances and Disease Registry: Toxicological profile for Perfluoroalkyls*. 2018.
- (23) Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaider, L. A.; Grandjean, P.; Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A.; et al. *Environ. Sci. Technol. Lett.* **2016**, *3*, 344–350.
- 15 (24) Andrews, D. Report: Up to 110 Million Americans Could Have PFAS–Contaminated Drinking Water <https://www.ewg.org/research/report-110-million-americans-could-have-pfas-contaminated-drinking-water> (accessed Jun 2, 2019).
- (25) Sun, M.; Arevalo, E.; Strynar, M.; Lindstrom, A.; Richardson, M.; Kearns, B.; Pickett, A.; Smith, C.; Knappe, D. R. U. *Environ. Sci. Technol. Lett.* **2016**, *3*, 415–419.
- 20 (26) Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; De Voogt, P. *Environ. Sci. Technol.* **2012**, *46*, 1708–1715.
- (27) Xiao, L.; Ching, C.; Ling, Y.; Nasiri, M.; Klemes, M. J.; Reineke, T. M.; Helbling, D. E.; Dichtel, W. R. (*Submitted to Chem. Mater. December 2018*) **2019**, 1–9.
- 25 (28) Mason, C. R.; Maynard-Atem, L.; Heard, K. W. J.; Satilmis, B.; Budd, P. M.; Friess, K.; Lanč, M.; Bernardo, P.; Clarizia, G.; Jansen, J. C. *Macromolecules* **2014**, *47*, 1021–1029.
- (29) Vojkovsk, T. *Pept. Res.* **1995**, *8*, 236–237.
- (30) Mařík, J.; Song, A.; Lam, K. S. *Tetrahedron Lett.* **2003**, *44*, 4319–4320.
- (31) Buckley, D.; Henbest, H. B.; Slade, P. *J. Chem. Soc.* **1957**, 4891, 4891.

30

## EQUIVALENTS

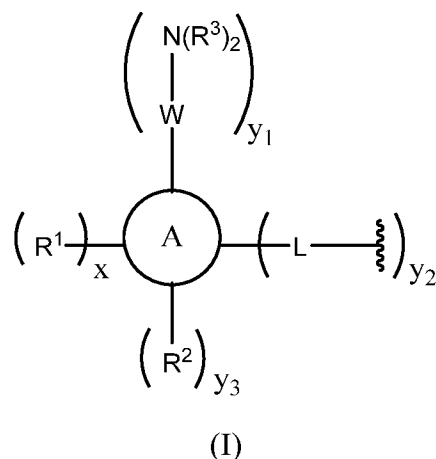
[0162] While the present invention has been described in conjunction with the specific embodiments set forth above, many alternatives, modifications and other variations thereof will be apparent to those of ordinary skill in the art. All such alternatives, modifications and variations are intended to fall within the spirit and scope of the present invention.

35

## CLAIMS:

1. A mesoporous polymeric material comprising a plurality of cyclodextrins crosslinked with a plurality of crosslinks comprising formula (I):

5



wherein

A is an aryl or heteroaryl moiety;

10 each  $\text{R}^1$  is independently selected from the group consisting of  $-\text{CF}_3$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{CN}$ ,  $-\text{C(O)}-\text{NH}_2$ ,  $-\text{N}_2^+$ ,  $-\text{NO}_2$ ,  $-\text{NO}$ ,  $-\text{NH-OH}$ ,  $-\text{N-C(O)-alkyl}$ ,  $-\text{halogen}$ ,  $-\text{N}_3$ ,  $-\text{CH}_2\text{-OH}$ ,  $-\text{CH}_2\text{-N}_3$ ,  $-\text{HC=O}$ ,  $-\text{C-NH-C(O)C-NH-}$ ,  $-\text{C-halogen}$ ,  $-\text{C-NH-C(O)-CO-alkyl}$ ,  $-\text{C-NH-C(O)-CO-aryl}$ ,  $-\text{C-NH-(SO}_2\text{)-aryl}$ ,  $-\text{C-NH-(SO}_2\text{)-alkyl}$ ,  $-\text{C=N-OH}$ ,  $-\text{C-NHC(O)-alkyl}$ , and  $-\text{NH-C(O)-NH}_2$ ;

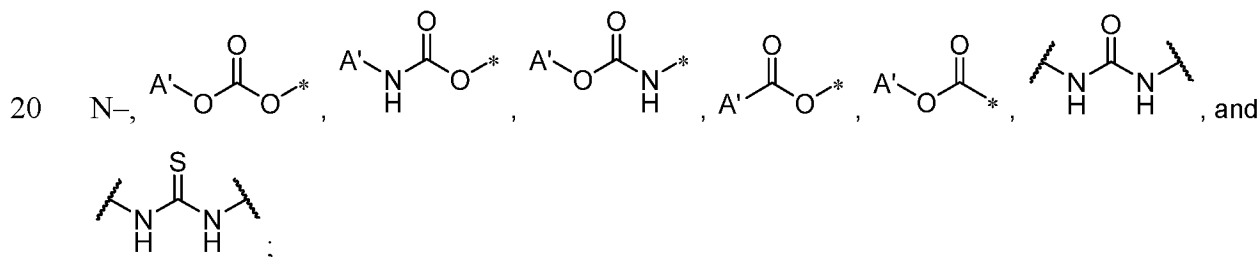
each  $\text{R}^2$  is independently  $-\text{OH}$ ,  $-\text{O-metal cation}$ ,  $\text{alkyl}$ ,  $-\text{SH}$ ,  $-\text{S-metal cation}$ ,  $-\text{S-alkyl}$ ;

15 each  $\text{R}^3$  is independently  $-\text{H}$ ,  $\text{C}_1\text{-C}_6$   $\text{alkyl}$ ,  $\text{C}_1\text{-C}_3$   $\text{haloalkyl}$ ,  $\text{aryl}$ ,  $-\text{C(O)N(R}^a\text{)(R}^b\text{)}$ ,  $-\text{C(O)R}^a$ ,  $-\text{CO}_2\text{R}^a$ ,  $-\text{SO}_2\text{N(R}^a\text{)(R}^b\text{)}$ , or  $-\text{SOR}^a$ ;

each  $\text{R}^a$  and  $\text{R}^b$  is independently  $\text{H}$ , or  $\text{C}_1\text{-C}_6$   $\text{alkyl}$ ;

each W is independently a bond, an alkylene group, or  $-(\text{O-CH}_2\text{-CH}_2)_x-$  wherein x is 1-100;

each L is independently a linking moiety selected from the group consisting of  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{N}-$ ,



$\text{A}'$  is a covalent bond to A;

\* is a covalent bond to  $\text{---}$ ;

$\zeta$  is a point of attachment to the plurality of cyclodextrin carbon atoms;

x is 0-8;

y<sub>1</sub> is 1-4;

y<sub>2</sub> is at least 2; and

5 y<sub>3</sub> is 0-4.

2. The mesoporous polymeric material of claim 1, wherein each W is  $-\text{CH}_2-$ .

3. The mesoporous polymeric material of claims 1 or 2, wherein each L is  $-\text{O}-$ .

4. The mesoporous polymeric material moiety of any of the preceding claims, wherein A is  
10 selected from the group consisting of phenyl, naphthyl, pyridyl, benzofuranyl, pyrazinyl,  
pyridazinyl, pyrimidinyl, triazinyl, quinoline, benzoxazole, benzothiazole, 1H-benzimidazole,  
isoquinoline, quinazoline, quinoxaline, pyrrole, indole, biphenyl, pyrenyl, anthracenyl.

5. The mesoporous polymeric material of any of the preceding claims, wherein A is phenyl.

6. The mesoporous polymeric material of any of the preceding claims, wherein each  
15 cyclodextrin is selected from the group consisting of  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin,  $\gamma$ -  
cyclodextrin, and combinations thereof.

7. The mesoporous polymeric material of any of the preceding claims, wherein each  
cyclodextrin is a  $\beta$ -cyclodextrin.

8. The mesoporous polymeric material of any of the preceding claims, wherein each R<sup>2</sup> is F.

20 9. The mesoporous polymeric material of any of the preceding claims, wherein x is 0-2.

10. The mesoporous polymeric material of any of the preceding claims, wherein x is 0.

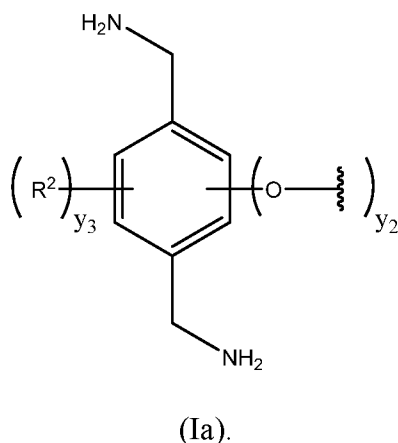
11. The mesoporous polymeric material of any of the preceding claims, wherein y<sub>1</sub> is 1-2.

12. The mesoporous polymeric material of any of the preceding claims, wherein y<sub>2</sub> is 2-3.

13. The mesoporous polymeric material of any of the preceding claims, wherein y<sub>3</sub> is 1-2.

25 14. The mesoporous polymeric material of claim 1, wherein x is 1 and R<sup>1</sup> is  $-\text{CN}$ .

15. The mesoporous polymeric material of claim 1, wherein the plurality of cyclodextrins are crosslinked with at least an equimolar amount of crosslinks comprising formula (Ia):



5

16. The mesoporous polymeric material of claim 15, wherein  $y_2$  and  $y_3$  are each 2.

17. The mesoporous polymeric material of claims 15 or 16, wherein each  $R^2$  is fluoro.

18. The mesoporous polymeric material of any of claims 15-17, wherein each cyclodextrin is  $\beta$ -cyclodextrin.

10 19. The mesoporous polymeric material of any of the preceding claims, wherein the molar ratio of cyclodextrin to crosslinks comprising formula (I) or formula (Ia) ranges from about 1:1 to about 1:X, wherein X is three times the average number of glucose subunits in the cyclodextrin.

15 20. The mesoporous polymeric material of claim 19, wherein the molar ratio of cyclodextrin to linking groups of formula (I) or formula (Ia) is about 1:6.

21. The mesoporous polymeric material of claim 19, wherein the molar ratio of cyclodextrin to crosslinks comprising formula (I) or formula (Ia) is about 1:5.

22. The mesoporous polymeric material of claim 19, wherein the molar ratio of cyclodextrin to crosslinks comprising formula (I) or formula (Ia) is about 1:4.

20 23. The mesoporous polymeric material of claim 19, wherein the molar ratio of cyclodextrin to crosslinks comprising formula (I) or formula (Ia) is about 1:3.

24. The mesoporous polymeric material of claim 19, wherein the molar ratio of cyclodextrin to crosslinks comprising formula (I) or formula (Ia) is about 1:2.

25. A supported porous polymeric material comprising porous particles affixed to a solid substrate, wherein said porous particles comprise a plurality of cyclodextrin moieties with a plurality of crosslinks comprising formula (I) or formula (Ia).

26. The supported porous polymeric material of claim 25, wherein the solid substrate is selected from the group consisting of, microcrystalline cellulose, cellulose nanocrystals, cellulose pulp, acrylate materials, methacrylate materials, styrenic materials, polystyrene materials, polyester materials, nylon materials, silicates, silicones, alumina, titania, zirconia, hafnia, hydroxyl-containing polymer beads, hydroxyl-containing irregular particles, amino-containing polymer beads, amino-containing irregular particles, fibrous materials, spun yarn, continuous filament yarn, staple nonwovens, continuous filament nonwovens, knit fabrics, woven fabrics, nonwoven fabrics, film membranes, spiral wound membranes, hollow fiber membranes, cloth membranes, powders, solid surfaces, polyvinylamine, polyethylenimine, proteins, protein-based fibers, wool, chitosan, amine-bearing cellulose derivatives, polyamide, vinyl chloride, vinyl acetate, polyurethane, melamine, polyimide, polyacryl, polyamide, acrylate butadiene styrene (ABS), Barnox, PVC, nylon, EVA, PET, cellulose nitrate, cellulose acetate, mixed cellulose ester, polysulfone, polyether sulfone, polyvinylidene fluoride, polytetrafluoroethylene, polyethylene, polypropylene, polycarbonate, silicon, silicon oxide, glass, glass microfibers, phosphine-functional materials, thiol-functional materials, fibrillating polyolefin materials, fibrillating regenerated cellulose materials, fibrillating acrylic materials, and combinations thereof.

27. The supported porous polymeric material of claim 26, wherein the fibrous material is selected from the group consisting of pulp fibers, short cut fibers, staple fibers, continuous filament fibers, and cellulosic fibers;

wherein the cellulosic fiber is selected from the group consisting of wood pulp, paper, paper fibers, cotton, regenerated cellulose, cellulose esters, cellulose ethers, starch, polyvinylalcohols, polyvinylphenols, and derivatives thereof.

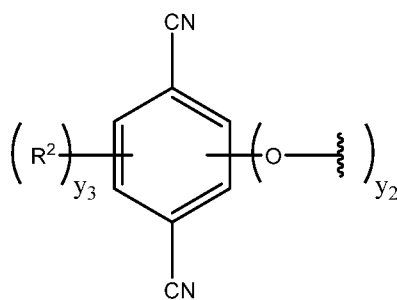
28. The supported porous polymeric material of claim 26, wherein the substrate is microcrystalline cellulose, cellulose nanocrystals, silica, glass, or beads made from synthetic polymers.

29. The supported porous polymeric material of claim 28, wherein the substrate is microcrystalline cellulose.
30. A method of purifying a fluid sample comprising one or more pollutants, the method comprising contacting the fluid sample with the mesoporous polymeric material of any of  
5 claims claim 1-24 or the supported porous polymeric material of claims 25-29, whereby at least 50 wt. % of the total amount of the one or more pollutants in the fluid sample is adsorbed by the mesoporous polymeric material.
31. The method of claim 30, wherein the fluid sample flows across, around, or through the mesoporous polymeric material or supported polymeric material.
- 10 32. The method of claim 30, wherein the fluid sample is contacted with the mesoporous polymeric material or supported polymeric material under static conditions for an incubation period and after the incubation period the fluid sample is separated from the mesoporous polymeric material.
- 15 33. The method of claim 30, wherein the fluid sample is drinking water, wastewater, ground water, aqueous extract from contaminated soil, or landfill leachate.
34. The method of claim 30, wherein the fluid sample is in the vapor phase.
35. The method of claim 34, wherein the fluid sample comprises one or more volatile organic compounds and air.
36. The method of claim 30, wherein the pollutants are one or more of anionic  
20 micropollutants, heavy metals, and/or dyes.
37. The method of claim 36, wherein the pollutant is an anionic micropollutant.
38. The method of claim 36, wherein the anionic micropollutant is a perfluorinated alkyl compound.
39. The method of claim 36, wherein the perfluorinated alkyl compound is PFOA.
- 25 40. The method of claim 36, wherein the pollutant is a heavy metal.
41. The method of claim 40, wherein the heavy metal is  $\text{Pb}^{2+}$ .

42. A method of removing one or more compounds from a fluid sample or determining the presence or absence of one or more compounds in a fluid sample comprising: a) contacting the sample with the mesoporous polymeric material of any of claims claim 1-24 or the supported porous polymeric material of claims 25-29 for an incubation period; b) separating  
5 the mesoporous polymeric material or supported porous polymeric material after the incubation period from the sample; and c) heating the mesoporous polymeric material or supported porous polymeric material separated in step b), or contacting the mesoporous polymeric material or supported porous polymeric material separated in step b) with a solvent, thereby releasing at least a portion of the compounds from the mesoporous polymeric  
10 material or supported porous polymeric material; and d1) optionally isolating at least a portion of the compounds released in step c); or d2) determining the presence or absence of the compounds released in step c), wherein the presence of one or more compounds correlates to the presence of the one or more compounds in the sample.
43. The method of claim 42, wherein said determining is carried out by gas chromatography,  
15 liquid chromatography, supercritical fluid chromatography, or mass spectrometry.
44. The method of claim 42, wherein the sample is a food and the compounds are volatile organic compounds.
45. The method of claim 42, wherein the sample is a perfume or fragrance and the compounds are volatile organic compounds.
- 20 46. The method of claim 42, wherein the compounds are anionic micropollutants, heavy metals, and/or dyes.
47. An article of manufacture comprising the mesoporous polymeric material of any of claims claim 1-24 or the supported porous polymeric material of claims 25-29.
48. The article of manufacture of claim 47, wherein the article is protective equipment.
- 25 49. The article of manufacture of claim 48, wherein the article is clothing.
50. The article of claim 47, wherein the article is a filtration medium.
51. The article of claim 47, wherein the article is an extraction device.

52. The article of claim 51, wherein the extraction device is a solid-phase extraction device capable of adsorbing polar and semi-polar organic molecules.

53. A method of making a crosslink comprising formula (Ia) comprising reducing one or more of the nitrile groups of a linking group of formula (II) with a suitable reducing agent



(II).

54. The method of claim 53, wherein the suitable reducing agent is selected from the group consisting of  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , diborane, DIBAL-H,  $\text{BH}_3\text{-THF}$ ,  $\text{BH}_3\text{-SMe}_2$ ,  $\text{H}_2 + \text{Raney Ni}$ , and  $\text{H}_2 + \text{Pd/C}$ .

10 55. The method of claim 54, wherein the suitable reducing agent is  $\text{BH}_3\text{-SMe}_2$ .

**Fig. 1**

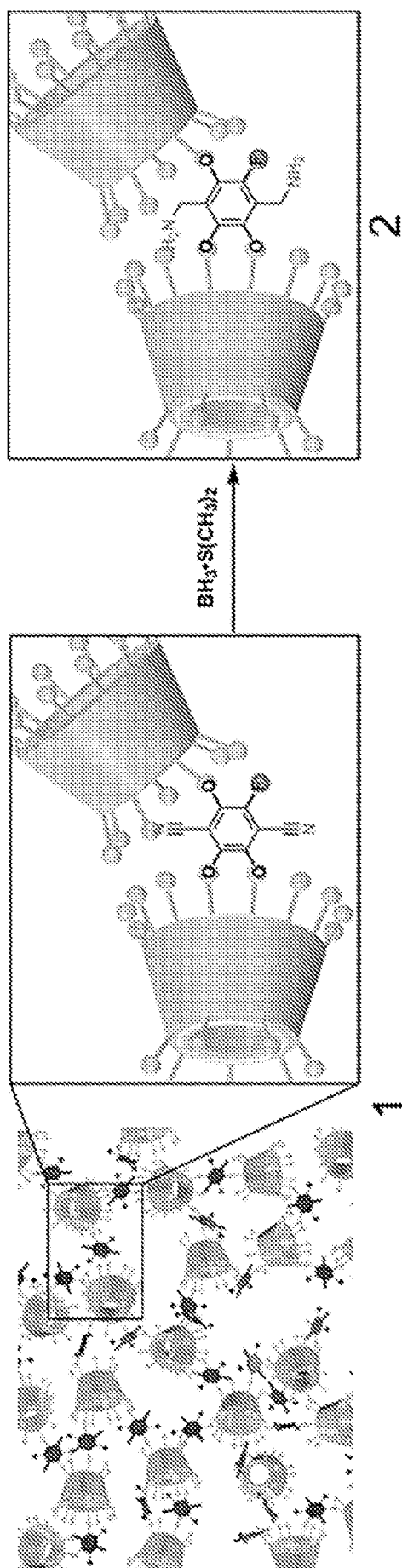


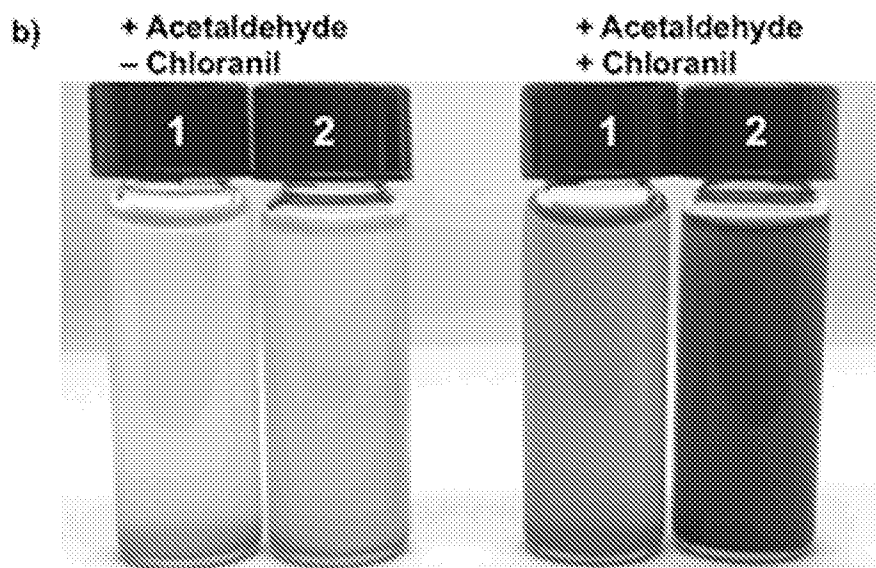
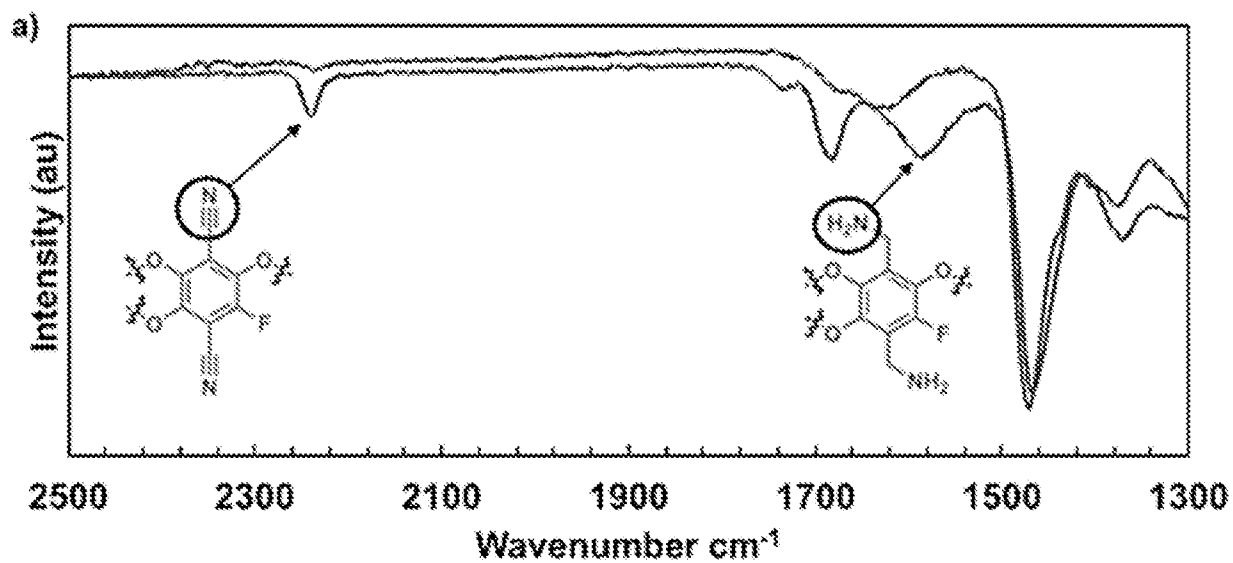
**Fig. 2**

**Fig. 3**

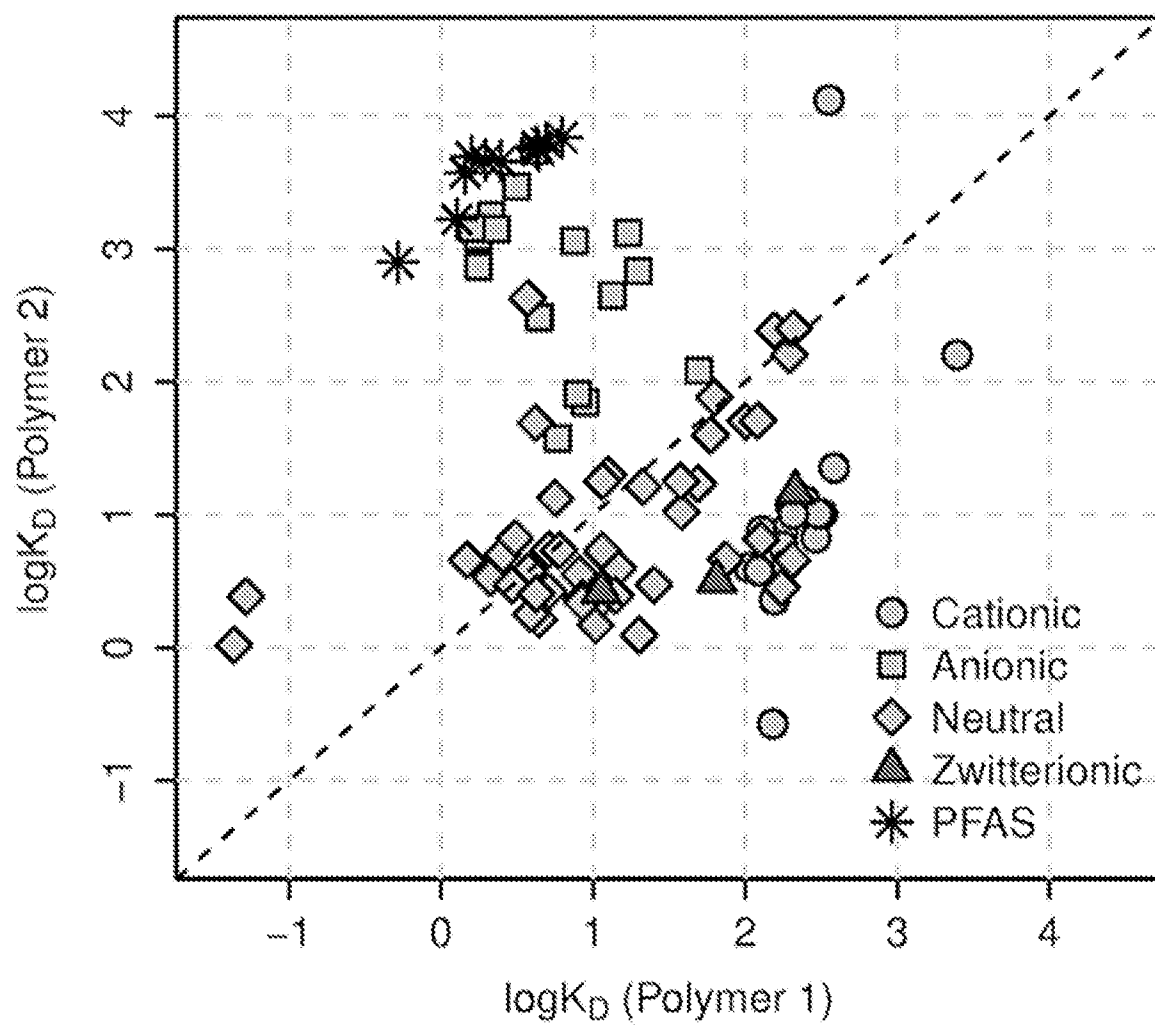


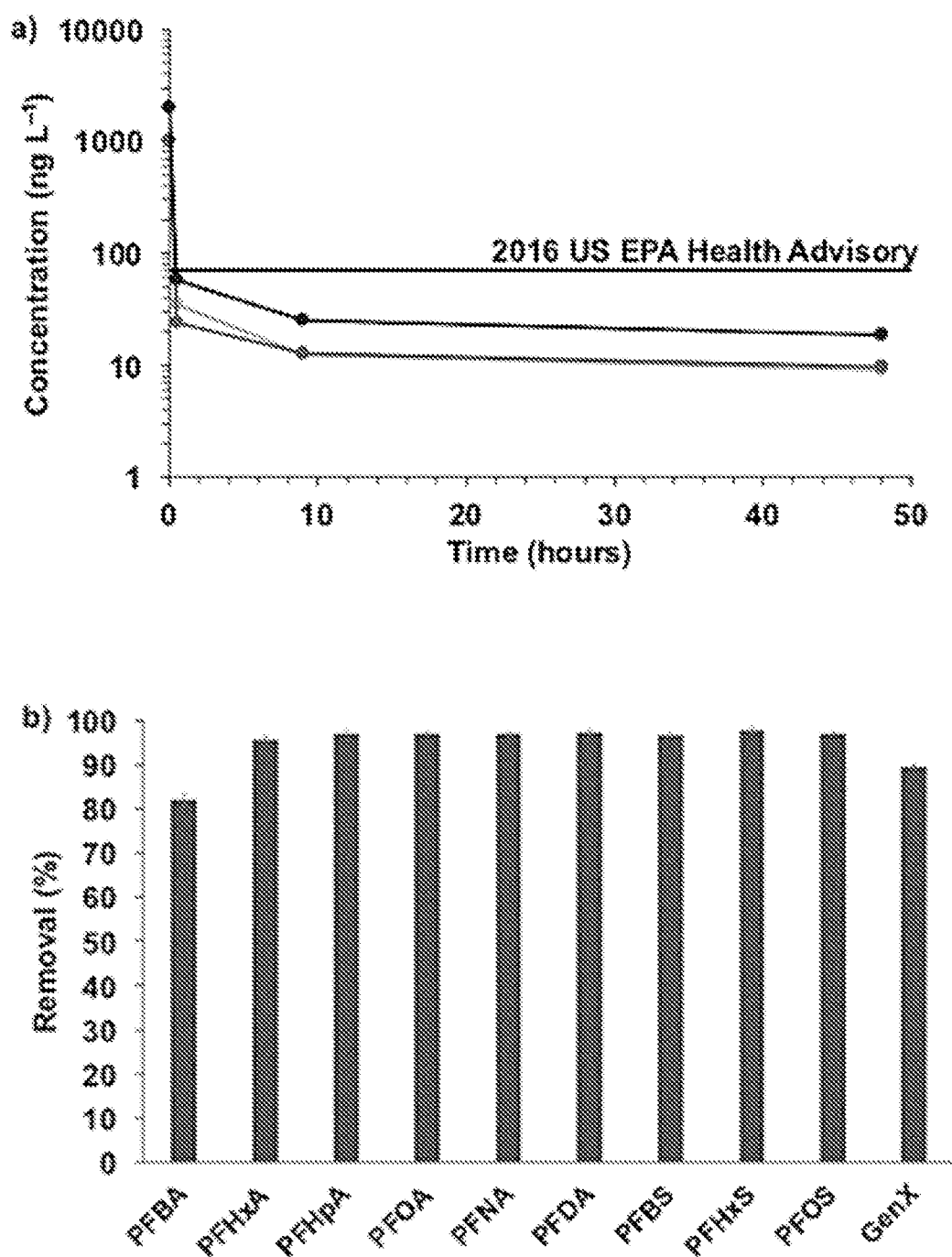
**Fig. 4**

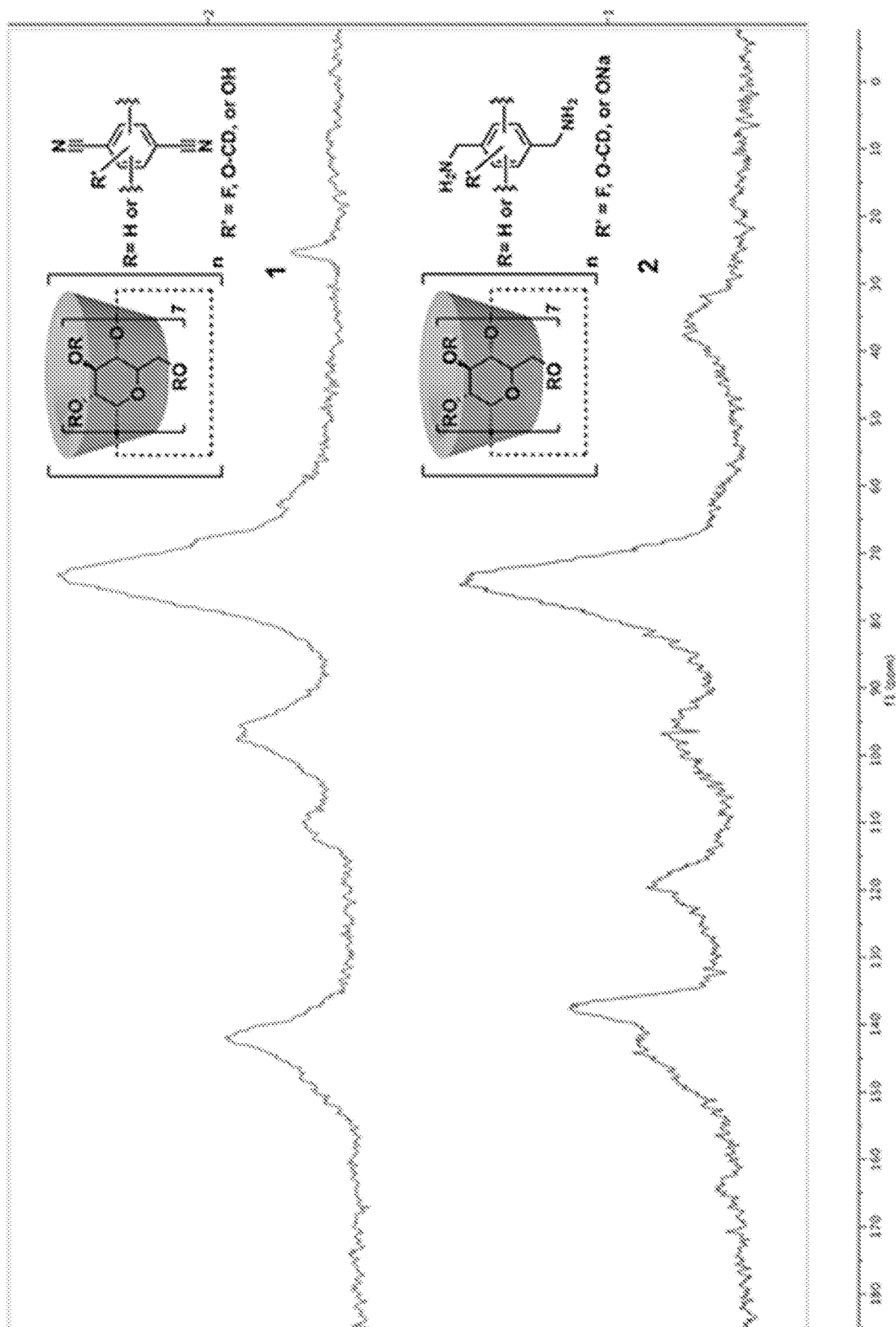
**Fig. 5**

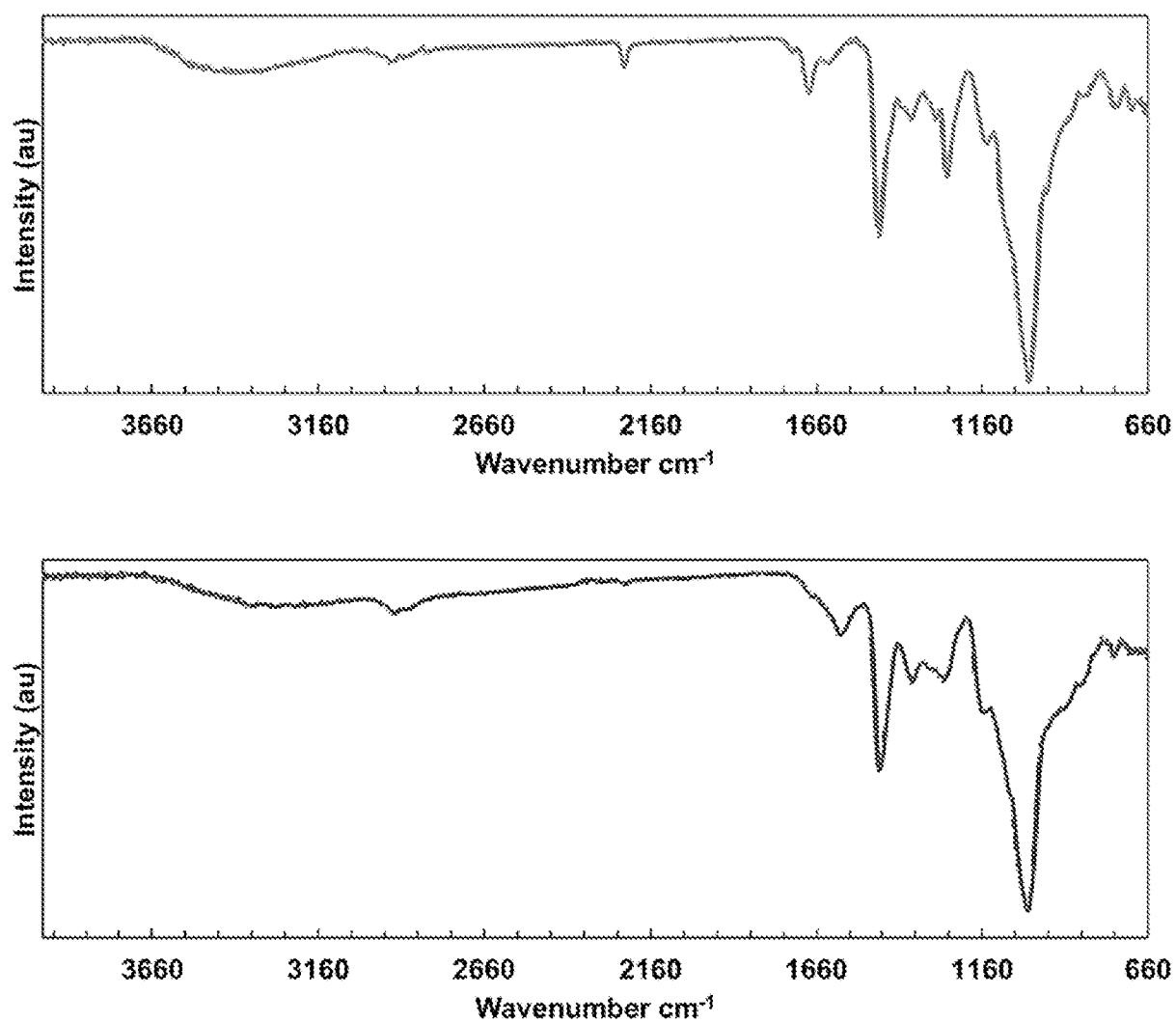
**Fig. 6**

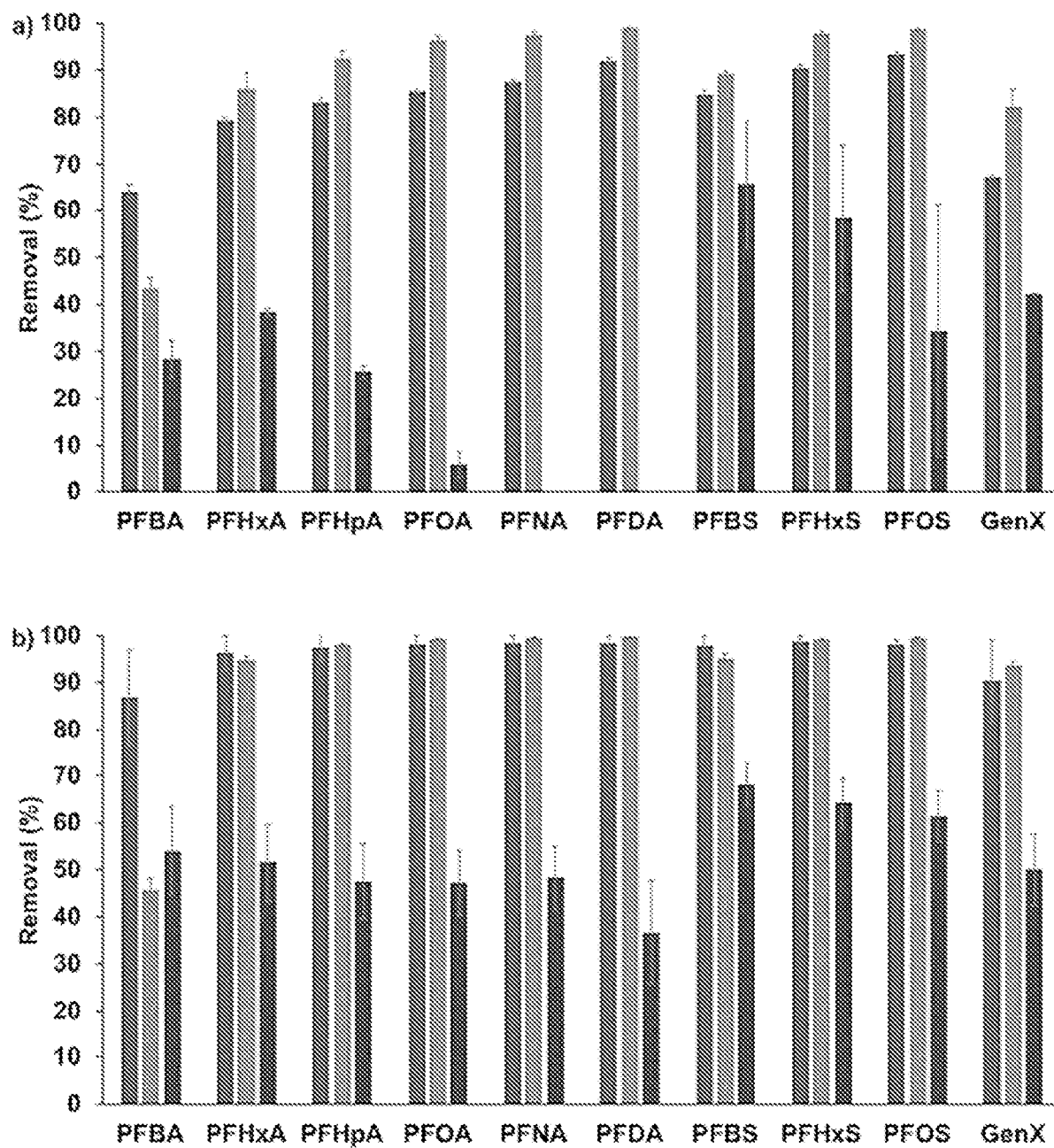
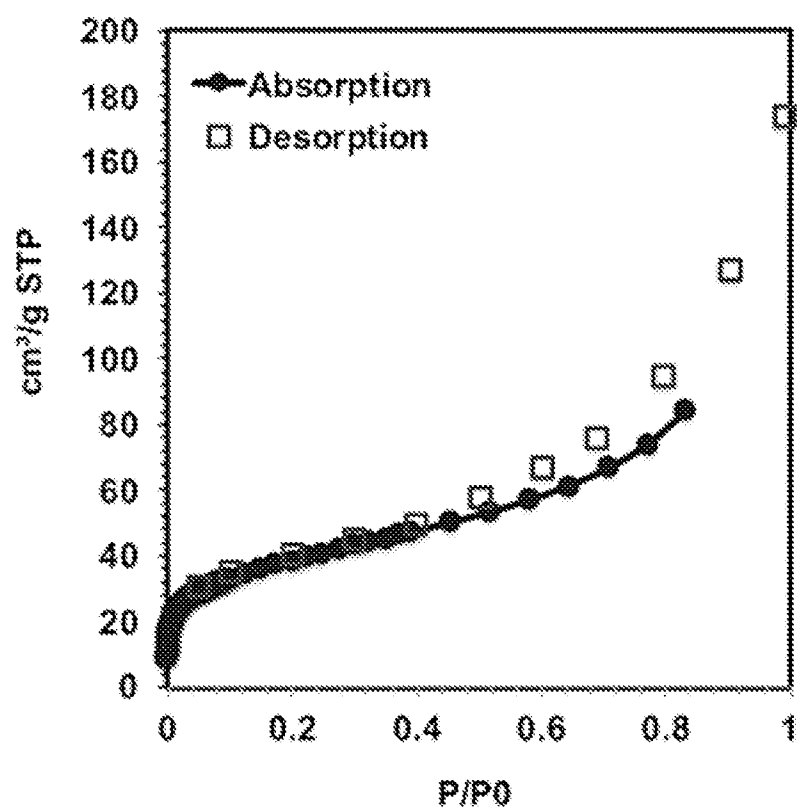
**Fig. 7**

**Fig. 8**

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/66641

## 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.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
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.: 4-13, 18-24 and 30-52  
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:

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.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/66641

## A. CLASSIFICATION OF SUBJECT MATTER

IPC - B01D 15/00; B01J 20/22; C02F 1/28 (2020.01)

CPC - A62D 3/33; B01D 15/00; B01J 20/22; C02F 1/28; C08B 37/0012

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)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                    | Relevant to claim No.    |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| Y         | WO 2018/200857 A1 (CORNELL UNIVERSITY et al.) 01 November 2018 (01.11.2018) para [0010];[0018];[0079];[0085];[0086];[0090];[0095];[0111];[0117]; pg. 19, ln 5-12; pg. 21; Figure 1; Claim 38                          | 1-3, 14-17, 25-29, 53-55 |
| Y         | DIENST et al. 'Selective Functionalization and Flexible Coupling of Cyclodextrins at the Secondary Hydroxyl Face', J. Org. Chem., 1995, Vol. 60, pp. 6537-6545. pg. 6540, Col 2, para 2, Scheme 2; pg. 6541, Chart 2, | 1-3, 14-17, 25-29, 53-55 |
| Y         | PARK et al. 'Preparation and Self-inclusion Properties of p-Xylylenediamine-modified beta-Cyclodextrins: Dependence on the Side of Modification', J. Chem. Soc. Perkin Trans. 2001, Vol. 2, pp. 2114-2118. pg. 2114   | 15-17, 53-55             |
| A         | ALSBAIEE et al. 'Rapid Removal of Organic Micropollutants From Water by a Porous beta-Cyclodextrin Polymer', Nature, 2016, Vol. 529, pp. 190-206. ENTIRE DOCUMENT                                                     | 1-3, 14-17, 25-29, 53-55 |
| A         | US 9,624,314 B2 (CORNELL UNIVERSITY) 18 April 2017 (18.04.2017) ENTIRE DOCUMENT                                                                                                                                       | 1-3, 14-17, 25-29, 53-55 |

☐ 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

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

13 FEBRUARY 2020

Date of mailing of the international search report

05 MAR 2020

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Lee Young

Telephone No. PCT Helpdesk: 571-272-4300