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

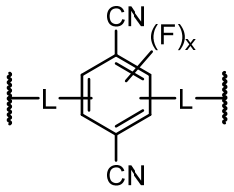
[0004] An alternative adsorbent material can be made from polymeric cyclodextrin materials produced from insoluble polymers of β-cyclodextrin (β-CD), which are toroidal macrocycles comprised of seven glucose units whose internal cavities are capable of binding organic compounds. β-CD is an inexpensive and sustainably produced monomer derived from cornstarch that is used extensively to formulate and stabilize pharmaceuticals, flavorants, and fragrances, as well as within chiral chromatography stationary phases. Insoluble β-CD polymers have been formed by crosslinking with epichlorohydrin and other reactive compounds, and feature well defined binding sites and high association constants. Insoluble β-CD polymers crosslinked with epichlorohydrin have been investigated as alternatives to AC for water purification, but their low surface areas result in inferior sorbent performance relative to ACs.

[0005] Thus there is a need for new sorbents that address the deficiencies of AC and the like and which will provide more effective sorption and/or sequestration properties for MPs (such as anionic MPs). There is a need for an adsorbent that provides rapid anionic MP extraction, high total uptake, and facile regeneration and reuse procedures. This invention meets those needs.

Summary

[0005a] In one aspect of the present disclosure, there is provided a porous polymeric material comprising:

(a) a plurality of cyclodextrins crosslinked with a plurality of crosslinks comprising structure (I):



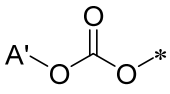
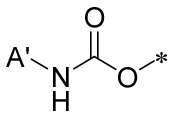
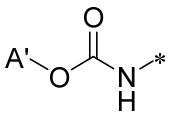
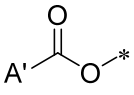
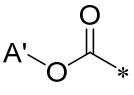
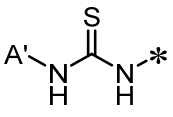
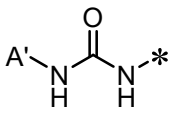
, and

structure (I)

(b) a plurality of crosslinks having a cationic moiety and a counteranion (X^-);

wherein:

x is 0, 1, or 2;

each L is independently selected from the group consisting of –O–, –S–, –N–, C_1-C_6 substituted or unsubstituted alkylene, C_1-C_3 haloalkylene, , , , , , , and ;

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

A' a covalent bond to the phenyl ring of structure (I); and

* is a covalent bond attached to .

[0005b] In another aspect of the present disclosure, there is provided a method of purifying a fluid sample comprising one or more pollutants, the method comprising contacting the fluid sample with the porous polymeric material disclosed herein, whereby at least 50 wt. % of the total amount of the one or more pollutants in the fluid sample is adsorbed by the porous polymeric material.

[0005c] In a further aspect of the present disclosure, there is provided a method of purifying a fluid sample comprising one or more pollutants, the method comprising contacting the fluid sample with the porous polymeric material disclosed herein, whereby at least 50 wt. % of the total amount of the one or more pollutants in the fluid sample is adsorbed by the porous polymeric material.

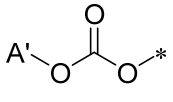
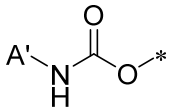
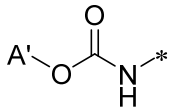
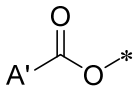
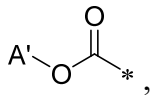
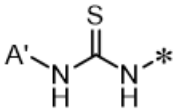
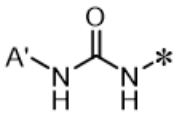
[0005d] In a further aspect of the present disclosure, there is provided a method of removing one or more compounds from a fluid sample or determining the presence or absence of one or more compounds in a fluid sample comprising: a) contacting the sample with the porous polymeric

material of claim 1 for an incubation period; b) separating the porous polymeric material after the incubation period from the sample; and c) heating the porous polymeric material separated in step b), or contacting the porous polymeric material separated in step b) with a solvent, thereby releasing at least a portion of the compounds from the porous polymeric material; and d1) optionally isolating at least a portion of the compounds released in step c); or d2) determining the presence or absence of the compounds released in step c), wherein the presence of one or more compounds correlates to the presence of the one or more compounds in the sample.

[0005e] In another aspect of the present disclosure, there is provided a solid-phase extraction device comprising the porous polymeric material of disclosed herein.

[0005f] In a further aspect of the present disclosure, there is provided a solid-phase extraction device comprising the porous polymeric material disclosed herein.

[0006] In some examples, the present disclosure provides a porous polymeric material comprising a plurality of cyclodextrins crosslinked with a plurality of crosslinks comprising formula (I):

each L is independently a linking moiety selected from the group consisting of –O–, –S–, –N–, C_1-C_6 substituted or unsubstituted alkylene, C_1-C_3 haloalkylene, , , , , , , and ;

A' is a covalent bond to A;

Z' is a covalent bond to Z;

* is a covalent bond to ;

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

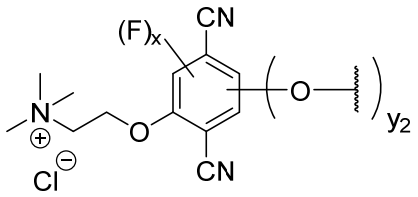
x is 0-8;

y_1 is 1-4;

y_2 is 1-4; and

y_3 is 0-4.

[0007] In some examples, the crosslinks of the porous polymeric material comprise formula (II):



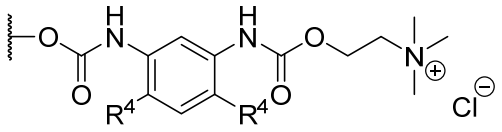
(II)

wherein

y_2 is 1 or 2; and

x is 1 or 2.

[0008] In some examples, the porous polymeric material of the present disclosure comprises a plurality of linkers of formula (III):



(III)

wherein one R^4 is –H and one R^4 is –Me.

[0009] In some examples, 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 with a plurality of crosslinks comprising formula (I), (II), or (III).

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

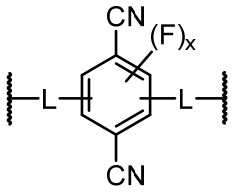
[0011] In some examples, the present disclosure provides a method of removing one or more compounds from a fluid sample or determining the presence or absence of one or more compounds in a fluid sample comprising: a) contacting the sample with the porous polymeric material or the supported porous polymeric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

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

CLAIMS:

1. A porous polymeric material comprising:

(a) a plurality of cyclodextrins crosslinked with a plurality of crosslinks comprising structure (I):



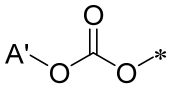
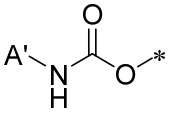
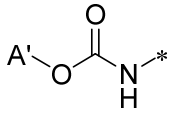
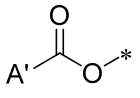
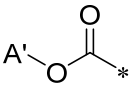
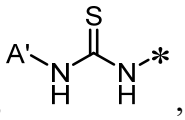
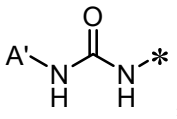
, and

structure (I)

(b) a plurality of crosslinks having a cationic moiety and a counteranion (X^-);

wherein:

x is 0, 1, or 2;

each L is independently selected from the group consisting of –O–, –S–, –N–, C_1-C_6 substituted or unsubstituted alkylene, C_1-C_3 haloalkylene, , , , , , , and ;

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

A' a covalent bond to the phenyl ring of structure (I); and

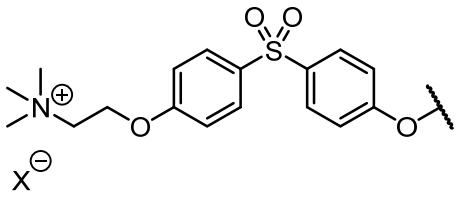
* is a covalent bond attached to .

2. The porous polymeric material of claim 1, wherein the cationic moiety is $–N(R^3)_3^+$, $–P(R^3)_3^+$, $–S(R^3)_2^+$, or -Heteroaryl$^+$, wherein each R^3 is independently –H, $–C_1$-C_6 alkyl, $–C_1$-C_3 haloalkyl, –aryl, $-C(O)N(R^a)(R^b)$, $-C(O)R^c$, $-CO_2R^c$, $-SO_2N(R^a)(R^b)$, or $-SOR^c$, and each R^a and R^b is independently H, or C_1-C_6 alkyl.

3. The porous polymeric material of claim 2, wherein the cationic moiety is $–N(R^3)_3^+$.

4. The porous polymeric material of claim 3, wherein the cationic moiety is $–N(CH_3)_3^+$.

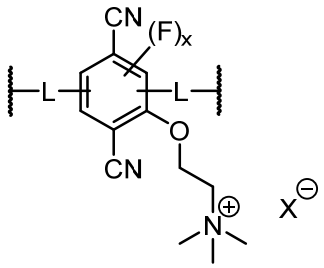
5. The porous polymeric material of claim 2, further comprising a plurality of linkers of structure (IV):



structure (IV).

6. The porous polymeric material of claim 5, wherein each cyclodextrin is β-cyclodextrin.

7. The porous polymeric material of claim 1, wherein the plurality of crosslinks having a cationic moiety and a counteranion (X^-) have structure (II):



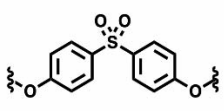
structure (II).

8. The porous polymeric material of claim 7, wherein each L is –O–.

9. The porous polymeric material of claim 8, wherein X^- is Cl^-.

10. The porous polymeric material of claim 7, wherein X^- is Cl^-.

11. The porous polymeric material of claim 7, further comprising a plurality of cyclodextrins crosslinked with a plurality of crosslinks of structure (III):

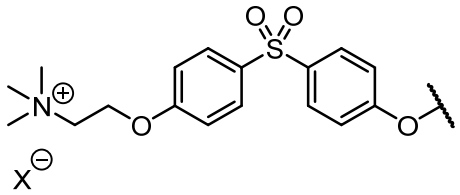


.

structure (III)

12. The porous polymeric material of claim 11, wherein each cyclodextrin is β-cyclodextrin.

13. The porous polymeric material of claim 7, further comprising a plurality of linkers of structure (IV):



structure (IV).

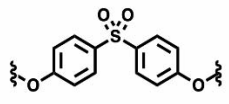
14. The porous polymeric material of claim 13, wherein each cyclodextrin is β-cyclodextrin.

15. The porous polymeric material of claim 7, wherein each cyclodextrin is β-cyclodextrin.

16. The porous polymeric material of claim 1, wherein each L is –O–.

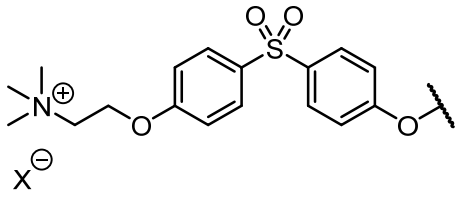
17. The porous polymeric material of claim 17, wherein X^- is Cl^-.

18. The porous polymeric material of claim 1, further comprising a plurality of cyclodextrins crosslinked with a plurality of crosslinks of structure (III):



structure (III)

19. The porous polymeric material of claim 18, further comprising a plurality of linkers of structure (IV):



structure (IV).

20. The porous polymeric material of claim 19, wherein each cyclodextrin is β-cyclodextrin.

21. The porous polymeric material of claim 18, wherein each cyclodextrin is β-cyclodextrin.

22. The porous polymeric material of claim 1, wherein each cyclodextrin is β-cyclodextrin.

23. A method of purifying a fluid sample comprising one or more pollutants, the method comprising contacting the fluid sample with the porous polymeric material of claim 1, whereby at least 50 wt. % of the total amount of the one or more pollutants in the fluid sample is adsorbed by the porous polymeric material.

24. A method of purifying a fluid sample comprising one or more pollutants, the method comprising contacting the fluid sample with the porous polymeric material of claim 7, whereby at least 50 wt. % of the total amount of the one or more pollutants in the fluid sample is adsorbed by the porous polymeric material.

25. A method of removing one or more compounds from a fluid sample or determining the presence or absence of one or more compounds in a fluid sample comprising: a) contacting the sample with the porous polymeric material of claim 1 for an incubation period; b) separating the porous polymeric material after the incubation period from the sample; and c) heating the porous polymeric material separated in step b), or contacting the porous polymeric material separated in step b) with a solvent, thereby releasing at least a portion of the compounds from the porous

polymeric material; and d1) optionally isolating at least a portion of the compounds released in step c); or d2) determining the presence or absence of the compounds released in step c), wherein the presence of one or more compounds correlates to the presence of the one or more compounds in the sample.

26. A solid-phase extraction device comprising the porous polymeric material of claim 1.

27. A solid-phase extraction device comprising the porous polymeric material of claim 7.