MODIFIED CLAY SORBENTS WITH MULTIFUNCTIONAL QUATERNARY AMMONIUM COMPOUNDS AND MONO-QUATERANRY AMMONIUM COMPOUNDS AND METHODS OF SORBING PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) FROM CONTAMINATED SAMPLES WITH THE MODIFIED CLAY SORBENTS

CROSS-REFENCE TO RELATED APPLICATION

[0001] The benefit of priority to U.S. Provisional Patent Application No. 63/029,261 filed May 22, 2020 is hereby claimed and the disclosure is incorporated herein by reference in its entirety.

BACKGROUND

Field of the Disclosure

[0002] The disclosure relates to methods of sorbing PFAS compounds, and in particular sorbing PFAS compounds using a clay modified with one or more multi-functional quaternary amine compounds having a functionality of three or more.

Brief Description of Related Technology

[0003] Perfluorinated compounds (PFCs) have wide application and as a result have become a global concern in contamination of water environments. Per- and polyfluoroalkyl substances (conventionally referred to collectively as PFAS) are a group of man-made chemicals that includes PFOA, PFOS, GenX, and many other chemicals. PFAS have been manufactured and used in a variety of industries, including in the United States since the 1940s. Perfluorooctane sulfonate (PFOS) is one of the typical PFCs and has been used in many industries as surfactants, fire retardants, lubricants, and polymer additives. Perfluorooctanoic acid (PFOA) and PFOS have been the most extensively produced and studied of these chemicals. PFCs can accumulate over time in the human body and many do not naturally break down. PFAS exposure has been demonstrated to be detrimental to human health. PFC removal from waste water sources is critical to the prevention of contamination of natural waterways. Since PFCs are generally very stable, they are difficult to decompose in ambient environments using some conventional technologies including bio- logical degradation, oxidation and reduction. Sorption has been used as an alternative method to effectively remove PFCs from wastewater, soil, and other contaminated sources with conventional sorbents including activated carbon, resin, and biosorbents.

SUMMARY

[0003a] In one aspect of the present disclosure, there is provided a modified clay sorbent for sorbing PFAS compounds from a contaminated sample, comprising:

a clay intercalated with one or more multifunctional-quaternary amine compounds having a functionality of 3 or more and one or more mono-quaternary amine compounds.

[0003b] In another aspect of the present disclosure, there is provided a modified clay sorbent for sorbing PFAS compounds from a contaminated sample, comprising:

a first modified clay comprising a clay intercalated with the one or more mono-quaternary amine compounds; and

a second modified clay comprising a clay intercalated with the one or more multifunctional-quaternary amine compounds having a functionality of 3 or more.

[0003c] In a further aspect of the present disclosure, there is provided a kit comprising: the modified clay sorbent disclosed herein and instructions for adding the clay sorbent to a contaminated sample for sorption of PFAS compounds.

[0003d] In another aspect of the present disclosure, there is provided a kit comprising:

the modified clay sorbent disclosed herein, wherein the first and second modified clays are present as separate components, and

instructions for adding the first modified clay and the second modified clay individually to a contaminated sample to form the modified clay sorbent in amounts such that the one or more multifunctional-quaternary amine compounds are present in an amount of 20 mol% to about 80 mol% based on the total moles of quaternary amine compounds added to the sample.

[0003e] In a further aspect of the present disclosure, there is provided a method of sorbing PFAS compounds from a contaminated sample, comprising:

admixing a modified clay sorbent with the sample, wherein the modified clay sorbent comprises a clay intercalated with a one or more mono-quaternary amine compounds and one or more multifunctional-quaternary amine compounds having a functionality of 3 or more, or

admixing a clay, one or more mono-quaternary amine compounds, and one or more multifunctional-quaternary amine compounds with the sample, wherein the clay is intercalated with the one or more mono-quaternary amine compounds and the one or more multifunctional-quaternary amine compounds in situ to form a modified clay sorbent for sorbing PFAS compounds from the contaminated sample.

[0003f] In another aspect of the present disclosure, there is provided a method of sorbing PFAS compounds from a contaminated sample, comprising:

admixing a modified clay sorbent with the sample, wherein the modified clay sorbent comprises a first modified clay comprising a clay intercalated with a one or more mono-quaternary amine compounds and a second modified clay comprising a clay intercalated with one or more multifunctional-quaternary amine compounds having a functionality of 3 or more.

[0004] The technical information set out below may in some respects go beyond the disclosure of the present disclosure, which is defined exclusively by the appended claims. The additional technical information is provided to place the actual disclosure in a broader technical context and to illustrate possible related technical developments. Such additional technical

information which does not fall within the scope of the appended claims, is not part of the present disclosure.

[0005] There is a need for improved methods of sorbing PFAS compounds from soils, wastewaters and other contaminated sources.

[0006] A modified clay sorbent in accordance with the disclosure can include a clay intercalated with one or more multifunctional-quaternary amine compounds having a functionality of 3 or more and one or more mono-quaternary amine compounds. In examples, the one or more multifunctional-quaternary amine compounds are present in a mole percent of about 25 mol% to about 95 mol% based on total moles of quaternary amine compounds present in the modified clay sorbent.

[0007] A modified clay sorbent in accordance with the disclosure can include a first modified clay comprising a clay intercalated with the one or more mono-quaternary amine compounds; and a second modified clay comprising a clay intercalated with the one or more multifunctional-quaternary amine compounds having a functionality of 3 or more. In examples, the second modified clay can be present in the modified clay sorbent in an amount such that the one or more multifunctional-quaternary amine compounds are present in an amount of about 25 mol% to about 95 mol% based on total moles of quaternary amine compounds present in the modified clay sorbent.

[0008] A method of sorbing PFAS compounds from a contaminated sample in accordance with the disclosure can include admixing a modified clay sorbent with the sample, wherein the modified clay sorbent comprises a clay intercalated with one or more multifunctional quaternary amine compounds having a functionality of 3 or more.

[0009] A method of sorbing PFAS compounds from a contaminated sample in accordance with the disclosure can include admixing a modified clay sorbent with the sample, wherein the modified clay sorbent comprises a clay intercalated with a one or more mono-quaternary amine compounds and one or more multifunctional-quaternary amine compounds having a functionality of 3 or more. In examples, the one or more multifunctional-quaternary amine compounds are present in an amount of about 25 mol% to about 95 mol% based on the total mole percent of the quaternary amine compounds in the modified clay sorbent.

[0010] A method of sorbing PFAS compounds from a contaminated sample can include admixing a modified clay sorbent with the sample, wherein the modified clay sorbent comprises a first modified clay comprising a clay intercalated with a one or more mono-quaternary amine

compounds and a second modified clay comprising a clay intercalated with one or more multifunctional-quaternary amine compounds having a functionality of 3 or more. In examples, a ratio of an amount of the first modified clay to the amount of the second modified clay is selected such that the one or more multifunctional-quaternary amine compounds are present in an amount of about 25 mol% to about 95 mol% based on the total mole percent of the quaternary amine compounds admixed with the sample.

[0011] In any of the modified clay sorbets or methods herein the multi-functional quaternary amine compound can be a trifunctional-quaternary amine compound (also referred to herein as "triquat").

BREIF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 is a graph showing the percent removal of various PFAS as a function of trifunctional quaternary amine compound mole percent; and

[0013] Figure 2 is a bar graph showing percent removal of various PFAS as a function of trifunctional quaternary amine compound mole percent.

DETAILED DESCRIPTION

[0014] The technical information set out below may in some respects go beyond the disclosure of the invention, which is defined exclusively by the appended claims. The additional technical information is provided to place the actual invention in a broader technical context and to illustrate possible related technical developments. Such additional technical information which does not fall within the scope of the appended claims, is not part of the invention.

[0015] Modified clay sorbents are disclosed herein for sorbing PFAS compounds. The modified clay sorbents can include a clay component modified with a blend of one or more mono-quaternary amine compounds and one or more multifunctional-quaternary amine compounds having a functionality of 3 or more. The modified clay sorbent can be modified with one or more multifunctional-quaternary amine compounds having a functionality of 3 or more. A method of sorbing PFAS compounds from a contaminated sample can include contacting or otherwise exposing the sample to one or more modified clay sorbents. In such methods, the modified clay sorbent can be modified with a multifunctional-quaternary amine compound having a functionality of 3 or more or with a blend of a mono-quaternary amine compound and a multifunctional-quaternary amine compound having a functionality of 3 or more. In any of the sorbents herein, the clay can be modified with more than one mono-quaternary amine

What is Claimed:

1. A modified clay sorbent for sorbing PFAS compounds from a contaminated sample, comprising:

a clay intercalated with one or more multifunctional-quaternary amine compounds having a functionality of 3 or more and one or more mono-quaternary amine compounds.

2. The modified clay sorbent of claim 1, wherein the clay is intercalated with the one or more multifunctional-quaternary amine compounds and one or more mono-quaternary amine compounds to at least 50% of the total cationic exchange capacity of the clay.

3. A modified clay sorbent for sorbing PFAS compounds from a contaminated sample, comprising:

a first modified clay comprising a clay intercalated with the one or more mono-quaternary amine compounds; and

a second modified clay comprising a clay intercalated with the one or more multifunctional-quaternary amine compounds having a functionality of 3 or more.

4. The modified clay sorbent of any one of the preceding claims, wherein the one or more multifunctional-quaternary amine compounds are present in a mole percent of about 20 mol% to about 80 mol% based on the total moles of quaternary amine compound present in the modified clay sorbent.

5. The modified clay sorbent of claims 3 or 4, wherein the first modified clay and the second modified clay are each intercalated with the respective one or more mono-quaternary amine compounds and multifunctional-quaternary amine compounds to at least about 50% of the cationic exchange capacity of the respective first or second modified clay.

6. The modified clay sorbent of any one of the preceding claims, wherein the one or more multifunctional-quaternary amine compounds have 18 or more carbons.

7. The modified clay sorbent of any one of the preceding claims, wherein the clay is one or more of attapulgite, bentonite, montmorillonite, nontronite, beidellite, volkonskoite, hectorite, sapponite, sauconite, sobockite, stevensite, svinfordite, vermiculite, palygorskite, kalonite, and sepiolite.

8. The modified clay sorbent of any one of the preceding claims, wherein the modified clay sorbent is present in a mat.

9. The modified clay sorbent of any one of the preceding claims, wherein the mono-functional quaternary amine is one or more of dimethyl di(C14-C18 alkyl) ammonium chloride.

10. A kit comprising: the modified clay sorbent of any one of the preceding claims and instructions for adding the clay sorbent to a contaminated sample for sorption of PFAS compounds.

11. A kit comprising:

the modified clay sorbent of claim 3, wherein the first and second modified clays are present as separate components, and

instructions for adding the first modified clay and the second modified clay individually to a contaminated sample to form the modified clay sorbent in amounts such that the one or more multifunctional-quaternary amine compounds are present in an amount of 20 mol% to about 80 mol% based on the total moles of quaternary amine compounds added to the sample.

12. The kit of claim 11, wherein the first and second modified clays are added in amounts such that the one or more multifunctional-quaternary amine compounds are present in an amount of 20 mol% to about 80 mol% based on the total moles of quaternary amine compounds added to the sample.

13. The kit of claim 11 or 12, wherein the first and second modified clays are added substantially simultaneously.

14. The kit of claim 11 or 12, wherein the first and second modified clays are added sequentially.

15. A method of sorbing PFAS compounds from a contaminated sample, comprising:

admixing a modified clay sorbent with the sample, wherein the modified clay sorbent comprises a clay intercalated with a one or more mono-quaternary amine compounds and one or more multifunctional-quaternary amine compounds having a functionality of 3 or more, or

admixing a clay, one or more mono-quaternary amine compounds, and one or more multifunctional-quaternary amine compounds with the sample, wherein the clay is intercalated with the one or more mono-quaternary amine compounds and the one or more multifunctional-quaternary amine compounds *in situ* to form a modified clay sorbent for sorbing PFAS compounds from the contaminated sample.

16. The method of claim 15, wherein the one or more multifunctional-quaternary amine compounds are present in an amount of at least about 20 mol% based on the total moles of the quaternary amine compounds in the modified clay sorbent.

17. A method of sorbing PFAS compounds from a contaminated sample, comprising:

admixing a modified clay sorbent with the sample, wherein the modified clay sorbent comprises a first modified clay comprising a clay intercalated with a one or more mono-quaternary amine compounds and a second modified clay comprising a clay intercalated with one or more multifunctional-quaternary amine compounds having a functionality of 3 or more.

18. The method of claim 17, wherein a ratio of an amount of the first modified clay to the amount of the second modified clay is selected such that the one or more multifunctional-quaternary amine compounds are present in an amount of about 20 mol% to about 80 mol% based on the total moles of the quaternary amine compounds admixed with the sample.

19. The method of any one of claims 15 to 18, wherein the one or more multifunctional-quaternary amine compounds comprises at least 18 carbons.

20. The method of any one of claims 15 to 19, wherein the clay is one or more of attapulgite, bentonite, montmorillonite, nontronite, beidellite, volkonskoite, hectorite, sapponite, sauconite, sobockite, stevensite, svinfordite, vermiculite, palygorskite, kalonite, and sepiolite.

21. The method of any one of claims 15 to 20, where the sorbent is capable of adsorbing at least 0.2 milligrams of PFAS compounds per gram of modified clay sorbent.

22. The method of any one of claims 15 to 21, wherein the sample is a contaminated soil, and the method comprises mixing the contaminated soil and the modified clay sorbent such that the modified clay sorbent is present in an amount of greater than about 0.5 wt% of the modified clay sorbent in the mixture.

23. The method of any one of claims 15 to 22, wherein the sample is a contaminated waste water stream, and the method comprises admixing the modified clay sorbent and the contaminated water stream by passing the contaminated water through a bed of the modified clay sorbent at a flow rate to maintain a contact time of the contaminated water with the bed of at least about 1 minute.

24. The method of any one of claims 15 to 22, wherein the modified clay sorbent in in the form of a prepacked permeable mat or gabion.

25. The method of any one of claims 15 to 22, wherein the modified clay sorbent in a granular or powder form into a body of water such that the modified clay forms a permeable reactive barrier layer.

26. The method of any one of claims 15 to 22, comprising the treatment of PFAS compounds from a contaminated water stream by mixing the modified clay and contaminated water in a tank.

27. The method of any one of claims 15 to 22, comprising the treatment of PFAS compounds from a contaminated water stream by injecting a suspension of the modified clay into contaminated soil and or a contaminated groundwater plume.