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(54) Title: GRAFTED POROUS CYCLODEXTRIN POLYMERIC MATERIAL AND METHODS OF MAKING AND USING SAME

(57) Abstract: Provided herein are compositions comprising mesoporous cyclodextrin (CD) containing polymers grafted to or bonded to a substrate. The compositions can be used for removing organic contaminants from water. The P-CDPs can rapidly sequester pharmaceuticals, pesticides, and other organic micropollutants, achieving equilibrium binding capacity in seconds with adsorption rate constants 15-200 times greater than activated carbon and nonporous CD sorbents. The composition can be regenerated several times, through a room temperature washing procedure, with no loss in performance.

GRAFTED POROUS CYCLODEXTRIN POLYMERIC MATERIAL AND METHODS OF MAKING AND USING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

5 **[0001]** This application claims the benefit of U.S. Provisional Application No. 62/490,162, filed April 26, 2017, the contents of which are incorporated herein by reference in their entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

10 **[0002]** This invention was made with government support under Grant Numbers 1413862 & 1541820 awarded by the National Science Foundation. The government has certain rights in the invention.

FIELD OF THE DISCLOSURE

15 **[0003]** The present disclosure relates to fluid purification with porous, high surface area cyclodextrin polymeric materials grafted or bonded to a support.

BACKGROUND OF THE INVENTION

20 **[0004]** As a consequence of population growth, continued industrialization, and climate change, communities in developed and developing countries face dwindling water supplies and are turning to drinking water resources that have been impacted by agricultural runoff or wastewater discharges. Drinking water, surface water, and groundwater impaired by these anthropogenic activities contain pollutants including trace organic chemicals, known as organic micropollutants, such as pesticides, pharmaceuticals, components of personal care products, and other industrial chemicals. As these pollutants have gained attention and analytical
25 techniques have improved, new emerging organic contaminants have been identified in water resources at a rapid pace. Toxicological data for these chemicals are limited, but significant developmental, reproductive, endocrine disrupting and other chronic health effects have been reported. Also, these pollutants can have negative effects on aquatic ecosystems, which serve as a basis of the food chain. Existing technologies for removing these emerging contaminants
30 can be energy intensive, expensive, and are not always effective. Conventional processes for drinking and wastewater purification like coagulation, flocculation, sedimentation, gravity settling, filtration, and biological processes do not adequately remove ions and other dissolved substances. These require more powerful separation processes like ultrafiltration, adsorption, and ion exchange. The sequestration of dissolved substances is done by passing water through

a column packed with an active material, for which the ability of the separation media to remove contaminants and the pressure drop are important factors. Managing this pressure drop to acceptable levels is achieved by tuning the particle size of the adsorbent, wherein large (typically tens of microns or larger) particle size and narrow particle size distribution enable rapid flow rates with minimal pressure drops.

[0005] There is also increasing interest in incorporating active materials into fabrics (including woven and nonwoven fabrics) for various purposes. For example, active materials incorporated into a sheet form (including pleated filters) have useful flow properties for removing contaminants from liquid or vapor streams. Active materials incorporated into fabrics (e.g., clothing) can be used to protect the wearer against potentially dangerous contaminants, or can be used to absorb odors (e.g., for outdoors, military, sanitary or medical applications).

[0006] Volatile organic compounds (VOCs) are a broad category of atmospheric contaminants (also termed pollutants) emitted from industrial syntheses, transportation, and commercial products including solvent thinners, paint, cleaners, and lubricants. Several techniques have been applied to remove VOCs from air, most commonly through adsorption and sequestration. 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. Because of the poorly defined structure and variation in the binding sites of ACs, optimal adsorption selectivities for processes employing ACs require empirical screening for each process design, 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.

[0007] To address some of the drawbacks associated with activated carbon, attention has turned to other adsorbents. One such 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 forming host-guest interactions with thousands of 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 that 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.

[0008] Improved mesoporous cyclodextrin-based absorbents have been described in US 9,624,314. Such materials have substantially improved absorption characteristics compared to ACs or epichlorohydrin crosslinked cyclodextrin polymers. The present application, in various embodiments, provides durable, mesoporous cyclodextrin-based absorbents supported on substrates with improved flow and mass transport characteristics, which allow utilization of such materials in forms and geometries which provide superior absorption characteristics.

SUMMARY OF THE INVENTION

[0009] The present disclosure provides porous, high surface area cyclodextrin polymeric materials grafted or bonded (or otherwise affixed) by various means (chemically, adhesively, and/or mechanically) to a solid substrate or support of known size and shape. Thus, the supported cyclodextrin-based absorbents of the present disclosure can be incorporated into durable forms which provide performance characteristics similar to and in some aspects superior to the unsupported adsorbent particles. For example, the fluid flow characteristics of the supported adsorbent particles of the present disclosure are superior to those of the unsupported particles, and the absorbent particles of the present disclosure can be readily be incorporated in to useful forms (e.g., textiles used in clothing, fluid filters, medical or sanitary fabrics, etc.). The present disclosure also provides methods of making and using these materials.

[0010] In some embodiments, the present disclosure provides a supported porous polymeric material comprising porous particles affixed to a solid substrate, wherein said porous particles comprise a plurality of cyclodextrin moieties crosslinked with one or more aryl moieties, and wherein the supported porous polymeric material has one or more performance characteristics which are nearly the same as or superior to the performance characteristics of the unsupported adsorbent of the same composition, for example which are at least about 50% of the same performance characteristics of unsupported porous particles of the same composition. In some embodiments, the performance characteristic is pollutant uptake. In some embodiments, the

performance characteristic is equilibrium adsorption capacity. In some embodiments, the performance characteristic is rate of attaining equilibrium adsorption. In some embodiments, the performance characteristic is specific permeability. In some embodiments, any of the performance characteristics recited above may be about the same or greater than the unsupported porous particles of the same composition. In some embodiments, the aryl moiety is TFN. In some embodiments, the support is microcrystalline cellulose (CMC). In some embodiments, the supported porous polymeric material is CD-TFN@CMC.

[0011] In one embodiment, the cyclodextrin polymer of the present disclosure is grafted or bonded onto a substrate of known size and shape. In another embodiment, the substrate is cellulose. In another embodiment, the cellulose is microcrystalline cellulose. In another embodiment, the size and morphology of the microcrystalline cellulose are tuned to optimize the desired properties of the grafted or bonded cyclodextrin polymer. In another embodiment, one of the desired properties is managing a pressure drop. In another embodiment, managing the pressure drop to acceptable levels is accomplished by tuning the particle size of the adsorbent. In another embodiment, tuning the particle size and morphology leads to grafted or bonded β -cyclodextrin polymer (e.g., CD-TFN, where “CD” refers to cyclodextrin, and TFN refers to the crosslinker “tetrafluoroterephthalonitrile”) on microcrystalline cellulose (e.g., CD-TFN@cellulose also referred to as CD-TFN@CMC) with improved flow characteristics. In another embodiment the improved flow characteristics of CD-TFN@cellulose material result from having a large particle size with a narrow particle size distribution. In another embodiment a large particle size is defined as particles tens of microns or larger. In still another embodiment, the improved flow characteristics enable more effective removal of pollutants, contaminants, and/or other unwanted compounds from liquids including but not limited to drinking and wastewater.

[0012] In some embodiments, the present disclosure provides a porous, high surface area cyclodextrin polymeric material. These materials may also be referred to herein as polymers, polymeric materials, or porous polymeric materials. In some embodiments, the high surface area cyclodextrin polymeric material may be non-porous. In various embodiments, the polymeric materials of the present disclosure comprise a plurality of cyclodextrin moieties and microcrystalline cellulose crosslinked by one or more aryl moieties.

[0013] In an embodiment, the porous polymeric material does not have an aliphatic ether bond to a crosslinking moiety.

[0014] In various embodiments, the molar ratio of cyclodextrin moieties to aryl moieties ranges from about 1:1 to about 1:X, wherein X is three times the average number of glucose subunits in the cyclodextrin moieties. In various embodiments, the molar ratio of microcrystalline cellulose to aryl moieties ranges from about 1:1 to about 1:X, wherein X is three times the average number of glucose subunits in the microcrystalline cellulose.

[0015] In various embodiments as described herein, the polymeric materials of the present disclosure comprise a plurality of cyclodextrin moieties and a substrate (e.g., a polymeric or inorganic support such as silica or alumina as described herein) functionalized with hydroxyl groups such that the cyclodextrin moieties and support are crosslinked by one or more aryl moieties. Alternatively, in other embodiments as described herein, the polymeric or inorganic supports are functionalized with reactive groups other than hydroxyl (e.g., carboxylic acids, acid chlorides, anhydrides or other activated forms of carboxylic acids known in the art; isocyanates, epoxides, amines, etc.) that can react with the polymeric materials of the present disclosure (which themselves may be functionalized with functional groups that can react with the substrate material), thereby grafting to the polymeric materials onto the substrate. In other embodiments, the polymeric materials of the present disclosure can be adhered to the substrate using a binder as described herein. Regardless of bonding or grafting mechanism, the supported polymeric materials of the present disclosure exhibit absorption characteristics that are substantially the same as the unsupported material. That is, the method and materials used to affix the polymeric materials of the present disclosure to the substrate do not substantially occlude or otherwise interfere with the absorption characteristics of the polymeric materials of the present disclosure.

[0016] In various embodiments, the cyclodextrin moieties comprise β -cyclodextrin. In various embodiments, the cyclodextrin moieties comprise β -cyclodextrin and the ratio of β -cyclodextrin moieties to crosslinking moieties is 1:1 to 1:21. In various embodiments, the porous polymeric material is mesoporous. In various embodiments, the porous polymeric material has a Brunauer-Emmett-Teller (BET) surface area of 1 m²/g to 2000 m²/g.

[0017] In various embodiments, the present disclosure is directed to compositions comprising any of the porous or non-porous polymeric materials described herein. In various embodiments, the composition comprises any of the porous or non-porous polymeric materials described herein covalently bonded to a support material, wherein the support material can be any support as described herein, including cellulosic materials, such as cotton, in any form, such as fibers, fabrics, etc. In various embodiments, the composition comprises any of the

porous or non-porous polymeric materials described herein adhesively bonded to a support material, wherein the support material can be any support as described herein, including cellulosic material, such as cotton, in any form, such as fibers, fabrics, etc.

[0018] In some embodiments, the present disclosure provides a method of purifying an aqueous sample comprising one or more organic pollutants, comprising contacting the aqueous sample with the supported porous polymeric material of the present disclosure, such that at least 50% to at least 99% of the one or more organic pollutants are removed from the aqueous sample. In some embodiments, the one or more cyclodextrin moieties are β -cyclodextrin moieties. In some embodiments, the supported porous polymeric material is CD-TFN@CMC.

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 aqueous sample is drinking water, wastewater, ground water, aqueous extracts from contaminated soils, or landfill leachates.

[0019] In some embodiments, the present disclosure provides a method of determining the presence or absence of compounds in a sample, comprising: a) contacting the sample with the supported porous polymeric material of the present disclosure for an incubation period; b) isolating the supported porous polymeric material from a) from the sample; and c) heating the supported porous polymeric material from b) or contacting the supported porous polymeric material from b) with a solvent such that at least part of the compounds are then released from the supported porous polymeric 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 the compounds. In some embodiments, the supported porous polymeric material is CD-TFN@CMC. In some embodiments, the compounds are organic compounds.

[0020] In various embodiments, the present disclosure is directed to methods of purifying a fluid sample comprising one or more unwanted compounds, wherein the sample is a fluid such as water or other liquids, air or other gases, by adsorbing the unwanted compounds with the porous polymeric material, typically in an amount of at least about 50% by weight of the total amount of said unwanted compounds. In other various embodiments, it is sufficient to remove at least 10% by weight of the total amount of said unwanted compounds. In other various embodiments, specific types of unwanted compounds are contaminants and pollutants, typically organic pollutants. In various embodiments, the present disclosure is directed to methods of determining the presence or absence of unwanted compounds, such as pollutants,

in a fluid sample as described herein, by contacting any of the porous polymeric materials herein with the fluid, adsorbing the compounds with the porous polymeric material, separating the porous polymeric material from the fluid sample, then releasing the compounds adsorbed on the porous polymeric material, for example by heating or solvent extraction, then
5 determining the presence or absence, and optionally the amount, of compound release from the porous polymeric material by detection methods (e.g., spectroscopic methods). In various embodiments, the present disclosure is directed to methods of removing compounds from a fluid (same as described herein) by contacting any of the porous polymeric materials herein with the fluid, adsorbing the compounds with the porous polymeric material, separating the
10 porous polymeric material from the fluid sample, then releasing the compounds adsorbed on the porous polymeric material, for example by heating or solvent extraction, and optionally isolating the compounds released from the porous polymeric material. In some embodiments, said removing is carried out to eliminate the adsorbed species from the fluid (gas or liquid), thereby purifying the fluid. Alternatively, said removing is carried out to isolate and purify, or
15 recover the adsorbed species from the fluid.

[0021] In some embodiments, the present disclosure provides an article of manufacture comprising a supported porous polymeric material or the present disclosure. In some embodiments, the article of manufacture is protective equipment (including protective clothing or respiratory devices). In some embodiments, the article of manufacture is clothing, for
20 example outdoors, exercise, or medical clothing designed to adsorb odors or biological and environmental contaminants. In some embodiments, the article of manufacture is a filtration medium. In some embodiments, the article of manufacture is an extraction device. In some embodiments, the extraction device is a solid-phase extraction device capable of adsorbing polar and semi-polar organic molecules.

BRIEF DESCRIPTION OF THE FIGURES

[0022] The skilled artisan will understand that the drawings primarily are for illustrative purposes and are not intended to limit the scope of the inventive subject matter described herein.

30 [0023] FIG. 1 is a schematic for the synthesis of CD-TFN@cellulose.

[0024] FIG. 2 is an FTIR of CD-TFN@cellulose and cellulose.

[0025] FIG. 3 shows A) A SEM image of unmodified cellulose and B) A SEM image of CD-TFN@cellulose.

[0026] FIG. 4 shows A) Time-dependent bisphenol A (0.1 mM) uptake of the CD-TFN@cellulose and the cellulose microcrystals (1 mg material/mL of solution). B) Bisphenol A uptake at equilibrium of the CD-TFN@cellulose and the cellulose microcrystals as a function of bisphenol A concentration (1 mg of material/mL of solution).

5 [0027] FIG. 5 shows A) The number of micropollutants removed in ten removal bins with equivalent masses (500 mg) of TFN-CDP and CD-TFN@cellulose (TFN-CDP on the left and CD-TFN@cellulose on the right in each pairing) and B) A comparison of specific micropollutant removal on equivalent masses of TFN-CDP and CD-TFN@cellulose.

10 [0028] FIG. 6 represents examples of suitable aryl moieties for crosslinking with β -cyclodextrins and microcrystalline cellulose.

[0029] FIG. 7 includes 85 examples of water contaminants that are of interest to be removed.

[0030] FIG. 8 Reaction scheme of the CD-TFN@CMC synthesis.

15 [0031] FIG. 9 PXRD data and SEM images of a) The as synthesized adsorbent, b) The solid with a particle size larger than 45 μm (CD-TFN@CMC), and c) The solid with a particle size smaller than 45 μm (CD-TFN).

[0032] FIG. 10 shows a) Electron image, b) Fluorine mapping, and c) Cross sectional TEM of CD-TFN@CMC; d) Electron image, e) Fluorine mapping, and f) Cross sectional TEM of CMC.

20 [0033] FIG. 11 shows a) BPA uptake of CMC, CD-TFN and CD-TFN@CMC as a function of the initial BPA concentration (1 mg of solid/mL of solution, measured at equilibrium), and b) BPA uptake by CMC, CD-TFN and CD-TFN@CMC and as a function of time (1 mg of solid/mL of solution, [BPA]=0.1mM).

25 [0034] FIG. 12 shows back pressure as a function of flow rate for CMC, CD-TFN, and CD-TFN@CMC packed in liquid chromatographic columns, using water as the mobile phase, and 200 mg of adsorbent.

[0035] FIG. 13 shows a) In-flow BPA uptake as a function of time for CD-TFN@CMC (200 mg) packed in a column at three different concentrations, and b) In-flow regeneration of CD-TFN@CMC (200 mg) packed in a column, saturation was performed with a 1.0 mM BPA solution and methanol was used for regeneration.

30 [0036] FIG. 14 shows in-flow uptake of 15 MPs (10 ppb each) by CD-TFN@CMC packed in a column (200 mg). Flow rate was 0.2 mL/min. Removal was calculated at 32 min for Atenolol, Atrazine, BPS, Gabapentin, Metolachlor, Metolachlor-ESA, Propanolol, and Valsartan. Removal was calculated at 10 min for 2,4-D, Bentazon, BPA, MCPA, Mecoprop, PFOA, and Sucralose.

[0037] FIG. 15 shows a) Mass yield calculated from the total mass at the beginning and at the end of the reaction. b) BPA thermodynamic uptake after 4h at room temperature, and 300 rpms, using 1 mg of polymer per mL of 1mM BPA solution.

[0038] FIG. 16 shows FTIR of CD-TFN, CD-TFN@CMC and CMC.

5 [0039] FIG. 17 shows a) F 1s XPS. b) N 1s XPS of CD-TFN, CD-TFN@CMC and CMC.

[0040] FIG. 18 shows a) Carbon, and b) Oxygen mapping of CMC. c) Carbon, and d) Oxygen mapping of CD-TFN@CMC.

[0041] FIG. 19 shows a) Electron image, and b) fluorine mapping of CD-TFN.

[0042] FIG. 20 shows cross sectional STEM zoom-in of CD-TFN@CMC.

10 [0043] FIG. 21 shows SEM image of CD-TFN.

[0044] FIG. 22 shows BPA uptake in terms of mg of BPA/g of β -CD of CD-TFN and CD-TFN@CMC as a function of the initial BPA concentration (1 mg of solid/mL of solution, measured at equilibrium).

15 [0045] FIG. 23 shows BPA uptake of a) CD-TFN and b) CD-TFN@CMC as a function of the equilibrium BPA concentration (1 mg of solid/mL of solution, measured at equilibrium).

[0046] FIG. 24 shows BPA uptake of a) CD-TFN and b) CD-TFN@CMC as a function of time (1 mg of solid/mL of solution, [BPA]=0.1mM).

20 [0047] FIG. 25 shows a) In flow BPA uptake as a function of time of the empty column at three different concentrations, and b) In flow BPA uptake as a function of time of the CMC (200 mg) packed in a column at three different concentrations.

[0048] FIG. 26 shows in flow vs batch BPA uptake of CD-TFN@CMC as a function of initial concentration.

[0049] FIG. 27 shows inflow uptake and breakthrough time of 8 MPs (10 ppb each) by CD-TFN@CMC packed in a column (200 mg). Flow rate was 0.2 mL/min.

25 [0050] FIG. 28 shows in flow MPs uptake as a function of time of CD-TFN@CMC (200 mg) packed in a column.

[0051] FIG. 29 shows structures of the adsorbed MPs.

[0052] FIG. 30 shows a) Electron image, and b) fluorine mapping of CD-TFN@CMS.

30 [0053] FIG. 31 shows a) BPA uptake of CD-TFN@CMS as a function of time (5 mg of solid/mL of solution, [BPA]=0.1mM) b) BPA uptake of CD-TFN@CMS as a function of the equilibrium BPA concentration (5 mg of solid/mL of solution, measured at equilibrium).

[0054] FIG. 32 shows back pressure as a function of flow rate packed in liquid chromatographic columns, using water as the mobile phase.

DETAILED DESCRIPTION OF THE INVENTION

[0055] 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.

5 [0056] As used herein, the terms “including,” “containing,” and “comprising” are used in their open, non-limiting sense.

[0057] 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.

10 [0058] The term "and/or" is used in this disclosure to mean either "and" or "or" unless indicated otherwise.

[0059] 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
15 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).

[0060] 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”
20 is used explicitly or not, every quantity given herein is meant to refer to the actual given value, and it can 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
25 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.

[0061] The present disclosure addresses a need for a supported adsorbent that provides rapid contaminant extraction, high total uptake, and facile regeneration and reuse procedures, as well
30 as a need for a supported purification adsorbent that is inexpensive and can be reliably mass produced.

[0062] The present disclosure provides a way to control the particle size and morphology of the adsorbent by covalently bonding a cyclodextrin polymer (e.g., β -cyclodextrin polymer) on a substrate of known size and shape. Various supports may be used in the context of the present

disclosure. In some embodiments, cellulose microcrystals are chosen as a support due to their availability in many sizes and shapes. Additionally, because cellulose and cyclodextrins such as β -cyclodextrin have similar chemical structures and available reactive functional groups, both cellulose and cyclodextrins can react with the crosslinker during the polymerization reaction, which bonds the polymer to the cellulose support. Similarly, the cyclodextrin polymers of the present invention can be bonded to substrates other than cellulose having available, reactive hydroxyl groups as described herein.

[0063] In various embodiments, the present disclosure is directed to methods of purifying a fluid sample comprising one or more unwanted compounds, wherein the sample is a fluid such as water or other liquids, air or other gases, by adsorbing the unwanted compounds with the supported porous polymeric material, typically in an amount of at least about 50% by weight of the total amount of said unwanted compounds. In other various embodiments the amount of unwanted compounds removed is at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 30%, at least about 35%, at least about 40%, at least about 45%, at least about 50%, at least about 55%, at least about 60%, at least about 65%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, about 100% and all values therebetween.

[0064] In various embodiments, the present disclosure is directed to methods of recovering or isolating one or more compounds from a fluid sample, wherein the sample is a fluid such as water or other liquids, air or other gases, by adsorbing the compounds with the supported porous polymeric material, typically in an amount of at least about 50% by weight of the total amount of said compounds. In other various embodiments the amount of unwanted compounds removed is at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 30%, at least about 35%, at least about 40%, at least about 45%, at least about 50%, at least about 55%, at least about 60%, at least about 65%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, about 100% and all values therebetween.

[0065] Flow characteristics are critical to the effectiveness of an adsorbent material in the removal of pollutants and/or contaminants from drinking and wastewater. The large and monodisperse particle size of a material enables rapid flow rates with minimal pressure drops, which are required for membrane, column and other filtration implementations.

[0066] The present disclosure provides porous, typically high surface area cyclodextrin polymeric materials ("P-CDP") grafted or bonded onto a variety of substrates as described

herein, such as microcrystalline cellulose, (i.e. CD-TFN@CMC), as well as methods of making and using these materials.

[0067] In some embodiments, the present disclosure provides a supported porous polymeric material comprising porous particles affixed to a solid substrate, wherein said porous particles
 5 comprise a plurality of cyclodextrin moieties crosslinked with one or more aryl moieties, and wherein the supported porous polymeric material has one or more performance characteristics which are at least about 50% of the same performance characteristics of unsupported porous particles of the same composition.

[0068] In some embodiments, the performance characteristic is pollutant uptake, and the
 10 pollutant uptake of the supported porous polymeric material is at least about 50% of the pollutant uptake of the unsupported porous particles of the same composition, wherein the pollutant uptake is the weight of pollutant absorbed (in milligrams) divided by the weight of porous particles (in grams). In some embodiments, the pollutant uptake of the supported porous polymeric material is about the same as the pollutant uptake of the unsupported porous particles
 15 of the same composition. In some embodiments, the pollutant uptake of the supported porous polymeric material is greater than the pollutant uptake of the unsupported porous particles of the same composition. In various embodiments, the pollutant uptake of the supported porous polymeric material relative to unsupported porous particles of the same composition ranges from about 50% to about 1000%, for example, about 50%, about 60%, about 70%, about 80%,
 20 about 90%, about 100%, about 120%, about 140%, about 160%, about 180%, about 200%, about 250%, about 30%, about 350%, about 400%, about 450%, about 500%, about 550%, about 600%, about 650%, about 700%, about 750%, about 800%, about 850%, about 900%, about 950%, about 1000%, including any ranges or subranges therebetween. In some embodiments, the supported porous polymeric material is CD-TFN@CMC. In some
 25 embodiments, the pollutant is bisphenol A.

[0069] In some embodiments, the performance characteristic is equilibrium adsorption capacity (q_e) for a pollutant, and the equilibrium adsorption capacity of the supported porous polymeric material is at least about 50% of the equilibrium adsorption capacity of unsupported porous particles having the same composition, wherein the q_e is measured as

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

wherein q_{max} (mg pollutant/g porous particles) is the maximum adsorption capacity the porous particles for the pollutant at equilibrium, K_L (mol^{-1}) is the equilibrium constant and C_e (mM) is the pollutant concentration at equilibrium. In some embodiments, the equilibrium adsorption

capacity of the supported porous polymeric material is about the same as the equilibrium adsorption capacity of the unsupported porous particles of the same composition. In some embodiments, the equilibrium adsorption capacity of the supported porous polymeric material is greater than the equilibrium adsorption capacity of the unsupported porous particles of the same composition. In various embodiments, the equilibrium adsorption capacity of the supported porous polymeric material relative to unsupported porous particles of the same composition ranges from about 50% to about 1000%, for example, about 50%, about 60%, about 70%, about 80%, about 90%, about 100%, about 120%, about 140%, about 160%, about 180%, about 200%, about 250%, about 30%, about 350%, about 400%, about 450%, about 500%, about 550%, about 600%, about 650%, about 700%, about 750%, about 800%, about 850%, about 900%, about 950%, about 1000%, including any ranges or subranges therebetween. In some embodiments, the supported porous polymeric material is CD-TFN@CMC. In some embodiments, the pollutant is bisphenol A.

[0070] In some embodiments, the performance characteristic is the rate at which equilibrium adsorption of a pollutant is reached (rate of equilibrium adsorption), and the rate of equilibrium adsorption of a pollutant of the supported porous polymeric material is at least about 50% of the rate of equilibrium adsorption of unsupported porous particles having the same composition and measured under the same conditions. In some embodiments, the rate of equilibrium adsorption of the supported porous polymeric material is about the same as the rate of equilibrium adsorption of the unsupported porous particles of the same composition measured under the same conditions. In some embodiments, the rate of equilibrium adsorption of the supported porous polymeric material is greater than the rate of equilibrium adsorption of the unsupported porous particles of the same composition measured under the same conditions. In various embodiments, the rate at which equilibrium adsorption capacity of the supported porous polymeric material is reached relative to unsupported porous particles of the same composition ranges from about 50% to about 1000%, for example, about 50%, about 60%, about 70%, about 80%, about 90%, about 100%, about 120%, about 140%, about 160%, about 180%, about 200%, about 250%, about 30%, about 350%, about 400%, about 450%, about 500%, about 550%, about 600%, about 650%, about 700%, about 750%, about 800%, about 850%, about 900%, about 950%, about 1000%, including any ranges or subranges therebetween. In some embodiments, the supported porous polymeric material is CD-TFN@CMC. In some embodiments, the pollutant is bisphenol A.

[0071] In some embodiments, the performance characteristic is the specific permeability of the supported polymeric material to a mobile phase at pressure P when the supported polymeric material is placed in a cylindrical column, wherein specific permeability (B_0) is:

$$B_0 = \frac{\eta L}{\pi r^2} \frac{F}{\Delta P}$$

5 wherein η (mPa*s) is the mobile phase viscosity, L (m) is the column length, r (m) is the column radius, and $F / \Delta P$ (m³/mPa*s) is the slope of the curve of flow rate vs back pressure. In some embodiments, the supported porous polymeric material has higher specific permeability compared to the unsupported porous particles having the same composition. In some embodiments, the specific permeability of the supported porous polymeric material is at
 10 least double the specific permeability of unsupported porous particles having the same composition. In various embodiments, the specific permeability of the supported porous polymeric material relative to unsupported porous particles of the same composition ranges from about 50% to about 1000%, for example, about 50%, about 60%, about 70%, about 80%, about 90%, about 100%, about 120%, about 140%, about 160%, about 180%, about 200%,
 15 about 250%, about 30%, about 350%, about 400%, about 450%, about 500%, about 550%, about 600%, about 650%, about 700%, about 750%, about 800%, about 850%, about 900%, about 950%, about 1000%, including any ranges or subranges therebetween. In some embodiments, the supported porous polymeric material is CD-TFN@CMC. In some embodiments, the supported porous polymeric material is CD-TFN@CMC and has a specific
 20 permeability at least about 4 times more than the unsupported porous particles having the same composition.

[0072] In some embodiments, the plurality of cyclodextrin moieties are crosslinked with at least an equimolar amount of one or more aryl moieties; wherein the aryl moiety is an aryl moiety of formula (I), (II), (III), or (IV), as described in detail below.

25 **[0073]** In some embodiments, the porous particles are affixed to the solid substrate covalently, adhesively, or mechanically. In some embodiments, the porous particles are affixed to the solid substrate covalently via a crosslinking moiety. In some embodiments, the crosslinking moiety is an aryl moiety of formula (I), (II), (III), or (IV).

[0074] In some embodiments, the aryl moiety is an aryl moiety of formula (I), as described
 30 in detail below. In some embodiments, the aryl moiety is an aryl moiety of formula (II), as described in detail below. In some embodiments, the aryl moiety is an aryl moiety of formula (III), as described in detail below. In some embodiments, the aryl moiety is an aryl moiety of formula (VI), as described in detail below.

[0075] In some embodiments, the molar ratio of cyclodextrin to aryl moiety ranges from about 1:1 to about 1:X, wherein X is three times the average number of glucose subunits in the cyclodextrin. In some embodiments, the molar ratio of cyclodextrin to aryl moiety is about 1:6.

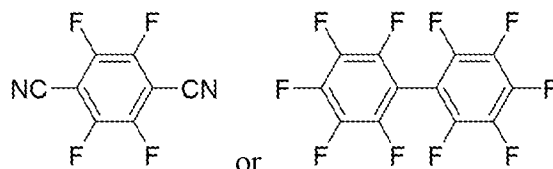
[0076] In some embodiments, the cyclodextrin is selected from the group consisting of α -, β -, γ -cyclodextrin, and combinations thereof. In some embodiments, the cyclodextrin is β -cyclodextrin.

[0077] In some embodiments, the aryl moiety is an aryl moiety of formula (I), and the molar ratio of β -cyclodextrin to aryl moiety is about 1:3. In some embodiments, the aryl moiety is an aryl moiety of formula (II), and the molar ratio of β -cyclodextrin to aryl moiety is about 1:3.

In some embodiments, the aryl moiety is an aryl moiety of formula (III), and the molar ratio of β -cyclodextrin to aryl moiety is about 1:3. In some embodiments, the aryl moiety is an aryl moiety of formula (IV), and the molar ratio of β -cyclodextrin to aryl moiety is about 1:3.

[0078] In some embodiments, 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. In some embodiments, 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, and derivatives thereof. In some embodiments, the substrate is microcrystalline cellulose, cellulose

nanocrystals, silica, glass, or beads made from synthetic polymer. In some embodiments, the substrate is microcrystalline cellulose. In some embodiments, the microcrystalline cellulose has a median particle size ranging from about 10 to about 500 μm . In some embodiments, the microcrystalline cellulose has a median particle size of about 50 μm . In some embodiments, the porous particles have a thickness on the solid substrate of from about 10 nm to about 2000 nm. In some embodiments, the porous particles have a polymer thickness of about 800 nm on the solid substrate.



[0079] In some embodiments, the aryl moiety is

In some embodiments, the supported porous polymeric material is CD-TFN@CMC or CD-DFB@CMC.

[0080] In some embodiments, the microcrystalline cellulose is spherical, rod-shaped, needle-like, flat, or flat and elongated. In some embodiments, the microcrystalline cellulose is spherical.

[0081] In some embodiments, the substrate is cellulose nanocrystals.

Cyclodextrin Polymers

[0082] The P-CDPs are comprised of insoluble polymers of cyclodextrin, which is an inexpensive, sustainably produced macrocycle of glucose. 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., α -, β -, γ -, comprising 6, 7, and 8 glucose units, respectively) or synthetic cyclodextrins. In some embodiments naturally occurring cyclodextrins are non-genetically modified 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 there between. 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 β -cyclodextrin (β -CD).

[0083] 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 -OR group can be a variety of functional groups, such as e.g., halide, acid halide, ester, or activated ester. 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 β -cyclodextrins), hydroxyalkylated cyclodextrins (e.g., hydroxypropyl- β -cyclodextrin and hydroxypropyl- γ -cyclodextrin), acetylated cyclodextrins (e.g., acetyl- γ -cyclodextrin), reactive cyclodextrins (e.g., chlorotriazinyl- β -CD), branched cyclodextrins (e.g., glucosyl- β -cyclodextrin and maltosyl- β -cyclodextrin), sulfobutyl- β -cyclodextrin, and sulfated cyclodextrins. Suitable cyclodextrins can also include cyclodextrins functionalized with photochemically reactive moieties such as vinyl, propargyl, acrylate, methacrylate groups, or thiol groups, so that after forming the P-CDP of the present disclosure, the P-CDP can be photochemically grafted to a suitably functionalized support using known methods (e.g., curing with a suitable wavelength of UV light in the presence of a photoinitiator and the photochemically reactive substrate). In addition to photochemical activation, the reactive moieties can be activated through chemical generation of radical species such as through the thermal decomposition of azo compounds (such as azobisisobutyronitrile).

[0084] The P-CDP can also be prepared from cyclodextrin derivatives as disclosed in U.S. Patent 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 $-\text{CH}_2\text{-CH(OH)-CH}_3$ or a $-\text{CH}_2\text{CH}_2\text{-OH}$ 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

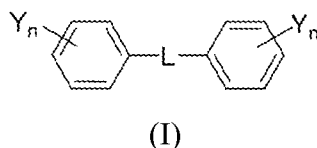
herein by reference for all purposes; and mixtures thereof. Other cyclodextrin derivatives are disclosed in U.S. Pat. No. 3,426,011, Parmerter et al., issued Feb. 4, 1969; U.S. Pat. Nos. 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued Jul. 1, 1969; U.S. Pat. No. 3,459,731, Gramera et al., issued Aug. 5, 1969; U.S. Pat. No. 10 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 for all purposes.

Aryl Crosslinking Moieties

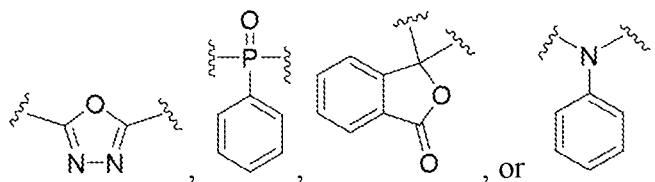
[0085] The P-CDP can also comprise a variety of aryl crosslinking moieties. The aryl crosslinking moiety is derived from an aryl compound that can react with a cyclodextrin to form an aryl ether bond. The aryl crosslinking moiety may comprise one or more electron withdrawing group (e.g., a halide group, such as -Cl and -F, -NO₂, and -CN group). The electron-withdrawing groups can be the same or different. Without intending to be bound by any particular theory, it is considered that the electron withdrawing group(s) facilitates a nucleophilic aromatic substitution reaction between the cyclodextrin and aryl compound. In various embodiments, the aryl crosslinking moiety has 0, 1, or 2 cyano groups and, optionally, 0, 1, 2, 3, or 4 halide groups.

[0086] The aryl moiety comprises one or more aromatic ring. The aromatic ring(s) comprise 4 to 40 carbons, including 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, and 40 carbons, including all ranges therebetween. The aryl moiety can be a fused aromatic ring structure or have at least two aromatic rings linked by a covalent bond (e.g., a biphenyl moiety). The aryl moiety can be a hydrocarbon aryl moiety or heteroaryl moiety. For example, the heteroaryl moiety has one or more heteroatom in an aryl ring or rings. Examples of aryl moieties include phenyl moieties, biphenyl moieties, naphthyl moieties, and anthracene moieties. In an embodiment, the aryl moiety is a dicyanophenyl moiety with 0, 1, or 2 halide groups (i.e., substituents).

[0087] In some embodiments, the aryl moiety is an aryl moiety of formula (I):



wherein L is Aryl, $-\text{S}(\text{O})_2-$, $-\text{C}(\text{O})-$, bond,

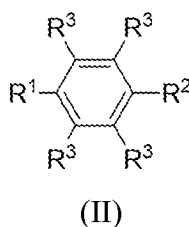


and

wherein each Y is independently H, F, Cl, CF_3 , SO_3H , or NO_2 , with the proviso that $n = 0-5$

and at least 2 of Y are F and/or Cl; or

5 an aryl moiety of formula (II):

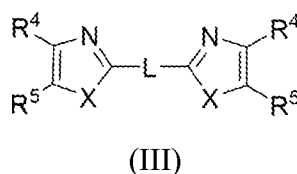


wherein R^1 is Cl, F or CN;

10 R^2 is Cl, F, CN, or NO_2 ; and

wherein each R^3 is independently H, F, or Cl, with the proviso at least 2 of R^1 , R^2 , or R^3 is F and/or Cl; or

an aryl moiety of formula (III):



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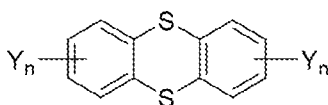
wherein L is Aryl;

X is O or S;

each R^4 is independently F, Cl, or CF_3 ; and

20 each R^5 is independently F, Cl, or NO_2 , with the proviso that at least 2 of R^4 and R^5 are F and/or Cl; or

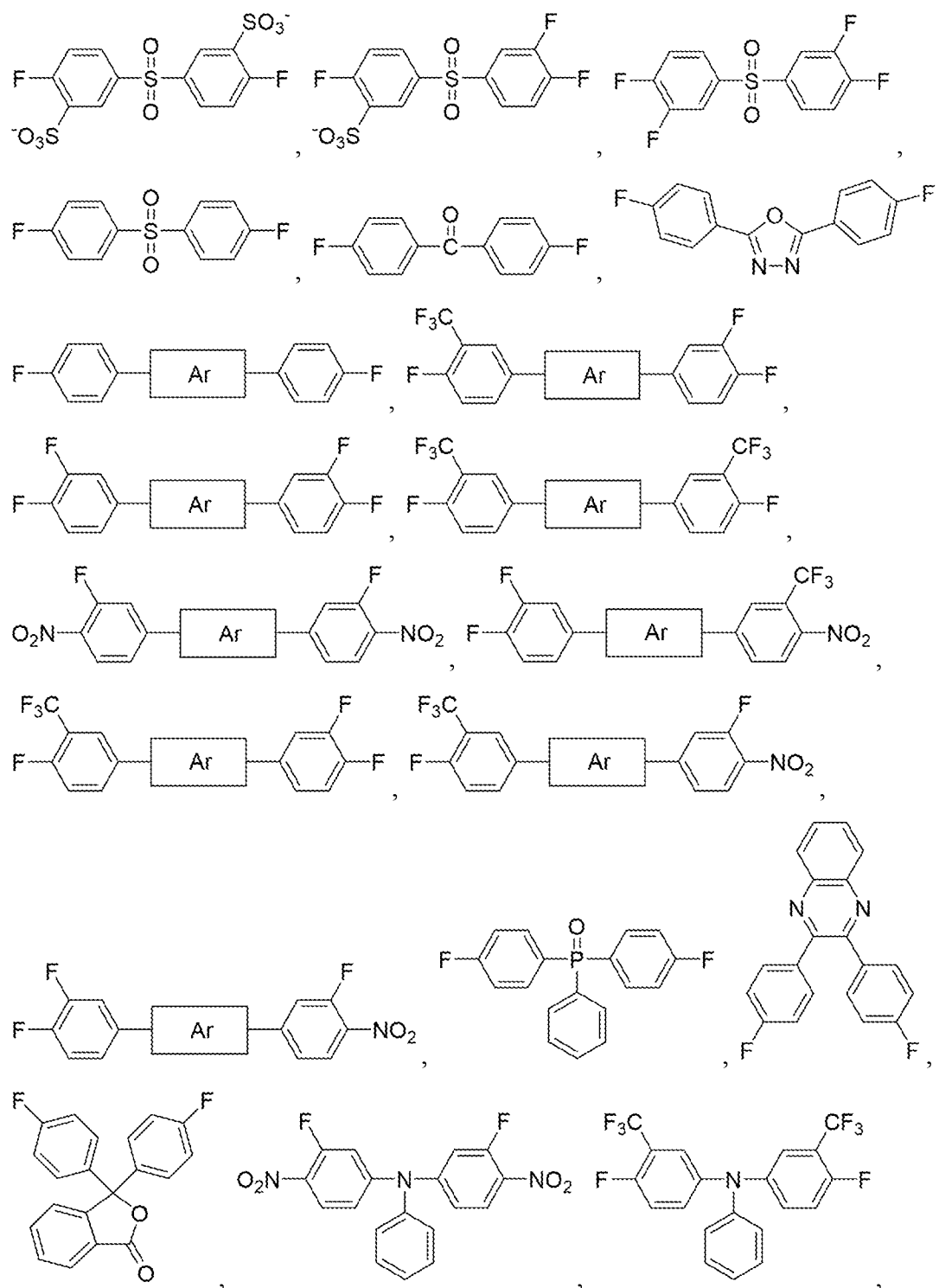
an aryl moiety of formula (IV):

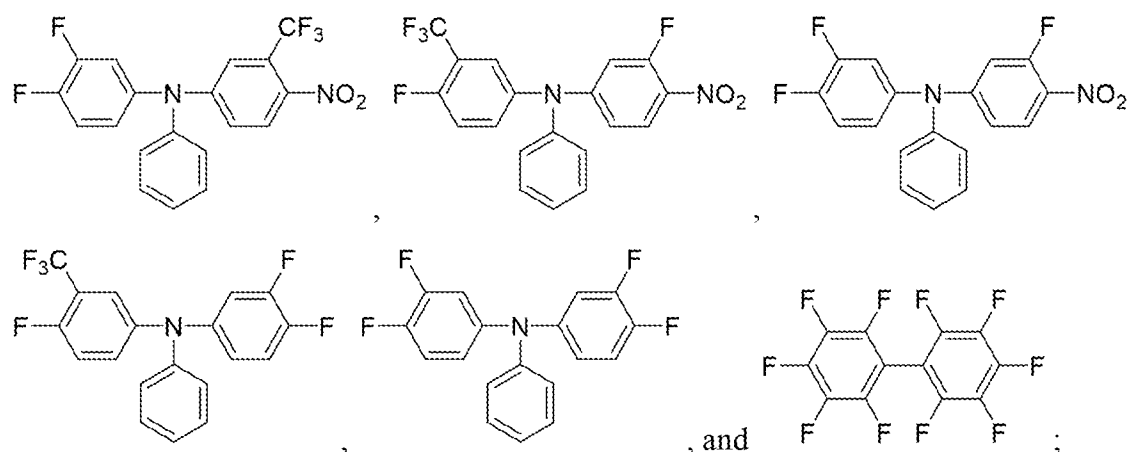


wherein each Y is independently H, F, Cl, CF_3 , SO_3H , or NO_2 , with the proviso that $n=0-5$ and

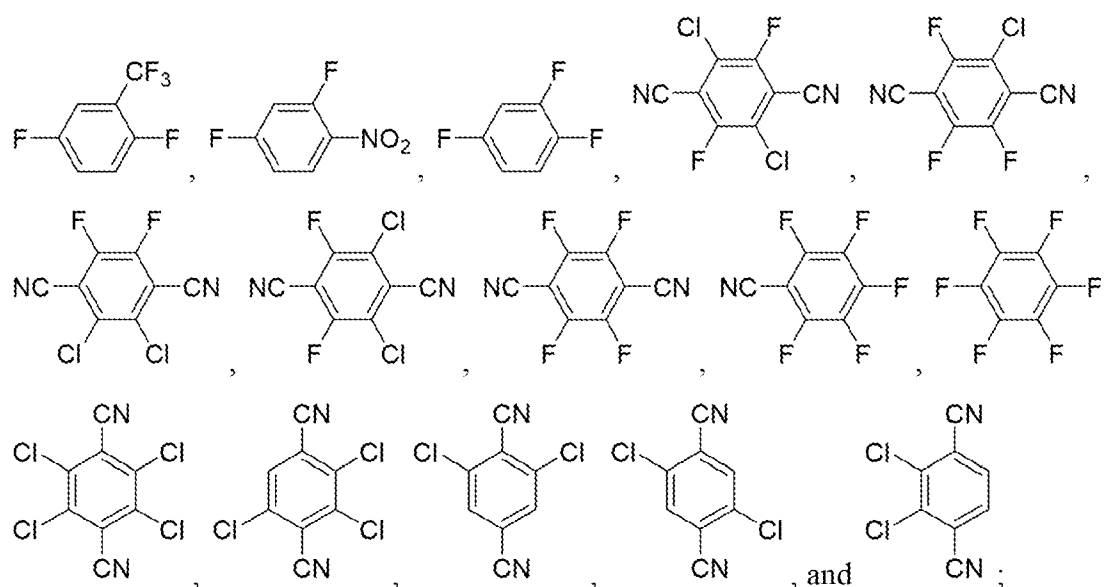
25 at least 2 of Y are F and/or Cl.

[0088] In some embodiments, the aryl moiety of formula (I) are selected from the group consisting of:

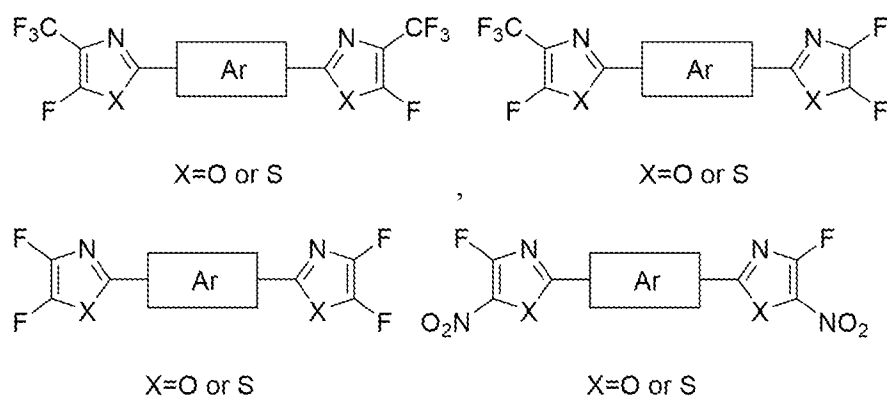


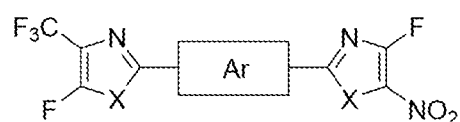


the aryl moiety of formula (II) are selected from the group consisting of:



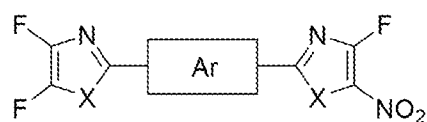
the aryl moiety of formula (III) are selected from the group consisting of:





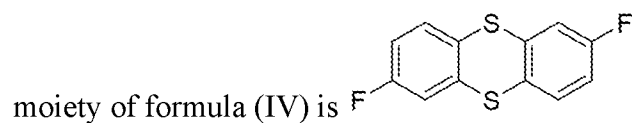
X=O or S

, and



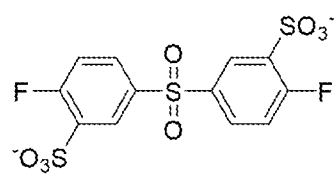
X=O or S

; and the aryl



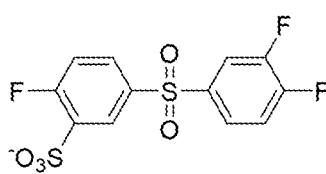
moiety of formula (IV) is

[0089] In some embodiments, the aryl moiety is an aryl moiety of formula (I) and is selected from the group consisting of:

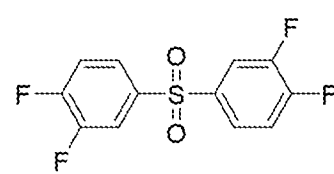


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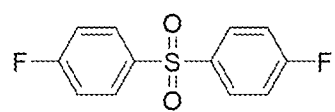
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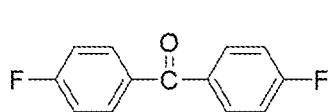
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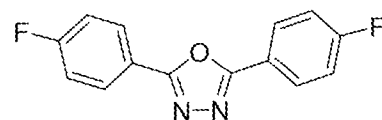
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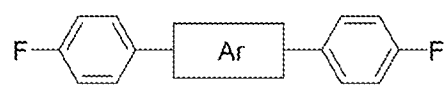
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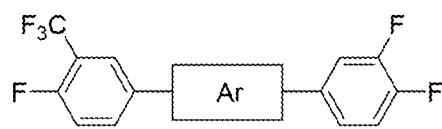
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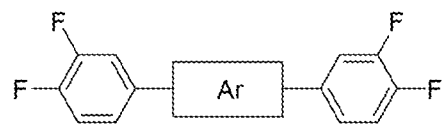
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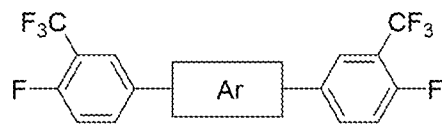
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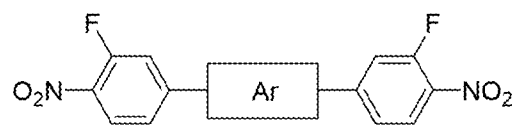
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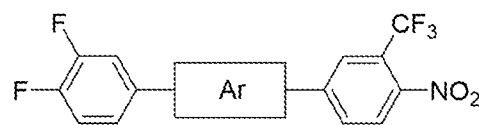
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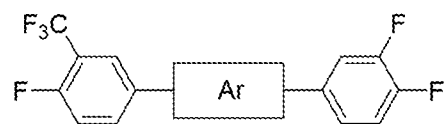
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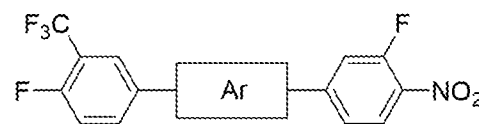
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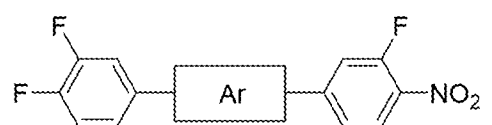
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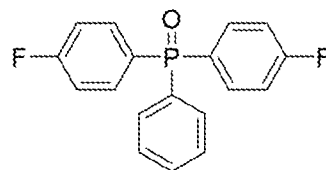
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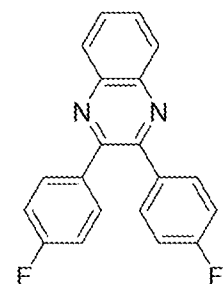
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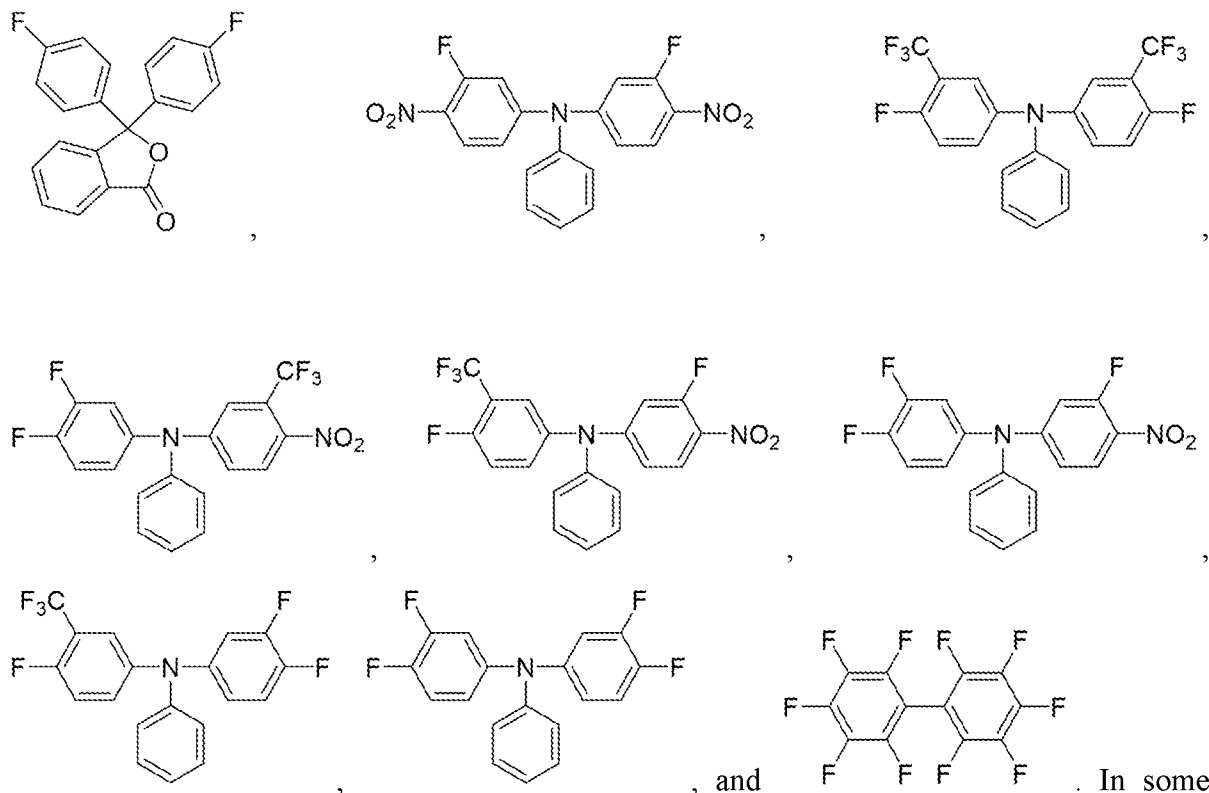


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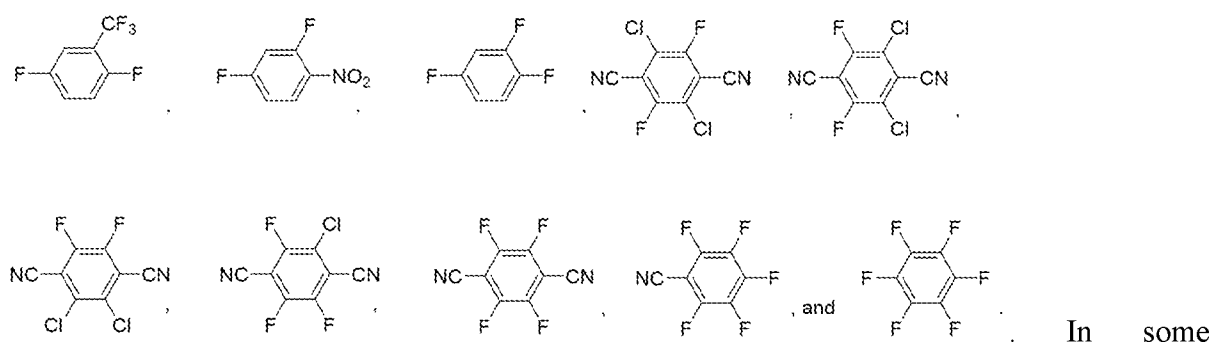
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embodiments, the aryl moiety is an aryl moiety of formula (I) and is

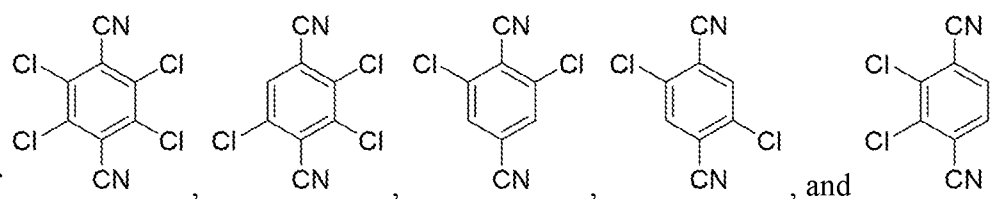
5 (DFB).

[0090] In some embodiments, the aryl moiety is an aryl moiety of formula (II), and is selected from the group consisting of:

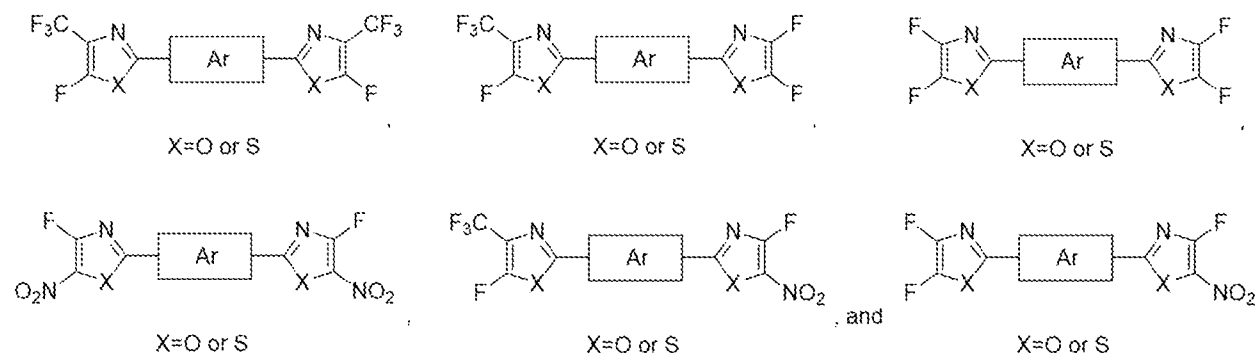


embodiments, the aryl moiety is an aryl moiety of formula (II), and is selected from the group

10 consisting of



[0091] In some embodiments, the aryl moiety is an aryl moiety of formula (III), and is selected from the group consisting of:



[0092] In some embodiments, for the aryl moieties of formulae (I)-(III) shown above, F can be replaced with Cl.

[0093] In some embodiments, suitable aryl moieties include, but are not limited to, the aryl moieties shown in FIG. 6 (In the examples, Ar is an aryl moiety as described herein).

[0094] As used herein, "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 14 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. As used herein, "aryl" also encompasses heteroaryl groups, which have 1 to 3 aromatic rings having 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. Exemplary ring systems of these heteroaryl groups 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, benzopyranlyl, 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]pyraziny, quinazolinyl, 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]pyrimidiny, tetrahydropyrrolo[1,2-a]pyrimidiny, 3,4-dihydro-2H-1 λ^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]thiaziny, 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]pyrimidiny, [1,2,4]triazolo[4,3-b]pyridaziny, 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]oxaziny, 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.

[0095] The porous polymeric material comprises a plurality of cyclodextrin moieties, for example β -cyclodextrin moieties. In an embodiment, the porous polymeric material comprises a plurality of β -cyclodextrin moieties crosslinked by one or more aryl (e.g., dicyanodifluorophenyl) moieties. For example, at least two of the plurality of β -cyclodextrin moieties are crosslinked by two or more aryl moieties. One of skill in the art will recognize that the polymeric material of the present disclosure can also include any of the cyclodextrin moieties disclosed herein, for example α - or γ -cyclodextrin moieties in addition to, or instead of the β -cyclodextrin moieties.

[0096] The aryl moieties can crosslink the primary and/or secondary groups on the cyclodextrin. The crosslinked cyclodextrin moieties can be covalently bonded to various positions. Similarly, the aryl moieties can crosslink the primary and/or secondary groups on CMC. The crosslinked CMC can also be covalently bonded to various positions. As an illustrative example, where the aryl crosslinking moiety comprises a phenyl moiety the crosslinking bonds can be to 1,2-, 1,3-, and/or 1,4-positions (relative positions) of the phenyl moiety on the aryl crosslinking moiety, depending on the available bonding sites on the phenyl moiety. Accordingly, the porous polymeric materials can include various regioisomers of the material. In an embodiment, the porous polymeric material comprises one or more regioisomer of the porous polymeric material.

[0097] The porous polymeric material of the present disclosure can have pores ranging in size (i.e., the longest dimension (e.g., diameter) of an orifice of a pore) from about 1 nm to about 50 nm, about 1 nm to about 20 nm, about 1 nm to about 10 nm, or about 1 nm to about 5 nm, including about 1 nm, about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 9 nm, about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, about 22 nm, about 23 nm, about 24 nm, about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, or about 50 nm, inclusive of all ranges therebetween. In an embodiment, the porous polymeric material is mesoporous. In an embodiment, the porous polymeric material comprises pores of about 1.5 nm to about 5 nm in size. In various embodiments, about 50% or more, about 80% or more, about 90% or more, about 95% or more, about 99% or more of the pores in the porous polymeric material are about 1 nm to about 50 nm in size. In various embodiments, about 50% or more, about 80% or more, about 90% or more, about 95% or more, about 99% or more of the pores in the porous polymeric material are about 10 nm or less in size.

[0098] The P-CDPs have a relatively large surface area, which substantially improves the adsorption kinetics and/or capacity compared to conventional nonporous P-CDPs. For example, the porous polymeric materials of the present disclosure can have a surface area ranging from about 50 m²/g to about 2000 m²/g, including all integer m²/g values and ranges therebetween. In particular embodiments, the surface area is about 50 m²/g, about 100 m²/g, about 150 m²/g, about 200 m²/g, about 250 m²/g, about 300 m²/g, about 350 m²/g, about 400 m²/g, about 450 m²/g, about 500 m²/g, about 550 m²/g, about 600 m²/g, about 650 m²/g, about 700 m²/g, about 750 m²/g, about 800 m²/g, about 850 m²/g, about 900 m²/g, about 950 m²/g, about 1000 m²/g, about 1100 m²/g, about 1200 m²/g, about 1300 m²/g, about 1400 m²/g, about 1500 m²/g, about 1600 m²/g, about 1700 m²/g, about 1800 m²/g, about 1900 m²/g, or about 2000 m²/g, inclusive of all ranges therebetween. In various embodiments, the surface area of porous polymeric material is 50 m²/g or greater, 100 m²/g or greater, or 200 m²/g or greater.

[0099] The ratio of cyclodextrin moieties to aryl crosslinking moieties is 1:1 to 1:X, where X is three times the average number of glucose subunits in the cyclodextrin moieties of the polymer. In various embodiments, the 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 ratio of cyclodextrin moieties to aryl crosslinking moieties is about 1:2.5 to about 1:10.

[0100] In various embodiments, the substrate may be microcrystalline cellulose, and the molar ratio of glucose subunits in the microcrystalline cellulose to aryl moieties covalently bonded to the glucose subunits in the microcrystalline cellulose ranges from about 1:1 to about 1:X, wherein X is three times the average number of glucose subunits in the microcrystalline cellulose. In various embodiments, the ratio of glucose subunits in the microcrystalline cellulose to aryl crosslinking moieties is about 1:0.01 to about 1:3, including about 1:0.01, about 1:0.02, about 1:0.03, about 1:0.04, about 1:0.05, about 1:0.06, about 1:0.07, about 1:0.08, about 1:0.09, about 1:0.1, about 1:0.2, about 1:0.3, about 1:0.4, about 1:0.5, about 1:0.6, about 1:0.7, about 1:0.8, about 1:0.9, about 1:1, about 1:1.1, about 1:1.2, about 1:1.3, about 1:1.4, about 1:1.5, about 1:1.6, about 1:1.7, about 1:1.8, about 1:1.9, about 1:2, about 1:2.1, about 1:2.2, about 1:2.3, about 1:2.4, about 1:2.5, about 1:2.6, about 1:2.7, about 1:2.8, about 1:2.9, or about 1:3, including all ranges of ratios therebetween. In an embodiment, the ratio of microcrystalline cellulose to aryl crosslinking moieties is about 1:0.02 to about 1:1.

[0101] In some embodiments, the present disclosure provides a composition comprising one or more porous polymeric materials (P-CDPs) of the present disclosure. For example, the composition comprises a support material supporting the porous polymeric materials of the present disclosure. In an embodiment, the composition consists essentially of one or more porous polymeric materials.

[0102] In an embodiment, a composition according to the present disclosure 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 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 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.

[0103] 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 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 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.

[0104] 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. Grafting includes an "in situ" process as described herein in which cyclodextrins, aryl crosslinking agents (e.g., aryl halides as described herein), and a substrate having surface bound nucleophiles (e.g., hydroxyls) are reacted together such that the aryl crosslinking agent 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 aryl groups to the substrate. The substrate having surface bound nucleophiles include, but are not limited to hydroxyls (such as microcrystalline cellulose), amines, phosphines, and thiols.

[0105] 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.

[0106] 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.

[0107] 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.

[0108] 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.

[0109] 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.

[0110] 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 μm to about 150 μm . 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 μm . 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.

[0111] 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., an aryl moiety as described herein or a linking moiety) 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.

[0112] 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 microfibers). Suitable materials further include textiles or synthetic or natural fiber-based materials. The material may exhibit
5 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.

[0113] 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,
10 chemical vapor 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
15 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.

[0114] The skilled artisan is well aware of the various possibilities of attaching polymers to optionally activated surfaces. These techniques generally involve the introduction of
20 amino-, silane-, thiol-, hydroxyl- and/or epoxy-functionalities to the surface, and the subsequent attachment thereto of the polymer.

[0115] 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
25 aminoalkylsilane.

[0116] The P-CDP may be bound to the substrate via a linker moiety, also referred to herein as a crosslinker moiety. 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
30 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. 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. As used herein, the linker moiety contains atoms interposed between the drug moiety 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.

[0117] 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 μm including about 10 μm , 20 μm , 45 μm , 50 μm , 65 μm , 75 μm , 100 μm , 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 AvicelTM. 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.

[0118] In some embodiments, the P-CDP-substrate complex (e.g., CD-TFN@CMC) 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 (e.g., CD-TFN@CMC) 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 (e.g., CD-TFN@CMC) has a polymer thickness of less than 1000 nm. In some embodiments, P-CDP-substrate complex (e.g., CD-TFN@CMC) 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.

[0119] In some embodiments, the P-CDP-substrate complex (e.g., CD-TFN@CMC) 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, 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 bisphenol A (BPA). In some embodiments, the cyclodextrin is β -cyclodextrin. In some embodiments, the aryl crosslinking moiety is TFN. In other embodiments, the aryl crosslinking agent is any aryl crosslinking agent disclosed herein.

[0120] In some embodiments, the P-CDP-substrate complex (e.g., CD-TFN@CMC) 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 bisphenol A (BPA). In some embodiments, the cyclodextrin is β -cyclodextrin. In some embodiments, the aryl crosslinking moiety is TFN. In other embodiments, the aryl crosslinking agent is any aryl crosslinking agent disclosed herein.

[0121] In some embodiments, the P-CDP-substrate complex (e.g., CD-TFN@CMC) has a relaxation time of less than 2 minutes. In some embodiments, the P-CDP-substrate complex (e.g., CD-TFN@CMC) has a relaxation time of about 0.99 ± 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 BPA. In some embodiments, the cyclodextrin is β -cyclodextrin. In some embodiments, the aryl crosslinking moiety is TFN.

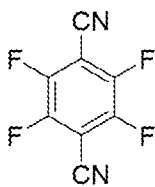
Microcrystalline Cellulose Supports

[0122] In some embodiments, any of the P-CDP materials disclosed herein (i.e., P-CDP materials prepared by reacting any of the disclosed aryl moieties with any of the disclosed cyclodextrins) is grafted or bonded onto CMC via any aryl linker disclosed herein. In some

embodiments, the P-CDP is homogenously distributed on the CMC surface. In some embodiments, the aryl linker is TFN. In some embodiments, the median particle size is about 50 μm . In other embodiments, the median particle size is from about 1 – about 250 μm .

[0123] 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 μm up to about 2 mm. For example, the particle sizes of CMC agglomerates can be about 200 μm , about 300 μm , about 400 μm , about 500 μm , about 600 μm , about 700 μm , about 800 μm , about 900 μm , 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.

[0124] In some embodiments, the P-CDP is grafted or bonded onto CMC via an aryl moiety of formula (I), (II), (III), or (IV) as described herein. In some embodiments, the P-CDP is



grafted or bonded onto CMC via or the tetrachloro analog thereof. In some embodiments, the P-CDP is grafted or bonded onto CMC via DFB or the decachloro analog thereof.

[0125] In some embodiments, P-CDP 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. In some embodiments, the aryl linker is DFB. In some embodiments, the median particle size is about 100 nm.

[0126] 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.

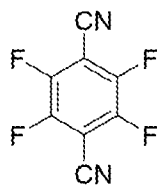
[0127] In some embodiments, it is desirable that the supported P-CDP materials disclosed herein (e.g., P-CDP@CMC) are in the form of particles having a narrow dispersity of particle sizes. In some embodiments, the particle size distribution has a low relative span of about 5 or less, where relative span is defined by the ratio $(D_{90}-D_{10})/D_{50}$, where D_{90} , D_{50} , and D_{10} are,

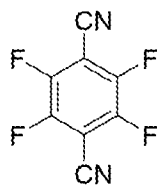
respectively the diameters at which 90%, 50%, and 10% of the particles in the distribution have a smaller diameter. Suitable spans are no more than 5, 4.5, 4, 3.5, 3, 2.5, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1, including all ranges therebetween.

5 Cellulose Nanocrystal Substrates

[0128] In other various embodiments, the P-CDP may be grafted or bonded onto 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.

[0129] In some embodiments, the P-CDP is grafted or bonded onto CNC via an aryl moiety of formula (I), (II), (III), or (IV) as described herein. In some embodiments, the P-CDP is



grafted or bonded onto CNC via  or the tetrachloro analog thereof. In some embodiments, the P-CDP is grafted or bonded onto CNC via DFB or the decachloro analog thereof.

[0130] In some embodiments, P-CDP is grafted or bonded onto CNC via an aryl linker, and the aryl linker is homogeneously distributed on the CNC crystal. In some embodiments, the aryl linker is TFN. In some embodiments, the aryl linker is DFB. In some embodiments, the median particle size is about 100 nm.

[0131] 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

[0132] 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 an aryl moiety of formula (I), (II), (III), or (IV), as described herein. In some embodiments, the fiber is a nonwoven fiber. In some embodiments, the present 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 an aryl moiety of formula (I), (II), (III), or (IV).

[0133] 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 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 (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 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 Japan) and fibers made from a 1:1
5 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-
10 (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
15 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
20 fibers, PIPD fibers, poly(6-hydroxy-2-naphthoic acid-co-4-hydroxybenzoic acid) fibers, carbon fibers, and combinations thereof.

[0134] 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
25 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.

[0135] 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
30 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.

[0136] 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.

[0137] 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.

[0138] 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.

[0139] 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.

[0140] 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.

[0141] 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.

[0142] 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.

10 Fibrillating Fiber Substrates

[0143] 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 Fybre®), fibrillating regenerated cellulose (such as Lenzing Tencel™) or fibrillating acrylic (such as Sterling Fibers CFF™) are deployed in wet 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 filtration applications such as point of use water filters or cabin air filters.

[0144] 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 Fybre®, 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 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 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.

[0145] The resultant powder loaded papers are amenable to a high loading of P-CDP 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.

5 [0146] 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)
10 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
15 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
20 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
25 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
30 and woven fabrics for use in apparel, upholstery, medical, displays, or other uses.

[0147] 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).

[0148] 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.

[0149] 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.

[0150] 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.

[0151] 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 from the vapor and liquid phase.

Performance

[0152] 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 CD-TFN material grafted to microcrystalline cellulose (CD-TFC@CMC) would have at least 50% of one or more of a particular performance characteristic found in unsupported CD-TFN (normalized to unit weight of CD-TFN in each material) tested under the same conditions.

[0153] 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 (mol^{-1}) is the equilibrium constant and C_e (mM) is the pollutant concentration at equilibrium.

[0154] 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 P-CDP of the present disclosure (or the comparator unsupported P-CDP) to reach equilibrium for a particular adsorbed species (or pollutant).

[0155] 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).

[0156] 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.

[0157] The performance characteristics of the present disclosure can be measured, for example based on bisphenol A 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

[0158] In some embodiments, the present disclosure provides an article of manufacture comprising one or more P-CDP-substrate complexes (e.g., CD-TFN@CMC) or a composition comprising one or more P-CDP-substrate complexes disclosed herein.

[0159] 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 porous polymeric material or a composition comprising one or more P-CDP-substrate complexes (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-CDP-substrate complexes or a composition comprising one or more P-CDP-substrate complexes. 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.

[0160] In another embodiment, the article is a solid phase microphase (SPME) extraction device comprising the P-CDP-substrate complexes (or a composition comprising the porous polymeric material), where the P-CDP-substrate complexes is the extracting phase the device.

[0161] In another embodiment, the article is a device for a solid-phase extraction of polar and semi-polar organic molecules. The device comprises the P-CDP-substrate complexes (or a composition comprising the porous polymeric material) instead of HLB media (hydrophilic/lipophilic balanced). The article with the P-CDP-substrate complexes outperforms the HLB media.

[0162] In another embodiment, the article is a device for liquid filtration of polar and semi-polar organic molecules. The device comprises the P-CDP-substrate 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

[0163] 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.

[0164] 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 aryl crosslinkers disclosed herein. One of skill in the art will recognize that crosslinking agents other than aryl crosslinkers can be used, provided they have similar ranges of flexibility. For example, 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.

[0165] In an embodiment, a method of making a porous polymeric material comprises contacting a cyclodextrin with a crosslinking agent, such as an aryl 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, if the crosslinking agent is an aryl compound) that can react with the 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 compound is a nucleophilic aromatic substitution reaction.

[0166] Examples of suitable aryl compounds that react to form aryl crosslinking moieties include the moieties shown in FIG 6, where Ar is an aryl moiety. Two or more of the functional groups (e.g., halide, -NO₂, and/or -CF₃ groups) react to form an aryl crosslinking group. In particular embodiments, the aryl compound is tetrafluoroterephthalonitrile, trichloroterephthalonitrile, dichloroterephthalonitrile, monochloroterephthalonitrile, decafluorobiphenyl (DFB), or octafluoronaphthalene. In another particular embodiment, the aryl compound is tetrafluoroterephthalonitrile.

[0167] 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 substrate (e.g., covalently, adhesively, or mechanically), for example by any of the methods described herein.

[0168] In some embodiments, the present disclosure provides a method of purifying an aqueous sample comprising one or more organic pollutants, the method comprising contacting the aqueous sample with the supported porous polymeric material of claim 1, such that at least 50% to at least 99% of the one or more organic pollutants are removed from the aqueous sample. In some embodiments, the one or more cyclodextrin moieties are β -cyclodextrin moieties. In some embodiments, the supported porous polymeric material is CD-TFN@CMC. 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 aqueous sample is drinking water, wastewater, ground water, aqueous extracts from contaminated soils, or landfill leachates.

[0169] 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 a P-CDP-substrate complex (e.g., CD-TFN@CMC) disclosed herein 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., β -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 P-CDP-substrate complex 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.

[0170] In an embodiment, a method of determining the presence or absence of compounds (e.g., organic compounds) in a sample comprises: a) contacting the sample with a P-CDP-substrate complex (e.g., CD-TFN@CMC) disclosed herein for an incubation period (e.g., 1 minute or less, 5 minutes or less, or 10 minutes or less); b) isolating the P-CDP-substrate complex from a) from the sample; and c) heating the P-CDP-substrate complex material from b) or contacting the P-CDP-substrate complex from b) with a solvent (e.g., methanol) such that at least part of the compounds are then released by the P-CDP-substrate complex; 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 P-CDP-substrate complex (or a composition comprising the porous polymeric material) can be the extracting phase in a solid phase microextraction (SPME) device.

[0171] In an embodiment, a method for removing compounds (e.g., organic compounds) from a sample comprises: a) contacting the sample with a P-CDP-substrate complex (e.g., CD-TFN@CMC) disclosed herein for an incubation period such that at least some of the compounds are sequestered in the polymer; b) isolating the P-CDP-substrate complex from a) from the sample; c) heating the P-CDP-substrate complex from b) or contacting the P-CDP-substrate 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.

[0172] 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.

[0173] 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.

[0174] In the methods, the P-CDP-substrate complex 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).

[0175] The following examples are provided to illustrate the present disclosure, and should not be construed as limiting thereof.

EXAMPLES

Example 1: Synthesis: Material and Methods

[0176] Various starting materials may be prepared in accordance with conventional synthetic methods well-known in the art.

[0177] The compounds of the present disclosure can be prepared from readily available starting materials by conventional methods and processes below. Different methods may also be used for manufacturing the inventive compounds, unless otherwise specified as typical or optimal process conditions (*i.e.*, reaction temperature, time, molar ratio of reactants, solvents, pressures, etc.). The optimal reaction conditions may vary depending on the particular reactants or solvents employed. Such conditions, however, can be determined by the skilled in the art by conventional optimization process.

[0178] In addition, those of ordinary skill in the art recognize that some functional groups can be protected/deprotected using various protecting groups before a certain reaction takes place. Suitable conditions for protecting and/or deprotecting specific functional group, and the use of protecting groups are well-known in the art.

[0179] For example, various kinds of protecting groups are described in T.W. Greene and G.M. Wuts, *Protecting Groups in Organic Synthesis*, Second edition, Wiley, New York, 1991, and other references cited above.

[0180] In general, the P-CDP materials referenced herein can be synthesized via nucleophilic aromatic substitution that crosslinks, for example, α , β , or γ -cyclodextrin, microcrystalline cellulose and a fluorinated aromatic compound of FIG. 6. A variety of bases can be used to facilitate the reaction including, but not limited to: K_2CO_3 , $KHCO_3$, K_3PO_4 , K_2HPO_4 , KH_2PO_4 , KH , NaH , Na_2CO_3 , $NaHCO_3$, CS_2CO_3 , NEt_3 , $iPrNEt_2$, pyridine, and DABCO. Solvents include but are not limited to THF, DMSO, CH_3CN , 1,4-dioxane, water, dimethylacetamide (DMA), DMF, and mixtures thereof. A range of temperatures from room temperature to 180 °C or greater can be employed.

[0181] Synthesis of Grafted β -cyclodextrin Polymer on Cellulose Microcrystals:

[0182] In one embodiment of the present invention, Grafted β -cyclodextrin polymer on cellulose microcrystals (CD-TFN@cellulose) was prepared by reacting 1.5 g of cellulose microcrystals, 3.2 g of β -cyclodextrin, 2.3 g of tetrafluorophthalonitrile, and 6.4 g of potassium carbonate in 150 mL of a 9:1 tetrahydrofuran/water solvent mixture at 85 °C for 2 days under a N₂ atmosphere in a 300 mL pressure vessel. The final suspension was cooled and filtered. The obtained solid was washed with THF, water, 1M HCl, and water again. Then, it was further washed with methanol using a Soxhlet extraction for 1 day. Finally, the solid was dried under high vacuum at 77 K for 3 h and then at room temperature for 9 h. 2.7 g (42.5% by mass) of CD-TFN@cellulose was isolated as a yellow solid (FIG. 1).

Analysis and Discussion

Characterization of the Synthesized CD-TFN@cellulose:

[0183] The elemental analysis of the obtained solid shows a Fluorine to Nitrogen ratio of 0.69, which indicates that on average, the aromatic crosslinker contains 2.6 substitutions of either β -cyclodextrin and/or cellulose. Additionally, from the Nitrogen to Carbon ratio, it can be calculated that the final material contains 16.6% crosslinker by mass. FT-IR spectrum of the CD-TFN@cellulose exhibits the typical bands for carbohydrates at 3350, 2900 and 1050 cm⁻¹. In addition, absorbances corresponding to the crosslinker are observed at 2233, 1680 and 1454 cm⁻¹. Peaks between 1200-900 cm⁻¹ have different intensities compared to the peaks of the unmodified cellulose (FIG. 2). SEM images of the unmodified cellulose (FIG. 3A) and CD-TFN@cellulose (Fig. 3B) demonstrate the coating of the β -cyclodextrin polymer on the cellulose microcrystals after the reaction. These images also suggest that the polymer adopts a sphere-like morphology on the surface of the cellulose, without any change in the size and shape of the cellulose microcrystals compared to the starting material.

Uptake of Bisphenol A from Water by CD-TFN@cellulose:

[0184] The capacity of the CD-TFN@cellulose to uptake bisphenol A from water solution as a function of contact time and initial concentration was investigated. As a function of contact time, CD-TFN@cellulose shows an order of magnitude greater uptake than cellulose microcrystals (15 mg BPA/g adsorbent versus 1 mg/g). Of added value, CD-TFN@cellulose reaches equilibrium within the first 10 min of contact time (FIG. 4A), showing its fast ability to sequester bisphenol A from water. Additionally, CD-TFN@cellulose is also superior to cellulose microcrystals as a function of bisphenol A concentration. CD-TFN@cellulose shows a maximum capacity of 86.7 mg BPA/g, compared to only a negligible adsorption by cellulose

at the studied concentration range (FIG. 4B). These findings show that CD-TFN@cellulose is a promising material for water purification in packed columns due to its fast and high adsorbance of pollutants.

Uptake of Micropollutants from Water by CD-TFN@cellulose:

5 **[0185]** The instant removal of 175 micropollutants with diverse chemical structures and uses through equivalent masses of the first-generation TFN-CDP and the CD-TFN@cellulose was measured (FIG. 5). The experiments were conducted in triplicate in columns packed with 500 mg of either TFN-CDP or CD-TFN@cellulose. The CD-TFN@cellulose was heated to 100 °C then cooled to ambient temperature, packed into the column, and conditioned with a mixture
10 of 5 mL of MeOH and 10 mL of nanopure water. The TFN-CDP was packed into the column and conditioned with a mixture of 5 mL of MeOH and 10 mL of nanopure water. One liter of nanopure water spiked with 500 ng/L of each of the 175 micropollutants was drawn over each cartridge using a conventional vacuum manifold. 8 mL samples were collected from the effluent of each cartridge at three separate time points through the filtration of the one liter of
15 water. Each sample was analyzed by means of high-resolution mass spectrometry to quantify the removal percentage of each of the micropollutants. The resulting data were partitioned into removal bins at intervals of 10% (e.g., 0-10% removal, 10-20% removal). The data in FIG. 5A show that the number of micropollutants classified in each removal bin was relatively stable between the two materials (TFN-CDP on the left and CD-TFN@cellulose on the right in each
20 pairing). This is surprising and unexpected considering that CD-TFN@cellulose has fewer cyclodextrin binding sites than an equivalent mass of TFN-CDP. The data in FIG. 5B show a direct comparison of the removal percentage for each micropollutant on TFN-CDP and CD-TFN@cellulose; each data point is the average of nine measurements (three samples each from triplicate experiments). The thick dashed line represent the situation in which the removal is
25 the same for each material, and the thinner dashed lines represent a 20% difference. There were 146 of 175 micropollutants that demonstrated equivalent removal between the two materials within a 20% deviation. Further, the residual difference between each data point and the equivalence point are normally distributed with a mean of one. This suggests random error, and no preferential removal of micropollutants by equivalent masses of each material.

Example 2: Deposition of β -Cyclodextrin on Cellulose Microcrystals: Synthesis and Use for In-flow Water Remediation

Materials and Instrumentation

[0186] Reagents: β -cyclodextrin (β -CD) (>97%), cellulose microcrystals (CMC) (50 μ m average particle size), tetrafluorophthalonitrile (TFN) (>99%), were purchased from Sigma Aldrich and used without further purification. Dimethyl sulfoxide (DMSO) (99.8%) and potassium carbonate (>99%) were purchased from Fisher Scientific and used without further purification. 200 μ m cellulose microspheres were kindly donated by KOBO products, Inc. Aqueous solutions of bisphenol A (BPA) were prepared using 18 M Ω deionized H₂O at neutral pH. All model compounds were obtained from commercial sources and used as received.

[0187] Instrumentation: Infrared spectroscopy was performed on a Thermo Nicolet iS10 with a diamond ATR attachment. Coating of the samples was done in a Denton Desk III TSC sputter coater. Scanning electron microscopy and energy dispersive spectroscopy were performed on a Hitachi S-3400N-II. Liquid chromatography was performed in a Bruker Amazon-X instrument, using a C-18 column for separation, and UV-VIS photodiode as a detector. Powder X-ray diffraction was done in a Stoe STADI-MP diffractometer, using pure Cu K α 1 radiation in transmission mode. Back pressure experiments were performed in a Shimadzu LC-20AD liquid chromatograph. Breakthrough experiments were done in a Hewlett Packard 1100 series, using a UV-VIS photodiode as a detector. The photoelectron spectra (XPS) were recorded with a Thermo Scientific ESCALAB 250Xi instrument, using Al K α X-ray source (1486.6 eV). The monochromated X-ray beam spot size is 500 μ m in diameter and the power is 150 watts. The pass energy of 100 eV and the step size of 1 eV were used for the survey scan. For the high resolution scan 50 eV of pass energy and 0.1 eV of step size were used.

Experimental protocols

[0188] Synthesis of CD-TFN@CMC: Functionalization of the cellulose microcrystals (CD-TFN@CMC) was performed by varying the previously reported synthesis of the cyclodextrin porous polymer. A 300 mL pressure vessel equipped with a magnetic stir bar was charged with TFN (7.5051 g, 37.52 mmol) and DMSO (170 mL), and the solution was stirred until TFN was completely dissolve. In another flask, β -CD (6.0052 g, 5.29 mmol), K₂CO₃ (18.4521 g, 133.51 mmol) and CMC (12.0011 g) were suspended in 73 mL of deionized H₂O. This suspension was then added dropwise into the DMSO solution, and the flask was bubbled with N₂ for 10 min. The N₂ inlet was removed, the flask was sealed, and the mixture was placed on a hot stirring plate at 85 °C and stirred at 500 r.p.m. for one day. The dark-red suspension was cooled down and then filtered, the solid was washed with THF (20 mL X 3),

water (20 mL X 3), HCl 1M (until CO₂ evolution stopped), water (20 mL X 3), and methanol (20 mL X 3). The yellow solid was washed with methanol using a Soxhlet extractor for 1 day, and then freeze-dried under high vacuum overnight. Giving 19.2759 g of a yellow solid (conversion: 82.1%). The functionalized cellulose was isolated from the non-bonded cyclodextrin polymer by using a 45 µm sieve, where the solid passing through the mesh is the free polymer (CD-TFN, 48.9%) and the solid staying on top of the sieve is the functionalized cellulose (CD-TFN@CMC, 51.1%).

[0189] Synthesis of m-CD-TFN: Synthesis of the β-CD polymer was performed by employing the same methodology used for CD-TFN@CMC. A 150 mL pressure vessel equipped with a magnetic stir bar was charged with TFN (3.7572 g, 18.78 mmol) and DMSO (72 mL), and the solution was stirred until TFN was completely dissolve. In another flask, β-CD (3.0066 g, 2.65 mmol) and K₂CO₃ (9.2510 g, 66.94 mmol) were suspended in 36 mL of deionized H₂O. This suspension was then added dropwise into the DMSO solution, and the flask was bubbled with N₂ for 10 min. The N₂ inlet was removed, the flask was sealed, and the mixture was placed on a hot stirring plate at 85 °C and stirred at 500 r.p.m. for one day. The dark-red suspension was cooled down and then filtered, the solid was washed with THF (20 mL X 3), water (20 mL X 3), HCl 1M (until CO₂ evolution stopped), water (20 mL X 3), and methanol (20 mL X 3). The yellow solid was washed with methanol using a Soxhlet extractor for 1 day, and then freeze-dried under high vacuum overnight. Giving 3.316 g of a yellow solid (yield: 57.2%).

[0190] Synthesis of CD-TFN@CMS: Functionalization of the cellulose microspheres (CD-TFN@CMS) was performed by a slight modification of the CD-TFN@CMC synthesis. A 300 mL Fast-Freeze flask was charged with TFN (3.7598 g, 18.80 mmol) and DMSO (84 mL), and the solution was stirred until TFN was completely dissolve. In another flask, β-CD (2.9999 g, 2.64 mmol), K₂CO₃ (9.2585 g, 66.99 mmol) and CMS (6.0117 g) were suspended in 36 mL of deionized H₂O. This suspension was then added dropwise into the DMSO solution, and the flask was bubbled with N₂ for 10 min. The N₂ inlet was removed, the flask was sealed and hooked to an overhead mechanical stirrer, and the mixture was placed on a hot stirring plate at 85 °C and stirred at 500 r.p.m. for one day. The dark-red suspension was cooled down and then filtered, the solid was washed with THF (20 mL X 3), water (20 mL X 3), HCl 1M (until CO₂ evolution stopped), water (20 mL X 3), and methanol (20 mL X 3). The yellow solid was washed with methanol using a Soxhlet extractor for 1 day, and then freeze-dried under high vacuum overnight. Giving 5.5684 g (yield: 46.6%). The functionalized spheres were isolated from the non-bonded cyclodextrin polymer by using a 90 µm sieve, where the solid

passing through the mesh is the free polymer (CD-TFN, 2.1%) and the solid staying on top of the sieve is the functionalized microsphere (CD-TFN@CMS, 97.9%).

[0191] Scanning electron microscopy: The following procedure was the same for all the samples. 5 mg of CD-TFN@CMC was suspended in 5 mL of water. The solution was stirred for 5 min, then a 20 μ L aliquot was taken and deposited in a stub covered with carbon tape, the water was allowed to evaporate overnight, and then the sample was coated with a 10 nm gold/palladium layer. The sample was transferred to the SEM instrument and both SEM and EDS were recorded using a working distance of 10 mm, and a charge voltage of 5 kV and 25 kV for SEM and EDS respectively.

Transmission electron microscopy:

[0192] Aqueous BPA kinetic uptake experiments: Adsorption kinetic studies were performed in 20 mL scintillation vials. All studies were conducted at ambient temperature and 300 rpms, and the procedure was the same for all the adsorbents tested. 8 mg of CD-TFN@CMC (40 mg for CD-TFN@CMS) was initially suspended in 7.2 mL of water and stirred for 5 min. Then, 0.8 mL of BPA (1 mM) was added to the stirring polymer suspension. After a specific contact time, a 0.5 mL aliquot was taken and filtered immediately by a Whatman 0.2 μ m inorganic membrane syringe filter into a LCGC vial. The residual concentration of BPA was determined by LC. Uptake was determined as the average of three independent experiments performed using different samples, each isolated from the same polymerization experiment.

[0193] Aqueous BPA thermodynamic uptake experiments: Thermodynamic adsorption studies were performed in 3 mL scintillation vials. All studies were conducted at ambient temperature and 300 rpms, and the procedure was the same for all the adsorbents tested. 2 mg of CD-TFN@CMC (10 mg for CD-TFN@CMS) were suspended in 2 mL of 0.125 mM BPA solution, and the suspension was stirred for 4h. After the equilibration time, 0.5 mL aliquot was taken and filtered immediately by a Whatman 0.2 μ m inorganic membrane syringe filter into a LCGC vial. This same procedure was repeated with the 0.25, 0.5, 0.75 and 1 mM BPA solutions. The residual concentration of BPA was determined by LC. Uptake was determined as the average of three independent experiments performed using different samples, each isolated from the same polymerization experiment.

[0194] Back pressure experiments: Back pressure experiments were done at ambient temperature and the procedure was the same for all the adsorbents tested. 200 mg of CD-TFN@CMC was packed in an empty column, by adding 20 mg of adsorbent at a time and

tapping the column. Then, the column was connected to a LC, and water was run through the column at 1 mL/min during 2h. Then, the flow rate was decreased to 0.1 mL/min, and the pressure was read after stabilization (1-2 min). Afterwards, the flow rate was increased to 0.2 mL/min and the pressure was read again. This procedure was repeated until the flow rate reached 1 mL/min (Back pressure for CD-TFN@CMS was measured in the range of 0.5-5 mL/min with 0.5 mL increments). Back pressure was determined as the average of three independent experiments performed using different samples, each isolated from the same polymerization experiment.

[0195] Aqueous BPA breakthrough and reusability experiment: Breakthrough experiments were done at ambient temperature and the procedure was the same for all the adsorbents tested, the flow rate was kept at 2mL/min during the entire experiment. 200 mg of CD-TFN@CMC was packed in an empty column, by adding 20 mg of adsorbent at a time and tapping the column. Then, the column was connected to a LC, and water was run through the column during 10 min. Then, the solvent was switched for BPA solution (0.1, 0.5, or 1.0 mM) and the UV-VIS signal was recorded until it reached a plateau. For the reusability experiment, the CD-TFN@CMC sample was packed and water equilibrated (200 mg, 10 min). First, a 1.0 mM BPA solution was run until it reached a plateau. Then, the solvent was switched for methanol and the column was rinsed until the UV-VIS signal went back to the initial value (approximately 5 min). Afterwards, the solvent was switched to water, and it was run for 10 min. Finally, the solvent was switched back to the BPA 1.0 mM solution, and the run started over. This procedure was repeated three times.

[0196] The characterization of the adsorbent reveals a core/shell structure where the polymer has a thickness of 800 ± 160 nm. Batch adsorption experiments demonstrate fast kinetics and access to more than 80% of the total number of cyclodextrins. The flow adsorption of bisphenol A by a packed column of the adsorbent indicates a non-linear increase in the saturation time as a function of the pollutant concentration. Furthermore, three adsorption/desorption experiments show the reusability of the adsorbent. Additionally, continuous adsorption of 15 micropollutants at relevant environmental concentration (10 ppb) confirms the potential utility of the adsorbent, where seven pollutants are removed completely and six are partially removed. Moreover, anaerobic and aerobic degradation of the adsorbent shows good stability towards bacterial aging. Finally, extrapolation of the synthesis to include cellulose microspheres proves the potential of the reaction to incorporate the cyclodextrin polymer into other cellulose substrates. Flow is preferred over batch adsorption because continuous removal of pollutants is more efficient and can be easily implemented in wastewater treatment plants.

Synthesis and Characterization

[0197] Deposition of the β -CD polymer on cellulose microcrystals (CMC) is done by reacting β -CD, TFN, CMC and K_2CO_3 in a mixture of DMSO:H₂O at 85°C for 1 day (Fig. 8). Based on previous results, a good quality polymer can be obtained with 6 eq. of TFN and 21 eq. of base with respect to β -CD (Klimes et al., In preparation. 2018). However, for these studies a loading of 7.1 eq. of TFN and 25.2 eq. of base to account for the presence of extra hydroxyl groups on the CMC is used. Doubling the amount of CMC compared to β -CD increases the odds of successful grafting. β -CD is highly soluble in DMSO, and is used as a solvent since it increases the yield of the reaction (Klimes et al., In preparation. 2018). Additionally, water aids in grafting the β -CD polymer on cellulose substrates (Alzate-Sánchez et al., Chem. Mater. 2016, 28 (22), 8340). A solvent screen with different combinations of DMSO and water, while keeping constant the reagent concentrations was performed. Based on the total mass yield and the capacity of the material to adsorb BPA (1 mg/mL in 1mM solution), mixture of 7:3 DMSO:H₂O for the large scale reaction was used (Fig. 15). After the polymerization and cleaning by soxhlet extraction of the material 19.3 g of a yellow powder was obtained. However, this material is a physical mixture of non-bonded β -CD polymer (CD-TFN) and β -CD polymer deposited on cellulose (CD-TFN@CMC), as depicted in the SEM image of Fig. 9a. Taking advantage of the initial particle size of the CMC (50 μ m) and the smaller particle size of the CD-TFN polymer, the initial solid was sieved to separate them; the solid on top of the sieve is enriched in CD-TFN@CMC, and the solid passing through the sieve is enriched in CD-TFN without cellulose. The effectiveness of the sieving is demonstrated by the PXRD data, in which the peaks corresponding to the crystalline domains of cellulose are enhanced in the CD-TFN@CMC sample and are barely discernable in the CD-TFN sample (Fig. 9, left panel). Additionally, the SEM images of the solids after sieving show that CD-TFN@CMC contains the solid with the biggest particle sizes and cellulose type morphology (Fig. 9b) while the CD-TFN sample holds particles with smaller size and rounded morphology (Fig. 9c).

[0198] Spectroscopic characterization of the CD-TFN and CD-TFN@CMC was performed with FT-IR. No significant differences in the position of the absorption bands for the solids after sieving are seen (Fig. 16). Yet, they exhibit typical bands for carbohydrates (3400 ± 200 and 1025 ± 50 cm^{-1}), in addition to absorbances at 2240 ± 20 and 1475 ± 25 cm^{-1} corresponding to the presence of the cross linker (Alsbaiee et al., Nature 2016, 529 (7585), 190 and Kačuráková, and Wilson, Carbohydr. Polym. 2001, 44 (4), 291). Superficial compositional analysis of CD-TFN and CD-TFN@CMC was performed using XPS, and in both samples, the

presence of nitrogen and fluorine was observed, confirming the incorporation of the crosslinker. As expected, XPS analysis of the starting cellulose (CMC) show no signal for these two elements (Fig. 17).

[0199] The composition analysis was performed as a combination of PXRD and combustion experiments. From the PXRD data, the amount of cellulose present was calculated using CMC to signify 100% cellulose, and 0% cellulose was signified by a CD-TFN polymer that does not contain cellulose (m-CD-TFN). By employing this methodology, 16.7 and 78.3 % CMC in CD-TFN and CD-TFN@CMC was calculated, respectively. Using combustion experiments and the amount of nitrogen quantified per sample, 38.05 and 8.1 % TFN for CD-TFN and CD-TFN@CMC was calculated, respectively. The combined amount of CMC + β -CD in each polymer by carbon content was determined, which was calculated by subtracting the carbon-based TFN from the total amount of carbon, and determined 61.95 and 91.9 % for CD-TFN and CD-TFN@CMC, respectively. Afterwards, combination of the PXRD results with the combustion experiments allows the determination of the amount of β -CD as 45.2 and 13.6 % for CD-TFN and CD-TFN@CMC, respectively. Moreover, a β -CD:TFN molar ratio of 3.9 and 2.1 and an average substitution in the TFN of 2.6 and 2.5 for CD-TFN and CD-TFN@CMC was calculated, respectively (Table 1).

Table 1. Composition parameters of CD-TFN@CMC and CD-TFN obtained from combination of PXRD and elemental analysis results.

Sample	CMC (%)	β -CD (%)	TFN (%)	β -CD/TFN ratio	TFN substitution
CD-TFN@CMC	78.3	13.6	8.1	2.1	2.5
CD-TFN	16.7	45.2	38.1	3.9	2.6

[0200] These results indicate that CD-TFN still contains cellulose. Also, the polymer that is deposited on the CMCs is less crosslinked than the free polymer, which is due to the presence of extra hydroxyl groups coming from the CMCs. However, the substitution pattern in the TFN is statistically the same for both samples, which supports a similar crosslinking reaction for both CD-TFN and CD-TFN@CMC formation.

[0201] Imaging experiments were performed using energy dispersive spectroscopy (EDS) and mapped elements that are in CD-TFN@CMC but not in the starting material (CMC). Oxygen and carbon mapping shows a higher contrast where the CD-TFN@CMC is located, which demonstrates the validity of the technique (Fig.18). Fluorine mapping has similar behavior, and identifies higher counts in the region where the particle is located. Therefore, it infers that TFN is present in the surface of the CMC and that it is homogeneously distributed

because areas of the particle with significantly higher counts are not seen (Fig. 10b). Additionally, the same EDS imaging on CMC was performed, and the fluorine mapping shows no significant contrast (Fig. 10e). Fluorine mapping for CD-TFN was performed, and it clearly shows a higher signal where the particle is located (Fig. 19). Scanning transmission electron microscopy (STEM) was used to study the morphology of CD-TFN@CMC. Initially, particle cross sections were obtained by cutting an embedded gel with the material to 1 μm thick sheets and then collected STEM images of these sheets. Depicted in Fig. 10c is a cross sectional image in which a core shell structure is seen, and the shell appears as a different feature surrounding the CMC core. As a control, slicing and imaging the CMC but the STEM image shows no core shell structure (Fig. 10f), which confirms that the morphology seen in CD-TFN@CMC is due to the presence of two different materials. A polymer thickness of 800 ± 160 nm was calculated (Fig. 20). Arguably, the shell is indeed the cyclodextrin polymer, and therefore the functionalization is produced only on the surface of the CMC. Additionally, the fact that the thickness of the β -CD polymer is below 1 μm enhances the possibility of much faster kinetics to adsorb MPs compared with the speed of CD-TFN which has a thickness on the order of tens of μm (Fig. 21).

BPA adsorption in batch experiments

[0202] β -CD is known to form a stable inclusion complex with BPA, so when the system is tested for BPA uptake; positive uptake would indicate that β -CD is present in the synthesized adsorbents, and the capacity and rate of the system for MP adsorption can be determined. The adsorption of BPA as function of concentration is depicted in Fig. 11a. Initially, it is clear that β -CD is present in both CD-TFN and CD-TFN@CMC due to their much higher capacity for BPA than CMC. Additionally, CD-TFN has a higher BPA capacity than CD-TFN@CMC due to a lower amount of non-adsorbent material (CMC) in this sample. However, if comparison of capacity in terms of mg BPA to g β -CD is performed, then their capacities are comparable (Fig. 22). Furthermore, fitting the BPA adsorption data as a function of concentration to a Langmuir model (Equation 1) to determine the thermodynamic parameters of the three materials tested (Fig. 23 and Table 2, Ghosal and Gupta, J. Mol. Liq. 2017, 225, 137).

[0203] The Langmuir model that consider homogeneous adsorption surface, is given as

$$q_e = q_{max} \frac{C_e K_L}{C_e K_L + 1} \quad (\text{Equation 1})$$

where q_e (mg BPA/g solid) is the amount of BPA adsorbed per gram of adsorbent at equilibrium. q_{max} (mg BPA/g solid) is the maximum adsorption capacity of adsorbent at equilibrium, K_L (mol^{-1}) is the equilibrium constant and C_e (mM) is the concentration at

equilibrium. By fitting the thermodynamic parameters using the curve fitting tool of IGOR Pro 6.3.7.2 the fitting curve was obtained as well as the thermodynamic parameters.

[0204] In the pseudo second order rate law, both the rate constant and the capacity at equilibrium are interrelated, making difficult the comparison in terms of speed of materials with different capacities towards a specific sorbate. To solve this problem, the relaxation time equation is used, given as

$$q_t = q_e \frac{t}{t+t_r} \text{ (Equation 2)}$$

where q_t (mg BPA/g solid) is the amount of BPA adsorbed per gram of adsorbent at a given time. q_e (mg BPA/g solid) is the amount of BPA adsorbed per gram of adsorbent at equilibrium at a given initial concentration, t (s) is the time, and t_r (s) is the relaxation time of the adsorption process, and it is the inverse of the rate constant. By fitting the kinetic parameters using the curve fitting tool of IGOR Pro 6.3.7.2 the fitting curve was obtained as well as the kinetic parameters.

Table 2. Thermodynamic and kinetic parameters of CD-TFN@CMC and CD-TFN obtained from Langmuir and relaxation time kinetic models respectively.

Sample	q_{max} (mg BPA/g solid)	K_L (mol ⁻¹)	q_e (mg BPA/g solid)	t_r (s)
CD-TFN@CMC	34.7±1.6	9599±1720	13.69±0.08	0.89±0.33
CD-TFN	193.6±7.8	5597±640	18.78±0.13	3.75±0.50

[0205] For CD-TFN, a maximum capacity of 193.6 ± 7.8 mg BPA / g solid was found, which corresponds to a combination of specific and nonspecific adsorption of BPA as seen in previous reports (Alsbaiee et al., Nature 2016, 529 (7585), 190). On the other hand, the maximum BPA capacity for CD-TFN@CMC is 34.7 ± 1.6 mg BPA / g solid. By assuming a 1:1 BPA:β-CD inclusion complex, a β-CD content of 16.8 ± 0.8 % for CD-TFN@CMC is calculated. The value calculated by PXRD/elemental analysis is 13.6%. These two values are very similar, and from them it was determined that at least 81% of β-CDs present in CD-TFN@CMC are being accessed. This high accessing rate could be due to the very thin film of polymer that is deposited on the surface of the CMCs. Finally, as expected, the BPA uptake by CMC could not be fitted to a Langmuir model, demonstrating nonspecific binding with BPA. However, the maximum adsorption value found was 1.7± 0.3 mg BPA / g solid. The speed BPA uptake from solution was evaluated by plotting the BPA adsorption as a function of time. CD-TFN has fast BPA uptake since it reached equilibrium within two minutes, which is comparable to our previously

reported β -CD polymers (Alsaiee et al., Nature 2016, 529 (7585), 190 and Ling et al., Environ. Sci. Technol. 2017, 51 (13), 7590). More remarkably, CD-TFN@CMC reached equilibrium within the first 20 s, which is the fastest BPA uptake for a β -CD material reported so far. The uptake of CMC is very low, and conclusions regarding its speed are hard to draw because the uptake does not follow any trend (Fig. 11b). In order to evaluate the speed of BPA uptake for materials with different capacities, the relaxation time (t_r) parameter was used, where processes with high relaxation times slowly reach equilibrium, while processes with small relaxation times adapt to equilibrium quickly (Liu, Colloids Surfaces A Physicochem. Eng. Asp. 2008, 320 (1–3), 275). By fitting the BPA kinetic uptake to equation 2, t_r of 3.75 ± 0.66 and 0.99 ± 0.03 s for CD-TFN and CD-TFN@CMC was calculated, respectively, corroborating the faster kinetics of CD-TFN@CMC compared to CD-TFN (Fig. 24 and Table 2). The fast kinetics of the deposited polymer is assumed to be due to more accessible β -CD for BPA due to a thinner layer of polymer (800 ± 160 nm) compared to a thicker layer of the polymer when it is not deposited on the CMC (16.0 ± 3.9 μ m).

Back pressure test

[0206] Low back pressure is an important characteristic of adsorbents meant to be used in packed columns for water purification. Back pressure is highly dependent on particle size, morphology, and distribution, and so larger, homogenous particles are desirable (Guiochon, G. J. Chromatogr. A 2007, 1168, 101). CD-TFN has an irregular shape and a broad size distribution, while CD-TFN@CMC has a regular shape and a size distribution centered at 50 μ m. It was speculated that this material should have a lower back pressure compare with CD-TFN. To investigate back pressure, chromatographic columns were packed with the adsorbents and an LC instrument was used to measure the pressure as a function of flow rate (Fig. 12). From the graph, CMC had the lowest back pressures and CD-TFN had the highest. CD-TFN@CMC had an intermediate back pressure and was close to that of CMC. By using the superficial velocity-based column permeability equation (Equation 3 and Table 3) (Neue, U. D. HPLC columns : theory, technology, and practice; Wiley-VCH, 1997), it was determined that CD-TFN@CMC is 3.4 times more permeable than CD-TFN. This higher permeability, combined with a fast uptake, makes CD-TFN@CMC a promising candidate for MP removal in flow.

[0207] Specific permeability can be determined from a graph of back pressure as a function of flow rate by using the following equation.

$$B_0 = \frac{\eta L}{\pi r^2} \frac{F}{\Delta P} \text{ (Equation 3)}$$

where η (mPa*s) is the mobile phase viscosity, L (m) is the column length, r (m) is the column radius, and $F / \Delta P$ (m³/mPa*s) is the slope of the curve of flow rate vs back pressure.

Table 3. Specific permeability of CMC, CD-TFN@CMC, CD-TFN and CD-TFN@CMS (water viscosity was 1.0016 mPa*s, and column radius was 4.0×10^{-3} m).

Sample	L (m)	B ₀ (m ²)
CMC	1.90×10^{-2}	2.2×10^{-12}
CD-TFN@CMC	1.85×10^{-2}	4.7×10^{-12}
CD-TFN	1.60×10^{-2}	1.6×10^{-11}
CD-TFN@CMS	1.45×10^{-2}	1.2×10^{-12}

Breakthrough adsorption of BPA

[0208] BPA kinetic adsorption and back pressure tests reveal that CD-TFN@CMC is faster and more permeable than CD-TFN. Driven by these insights, in-flow removal of BPA was evaluated by packing a column with CD-TFN@CMC and then flowing solutions of BPA (0.1, 0.5 and 1.0 mM) through it. It was expected to not see a BPA signal initially due to the adsorption of this pollutant in the column. Eventually, due to continuous injection of BPA, the CD-TFN@CMC would be saturated, and subsequent leaching of BPA would be expected. By monitoring the BPA signal using a UV-VIS detector, typical breakthrough curves were recorded for CD-TFN@CMC. Higher BPA concentrations required lower times to saturate the adsorbent. Additionally, a non-linear relation between the initial BPA concentration and the time required to saturate the CD-TFN@CMC was observed (Fig. 13a). Furthermore, control experiments of the CMC and the empty column showed no difference in their breakthrough time, indicating the CMC is not a BPA adsorbent by itself (Fig. 25). The breakthrough time (BT) was calculated as the time when 10% of the influent concentration is measured, and the bed volume was determined, as the ratio of the treated water before breakthrough volume, and the column volume (Table 4, Hori et al., JAPCA 1988, 38, 269). The highest bed volume found for the CD-TFN@CMC is 82.2, which is not particularly high. However, this BPA concentration (22.8 ppm) is 407 times higher than the maximum amount detected in surface water (56 ppb) (Corrales et al., Dose Response . 2105, 13(3), 1559325815598308). Therefore, higher bed volumes are expected when environmentally relevant concentrations of micropollutants are tested. Additionally, assuming the UV-VIS signal has a linear response to BPA concentration, the amount of BPA adsorbed in each experiment calculated and the adsorption values determined are very close to the values found in batch experiments (Fig. 26). This validates the use of batch experiments to estimate the capacity in-flow.

	CD-TFN@CMC			CMC		
Concentration (mM)	BT (min)	BV	BPA uptake (mg/g)	BT (min)	BV	BPA uptake (mg/g)
0.1	37.0	82.2	9.7	1.9	3.8	0.6
0.5	14.5	32.3	20.7	1.8	3.5	3.3
1.0	10.6	23.6	30.1	1.8	3.5	5.1

Table 4. Breakthrough time (BT), bed volumes (BV) and BPA uptake of CD-TFN@CMC and CMC from in-flow experiments.

- 5 **[0209]** Another important characteristic for next-generation adsorbents is the feasibility to regenerate them. Fast and low energy consumption is desired for the regeneration of adsorbents to avoid one of the biggest drawbacks of standard (activated carbons) materials. Moreover, regeneration that does not involve the removal of the adsorbent from the system would allow for a continues process that guaranties a more efficient water purification procedure.
- 10 Previously, it was demonstrated that β -CD polymers are easily regenerated in batch experiments upon washing with methanol (Alsaiee et al., Nature 2016, 529 (7585), 190). This regeneration was extrapolated to an in-flow system by saturating the CD-TFN@CMC with a 1.0 mM (228 ppm) BPA solution, followed by a methanol wash to remove the adsorbed BPA, and after attaining equilibrium with water this procedure was repeated. After three consecutive
- 15 cycles of BPA adsorption/methanol washes, no change in capacity or breakthrough time was observed, which demonstrates CD-TFN@CMC can be easily and completely regenerated by a simple methanol wash with no need to remove the adsorbent from the column (Fig. 13b).

Micropollutant removal

- 20 **[0210]** Micropollutants (MPs) are contaminants which exist in a sub-ppm concentration in the environment. Therefore, a more complete assessment of an adsorbent is accomplished by testing its performance to remove MPs as such concentrations. Consequently, it was decided to test the performance of CD-TFN@CMC to remove micropollutants at environmentally relevant concentrations (10 ppb). A cocktail of 15 micropollutants in water was generated and this solution was passed through a column packed with CD-TFN@CMC, and the breakthrough
- 25 time of each micropollutant was monitored. After 60 minutes, seven micropollutants did not breakthrough, so 100% removal for them was calculated. On the other hand, 8 micropollutants were detected during the run, and the removal was calculated at 10 min (32 min for Valsartan) (Fig. 14). Nine micropollutants had removals higher than 80%, which means their concentration in water after passing through the adsorbent is below 2 ppb. Even more

remarkable, this reduction in the individual concentration occurs in the presence of other micropollutants. The breakthrough time of the micropollutants which were not completely removed was determined, and compared with the percent removal previously calculated (Fig. 27). In general, there is a direct relation between these two parameters, and MPs with high removal need longer times to break through the column. Furthermore, a structural analysis of the MPs gives an insight about the physicochemical properties of the adsorbent. Depicted in Fig. 29 are the chemical structures of each micropollutant and, by comparing the percent removal, it can be stated that MPs with carboxylic or sulfonic acid functionalities are poorly removed. On the contrary, MPs with amino functional groups are highly removed. This behavior is exemplified by the couple Metolachlor and Metolachlor-ESA, where the change of a chloride group (Metolachlor) for a sulfonic acid group (Metolachlor-ESA) decreased the removal from $99.7 \pm 0.2\%$ to $70.9 \pm 5.2\%$, respectively. Therefore, CD-TFN@CMC has affinity towards basic molecules, most likely due to the presence of acidic functionalities. This assertion is supported by a previous study published in which the incorporation of highly acidic phenol groups during the polymerization of β -CD with TFN due to the electro deficient character of the crosslinker was detected (Klemes et al., In preparation. 2018)

Extrapolation to cellulose microspheres

[0211] Although the feasibility of depositing the β -CD polymer onto cellulose microcrystals was demonstrated, this substrate is not ideal for column packing because it has an elongated morphology. Spherical particles are more desirable because they pack better and, consequently, less energy required to pass water through them. The synthesis of CD-TFN@CMC to cellulose microspheres with a particle size of $200 \mu\text{m}$ was extrapolated and the microspheres (CD-TFN@CMS) were modified by employing mechanical stirring instead of magnetic stirring to avoid breaking down of the initial material. After the synthesis, a $90\mu\text{m}$ sieve was used to isolate the CD-TFN from the CD-TFN@CMS. Interestingly, this time the amount of free polymer isolated was just 2.1% since 97.9% of the sample is CD-TFN@CMS. The SEM image of CD-TFN@CMS indicates the spheres are stable under the modified reaction conditions. Additionally, fluorine mapping once again served as a probe of the crosslinker presence on the surface of the particle (Fig. 30). The thermodynamic uptake of the CD-TFN@CMS was also tested (Fig. 31 and Table 5). The microspheres had a maximum capacity for BPA at $5.3 \pm 0.3 \text{ mg/g}$, which is 6.5 times lower than the capacity of the CD-TFN@CMC, so optimization of the reaction is required to increase incorporation of the β -CD polymer onto the cellulose, but it will part of future efforts. Finally, a pressure drop test for the CD-TFN@CMS was conducted

under the same conditions as for CD-TFN@CMC. The outcome of the experiment reflected a much lower back pressure compared to the previously tested materials, with a permeability 1.8 times lower than CMC (Fig. 32, Table 3).

Sample	q_{max} (mg BPA/g solid)	K_L (mol ⁻¹)	q_e (mg BPA/g solid)	t_r (s)
CD-TFN@CMC	5.28±0.34	9112±2300	1.55±0.04	45.1±7.3

Table 5. Thermodynamic and kinetic parameters of CD-TFN@CMS obtained from Langmuir and relaxation time kinetic models respectively.

Conclusions

[0212] A new adsorbent based on renewable resources for the continuous sequestration of organic micropollutants from water was developed. The adsorbent had a core/shell structure in which the shell polymer has a thickness of 800 ± 160 nm and is homogeneously distributed on the surface of the cellulose microcrystal. This homogeneity imparts outstanding properties to the adsorbent, including fast kinetics, high cyclodextrin access, and allowed for the possibility to pack columns for in-flow water treatment.

[0213] The sequestration of BPA by a packed column of CD-TFN@CMC was tested, and a non-linear relation was found between saturation time and pollutant concentration. Moreover, a bed volume of 82.2 for the 22.8 ppm BPA concentration was determined, which is a promising result when one takes into account the maximum levels of this pollutant in surface water (56 ppb). Additionally, the in-flow reusability of the adsorbent by saturation of the CD-TFN@CMC with a solution of BPA followed by a methanol rinse to remove the pollutant was probed, and neither a decrease in the saturation time nor a maximum in capacity was recorded. Furthermore, in the continuous sequestration of organic pollutants at environmentally relevant concentrations, it was found that seven of fifteen pollutants were completely removed over the course of the experiment. Six pollutants were partially removed and had breakthrough times ranging from 10 to 40 min, while two pollutants were poorly removed. Structural analysis of the micropollutants revealed a charge-based selectivity of CD-TFN@CMC. Extrapolation of the synthesis to cellulose microspheres was explored and demonstrated the utility of the reaction to produce adsorbents in an application-based fashion. Novel adsorbents for in-flow water remediation are desirable.

EQUIVALENTS

[0214] 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.

INCORPORATION BY REFERENCE

[0215] US Patent Application No. 15/134,030 and all documents cited herein are each incorporated by reference in their entirety for all purposes. However, mention of any reference, article, publication, patent, patent publication, and patent application cited herein is not, and should not be taken as acknowledgment or any form of suggestion that they constitute valid prior art or form part of the common general knowledge in any country in the world.

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We claim:

1. A supported porous polymeric material comprising porous particles affixed to a solid substrate, wherein said porous particles comprise a plurality of cyclodextrin moieties crosslinked with one or more aryl moieties, and wherein the supported porous polymeric material has one or more performance characteristics which are at least about 50% of the same performance characteristics of unsupported porous particles of the same composition.
2. The supported porous polymeric material of claim 1, wherein the performance characteristic is pollutant uptake, and the pollutant uptake of the supported porous polymeric material is at least about 50% of the pollutant uptake of the unsupported porous particles of the same composition, wherein the pollutant uptake is the weight of pollutant absorbed (in milligrams) divided by the weight of porous particles (in grams).
3. The supported porous polymeric material of claim 2, wherein the pollutant uptake of the supported porous polymeric material is about the same as the pollutant uptake of the unsupported porous particles of the same composition.
4. The supported porous polymeric material of claim 2, wherein the pollutant uptake of the supported porous polymeric material is greater than the pollutant uptake of the unsupported porous particles of the same composition.
5. The supported porous polymeric material of any of claims 2-4, wherein the supported porous polymeric material is CD-TFN@CMC.
6. The supported porous polymeric material of claim 2-5, wherein the pollutant is bisphenol A.
7. The supported porous polymeric material of claim 1, wherein the performance characteristic is equilibrium adsorption capacity (q_e) for a pollutant, and the equilibrium adsorption capacity of the supported porous polymeric material is at least about 50% of the equilibrium adsorption capacity of unsupported porous particles having the same composition, wherein the q_e is measured as

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

wherein q_{max} (mg pollutant/g porous particles) is the maximum adsorption capacity the porous particles for the pollutant at equilibrium, K_L (mol⁻¹) is the equilibrium constant and C_e (mM) is the pollutant concentration at equilibrium.

5

8. The supported porous polymeric material of claim 7, wherein the equilibrium adsorption capacity of the supported porous polymeric material is about the same as the equilibrium adsorption capacity of the unsupported porous particles of the same composition.

10

9. The supported porous polymeric material of claim 7, wherein the equilibrium adsorption capacity of the supported porous polymeric material is greater than the equilibrium adsorption capacity of the unsupported porous particles of the same composition.

15

10. The supported porous polymeric material of any of claims 7-9, wherein the supported porous polymeric material is CD-TFN@CMC.

11. The supported porous polymeric material of any of claims 7-10, wherein the pollutant is bisphenol A.

20

12. A supported porous polymeric material of claim 1, wherein the performance characteristic is the rate at which equilibrium adsorption of a pollutant is reached (rate of equilibrium adsorption), and the rate of equilibrium adsorption of a pollutant of the supported porous polymeric material is at least about 50% of the rate of equilibrium adsorption of unsupported porous particles having the same composition and measured under the same conditions.

25

13. The supported porous polymeric material of claim 12, wherein the rate of equilibrium adsorption of the supported porous polymeric material is about the same as the rate of equilibrium adsorption of the unsupported porous particles of the same composition measured under the same conditions.

30

14. The supported porous polymeric material of claim 12, wherein the rate of equilibrium adsorption of the supported porous polymeric material is greater than the rate of equilibrium

adsorption of the unsupported porous particles of the same composition measured under the same conditions.

15. The supported porous polymeric material of any of claims 12-14, wherein the supported
5 porous polymeric material is CD-TFN@CMC.

16. The supported porous polymeric material of any of claims 12-15, wherein the pollutant is bisphenol A.

10 17. The supported porous polymeric material of claim 1, wherein the performance characteristic is the specific permeability of the supported polymeric material to a mobile phase at pressure P when the supported polymeric material is placed in a cylindrical column, wherein specific permeability (B_0) is:

$$B_0 = \frac{\eta L}{\pi r^2} \frac{F}{\Delta P}$$

15 wherein η (mPa*s) is the mobile phase viscosity, L (m) is the column length, r (m) is the column radius, and $F / \Delta P$ (m³/mPa*s) is the slope of the curve of flow rate vs back pressure.

18. The supported porous polymeric material of claim 17, wherein the supported porous
20 polymeric material has higher specific permeability compared to the unsupported porous particles having the same composition.

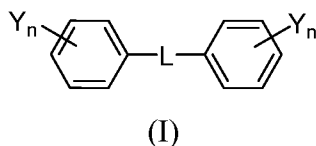
19. The supported porous polymeric material of claim 18, wherein the specific permeability of the supported porous polymeric material is at least double the specific permeability of
25 unsupported porous particles having the same composition.

20. The supported porous polymeric material of any of claims 17-19, wherein the supported porous polymeric material is CD-TFN@CMC.

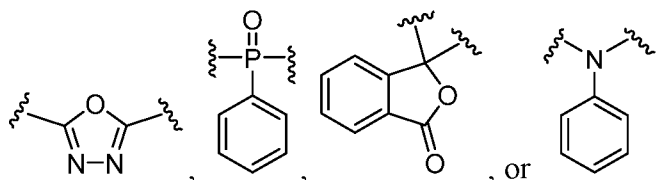
30 21. The supported porous polymeric material of claim 17, wherein the supported porous polymeric material is CD-TFN@CMC and has a specific permeability at least about 4 times more than the unsupported porous particles having the same composition.

22. The supported porous polymeric material of claim 1, wherein the plurality of cyclodextrin moieties are crosslinked with at least an equimolar amount of one or more aryl moieties; and

wherein the aryl moiety is an aryl moiety of formula (I):



wherein L is Aryl, -S(O)₂-, -C(O)-, bond,

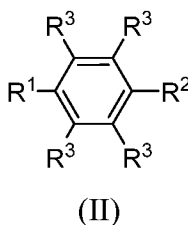


and

wherein each Y is independently H, F, Cl, CF₃, SO₃H, or NO₂, with the proviso that n = 0-5

10 and at least 2 of Y are F and/or Cl; or

an aryl moiety of formula (II):

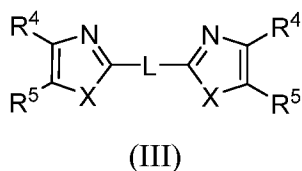


15 wherein R¹ is Cl, F or CN;

R² is Cl, F, CN, or NO₂; and

wherein each R³ is independently H, F, or Cl, with the proviso at least 2 of R¹, R², or R³ is F and/or Cl; or

an aryl moiety of formula (III):



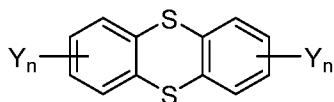
wherein L is Aryl;

X is O or S;

25 each R⁴ is independently F, Cl, or CF₃; and

each R⁵ is independently F, Cl, or NO₂, with the proviso that at least 2 of R⁴ and R⁵ are F and/or Cl; or

an aryl moiety of formula (IV):



5 wherein each Y is independently H, F, Cl, CF₃, SO₃H, or NO₂, with the proviso that n=0-5 and at least 2 of Y are F and/or Cl.

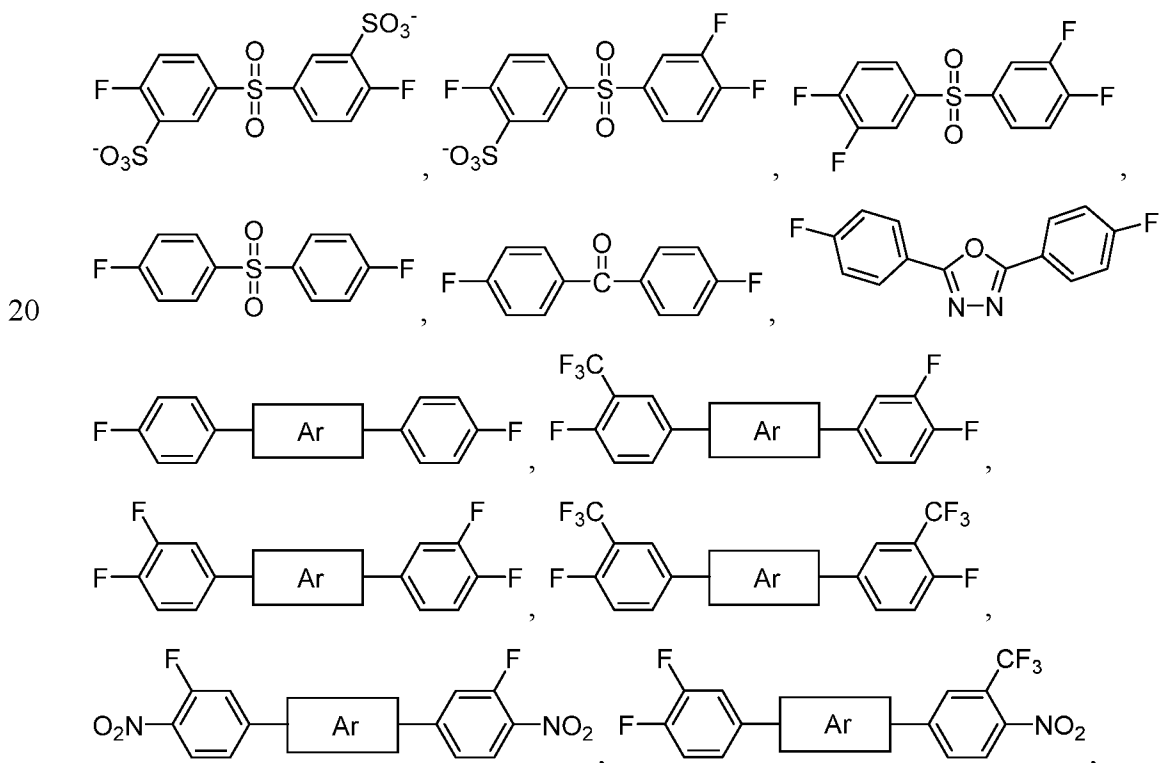
23. The supported porous polymeric material of claim 1, wherein the porous particles are affixed to the solid substrate covalently, adhesively, or mechanically.

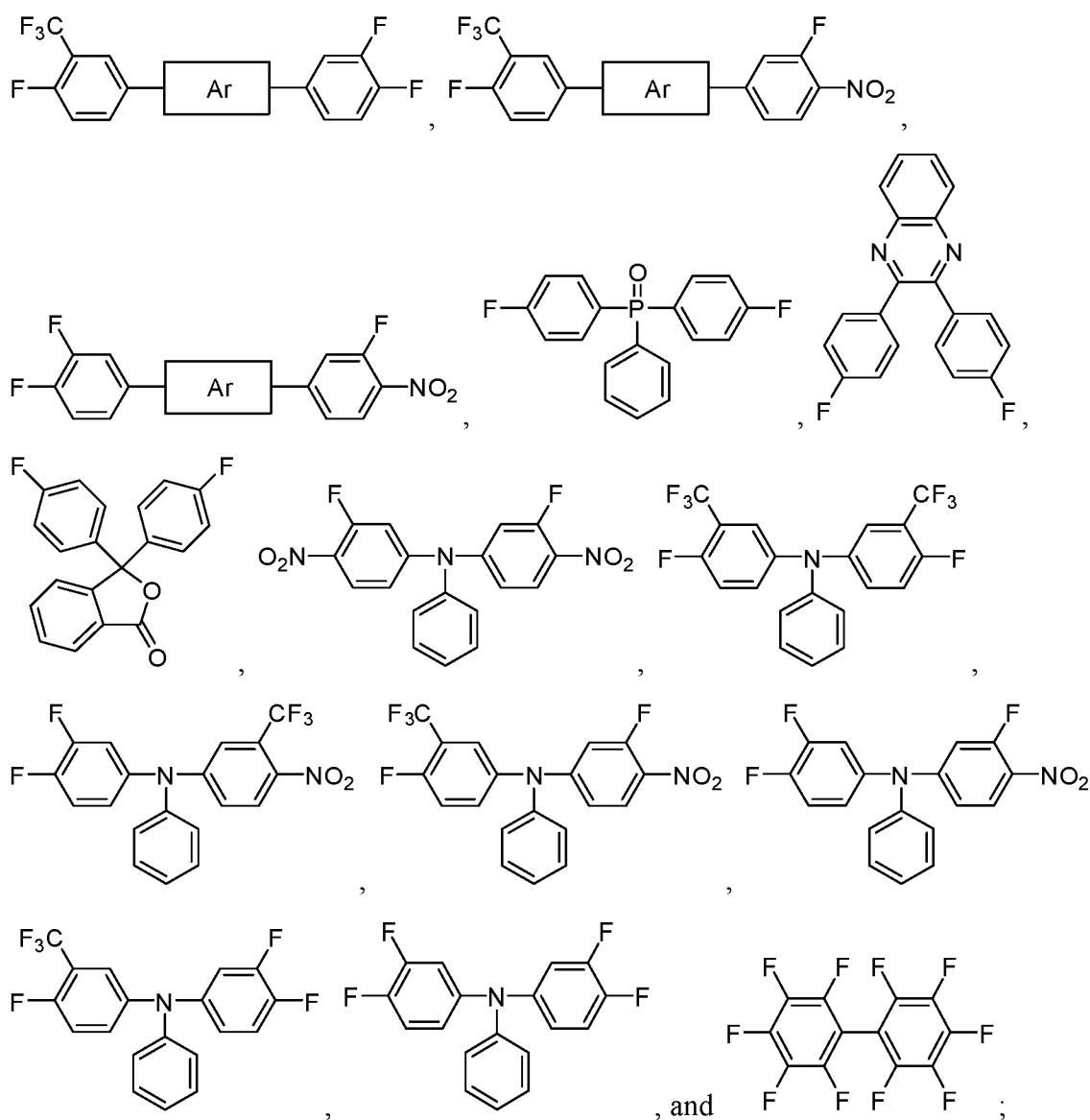
10

24. The supported porous polymeric material of claim 23, wherein the porous particles are affixed to the solid substrate covalently via a crosslinking moiety.

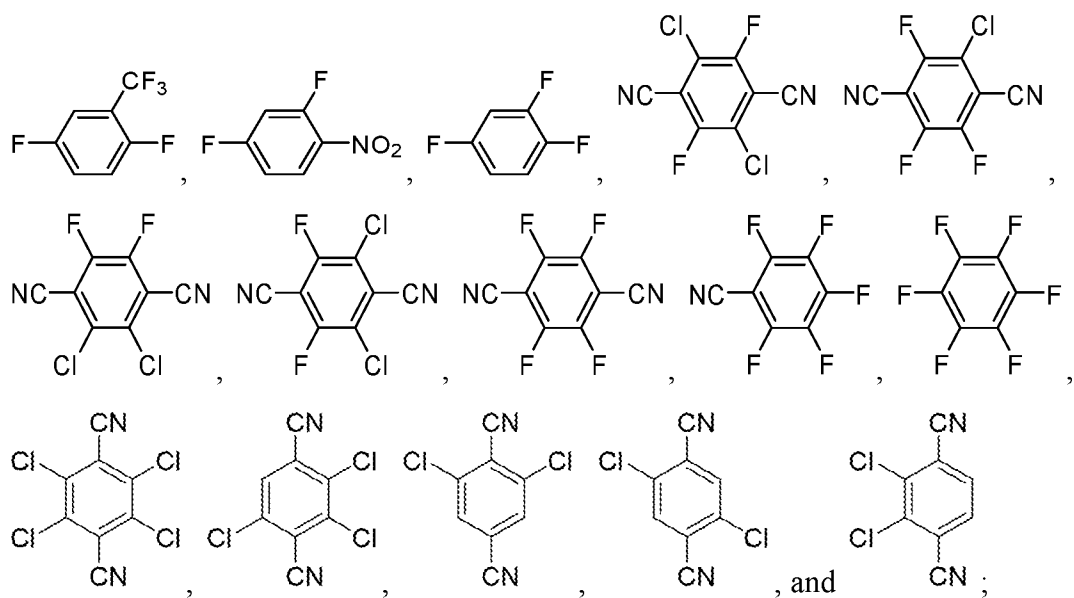
25. The supported porous polymeric material of claim 24, wherein the crosslinking moiety is
15 an aryl moiety of formula (I), (II), (III), or (IV).

26. The supported porous polymeric material of claim 25, wherein the aryl moiety of formula (I) is selected from the group consisting of:

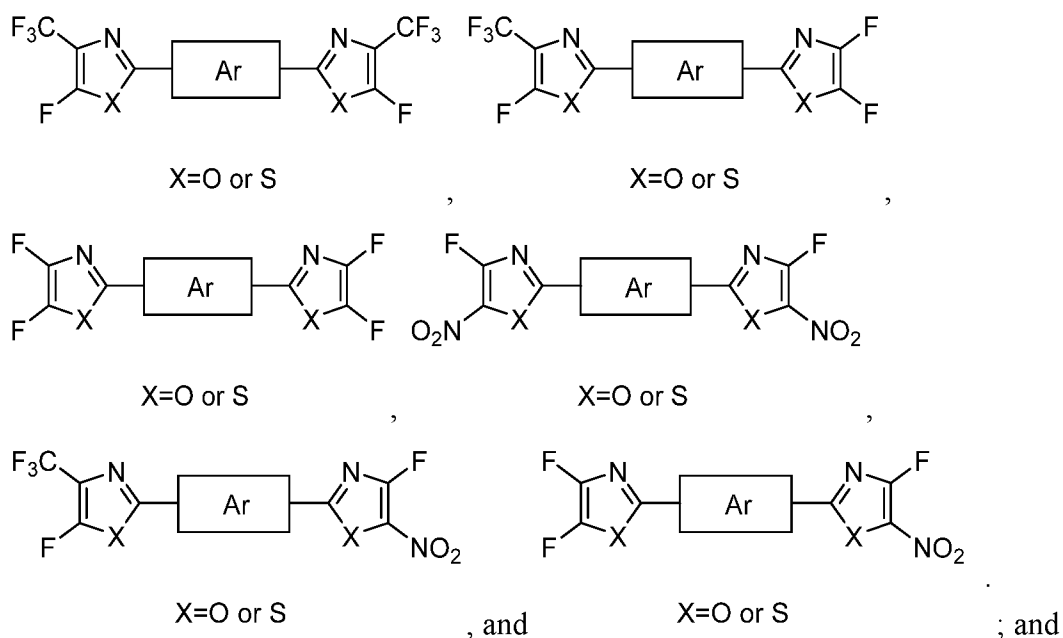




the aryl moiety of formula (II) is selected from the group consisting of:

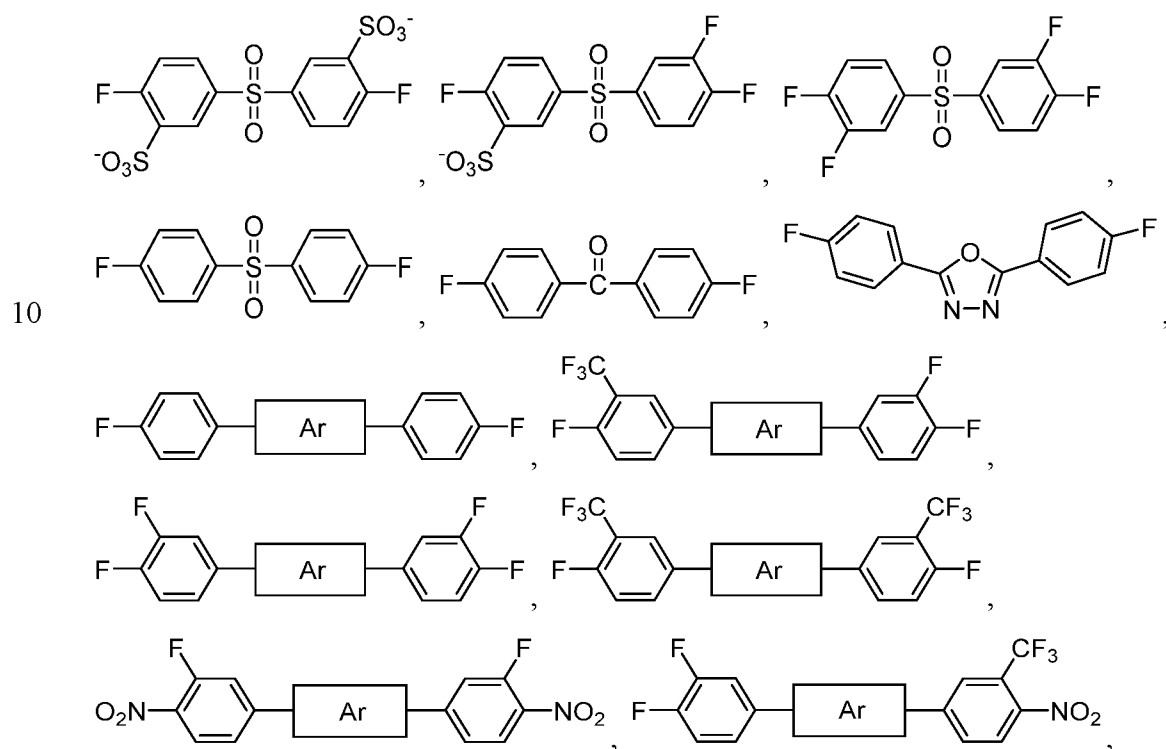


the aryl moiety of formula (III) is selected from the group consisting of:



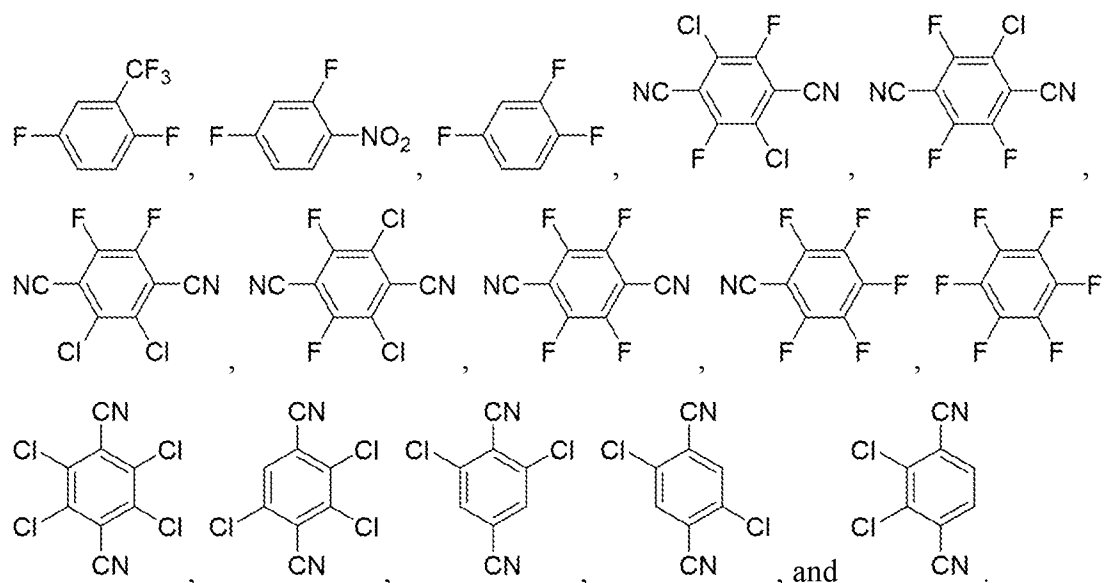
5 the aryl moiety of formula (IV) is

27. The supported porous polymeric material of claim 26, wherein the aryl moiety is an aryl moiety of formula (I) and is selected from the group consisting of:

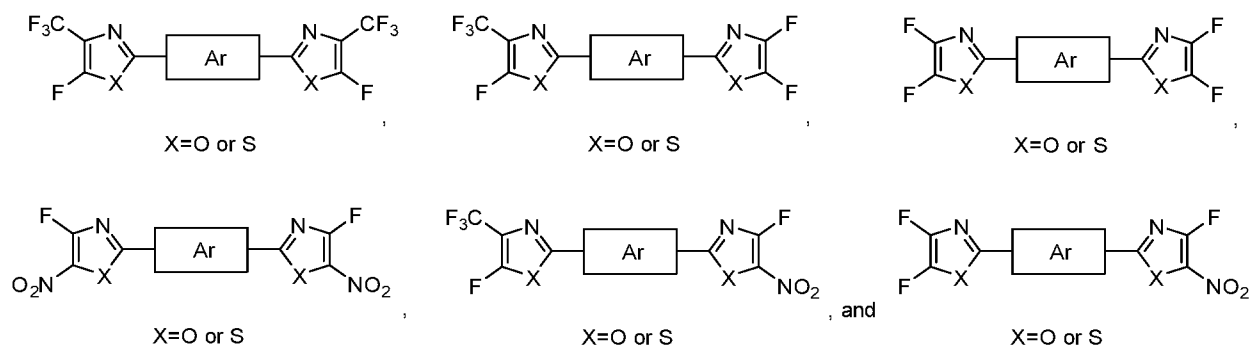




- 77 -



- 5 29. The supported porous polymeric material of claim 26, wherein the aryl moiety is an aryl moiety of formula (III), and is selected from the group consisting of:



- 10 30. The supported porous polymeric material of claim 26, wherein the molar ratio of cyclodextrin to aryl moiety ranges from about 1:1 to about 1:X, wherein X is three times the average number of glucose subunits in the cyclodextrin.

- 15 31. The supported porous polymeric material of claim 30, wherein the molar ratio of cyclodextrin to aryl moiety is about 1:6.

32. The supported porous polymeric material of claim 1, wherein the cyclodextrin is selected from the group consisting of α -, β -, γ -cyclodextrin, and combinations thereof.

- 20 33. The supported porous polymeric material of claim 32, wherein the cyclodextrin is β -cyclodextrin.

34. The supported porous polymeric material of claim 26, wherein the aryl moiety is an aryl moiety of formula (I), and the molar ratio of β -cyclodextrin to aryl moiety is about 1:3.

5 35. The supported porous polymeric material of claim 26, wherein the aryl moiety is an aryl moiety of formula (II), and the molar ratio of β -cyclodextrin to aryl moiety is about 1:3.

36. The supported porous polymeric material of claim 26, wherein the aryl moiety is an aryl moiety of formula (III), and the molar ratio of β -cyclodextrin to aryl moiety is about 1:3.

10

37. The supported porous polymeric material of claim 1, 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.

38. The supported porous polymeric material of claim 37, 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, and derivatives thereof.

39. The supported porous polymeric material of claim 37, wherein the substrate is microcrystalline cellulose, cellulose nanocrystals, silica, glass, or beads made from synthetic polymers.

5

40. The supported porous polymeric material of claim 39, wherein the substrate is microcrystalline cellulose.

10

41. The supported porous polymeric material of claim 40, wherein the microcrystalline cellulose has a median particle size ranging from about 10 to about 500 μm .

42. The supported porous polymeric material of claim 41, wherein the microcrystalline cellulose has a median particle size of about 50 μm .

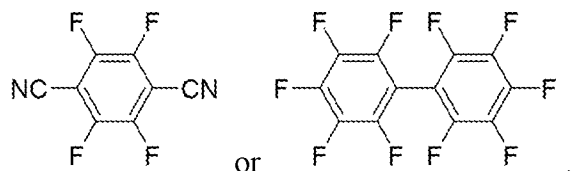
15

43. The supported porous polymeric material of any of claim 40, wherein the porous particles have a thickness on the solid substrate of from about 10 nm to about 2000 nm.

44. The supported porous polymeric material of claim 43, wherein the porous particles have a polymer thickness of about 800 nm on the solid substrate.

20

45. The supported porous polymeric material of claim 1, wherein the aryl moiety is



25

46. The supported porous polymeric material of claim 45, wherein the supported porous polymeric material is CD-TFN@CMC or CD-DFB@CMC.

47. The supported porous polymeric material of claim 40, wherein the microcrystalline cellulose is spherical, rod-shaped, needle-like, flat, or flat and elongated.

30

48. The supported porous polymeric material of claim 47, wherein the microcrystalline cellulose is spherical.

49. The supported porous polymeric material of claim 39, wherein the substrate is cellulose nanocrystals.

5 50. An article of manufacture comprising a supported porous polymeric material of claim 1.

51. The article of manufacture of claim 50, wherein the article is protective equipment.

52. The article of manufacture of claim 51, wherein the article is clothing.

10

53. The article of claim 50, wherein the article is a filtration medium.

54. The article of claim 50, wherein the article is an extraction device.

15 55. The article of claim 54, wherein the extraction device is a solid-phase extraction device capable of adsorbing polar and semi-polar organic molecules.

56. A method of purifying an aqueous sample comprising one or more organic pollutants, comprising contacting the aqueous sample with the supported porous polymeric material of
20 claim 1, such that at least 50% to at least 99% of the one or more organic pollutants are removed from the aqueous sample.

57. The method of claim 56, wherein the one or more cyclodextrin moieties are β -cyclodextrin moieties.

25

58. The method of claim 56, wherein the supported porous polymeric material is CD-TFN@CMC.

59. The method of claim 56, wherein said contacting is by flowing the aqueous phase across,
30 over, around, or through the supported porous polymeric material.

60. The method claim 56, wherein 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.

61. The method of claim 56, wherein the aqueous sample is drinking water, wastewater, ground water, aqueous extracts from contaminated soils, or landfill leachates.

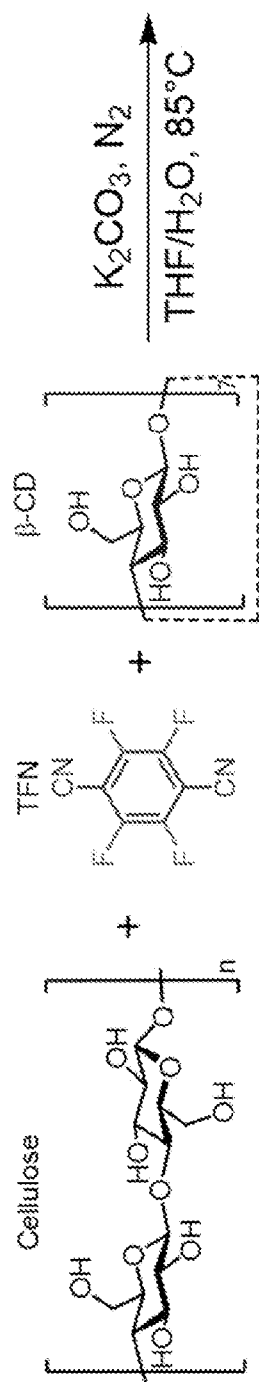
5 62. A method of determining the presence or absence of compounds in a sample, comprising: a) contacting the sample with the supported porous polymeric material of claim 1 for an incubation period; b) isolating the supported porous polymeric material from a) from the sample; and c) heating the supported porous polymeric material from b) or contacting the supported porous polymeric material from b) with a solvent such that at least part of the
10 compounds are then released from the supported porous polymeric 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 the compounds.

15 63. The method of claim 62, wherein the supported porous polymeric material is CD-TFN@CMC.

64. The method of claim 62, wherein compounds are organic compounds.

20

FIG. 1



CD-TFN@cellulose

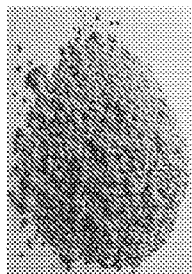


FIG. 2

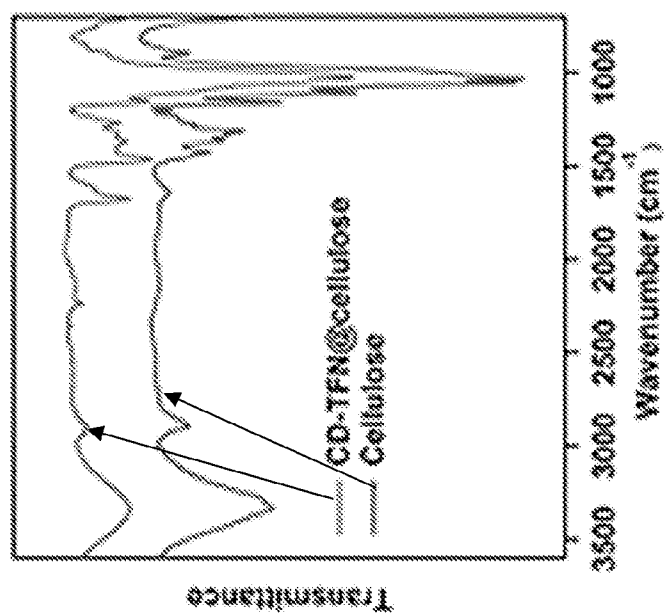


FIG. 3

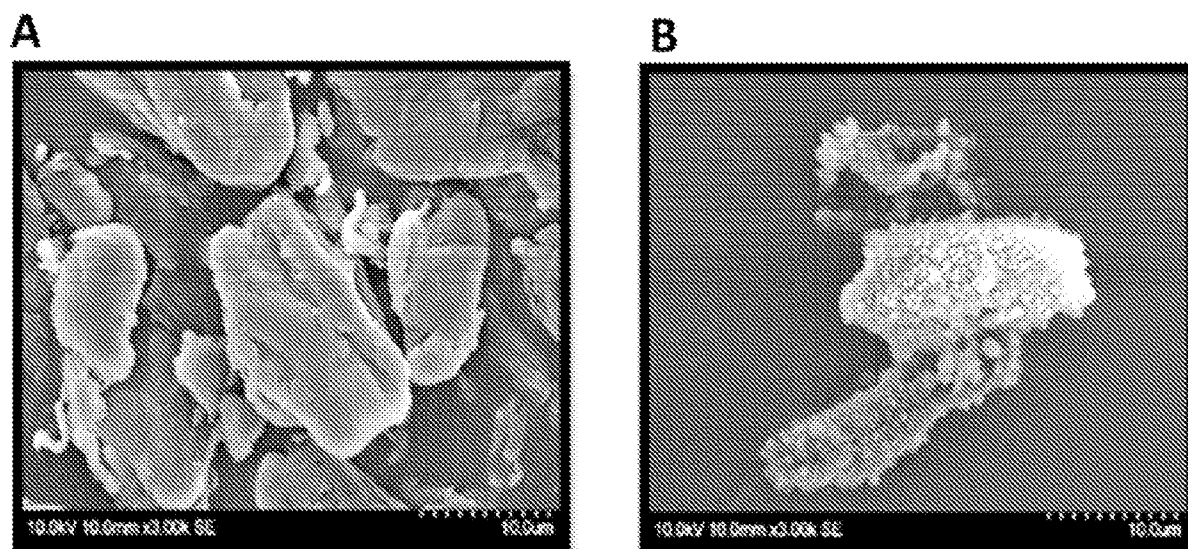


FIG. 4

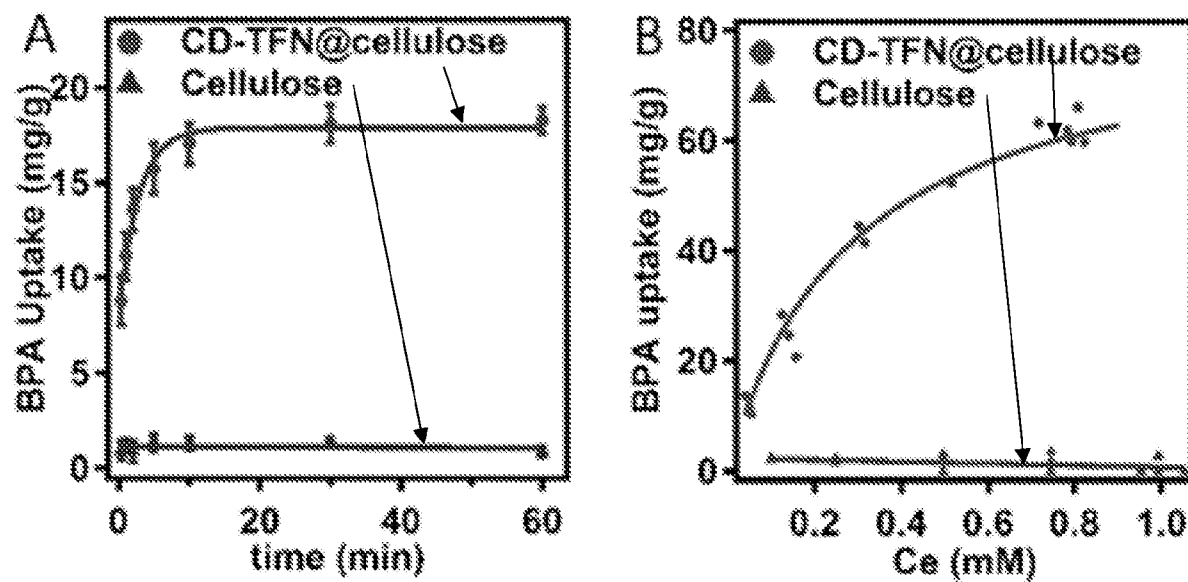


FIG. 5

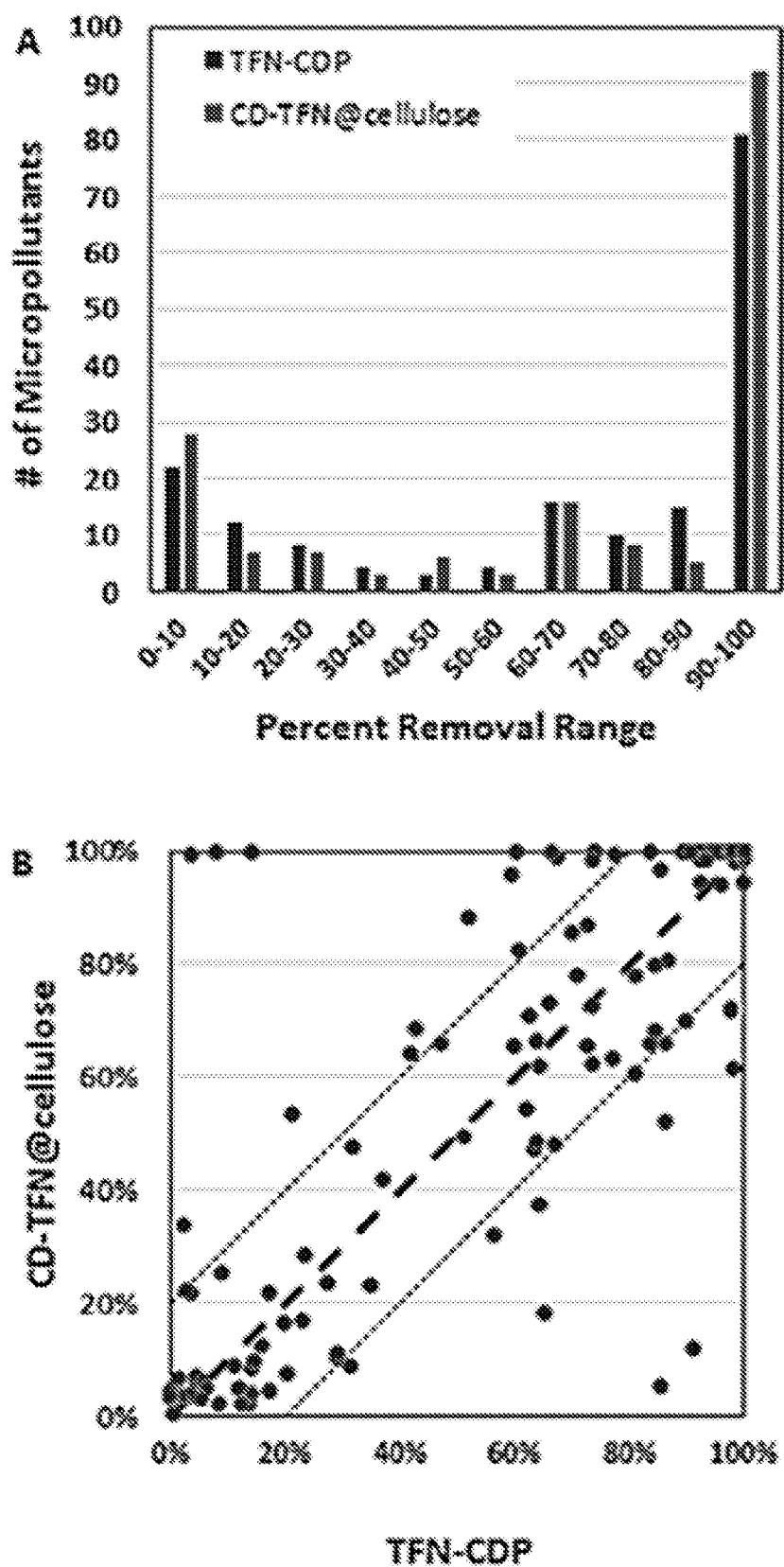


FIG. 6

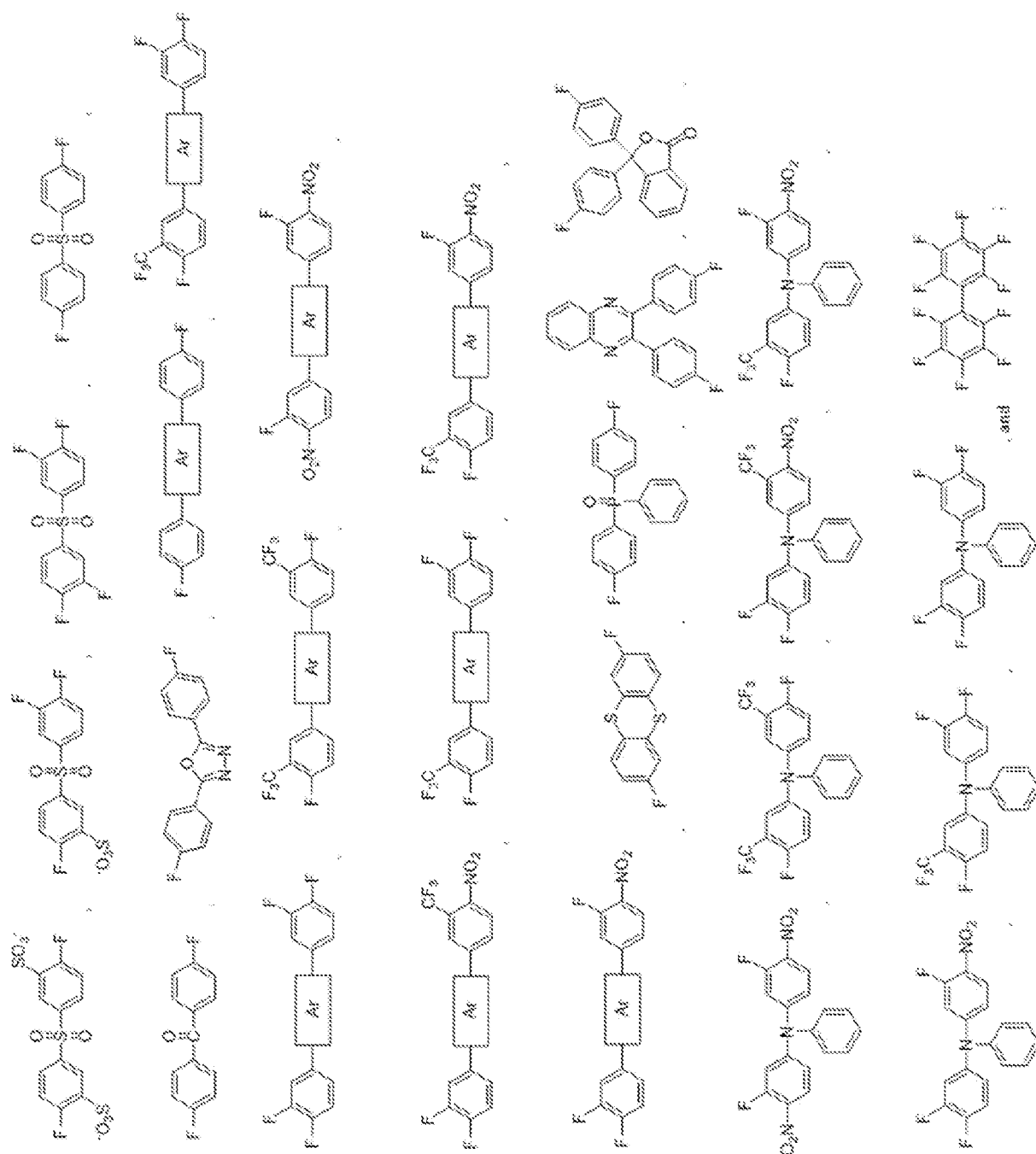


FIG. 6 (continued)

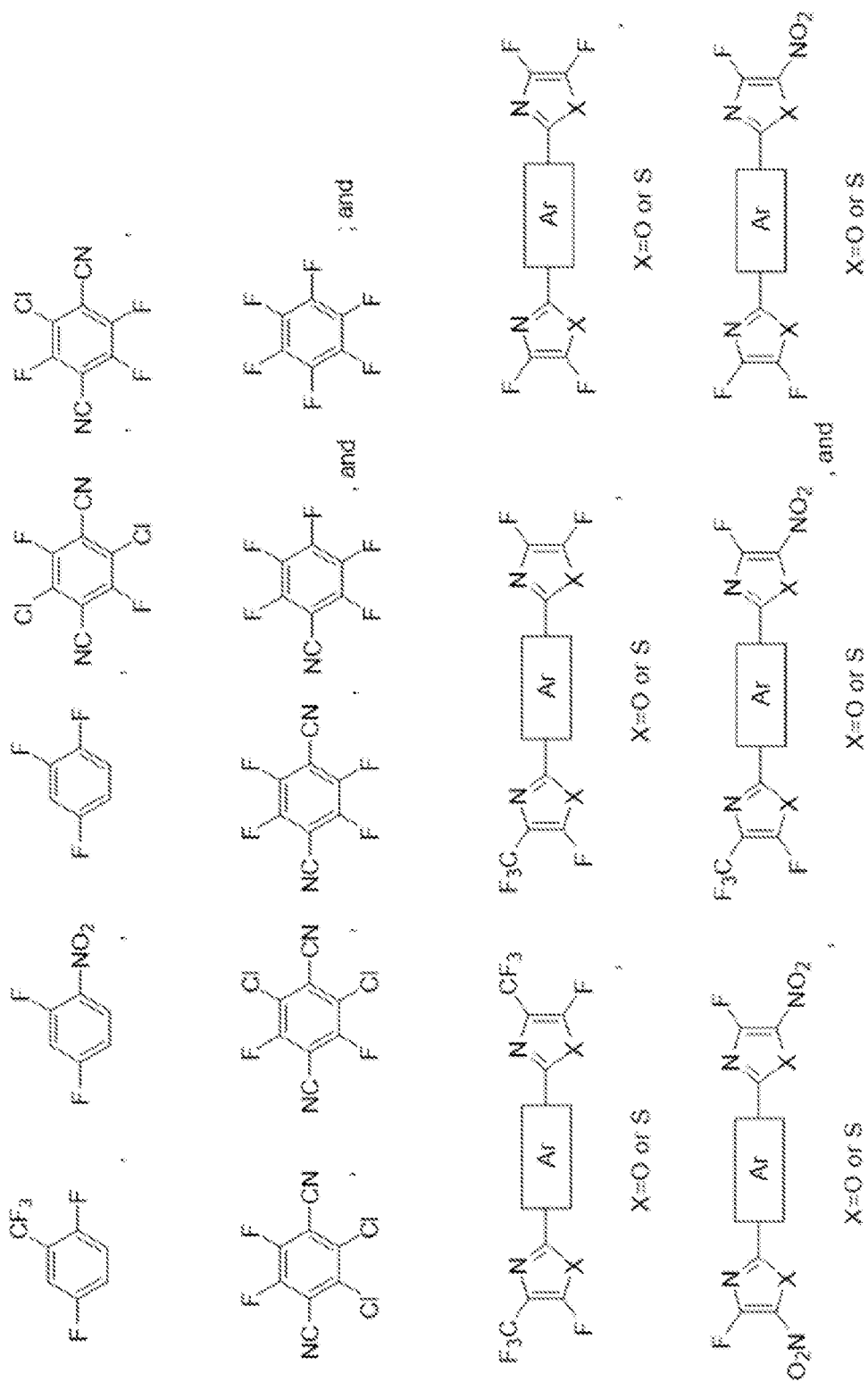


FIG. 7

Compound Name	Compound Name
2,4-D	Linuron
Abacavir	Malaoxon
Acebutolol	MCPA
Acetaminophen	Mecoprop
Acetochlor	Meproamate
Albuterol	Methomyl
Allopurinol	Metolachlor
Amphetamine	Metoprolol
Atenolol	Metribuzin
Atenolol Acid	Molinate
Atrazine	Morphine
Benzotriazole-methyl-1H	Nadolol
Bromacil	Naproxen
Bupropion	Oxcarbazepine
Caffeine	Oxybenzone
Carbamazepine	Paraxanthine
Carbaryl	Penciclovir
Carbofuran	Pentoxifylline
Chloridazon	PFBA
Chloroxylenol	PFOA
Cimetidine	Phenytoin
Clofibrilic Acid	Progesterone
Codeine	Prometon
Cotinine	Propachlor
DEET	Ranitidine
Diazinon	Siduron
Diclofenac	Simazine
Dimethoate	Sitagliptin
Diuron	Sucralose
Efavirenz	Sulfamethoxazole
Erythromycin	Sulfathiazole
Estrone	TCEP
Famotidine	Testosterone
Fluconazole	Tramadol
Fluoxetine	Tributyl Phosphate
Gemfibrozil	Triclosan
Hydrocodone	Trimethoprim
Ibuprofen	Valsartan
Imidacloprid	Venlafaxine
Iopromid	Warfarin
Ioxynil	1,4-dioxane
Isoproturon	chlorpyrifos
Ketoprofen	

FIG. 8

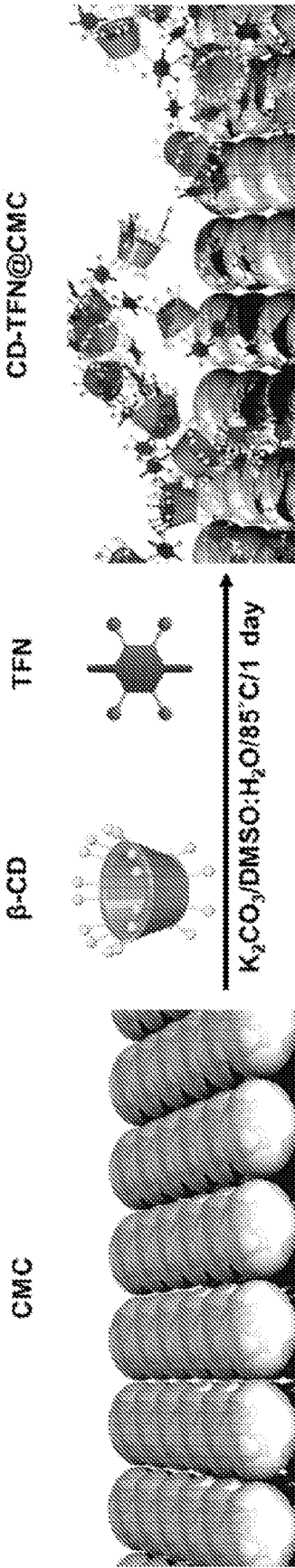
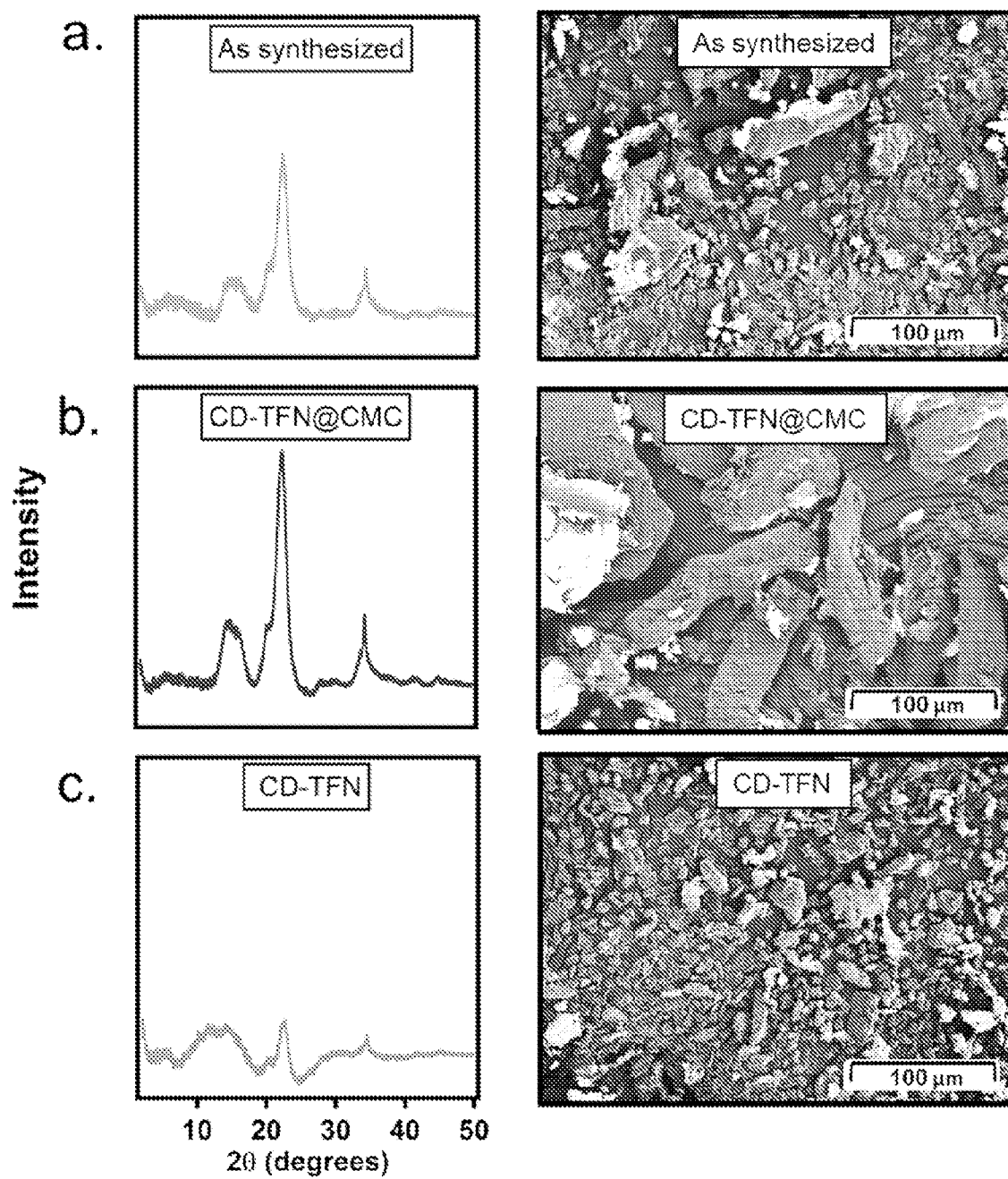
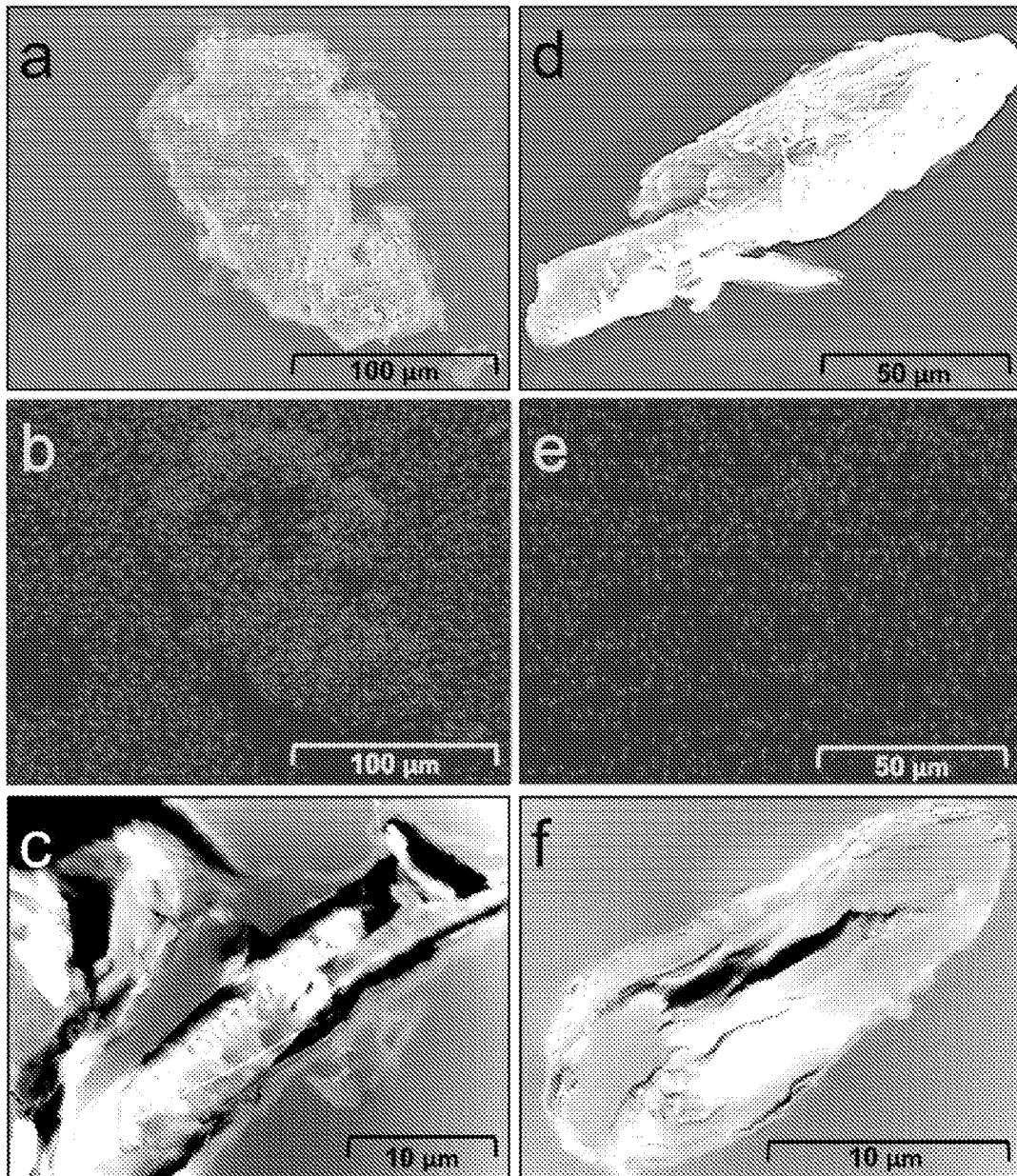


FIG. 9



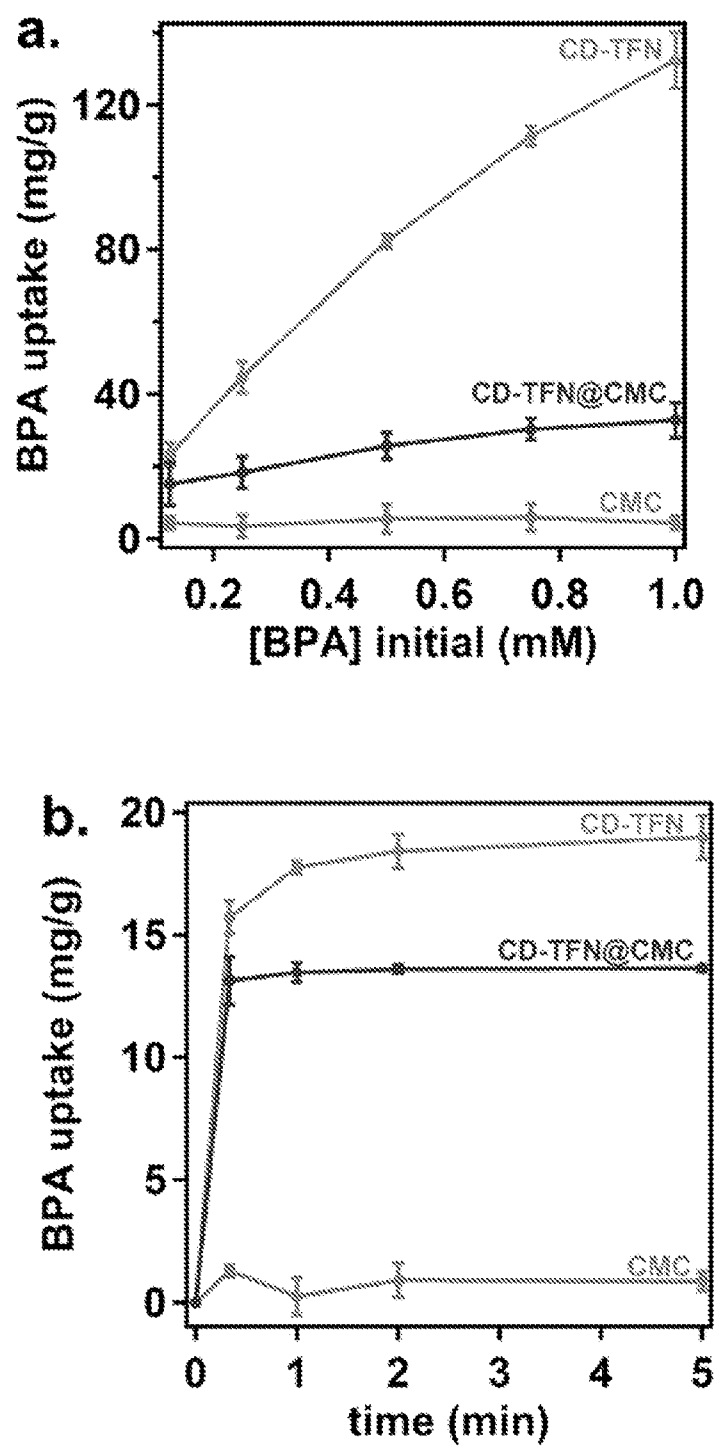
9/28

FIG. 10



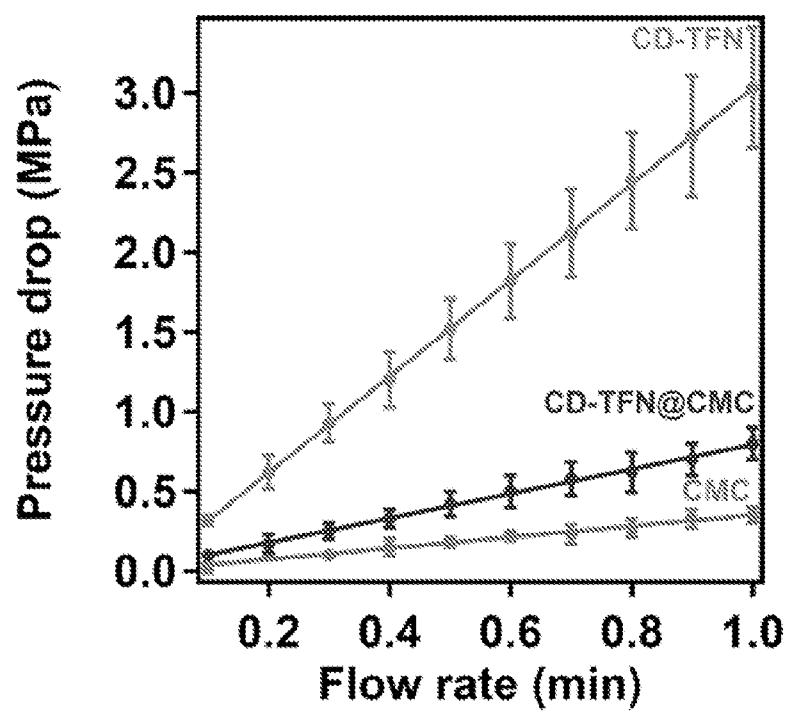
10/28

FIG. 11



11/28

FIG. 12



12/28

FIG. 13

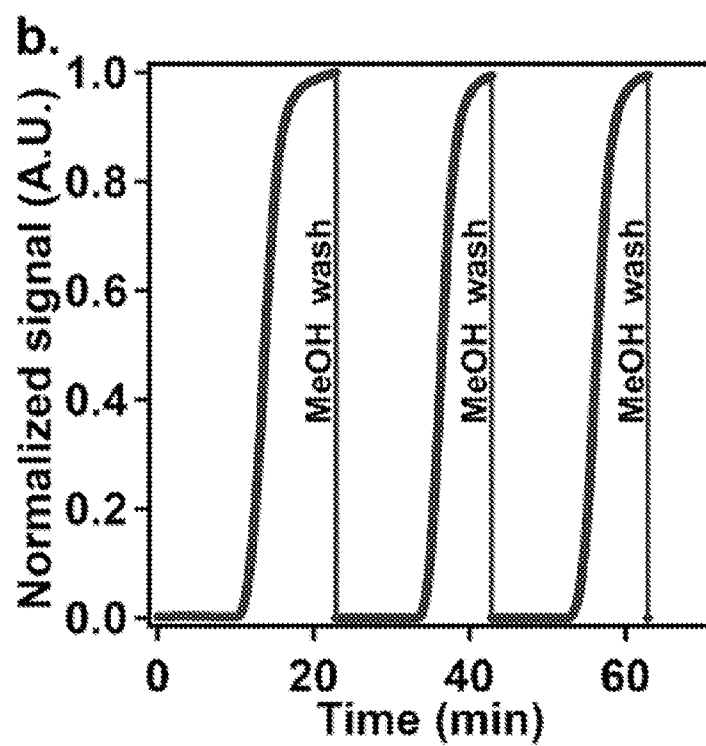
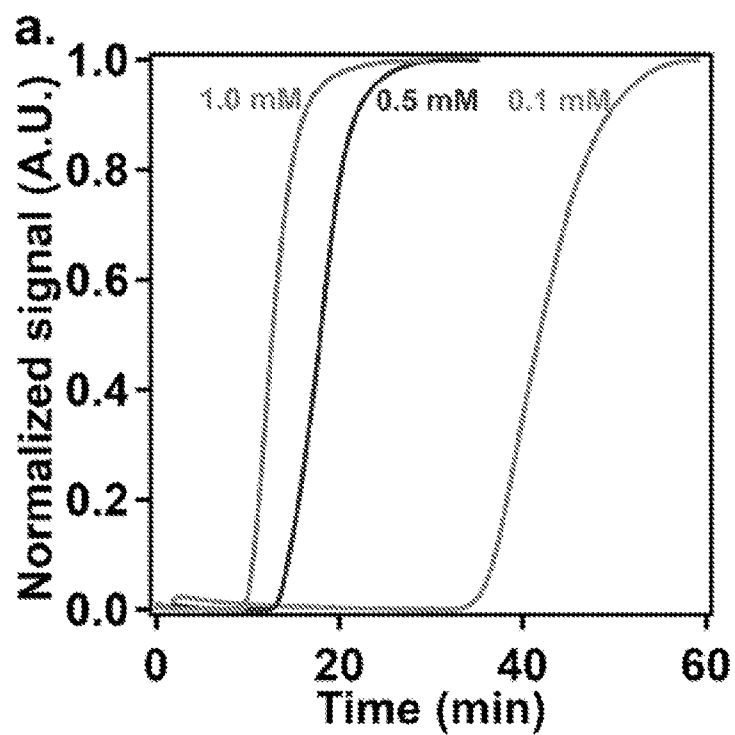
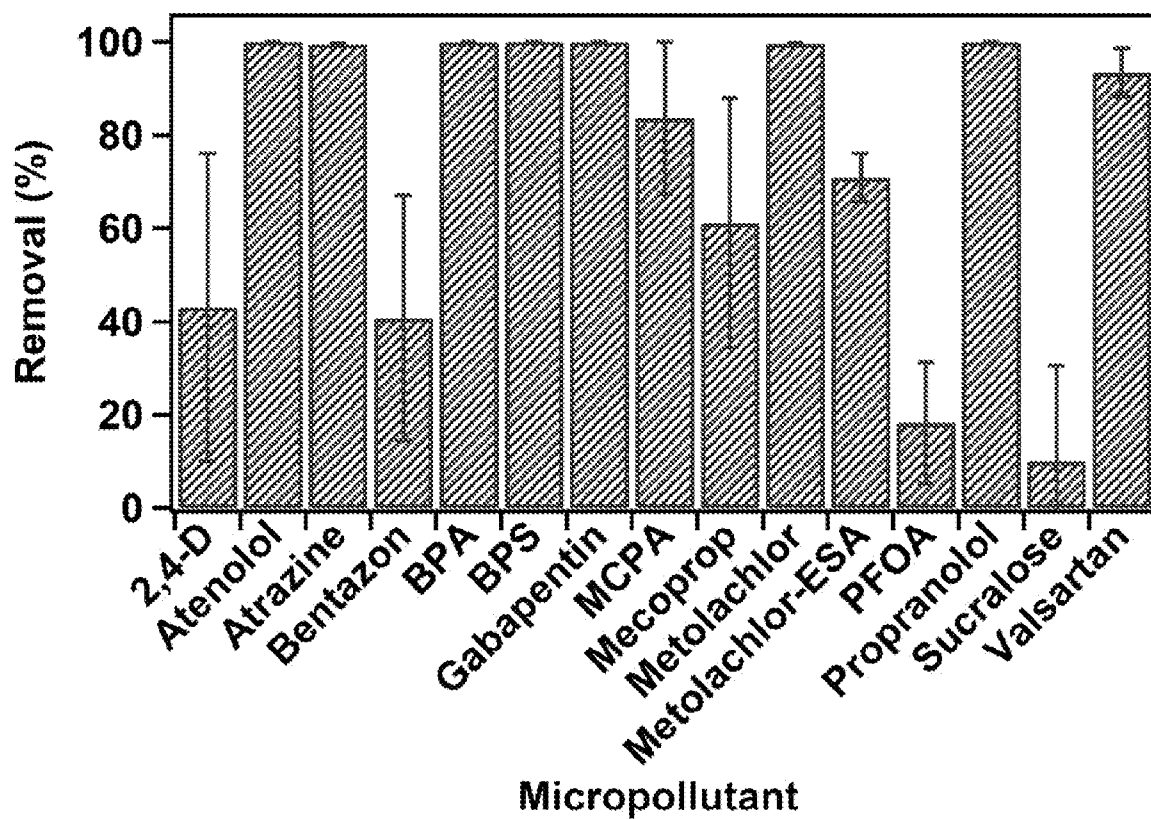


FIG. 14



14/28

FIG. 15

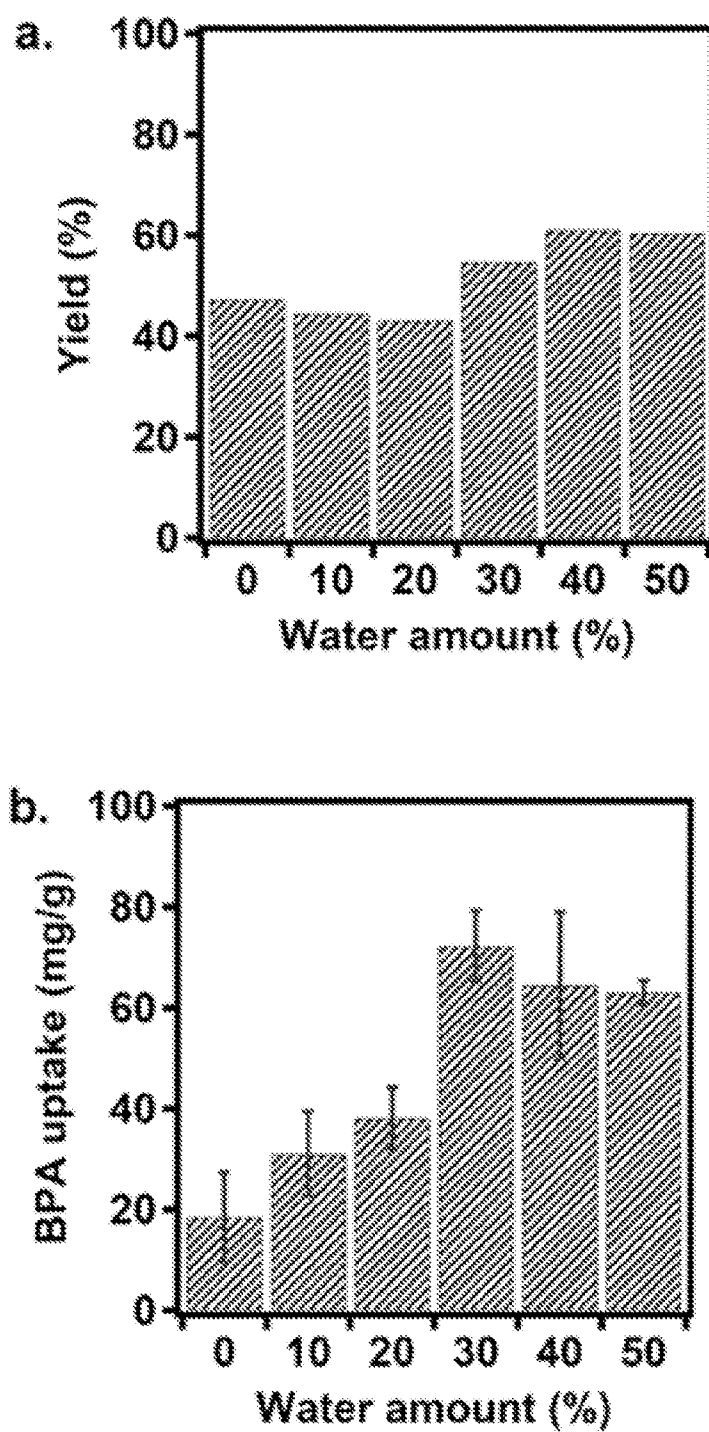


FIG. 16

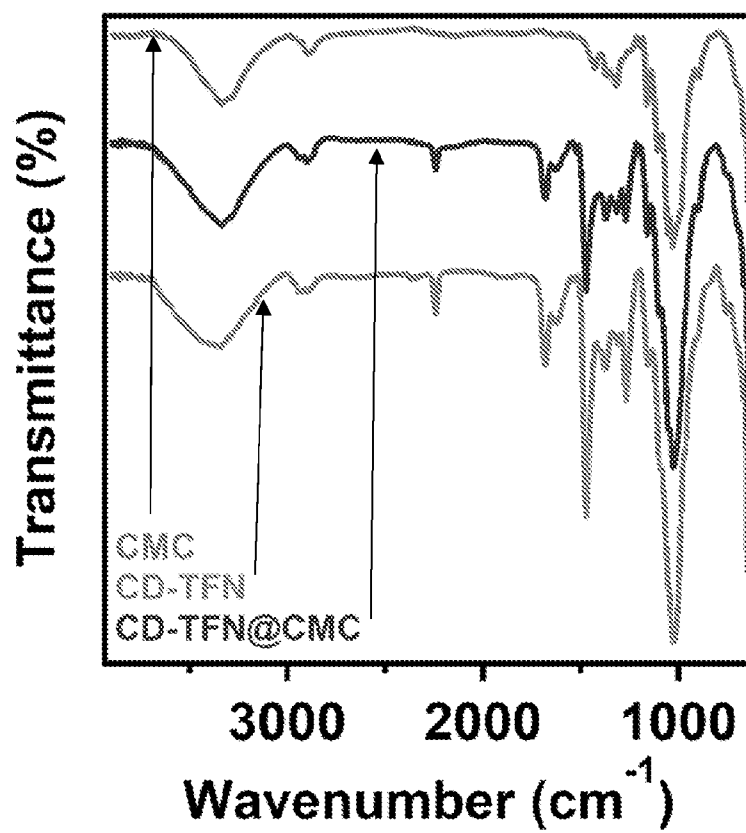
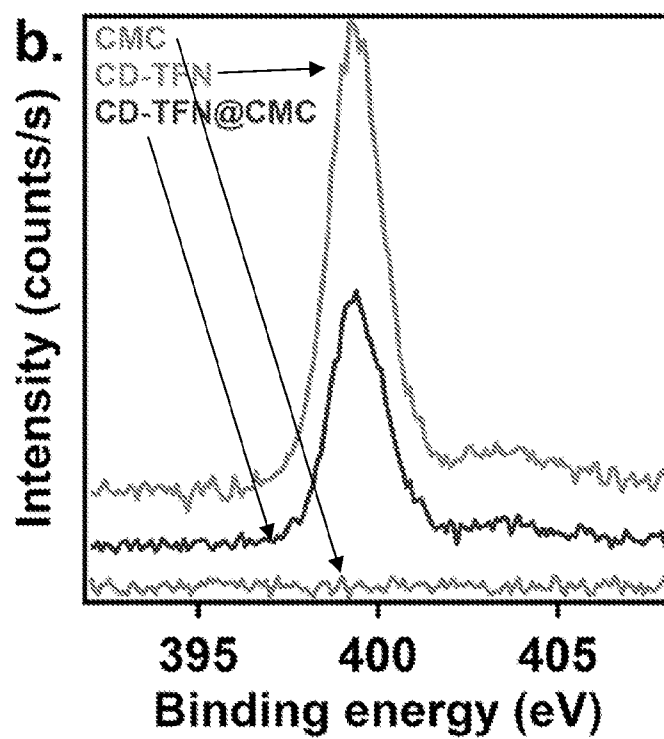
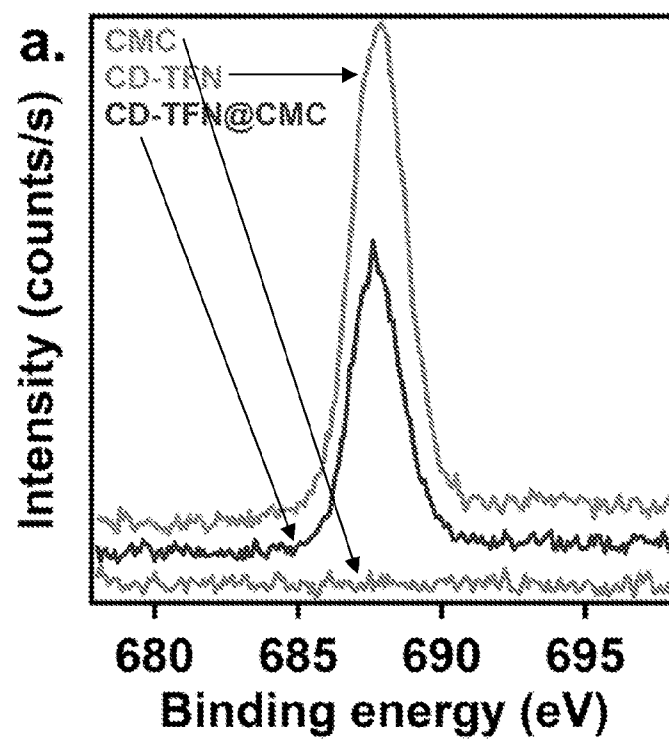


FIG. 17



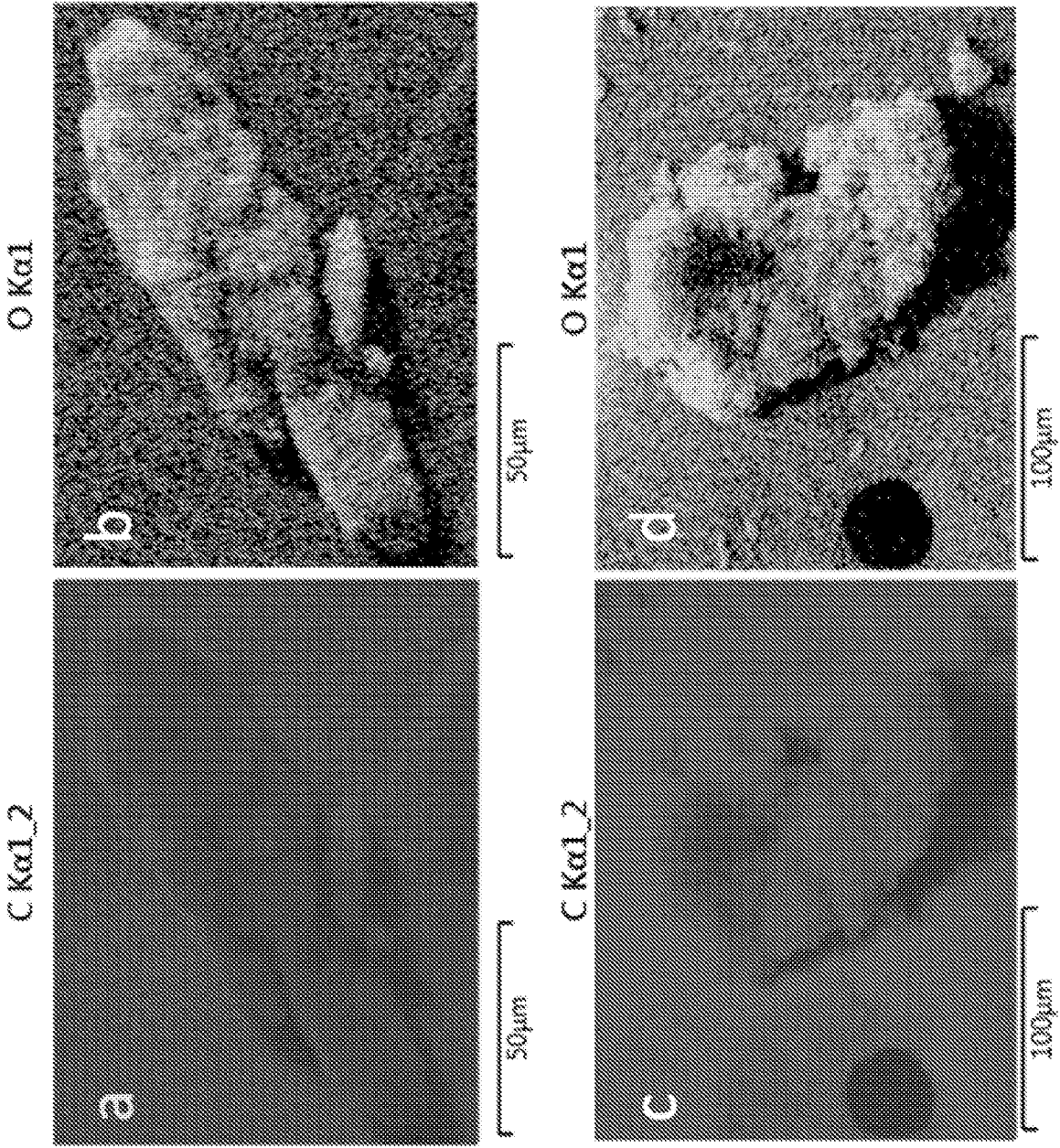
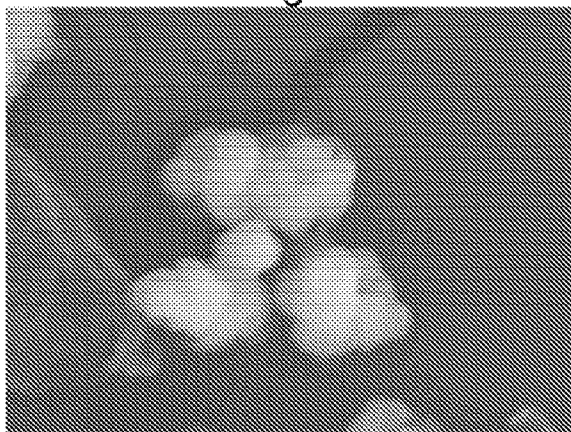


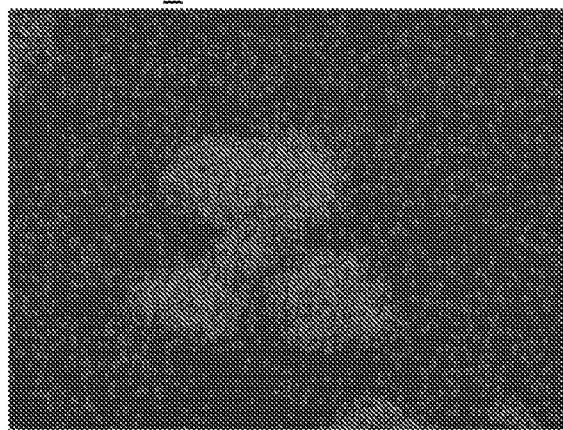
FIG. 18

FIG. 19

a. Electron image

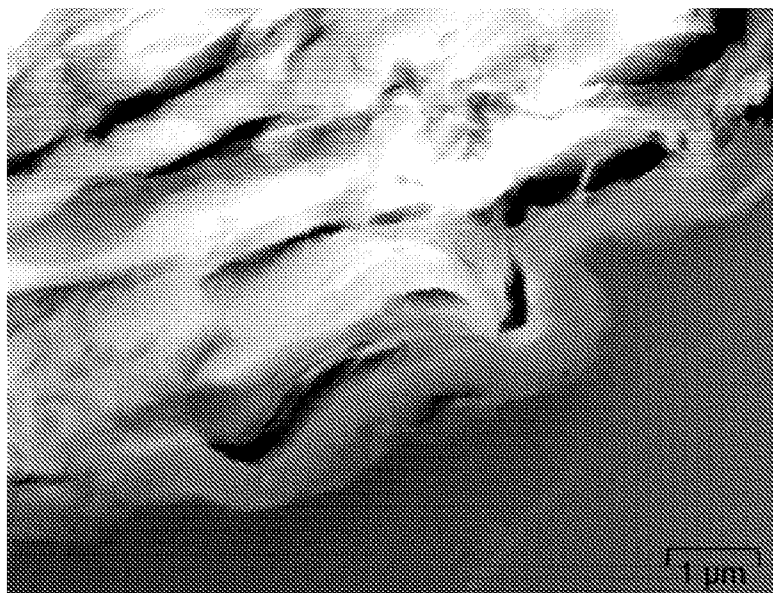


10 μm

b. F K α 1_2

10 μm

FIG. 20



1 μm

FIG. 21

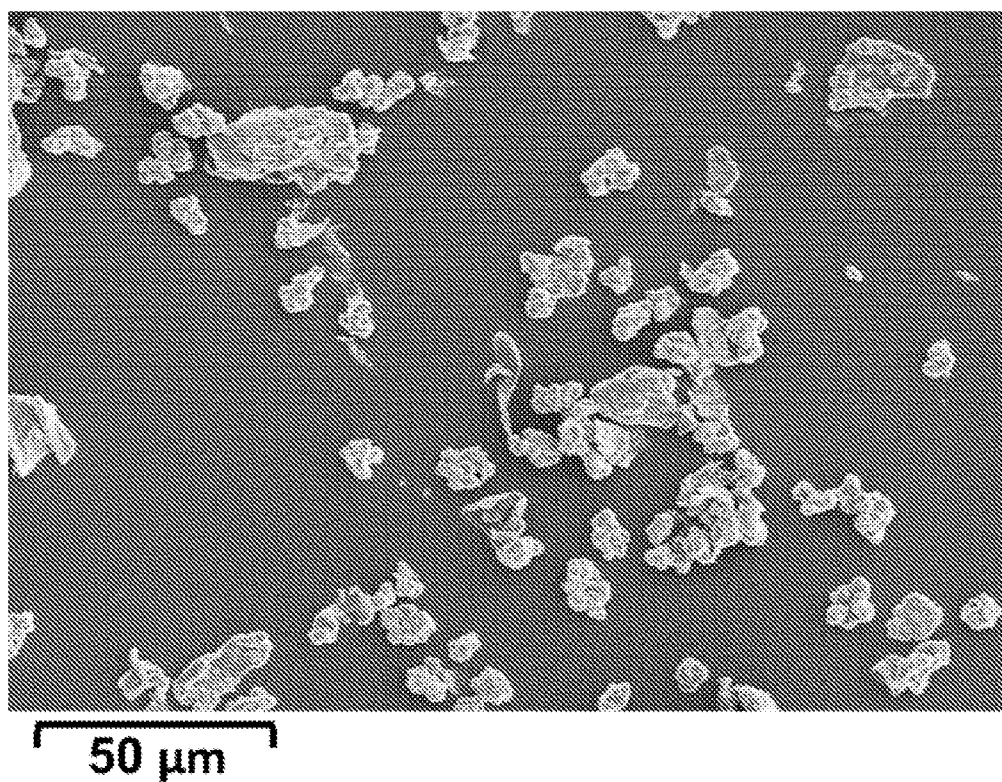


FIG. 22

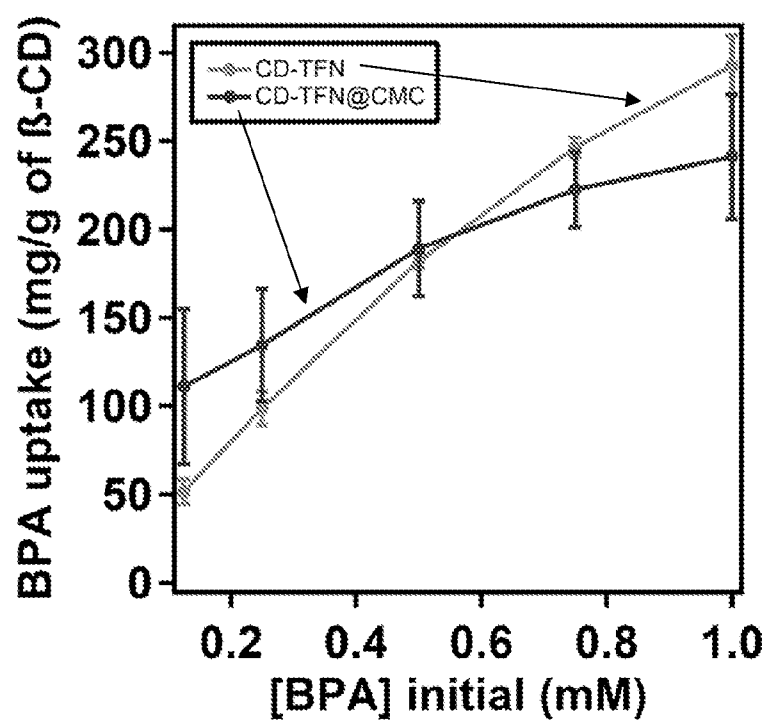


FIG. 23

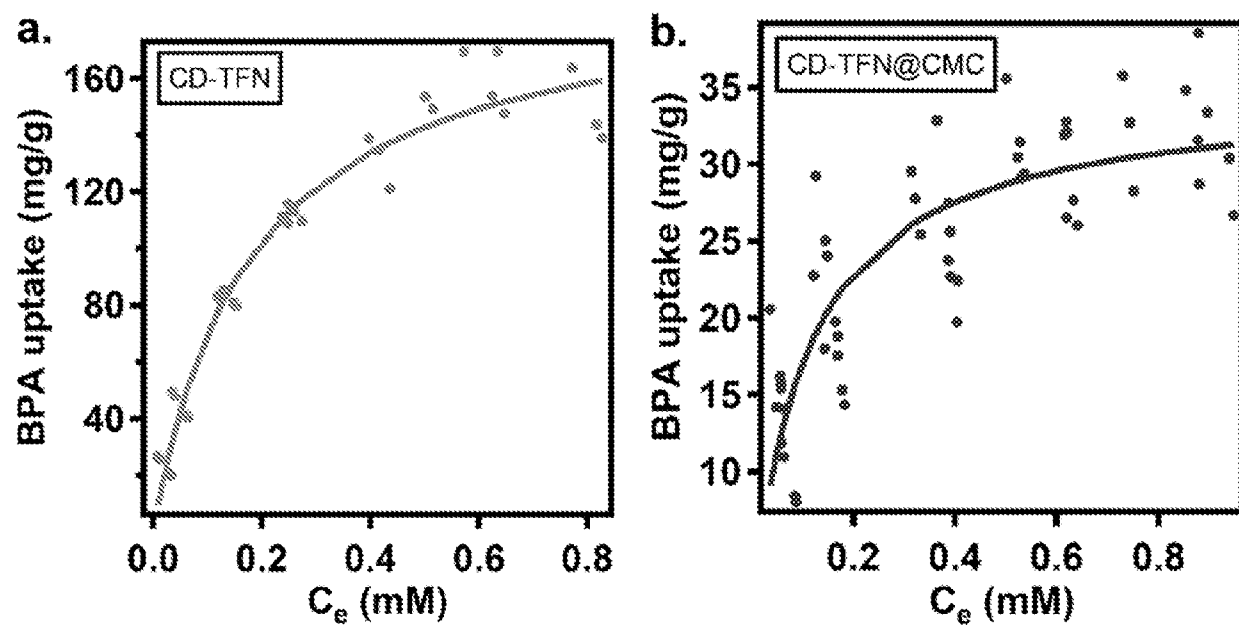


FIG. 24

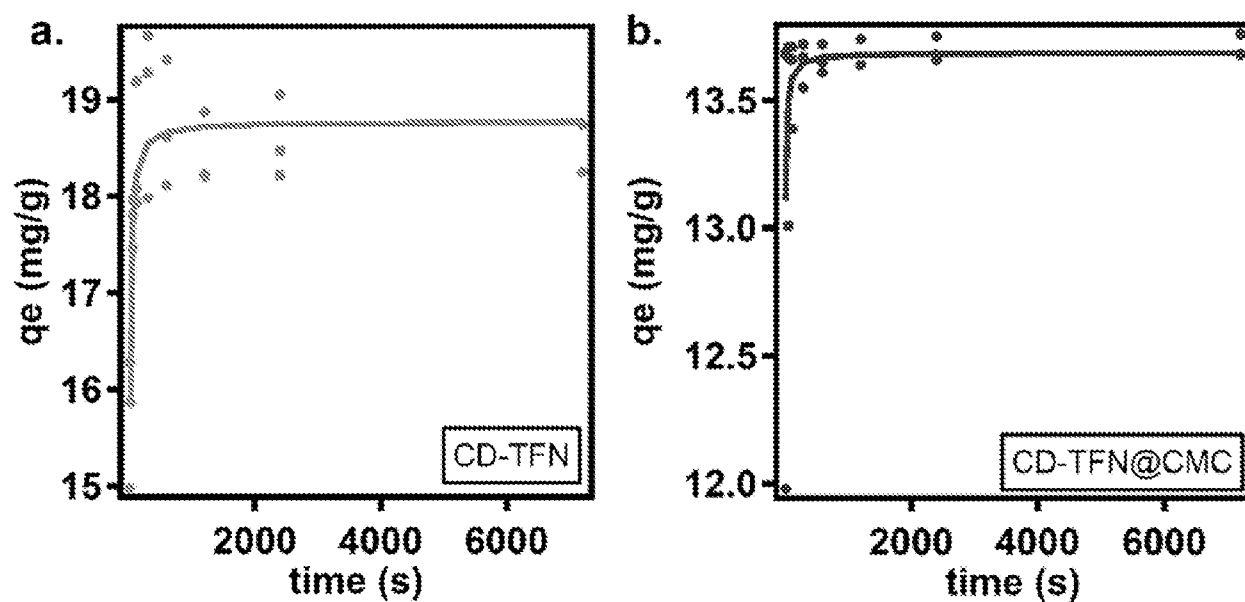
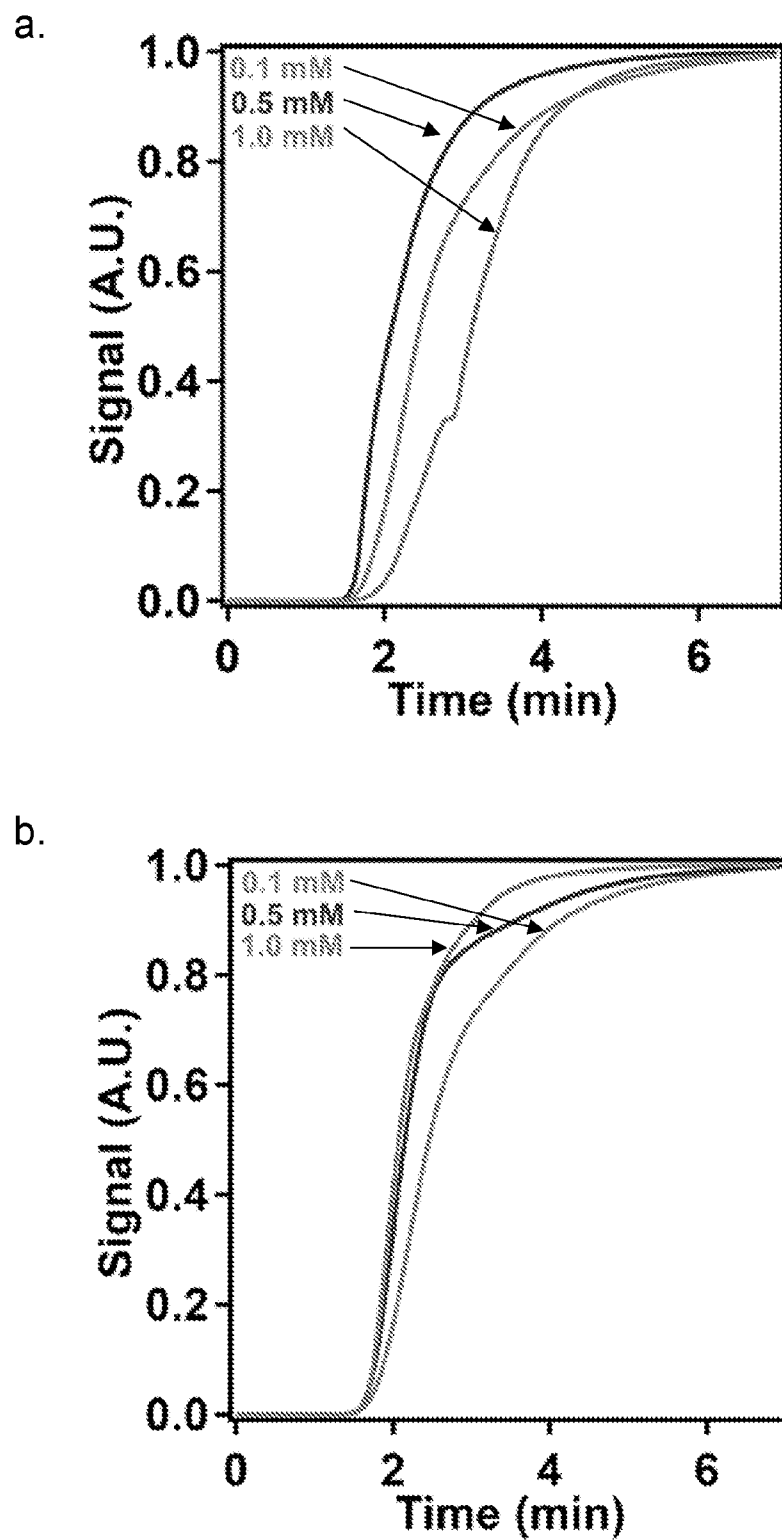


FIG. 25



22/28

FIG. 26

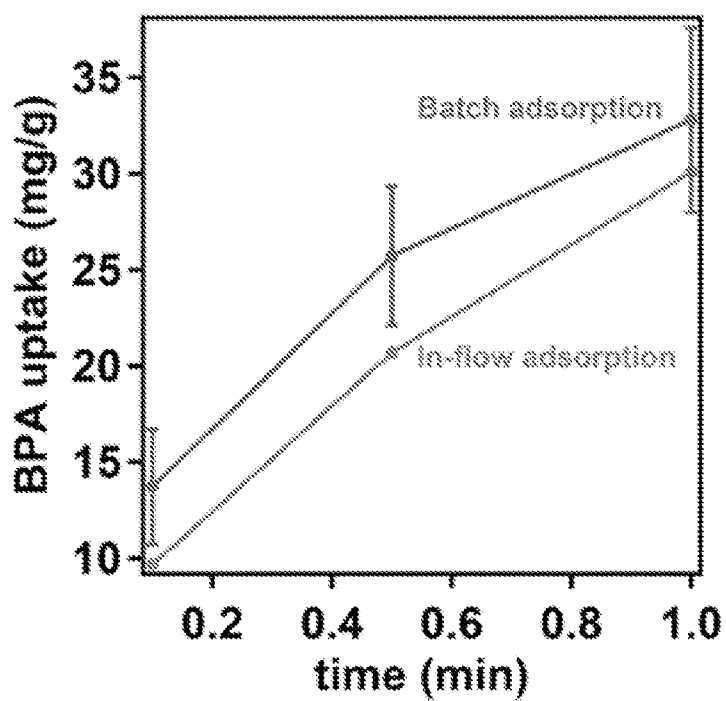
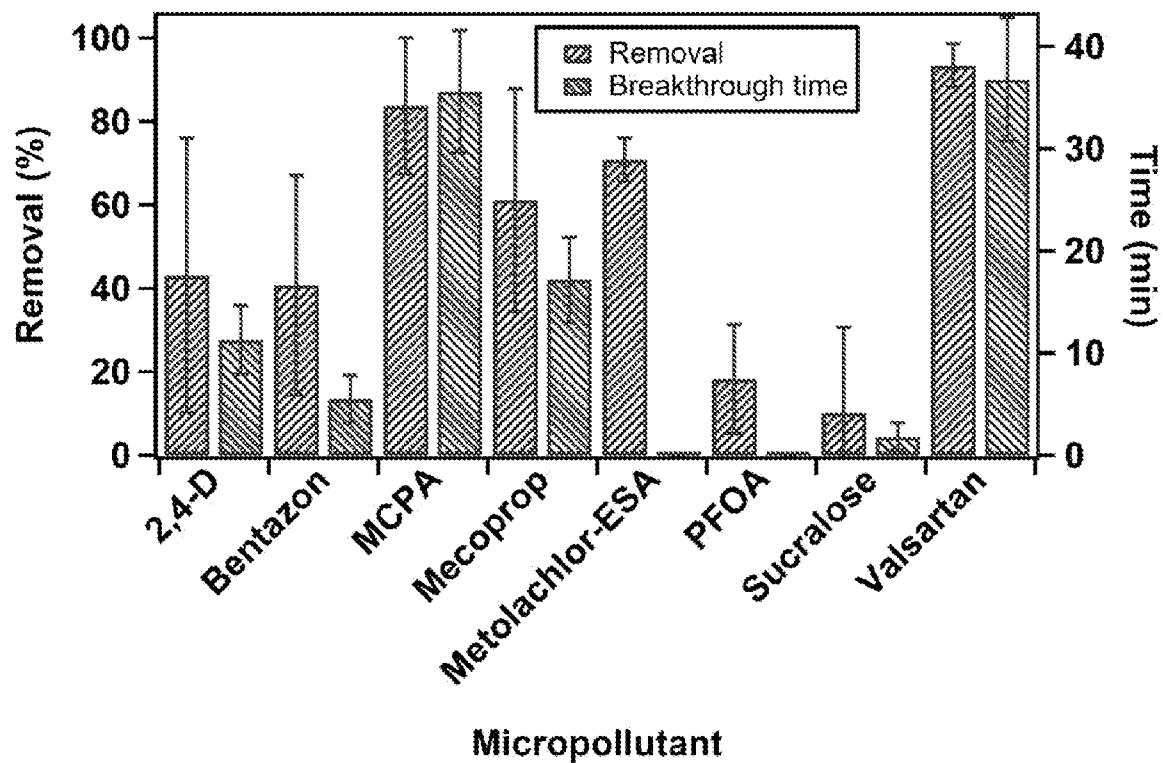
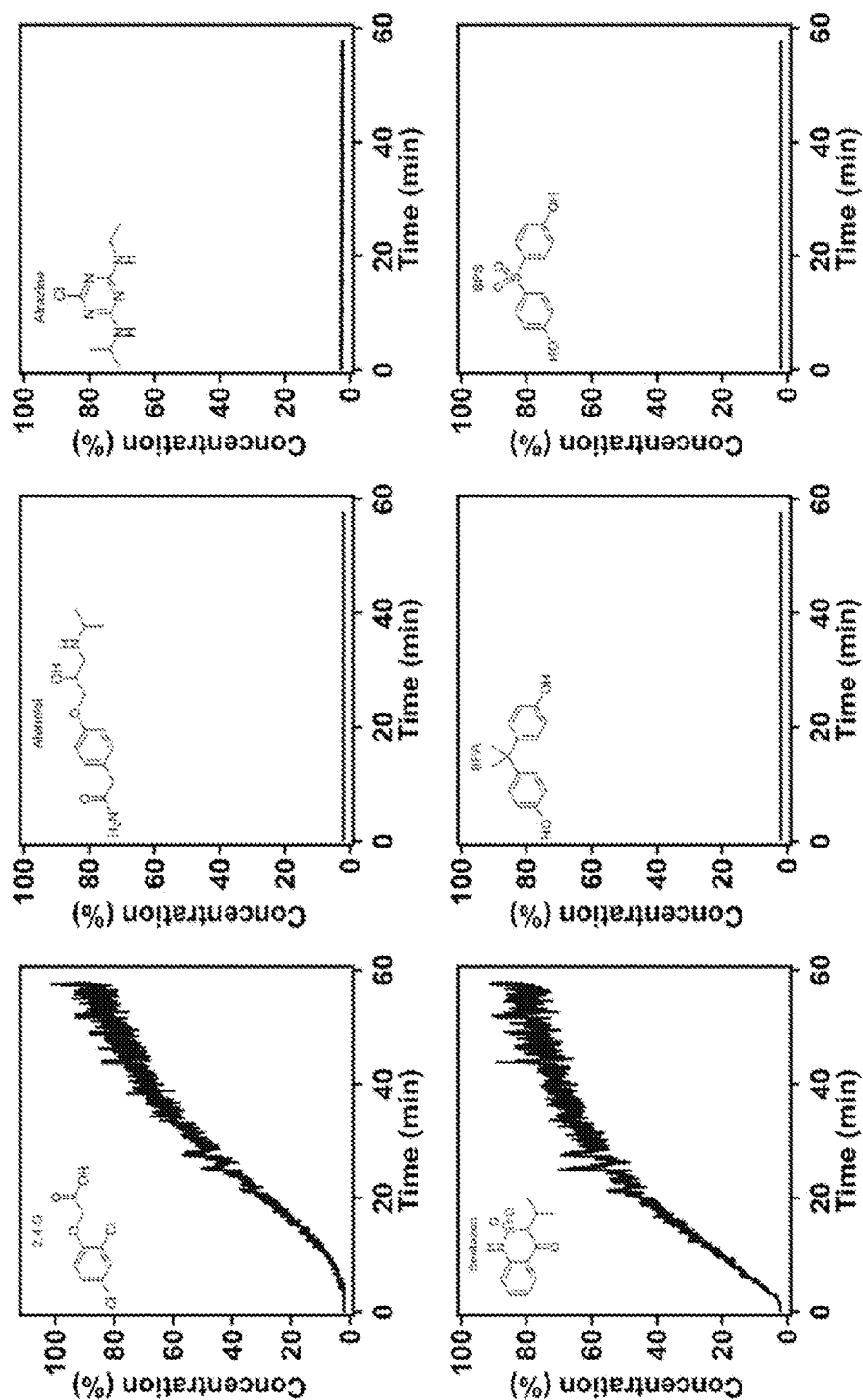


FIG. 27



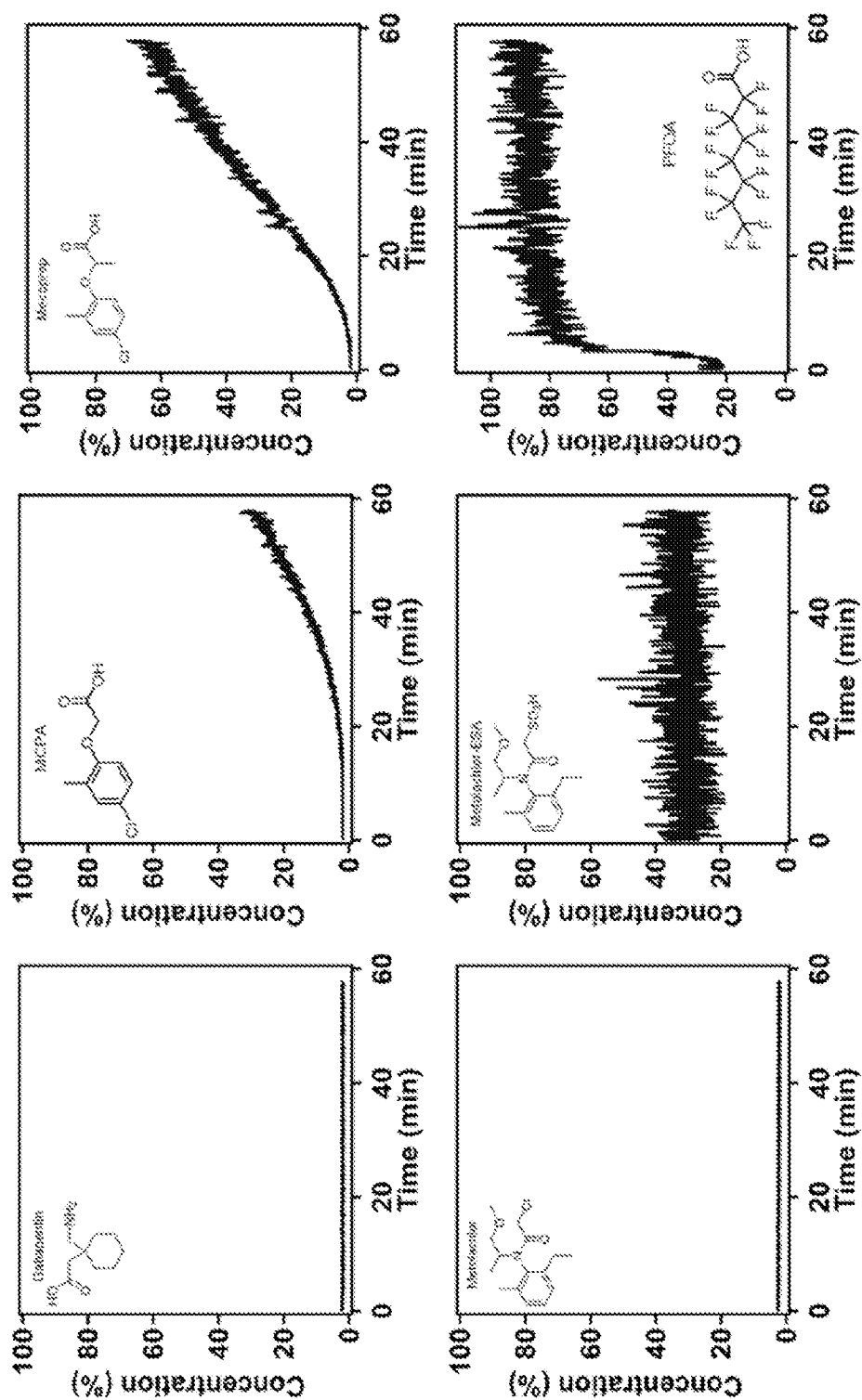
23/28

FIG. 28



24/28

FIG. 28 (continued)



25/28

FIG. 28 (continued)

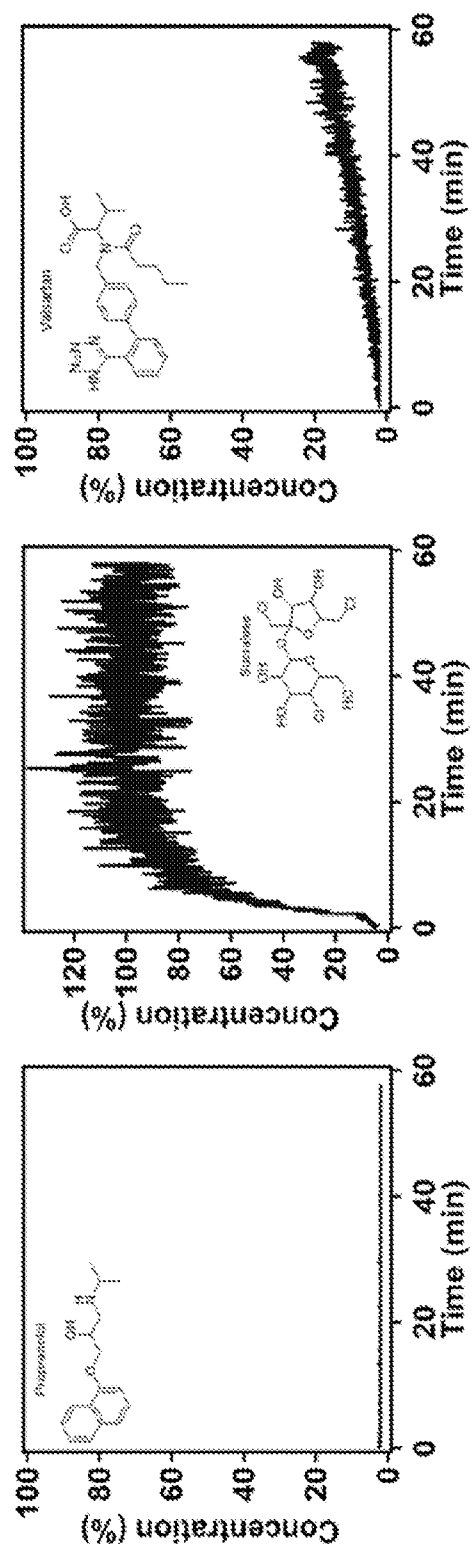


FIG. 29

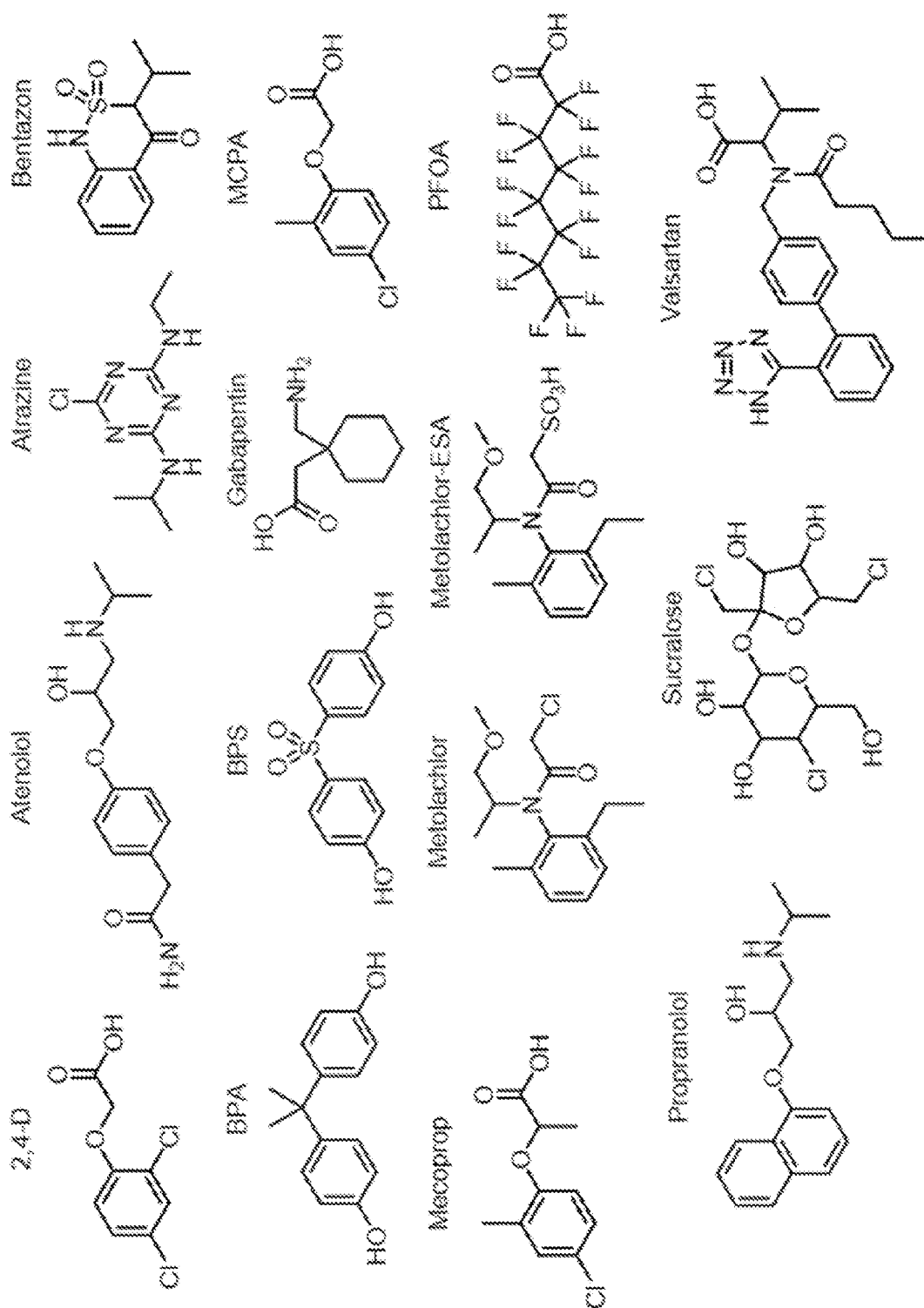


FIG. 30

a. Electron image

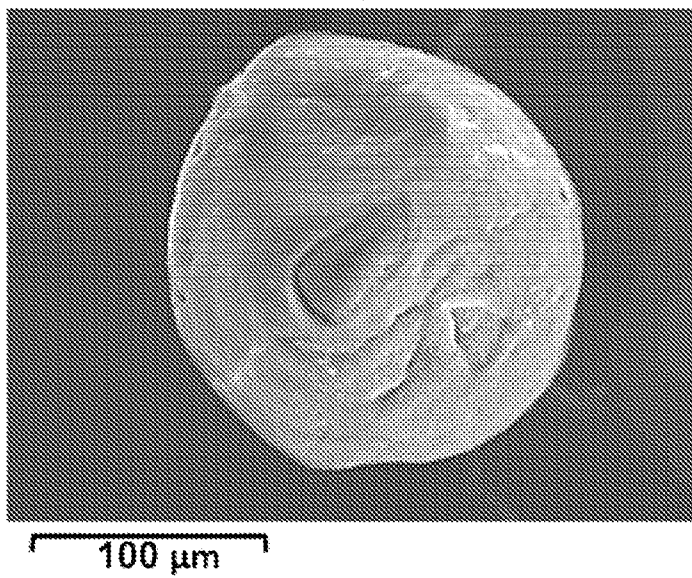
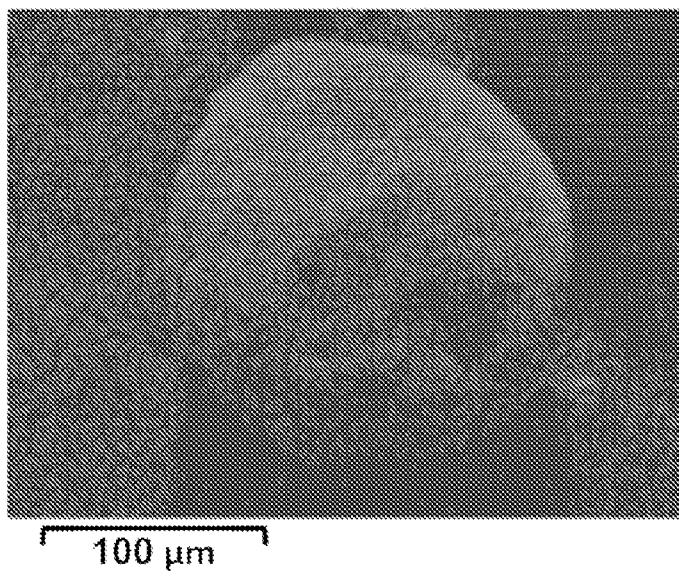
b. F K α 1_2

FIG. 31

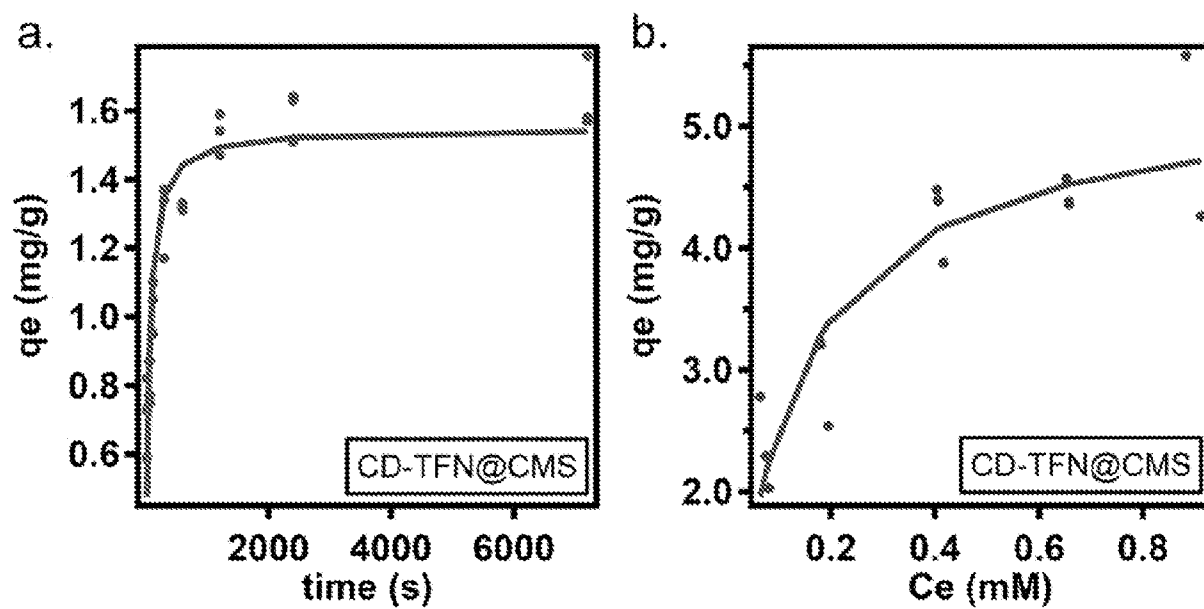
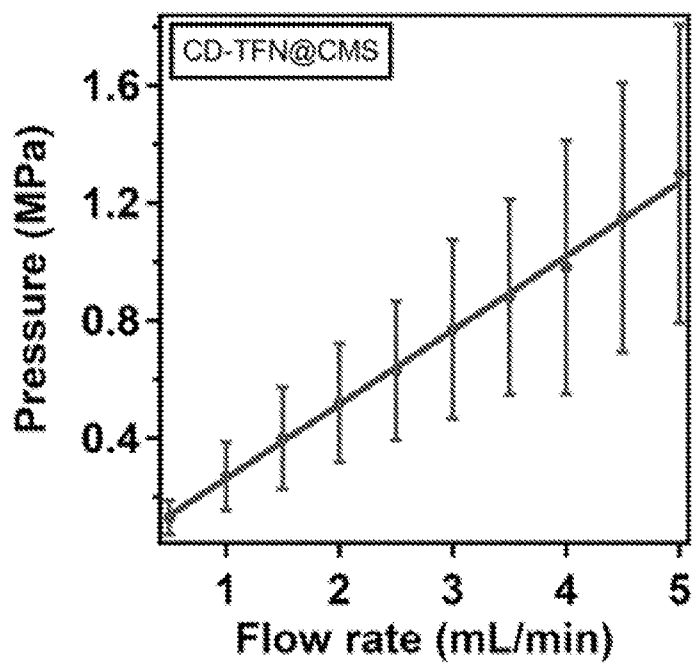


FIG. 32



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/29628

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.: 6, 11, 16
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:
Please see attached sheet--

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.: 1-5, 22-27, 30-34, 37, 39-44, 47-48, 50-52

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 18/29628

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C02F 1/28; G01N 30/02; C08B 15/00 (2018.01)

CPC - B01D 15/08; B01J 20/24; B01J 20/28033; B01J 20/286; B01J 20/3212; B01J 20/3272; C08F 1/285; C08B 15/00; C08B 37/0012; G01N 30/02

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.
X	US 2016/0304630 A1 (CORNELL UNIVERSITY) 20 October 2016 (20.10.2016); para [0006], [0008], [0010], [0075], [0101], [0110]-[0111], [0113], [0119], [0123]-[0128], [0153], [0160], [0174], [0208], [0223]; Figs. 3, 7-9	1, 22-27, 30-34, 37, 39-40, 50-52
-		-----
Y		2-5, 41-44, 47-48
Y	US 4,902,788 A (ZEMEL et al.) 20 February 1990 (20.02.1990); col 2 ln 44-52, col 6 ln 63-68	2-5
Y	US 6,149,943 A (MCTEIGUE et al.) 21 November 2000 (21.11.2000); col 1 ln 41-42; col 2 ln 43-44; col 3 ln 2-4, 10-12	41-42, 47-48
Y	US 2012/0107459 A1 (WOOD et al.) 03 May 2012 (03.05.2012); para [0024], [0062], [0066]	43-44

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

14 August 2018

Date of mailing of the international search report

17 SEP 2018

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 W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/29628

Attachment to Box.No.III:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I+: Claims 1-5, 7-10, 12-15 and 17-55, directed to a supported porous polymeric material comprising porous particles affixed to a solid substrate, wherein said porous particles comprise a plurality of cyclodextrin moieties crosslinked with one or more aryl moieties selected from formula (I), (II), (III) and (IV), represented by the structures specified in claim 26; wherein the supported porous polymeric material has one or more performance characteristics; and to an article of manufacture comprising the supported porous polymeric material, selected from protective equipment, a filtration medium and an extraction device.

The supported porous polymeric material will be searched to the extent that the material encompasses porous particles covalently affixed to microcrystalline cellulose, comprising a plurality of cyclodextrin moieties crosslinked with one or more aryl moieties of formula (I), represented by the first structure of claim 26; wherein the performance characteristic is pollutant uptake (first choice in claim 2) and wherein the article of manufacture comprising the supported porous polymeric material, is a protective equipment which is clothing. It is believed that claims 1-5, 22-27, 30-34, 37, 39-44, 47-48, 50-52 read on this first named invention, and thus these claims will be searched without fee to the extent that they encompass the supported porous polymeric material, described above.

Applicant is invited to elect additional supported porous polymeric material(s), wherein each additional material elected will require one additional invention fee. Applicants must specify the claims that encompass any additionally elected material(s). Applicants must further indicate, if applicable, the claims which encompass the first named invention, if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the '+' group(s) will result in only the first claimed invention to be searched.

Additionally, an exemplary election wherein different actual variables are selected is suggested. An exemplary election would be a porous polymeric material comprising porous particles covalently affixed to microcrystalline cellulose, comprising a plurality of cyclodextrin moieties crosslinked with one or more aryl moieties of formula (II), represented by the first structure of claim 45; wherein the performance characteristic is equilibrium adsorption capacity (qe) for a pollutant and wherein the article of manufacture comprising the supported porous polymeric material, is a filtration medium (i.e., claims 1-5, 7-10, 22-26, 28, 30-33, 35, 37, 39-48, 50 and 53).

Group II: Claims 56-61, directed to a method of purifying an aqueous sample comprising one or more organic pollutants, comprising contacting the aqueous sample with the supported porous polymeric material, such that at least 50% to at least 99% of the one or more organic pollutants are removed from the aqueous sample.

Group III: Claims 62-64, directed to a method of determining the presence or absence of compounds in a sample, comprising: a) contacting the sample with the supported porous polymeric material for an incubation period; b) isolating the supported porous polymeric material from a) from the sample; and c) heating the supported porous polymeric material from b) or contacting the supported porous polymeric material from b) with a solvent such that at least part of the compounds are then released from the supported porous polymeric material; and d) determining the presence or absence of any compounds.

The group of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I+ includes the technical feature of a unique supported porous polymeric material and an article comprising the same, which is not required by any other invention of Group I+.

Group II includes the technical feature of a method of purifying an aqueous sample, not required by Group I+ or Group III.

Group III includes the technical feature of a method of determining the presence or absence of compounds in a sample, which is not required by Groups I+ and Group II.

The inventions of Group I+ as well as Groups I+, II and III, share the technical feature of a supported porous polymeric material comprising porous particles affixed to a solid substrate, wherein said porous particles comprise a plurality of cyclodextrin moieties crosslinked with one or more aryl moieties, and wherein the supported porous polymeric material has one or more performance characteristics which are at least about 50% of the same performance characteristics of unsupported porous particles of the same composition.

This shared technical feature, however, does not provide a contribution over the prior art, as being obvious over US 2016/0304630 A1 to Cornell University (hereinafter Cornell).

Cornell discloses a supported porous polymeric material comprising porous particles affixed to a solid substrate (para [0008]: "the composition comprises any of the porous polymeric materials described herein covalently bonded to a support material"), wherein said porous particles comprise a plurality of cyclodextrin moieties crosslinked with one or more aryl moieties (para [0008]: "the polymeric materials of the present disclosure comprise a plurality of cyclodextrin moieties crosslinked by one or more aryl moieties"), and wherein the supported porous polymeric material has one or more performance characteristics (para [0110]: "the porous polymeric material has a relatively large surface area, which substantially improves the adsorption kinetics and/or capacity compared to conventional nonporous cyclodextrin polymers"; para [0126]: "significant capacity beyond 1:1 CD [cyclodextrin] inclusion complexes").

Whereas Cornell does not specifically disclose which are at least about 50% of the same performance characteristics of unsupported porous particles of the same composition, in view of the above disclosure (especially, para [0126]), it would have been obvious for the person of ordinary skill in the art to adjust the aforementioned performance characteristics (e.g., surface area, pollutant uptake, adsorption capacity, para [0153], [0160]) in the course of routine experimentation (e.g., variation of polymer and/or substrate chemical composition, particle morphology, size and/or surface area, etc.) in order to enhance pollutant removal (para [0127]).

As said supported porous polymeric material was known in the art at the time of the invention, this cannot be considered a special technical feature, which would otherwise unify the inventions of Group I+ or those of Groups I+, II and III.

---Continued on next sheet---

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/29628

Continuation of previous sheet:

The inventions of Group I+ also share the technical feature of an article comprising the porous polymeric material. This shared technical feature, however, does not provide a contribution over the prior art, as being obvious over Cornell, which discloses a supported porous polymeric material, as described above, and further discloses an article comprising the porous polymeric material (para [0233]). As said article was known in the art at the time of the invention, this cannot be considered a special technical feature, which would otherwise unify the inventions of Group I+.

Groups II and III further share the technical feature of contacting the supported porous polymeric material with a sample. This shared technical feature, however, does not provide a contribution over the prior art, as being obvious over Cornell, which discloses a method comprising contacting the supported porous polymeric material with a sample (para [0228]). As said article was known in the art at the time of the invention, this cannot be considered a special technical feature, which would otherwise unify the inventions of Groups II-III.

The inventions of Group I+-III thus lack unity under PCT Rule 13.

Note reg. item 4: Claims 6, 11 and 16 are unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).