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(71) Applicant: **GEOSYNTEC CONSULTANTS, INC.** [US/US]; 900 Broken Sound Pkwy NW Ste 200, Boca Raton, Florida 33487 (US).

(72) Inventors: **ZHOU, Chao**; c/o Geosyntec Consultants, Inc., 900 Broken Sound Pkwy NW Ste 200, Boca Raton, Florida 33487 (US). **FAN, Dimin**; c/o Geosyntec Consultants, Inc., 900 Broken Sound Pkwy NW Ste 200, Boca Raton, Florida 33487 (US).

(74) Agent: **SCHNEIDER, Ryan A.** et al.; Troutman Pepper Hamilton Sanders LLP, 600 Peachtree Street NE, Suite 3000, Atlanta, Georgia 30308 (US).

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(54) Title: DESTRUCTION SYSTEMS AND METHODS FOR ENVIRONMENTAL CONTAMINANTS

(57) Abstract: A system and method to generate highly reactive species that can destruct PFAS via approaches that are practical to implement *in situ*. Electrons are activated from chemically reduced TMOs (e.g., reduced titanium dioxide (r-TiO_2) or reduced zinc oxide (r-ZnO)) under mildly elevated temperature (for example, < 80°C) and reactive effectively with PFAS to generate inorganic fluoride and other degradation products. The electrons are believed to exist in shallow trap states close to the conduction band of the reduced material, and therefore can be excited by a mild form of energy such as mild heat or far infrared (IR) irradiation, instead of ultraviolet or visible light, which requires much higher energy and is difficult to implement *in situ*.

DESTRUCTION SYSTEMS AND METHODS FOR ENVIRONMENTAL CONTAMINANTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit under 35 USC § 119(e) of US Provisional Patent Application No. 63/489,959 filed 13 March 2023, the entirety of which is incorporated herein by reference as if set forth herein in their entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] Not Applicable

THE NAMES OF THE PARTIES TO A JOINT RESEARCH AGREEMENT

[0002] Not Applicable

SEQUENCE LISTING

[0003] Not Applicable

STATEMENT REGARDING PRIOR DISCLOSURES BY THE INVENTOR OR A JOINT INVENTOR

[0004] Not Applicable

BACKGROUND OF THE DISCLOSURE

1. Field of the Invention

[0005] The present invention relates to destruction systems and methods for environmental contaminants, including compositions and methods for removing one or more contaminants from media such as air, soil, and/or water.

2. Description of Related Art

[0006] Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that includes perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), GenX, and many other chemicals. Examples of where PFAS can be found include cleaners, textiles, leather, paper and paints, fire-fighting foams, and wire insulation.

[0007] PFAS are synthetic chemical substances with special properties and hundreds of manufacturing and industrial applications. PFOA is a long-chain perfluoroalkyl carboxylic acid (PFCA), a subset of PFAS, that does not occur naturally in the environment. The EPA has investigated PFOA for its persistence in the environment. It is found both in the environment and in the blood of the general US population, remains in people for a long time, and shown to cause developmental and other adverse effects in laboratory animals. There is also evidence that exposure to PFAS can lead to adverse health outcomes in humans.

[0008] PFOA was used as an aqueous dispersing agent to make fluoropolymers. PFOA is no longer used in US to manufacture fluoropolymers but some fluoropolymers containing PFOA are imported domestically as part of articles. Fluoropolymers impart valuable properties, including fire resistance and oil, stain, grease, and water repellency to articles, and are used in many industry segments, including the aerospace, automotive, building/construction, chemical processing, electronics, semiconductors, and textile industries.

[0009] PFOA can also be produced by the breakdown of some fluorinated telomers, substances that are used in surface treatment products to impart soil, stain, grease, and water resistance. Some telomers are also used as high performance surfactants in products that must flow evenly, such as paints, coatings, and cleaning products, fire-fighting foams for use on liquid fuel fires, or the engineering coatings used in semiconductor manufacture.

[0010] Thus, the need is clear that remediation of PFAS and other contaminants that ill-effect the environment is important.

[0011] PFAS destruction in various impacted environmental matrices, especially groundwater, remains a top priority and challenge for the remediation industry. Recent studies have investigated/developed a number of promising thermal and non-thermal technologies for aqueous-phase PFAS destruction, including UV photocatalysis, electron beam, electrochemical oxidation, ultrasound, plasma, or high-temperature heating.

[0012] However, these technologies are primarily for *ex situ* treatment and exclusively *ex situ* treatments are unlikely to be cost-effective for managing PFAS-contaminated groundwater in the long term; thus, new approaches for *in situ* PFAS destruction are urgently needed.

[0013] Earlier PFAS destruction research showed that conventional *in situ* chemical reduction or oxidation approaches are inefficient for PFAS destruction. As a result, more recent *in situ* PFAS treatment technologies for groundwater have mostly focused on sorptive amendments, but without a destructive natural attenuation mechanism, future handling of PFAS-laden sorptive media will be a concern once sorption capacity is exhausted.

[0014] Therefore, a need still exists for successful compositions and methods that remove/breakdown/destroy environmentally-dangerous contaminants, including heat activation of chemically reduced transition metal oxides (TMOs) or derivatives for *in situ* PFAS degradation. These and other objects, features, and advantages of the present invention will become more apparent upon reading the following specification in conjunction with the accompanying drawings.

BRIEF SUMMARY OF THE INVENTION

[0015] Briefly described, in a preferred form, the present invention is a system for the destruction of one or more environmental contaminants that are reactive towards a reductive treatment. The destruction can be *in situ*. The destruction can be *ex situ*. The environmental contaminants can be PFAS.

[0016] The reductive treatment can comprise activating electrons from chemically reduced TMOs (e.g., reduced titanium dioxide (r-TiO_2) or reduced zinc oxide (r-ZnO)) under mildly elevated temperature (< 80°C).

[0017] In another exemplary embodiment, the present invention is a system that generates highly reactive species that can destruct PFAS that are practical to implement *in situ.*

[0018] In another exemplary embodiment, the present invention is a destruction method for one or more environmental contaminants that are reactive towards a reductive treatment. The destruction can be *in situ*. The destruction can be *ex situ*. The environmental contaminants can be PFAS.

[0019] In another exemplary embodiment, the present invention is a method of generating highly reactive species that can destruct PFAS that are practical to implement *in situ.*

[0020] In another exemplary embodiment, the present invention is an *in situ* treatment with controlled activation of reactive electrons comprising chemically reducing a TMO, presenting the

reduced TMO into a contaminant-impacted treatment zone for source reduction, and heating the treatment zone to a desired temperature to activate stored electrons to degrade the contaminant.

[0021] In any of the exemplary embodiments, the controlled activation reactive electrons can comprise the controlled activation of highly reactive electrons.

[0022] In any of the exemplary embodiments, chemically reducing the TMO can comprise creating excess electrons in the TMO via reduction with a strong chemical reductant.

[0023] In any of the exemplary embodiments, presenting the reduced TMO can comprise injecting and/or delivering the reduced TMO in a slurry form. Presenting the reduced TMO can comprise injecting and/or delivering the reduced TMO in a slurry form into a PFAS-impacted aquifer to form a treatment zone for source reduction and/or a permeable reactive barrier for plume treatment

[0024] In any of the exemplary embodiments, the contaminant can be PFAS.

[0025] In any of the exemplary embodiments, heating of the treatment zone/barrier can be heating to < 80 °C to activate stored electrons in the reduced TMO to degrade the PFAS.

[0026] In another exemplary embodiment, the present invention is a method of forming a reactive species that can destruct per- and polyfluoroalkyl substances (PFAS).

[0027] In any of the exemplary embodiments, the reactive species can destruct PFAS in an *in situ* treatment.

[0028] In any of the exemplary embodiments, the forming can comprise reducing a transition metal oxide (TMO). The reducing can be chemically reducing.

[0029] In any of the exemplary embodiments, the method can further comprise applying in a treatment zone the reactive species in proximity to one or more environmental contaminants comprising PFAS and heating the treatment zone from between 50°C to 100°C.

[0030] In another exemplary embodiment, the present invention is a method comprising applying in a treatment zone a reactive species in proximity to one or more environmental contaminants comprising per- and polyfluoroalkyl substances (PFAS) and activating the reactive species in the treatment zone from between 50°C to 100°C.

[0031] In any of the exemplary embodiments, the activating can be selected from the group consisting of heating the reactive species, presenting the reactive species to infrared, and presenting the reactive species to microwave.

[0032] In any of the exemplary embodiments, the activating can comprise heating the reactive species in the treatment zone from between 50°C to 100°C.

[0033] In any of the exemplary embodiments, the method can be an *in situ* treatment of the one or more environmental contaminants.

[0034] In any of the exemplary embodiments, the method can be an *ex situ* treatment of the one or more environmental contaminants.

[0035] In any of the exemplary embodiments, the method can further comprise chemically reducing a metal oxide to form the reactive species.

[0036] In any of the exemplary embodiments, the metal oxide can be a transition metal oxide (TMO).

[0037] In any of the exemplary embodiments, the reactive species can be selected from a group consisting of reduced titanium dioxide (r-TiO_2) or reduced zinc oxide (r-ZnO).

[0038] In any of the exemplary embodiments, the method can further comprise catalyzing release and activation of stored electrons in the reactive species in the treatment zone and reductively destroying and mineralizing the PFAS in the treatment zone, wherein the method is an *in situ* treatment of PFAS in ground water, wherein the applying comprises applying a slurry of the reactive species, and wherein the treatment zone has a treatment pH range from between 5 to 9.

[0039] In another exemplary embodiment, the present invention is an *in situ* treatment of one or more environmental contaminants with controlled activation of reactive electrons comprising presenting a material with a negative band gap into a treatment zone comprising the one or more environmental contaminants and heating the treatment zone to a treatment temperature to activate stored electrons to degrade one or more of the environmental contaminants.

[0040] In any of the exemplary embodiments, one of the environment contaminants can be PFAS, and the heating degrades the PFAS.

[0041] In any of the exemplary embodiments, the presented material can comprise a reduced TMO.

[0042] In any of the exemplary embodiments, the method can further comprise forming the material with the negative band gap by chemically reducing a TMO.

[0043] In any of the exemplary embodiments, the presenting cam comprise presenting the reduced TMO via injecting and/or delivering the reduced TMO in a slurry form.

[0044] In any of the exemplary embodiments, the presenting can comprise presenting the reduced TMO via injecting and/or delivering the reduced TMO in a slurry form into a PFAS-impacted aquifer to form the treatment zone for source reduction and/or a permeable reactive barrier for plume treatment.

[0045] In any of the exemplary embodiments, the heating can comprise heating the treatment zone/barrier to activate stored electrons in the reduced TMO to degrade the PFAS.

[0046] In any of the exemplary embodiments, the heating can comprise heating the treatment zone/barrier to between 50°C to 100°C.

[0047] In another exemplary embodiment, the present invention is an *in situ* treatment with controlled activation of highly reactive electrons comprising creating an excess of electrons in a TMO by reduction with a strong chemical reductant, injecting/delivering the reduced TMO in a slurry into a PFAS-impacted aquifer to form at least one of (i) a treatment zone for PFAS reduction or (ii) a permeable reactive barrier for plume treatment of the PFAS, and heating the treatment zone/barrier to between 50°C to 100°C to activate the stored electrons to degrade the PFAS.

[0048] In another exemplary embodiment, the present invention is a system comprising a reactive species, a treatment zone comprising one or more environmental contaminants comprising per- and polyfluoroalkyl substances (PFAS), and a heating means to heat the treatment zone, wherein upon application of the reactive species in the treatment zone and heating of the treatment zone, the PFAS is degraded.

[0049] In any of the exemplary embodiments, the heating means can be configured to heat the treatment zone from between 50°C to 100°C.

[0050] In any of the exemplary embodiments, the reactive species can comprise a reduced TMO.

[0051] In another exemplary embodiment, the present invention is a system for the destruction of one or more environmental contaminants that are reactive towards a reductive treatment that activates electrons in a material, wherein the material is selected from the group consisting of a material prepared from a starting TMO material and using a chemical reduction method to create shallowly-trapped electrons within -0.3 eV of the conduction band which has a sufficiently negative reduction potential on the order of -0.3 eV, and a starting reduced TMO material modified or combined with other solid-state materials or chemical elements whose desirable electronic or adsorptive properties improve the overall treatment performance of the system.

[0052] In any of the exemplary embodiments, the system can further comprise a non-solid amendment to improve one or more of reactivity, selectivity, and/or longevity of the material.

[0053] In any of the exemplary embodiments, the system can further comprise one or more heating methods and/or heating apparatus.

[0054] In another exemplary embodiment, the present invention an *in situ* treatment with controlled activation of highly reactive electrons comprising creating an excess electrons in TMOs by reduction with a strong chemical reductant, injecting/delivering the reduced TMO slurry into a PFAS-impacted aquifer to form one or both (i) a treatment zone for source reduction or (ii) a permeable reactive barrier for plume treatment, and heating the treatment zone/barrier to < 80 °C to activate the stored electrons to degrade PFAS.

[0055] In another exemplary embodiment, the present invention a system for the destruction of one or more environmental contaminants that are reactive towards a reductive treatment that activates electrons in a material, wherein the material is selected from the group consisting of a material prepared from a starting TMO material and using a chemical reduction method to create shallowly-trapped electrons within -0.3 eV of the conduction band which has a sufficiently negative reduction potential on the order of -0.3 eV, a starting reduced TMO material modified or combined with other solid-state materials or chemical elements whose desirable electronic or adsorptive properties improve the overall treatment performance of the system, and a combination thereof.

[0056] In any of the exemplary embodiments, the system can further comprise a non-solid amendment (e.g., gas or liquid, or their aqueous solutions) to improve one or more of reactivity, selectivity, and/or longevity.

[0057] In any of the exemplary embodiments, the system can further comprise one or more heating methods and/or heating apparatus.

[0058] In another exemplary embodiment, the present invention is an *in situ* treatment with controlled activation of reactive electrons comprising chemically reducing a TMO, presenting the reduced TMO into a contaminant-impacted treatment zone for source reduction, and activating stored electrons in the reduced TMO in the treatment zone to degrade the contaminant.

[0059] In any of the exemplary embodiments, the activating can be selected from the group consisting of heating the reduced TMO, presenting the reduced TMO to infrared, and presenting the reduced TMO to microwave.

BRIEF DESCRIPTION OF THE DRAWINGS

[0060] The accompanying Figures, which are incorporated in and constitute a part of this specification, illustrate several aspects described below.

[0061] FIG. 1 is a schematic of the present invention according to a preferred embodiment, illustrating *in situ* PFAS destruction with chemically reduced TMOs under mild heating conditions in a shallow aquifer under an aqueous film-forming foam (AFFF)-impacted source area.

[0062] FIG. 2 is a schematic of various ways to form the reactive species from a metal oxide according to exemplary embodiments of the present invention.

[0063] FIGS. 3 and **4** are flow diagrams of process steps of exemplary embodiments of the present invention.

[0064] FIG. 5 shows an exemplary form of a chemically reduced TMO lattice.

[0065] FIG. 6 is a graph illustrating F-production from 200 ppb PFOS in DI Water with defluorination percentiles of the PFOS after 24 hrs incubation with chemically reduced ZnO, TiO_2, and activated carbon-supported titanate nanotubes (TNTs@AC) at pH =7 and 80 °C under anoxic conditions.

[0066] FIG. 7 is a graph illustrating PFOS data in rTMO reactors.

[0067] FIGS. 8A-8D are graphs exploring an additional commercial rTMO and different temperatures. **FIGS. 8A** and **8B** were conducted at 50°C illustrating the percent defluorination at

4 hours and 24, respectively. **FIGS. 8C** and **8D** were conducted at 80°C illustrating the percent defluorination at 4 hours and 24, respectively.

[0068] FIGS. 9-10 are **TABLES** with supporting technical data, where **TABLE 1** presents raw data of three types of reduced TMO (r-TMO) (Conditions: 1 g/L r-TMO, 25 mL 200 ppb PFOS, pH 7±0.1, 80 °C, dark, and 24 hrs reaction duration and **TABLE 2** presents raw data of three types of r-TMO (Conditions: 2 g/L r-TMO, 25 mL 200 ppb PFOS, pH 7±0.1, 80 °C, dark, and 24 hrs duration. F- was not detected in all blank controls. The total F^- number in 200 ppb PFOS is 129.1528 ppb if completely defluorinated.

[0069] FIG. 11 is a photograph of chemically-reduced TNTs@AC.

[0070] FIGS. 12-13 are graphs of results of defluorination of three samples from the TABLES of **FIGS. 9-10**.

DETAIL DESCRIPTION OF THE INVENTION

[0071] To facilitate an understanding of the principles and features of the various embodiments of the invention, various illustrative embodiments are explained below. Although exemplary embodiments of the invention are explained in detail, it is to be understood that other embodiments are contemplated. Accordingly, it is not intended that the invention is limited in its scope to the details of construction and arrangement of components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments and of being practiced or carried out in various ways. Also, in describing the exemplary embodiments, specific terminology will be resorted to for the sake of clarity.

[0072] It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural references unless the context clearly dictates otherwise. For example, reference to a component is intended also to include composition of a plurality of components. References to a composition containing "a" constituent is intended to include other constituents in addition to the one named.

[0073] Also, in describing the exemplary embodiments, terminology will be resorted to for the sake of clarity. It is intended that each term contemplates its broadest meaning as understood by those skilled in the art and includes all technical equivalents which operate in a similar manner to accomplish a similar purpose.

[0074] Ranges may be expressed herein as from "about" or "approximately" or "substantially" one particular value and/or to "about" or "approximately" or "substantially" another particular value. When such a range is expressed, other exemplary embodiments include from the one particular value and/or to the other particular value.

[0075] Similarly, as used herein, "substantially free" of something, or "substantially pure", and like characterizations, can include both being "at least substantially free" of something, or "at least substantially pure", and being "completely free" of something, or "completely pure".

[0076] By "comprising" or "containing" or "including" is meant that at least the named compound, element, particle, or method step is present in the composition or article or method, but does not exclude the presence of other compounds, materials, particles, method steps, even if the other such compounds, material, particles, method steps have the same function as what is named.

[0077] It is also to be understood that the mention of one or more method steps does not preclude the presence of additional method steps or intervening method steps between those steps expressly identified. Similarly, it is also to be understood that the mention of one or more components in a composition does not preclude the presence of additional components than those expressly identified.

[0078] The materials described as making up the various elements of the invention are intended to be illustrative and not restrictive. Many suitable materials that would perform the same or a similar function as the materials described herein are intended to be embraced within the scope of the invention. Such other materials not described herein can include, but are not limited to, for example, materials that are developed after the time of the development of the invention.

[0079] While exemplary embodiments provide for the *in situ* remediation of PFAS, the present technology can be applied in *ex situ* environments.

[0080] In exemplary remediation systems and methods, the present invention destroys containments in a treatment zone with the application of a reactive species, wherein efficient destruction of the containment occurs within a treatment pH range and within a treatment temperature range.

[0081] In exemplary embodiments, the treatment pH range is from 5-9, and the treatment temperature range is from 50°C to under 100°C.

[0082] In exemplary *in situ* embodiments, the reactive species is activated without light, but with heat. In exemplary *ex situ* embodiments, the reactive species can be activated with or without light.

[0083] In exemplary embodiments, the reactive species comprises a reduced metal oxide. The metal oxide can include binary, i.e., an oxide containing one type of metal (for example, TiO_2, ZnO, and other 3d transition metal oxides including, but not limited, to V, Cr. Mn, Fe, Co, Ni, and Cu), and tertiary, i.e., an oxide containing two types of metals (for example, Zinc Ferrite ($ZnFe_2O_4$, or ZFO) and other similar oxides that include multiple metals with oxygen).

[0084] The metal oxide can comprise a transition metal oxide (TMO), for example, a transition metal incorporated Bi-based metal oxide.

[0085] Of course, 3d transition metals may be preferred simply for their relative abundance, low costs, and low toxicity/biocompatibity.

[0086] In an exemplary embodiment as illustrated in **FIG. 1**, the present invention generates highly reactive species that can destruct PFAS via approaches that are practical to implement *in situ*. For example, electrons are activated from chemically reduced TMOs (e.g., reduced titanium dioxide (r-TiO_2) or reduced zinc oxide (r-ZnO)) in the treatment temperature range (e.g., a mildly elevated temperature (< 80 °C)) and reactive effectively with PFAS to generate inorganic fluoride and other degradation products.

[0087] The electrons are believed to exist in the shallow trap states close to the conduction band of the reduced material and therefore can be excited by a mild form of energy such as mild heat or far infrared (IR) irradiation, instead of ultraviolet or visible light, which requires much higher energy and is difficult to implement *in situ*.

[0088] While the activities of those heat- or IR-activated electrons have been harvested to drive reduction of small molecules such as water to H_2 and N_2 to NH_3, it is innovative to apply such reducing power to destruct a much larger and more complex molecule, such as a PFAS.

[0089] As shown in **FIG. 2**, forming the reactive species from a metal oxide can take many forms. For example, the preparation can include chemical reduction, hydrogenation, annealing in a reducing atmosphere or vacuum, electrochemical reduction, plasma, laser ablation, oxidation approaches and other methods.

[0090] The reduction of the metal oxide by chemicals can include $NaBH_4$ and other chemicals including low/zero valent metals, inorganic or organic carbonaceous materials - which would include activated carbon, biochar, carbon black, etc. Hydrogenation is at relatively high temperatures. The reduction can include oxidation of elemental/low valent metals (e.g., growing ZnO by oxidizing it in organic solvents). For ZFO, and similar tertiary oxides, annealing at a relatively high temperature, but in air, can also produce the reactive species with the necessary functionality.

[0091] As shown in **FIG. 3**, the present inventive approach **300** is a practical scenario for *in situ* treatment with controlled activation of highly reactive electrons, which can include the steps of introducing a reactive species into a contamination zone including contaminate **310**, activating the reactive species **320**, and reductively destroying the contaminate **330**.

[0092] In an exemplary embodiment, after creation of excess electrons in TMOs by reduction with a strong chemical reductant, injection/delivery **310** of a reduced TMO slurry into a PFAS-impacted contamination zone of an aquifer can form a treatment zone for source reduction or a permeable reactive barrier for plume treatment, following the best practice of *in situ* amendment injection, and the treatment zone/barrier is heated **320** to a desired temperature in the treatment temperature range (< 80 °C) to activate the stored electrons, which then degrades **330** the PFAS.

[0093] As shown in **FIG. 4**, the present inventive approach **400** can include introducing **410** a rTMO slurry into a subsurface contamination zone comprising PFAS, chlorinated solvents, etc., forming a subsurface treatment zone defined by a location of the rTMO slurry **412**, concentrating the contaminant from the subsurface contamination zone into the treatment zone **414**, increasing the temperature of the treatment zone to within the treatment temperature range (for example, below water's boiling point) **420**, catalyzing the release and activation of stored electrons in the rTMO in the treatment zone **422**, and reductively destroying and mineralizing target contaminants in the treatment zone that produces simple nontoxic end products **430**.

[0094] One of ordinary skill in the art will appreciate that the present invention works with general governing principals that extend the exemplary embodiments of materials and processes disclosed herein.

[0095] For example, one of ordinary skill in the art will appreciate that the reactive species needs to embody a sufficiently negative conduction band minimum (CBM) in order to be "negative

enough" to reduce PFAS, which is more negative than -0.3 eV. That within generally 0.3-0.5 eV below the CBM lie one or more defects states of the reduced metal oxide, which are generally created by reduction of the starting metal oxide and other means described herein. Generally, the higher the degree of the reduction, the better. With that said, commercially available TiO_2-X also worked to some degree in experiments.

[0096] Further, one of ordinary skill in the art will appreciate other terminologies associated with the defect states include oxygen vacancies (Ovs)/defects, shallow donors/donor states, and shallow traps. Some other ways to describe the materials are black TiO_2/tatania (or ZnO), TiO_2-2, ZnO_1-X, etc.)

[0097] Further, one of ordinary skill in the art will appreciate that "mild" heat (50°C to just below 100°C) is enough to mobilize the e^- in the defect states to the conduction band (CB), which is then able to reductively react with target contaminants.

[0098] Further, one of ordinary skill in the art will appreciate that adsorption on the surface of the material is believed to facilitate the reduction reaction and improve selectivity towards the target contaminant (vs. other solutes and water).

[0099] Further, one of ordinary skill in the art will appreciate that composite materials with carbon can provide additional adsorptive capacities and may increase efficacy.

[0100] Further, one of ordinary skill in the art will appreciate the present innovation need not involve the use of high-cost, low-abundance elements, including precious metals and rare earth elements.

[0101] The present inventive approach is a practical scenario for *in situ* treatment with controlled activation of highly reactive electrons, which itself can incorporate three steps: (i) creation of excess electrons in TMOs by reduction with a strong chemical reductant; (ii) injection/delivery of the reduced TMO slurry into PFAS-impacted aquifer to form a treatment zone for source reduction or a permeable reactive barrier for plume treatment, following the best practice of *in situ* amendment injection; and (iii) heating of the treatment zone/barrier to the desired temperature (< 80 °C) to activate the stored electrons to degrade PFAS.

[0102] Preliminary tests/results shown in **FIG. 6** illustrate feasibility of the inventive approach. Three chemically reduced TMOs or derivatives (ZnO, TiO_2, and activated carbon-supported

titanate nanotubes (TNTs@AC)) were prepared following the published protocol and incubated at 80°C with 200 μg/L (which is environmentally relevant, especially for source zones) of perfluorooctane sulfonic acid (PFOS) in buffered deionized water (pH = 7) for 24 hrs. The fluoride production at 24 hrs indicated defluorination ranging from ~33% to ~62% with the reduced ZnO and TNTs@AC showing the best performance.

[0103] This initial PFOS defluorination was conducted at neutral pH. This is a distinctive advantage of using a solid-phase electron source compared to a homogeneous system in which electrons are generated by other means in the solvated (or "free") form. In those systems, PFAS removal and defluorination is highly unfavorable at pH < 9.5 due to the reactions between the solvated electrons and protons at lower pH (i.e., relatively high proton concentrations). Being able to compete with protons and destruct PFAS under neutral pH makes the present invention much more feasible to implement *in situ*.

[0104] **FIGS. 8A-8D** illustrates three lab-prepared rTMOs plus one commercial rTMO (RC-TiO_2) at 50°C and 80°C. The results confirmed that deF was occurring in all materials (generally 80°C > 50°C). Fastest DeF kinetics based on F production at 4 hrs for 80°C with R-TNTs@AC.

[0105] In an exemplary embodiment, the present remediation technology can be implemented by a treatment system comprising materials prepared by a starting TMO material (such as TiO_2, ZnO) and any chemical reduction method that creates abundant shallowly trapped electrons within -0.3 eV of the conduction band which has a sufficiently negative reduction potential on the order of -0.3 eV, and/or reduced TMO materials modified or combined with other solid-state materials or chemical elements whose desirable electronic or adsorptive properties can improve the overall treatment performance, and/or a non-solid amendment (e.g., gas or liquid, or their aqueous solutions) added to the reaction system to improve reactivity, selectivity, and longevity, and/or heating methods and apparatus, and temporal and spatial temperature profile as a result, and/or alternative activation methods such as infrared or microwave heating, and other synergistic PFAS treatment systems that can work in tandem with the heat-activated reduced TMO system which include systems that convert perfluoroalkyl acid (PFAA) precursors to PFAAs or treat reaction byproducts (e.g., short chain PFAS).

[0106] In addition to the application of *in situ* groundwater remediation and destruction of PFAS, the present invention includes other embodiments, for example, *ex situ* destruction of PFAS by a

mixed-bed or fix-bed reactor with the reduced TMO as the reactant/media and an activation method such as heat, infrared irradiation (artificial or natural sunlight), and microwave heating, and/or *in situ* and *ex situ* destruction of other environmental contaminants that are reactive towards reductive treatment, such as chlorinated volatile organic compounds, metal and non-metal oxyanion (e.g., perchlorate, nitrate, chromate, arsenate/arsenite, selenate/selenite), insensitive munition compounds including 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine (NQ), and metal cations (copper, lead, mercury, cadmium).

[0107] The present disclosure incorporates by reference the entirety of the contents of the following documents:

[0108] SERDP. *2022 PFAS Workshop Summary Report.pdf.* https://serdp-estcp-storage.s3.us-gov-west-1.amazonaws.com/s3fs-public/2022-11/2022%20PFAS%20Workshop%20Summary%20Report.pdf?VersionId=QQn6tLnl7ezdnZypKtTJlTCGiLYxZfuP (accessed 2023-01-04).

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[0112] McGregor, R. *In Situ* Treatment of PFAS-Impacted Groundwater Using Colloidal Activated Carbon. *Remediat. J.* 2018, *28* (3), 33–41. https://doi.org/10.1002/rem.21558.

[0113] Carey, G. R.; Hakimabadi, S. G.; Singh, M.; McGregor, R.; Woodfield, C.; Van Geel, P. J.; Pham, A. L.-T. Longevity of Colloidal Activated Carbon for *in Situ* PFAS Remediation at

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[0114] McGregor, R. Six Pilot-scale Studies Evaluating the *in Situ* Treatment of PFAS in Groundwater. *Remediat. J.* 2020, *30* (3), 39–50. https://doi.org/10.1002/rem.21653.

[0115] Liu, C.; Hatton, J.; Arnold, W. A.; Simcik, M. F.; Pennell, K. D. *In Situ* Sequestration of Perfluoroalkyl Substances Using Polymer-Stabilized Powdered Activated Carbon. *Environ. Sci. Technol.* 2020, *54* (11), 6929–6936. https://doi.org/10.1021/acs.est.0c00155.

[0116] Zhang, X.; Zhang, G.; Zou, J. Nitrogen Reduction Utilizing Solvated Electrons Produced by Thermal Excitation of Trapped Electrons in Reduced Titanium Oxide. *New J. Chem.* 2018, *42* (8), 6084–6090. https://doi.org/10.1039/C8NJ00560E.

[0117] Zhang, G.; Zou, J.; Xu, X. Reduced 3d Transition Metal Oxides Work as Solid-State Sources of Solvated Electrons and Directly Inject Electrons into Water for H2 Production under Mild Thermal or IR Excitation. *Adv. Sustain. Syst.* 2018, *2* (1), 1700139. https://doi.org/10.1002/adsu.201700139.

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Implications to PFAS Remediation and Management. *Environ. Sci. Technol.* 2019, *53* (7), 3718–3728. https://doi.org/10.1021/acs.est.8b06648.

[0123] Bentel, M. J.; Liu, Z.; Yu, Y.; Gao, J.; Men, Y.; Liu, J. Enhanced Degradation of Perfluorocarboxylic Acids (PFCAs) by UV/Sulfite Treatment: Reaction Mechanisms and System Efficiencies at PH 12. *Environ. Sci. Technol. Lett.* 2020, *7* (5), 351–357. https://doi.org/10.1021/acs.estlett.0c00236.

[0124] Numerous characteristics and advantages have been set forth in the foregoing description, together with details of structure and function. While the invention has been disclosed in several forms, it will be apparent to those skilled in the art that many modifications, additions, and deletions, especially in matters of shape, size, and arrangement of parts, can be made therein without departing from the spirit and scope of the invention and its equivalents as set forth in the following claims. Therefore, other modifications or embodiments as may be suggested by the teachings herein are particularly reserved as they fall within the breadth and scope of the claims here appended.

CLAIMS

What is claimed is:

1. A method of forming a reactive species that can destruct per- and polyfluoroalkyl substances (PFAS).

2. The method of Claim 1, wherein the reactive species destructs PFAS in an *in situ* treatment.

3. The method of Claim 1, wherein the forming comprises reducing a transition metal oxide (TMO).

4. The method of Claim 3, wherein the reducing is chemically reducing.

5. The method of Claim 1 further comprising:

applying in a treatment zone the reactive species in proximity to one or more environmental contaminants comprising PFAS; and

heating the treatment zone from between 50°C to 100°C.

6. A method comprising:

applying in a treatment zone a reactive species in proximity to one or more environmental contaminants comprising per- and polyfluoroalkyl substances (PFAS); and

activating the reactive species in the treatment zone from between 50°C to 100°C.

7. The method of Claim 6, wherein the activating is selected from the group consisting of heating the reactive species, presenting the reactive species to infrared, and presenting the reactive species to microwave.

8. The method of Claim 6, wherein the activating comprises heating the reactive species in the treatment zone from between 50°C to 100°C.

9. The method of Claim 8, wherein the method is an *in situ* treatment of the one or more environmental contaminants.

10. The method of Claim 8, wherein the method is an *ex situ* treatment of the one or more environmental contaminants.

11. The method of Claim 8 further comprising chemically reducing a metal oxide to form the reactive species.

12. The method of Claim 11, wherein the metal oxide is a transition metal oxide (TMO).

13. The method of Claim 8, wherein the reactive species is selected from a group consisting of reduced titanium dioxide (r-TiO_2) or reduced zinc oxide (r-ZnO).

14. The method of Claim 8 further comprising:

catalyzing release and activation of stored electrons in the reactive species in the treatment zone; and

reductively destroying and mineralizing the PFAS in the treatment zone;

wherein the method is an *in situ* treatment of PFAS in ground water;

wherein the applying comprises applying a slurry of the reactive species; and

wherein the treatment zone has a treatment pH range from between 5 to 9.

15. An *in situ* treatment of one or more environmental contaminants with controlled activation of reactive electrons comprising:

presenting a material with a negative band gap into a treatment zone comprising the one or more environmental contaminants; and

heating the treatment zone to a treatment temperature to activate stored electrons to degrade one or more of the environmental contaminants.

16. The method of Claim 15, wherein one of the environment contaminants is PFAS; and

wherein the heating degrades the PFAS.

17. The method of Claim 15, wherein the presented material comprises a reduced TMO.

18. The method of Claim 15 further comprising forming the material with the negative band gap by chemically reducing a TMO.

19. The method of Claim 17, wherein the presenting comprises presenting the reduced TMO via injecting and/or delivering the reduced TMO in a slurry form.

20. The method of Claim 17, wherein the presenting comprises presenting the reduced TMO via injecting and/or delivering the reduced TMO in a slurry form into a PFAS-impacted aquifer to form the treatment zone for source reduction and/or a permeable reactive barrier for plume treatment.

21. The method of Claim 20, wherein the heating comprises heating the treatment zone/barrier to activate stored electrons in the reduced TMO to degrade the PFAS.

22. The method of Claim 21, wherein the heating comprises heating the treatment zone/barrier to between 50°C to 100°C.

23. An *in situ* treatment with controlled activation of highly reactive electrons comprising:

creating an excess of electrons in a TMO by reduction with a strong chemical reductant;

injecting/delivering the reduced TMO in a slurry into a PFAS-impacted aquifer to form at least one of (i) a treatment zone for PFAS reduction or (ii) a permeable reactive barrier for plume treatment of the PFAS; and

heating the treatment zone/barrier to between 50°C to 100°C to activate the stored electrons to degrade the PFAS.

24. A system comprising:

a reactive species;

a treatment zone comprising one or more environmental contaminants comprising per- and polyfluoroalkyl substances (PFAS); and

a heating means to heat the treatment zone;

wherein upon application of the reactive species in the treatment zone and heating of the treatment zone, the PFAS is degraded.

25. The system of Claim 24, wherein the heating means is configured to heat the treatment zone from between 50°C to 100°C.

26. The system of Claim 24, wherein the reactive species comprises a reduced TMO.

27. A system for the destruction of one or more environmental contaminants that are reactive towards a reductive treatment that activates electrons in a material;

wherein the material is selected from the group consisting of:

a material prepared from a starting TMO material and using a chemical reduction method to create shallowly-trapped electrons within -0.3 eV of the conduction band which has a sufficiently negative reduction potential on the order of -0.3 eV; and

a starting reduced TMO material modified or combined with other solid-state materials or chemical elements whose desirable electronic or adsorptive properties improve the overall treatment performance of the system.

28. The system of Claim 27 further comprising a non-solid amendment to improve one or more of reactivity, selectivity, and/or longevity of the material.

29. The system of Claim 27 further comprising one or more heating methods and/or heating apparatus.

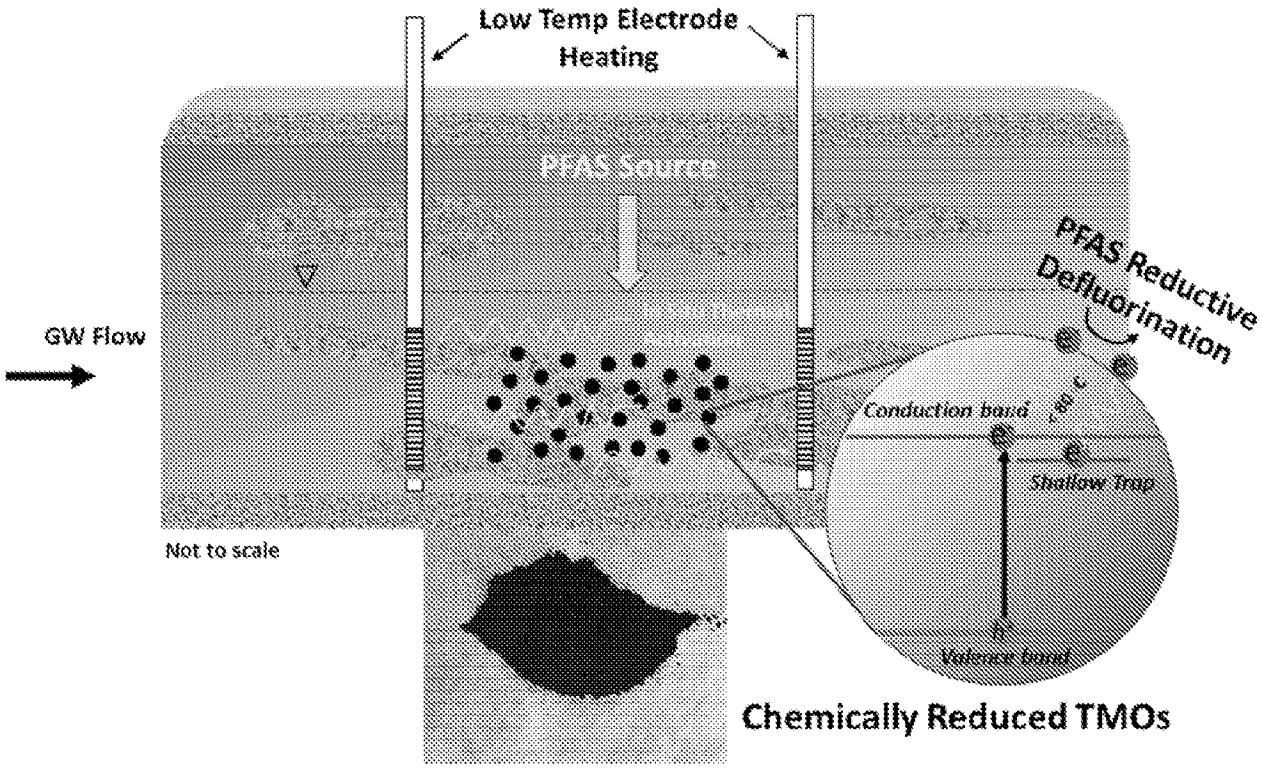
Low Temp Electrode Heating
PFAS Source
GW Flow
Not to scale
PFAS Reductive Defluorination
Conduction band
Shallow Trap
Valence band
Chemically Reduced TMOs

FIG. 1

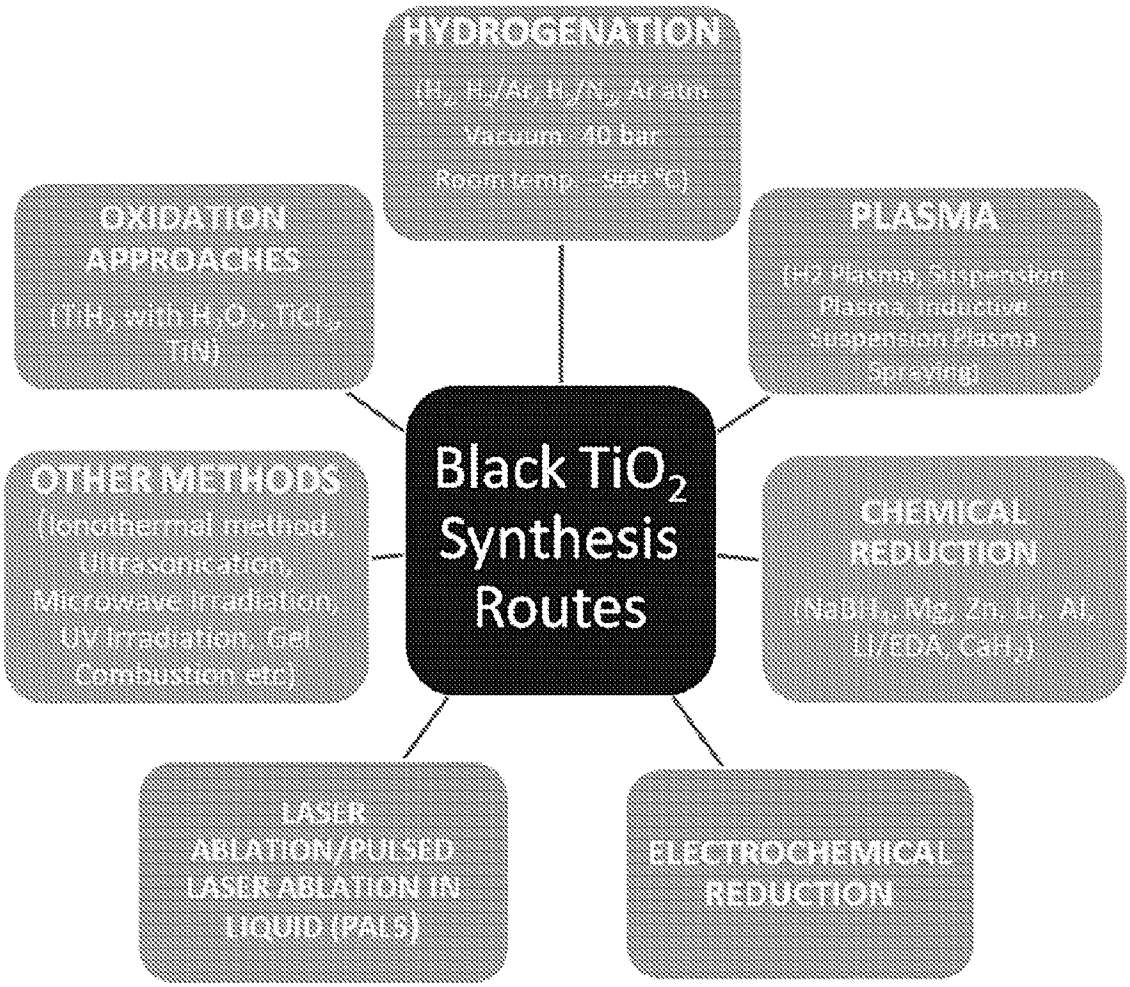
HYDROGENATION
(H_2, H_2/Ar, B_2H_6/N_2, Ar gas
Vacuum - 10 bar
Room temp. - 500 °C)
OXIDATION APPROACHES
(H_2 with H_2O_2, $TiCl_4$, TiN)
PLASMA
(H_2 plasma, Supersonic Plasma, Inductive suppression Plasma Spraying)
Black TiO_2 Synthesis Routes
OTHER METHODS
(Ionothermal method, Ultrasonication, Microwave Irradiation, UV Irradiation, Gel Combustion etc.)
CHEMICAL REDUCTION
($NaBH_4$, Mg, Zn, Li, Al, Li/EDA, C_8H_8)
LASER ABLATION/PULSED LASER ABLATION IN LIQUID (PALS)
ELECTROCHEMICAL REDUCTION

FIG. 2

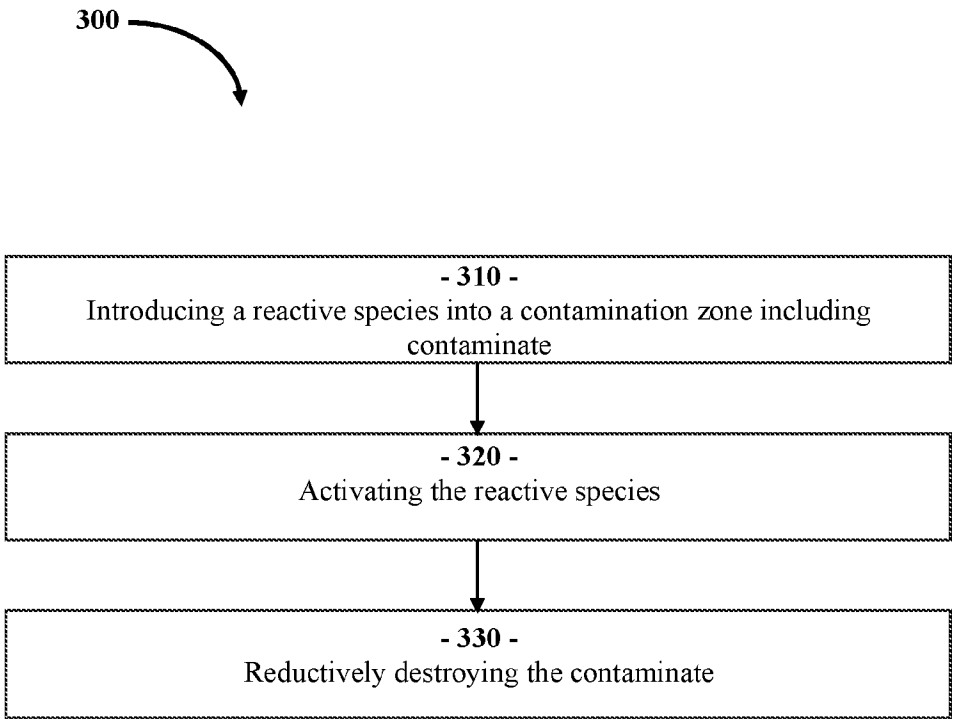
300
- 310 -
Introducing a reactive species into a contamination zone including contaminate
- 320 -
Activating the reactive species
- 330 -
Reductively destroying the contaminate

FIG. 3

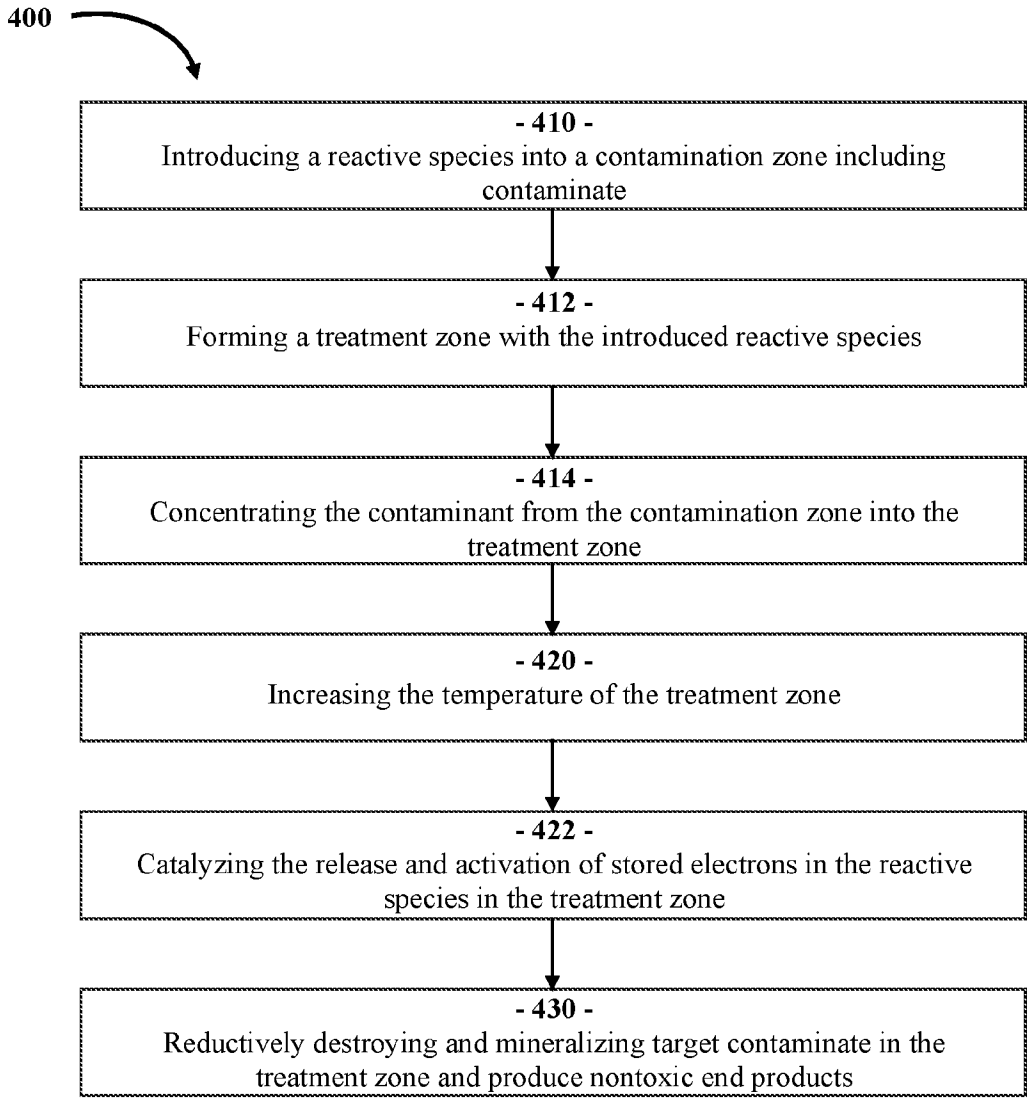
400
- 410 -
Introducing a reactive species into a contamination zone including contaminate
- 412 -
Forming a treatment zone with the introduced reactive species
- 414 -
Concentrating the contaminant from the contamination zone into the treatment zone
- 420 -
Increasing the temperature of the treatment zone
- 422 -
Catalyzing the release and activation of stored electrons in the reactive species in the treatment zone
- 430 -
Reductively destroying and mineralizing target contaminate in the treatment zone and produce nontoxic end products

FIG. 4

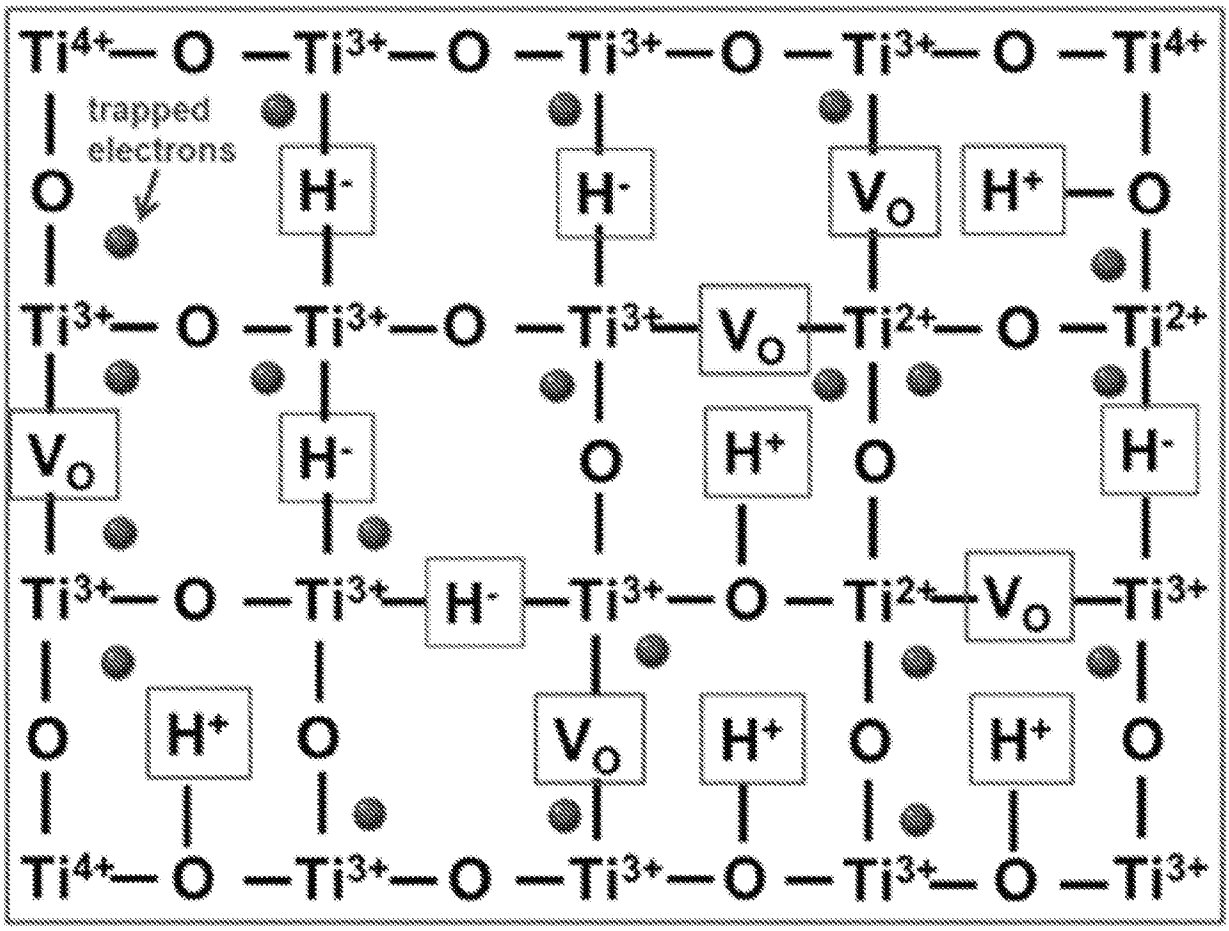

FIG. 5

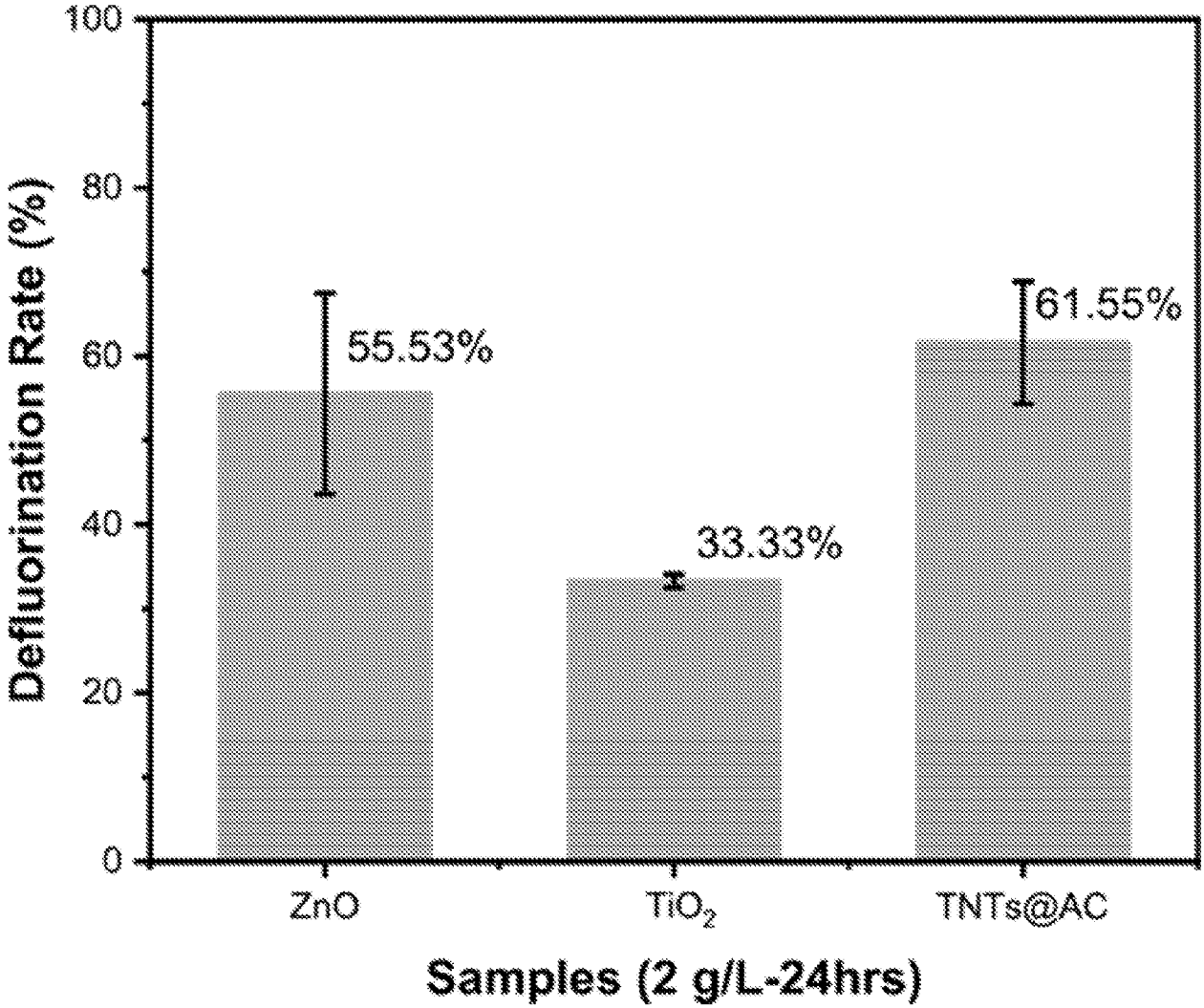
Defluorination Rate (%)
100
80
60
40
20
0
55.53%
33.33%
61.55%
ZnO
TiO2
TNTs@AC
Samples (2 g/L-24hrs)

FIG. 6

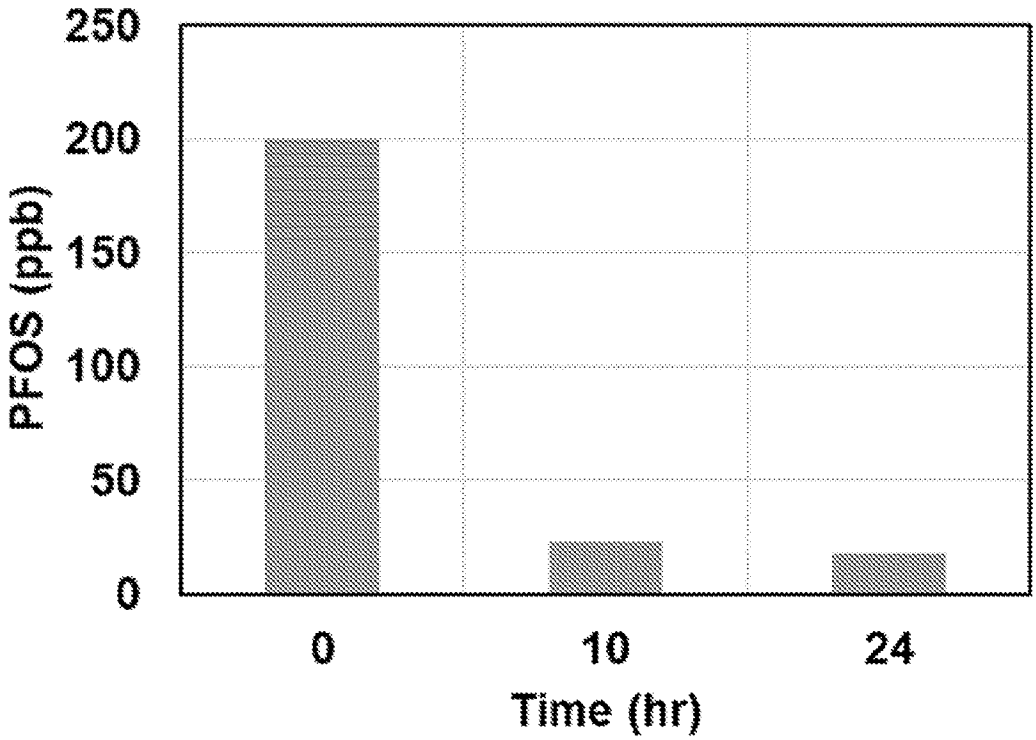

FIG. 7

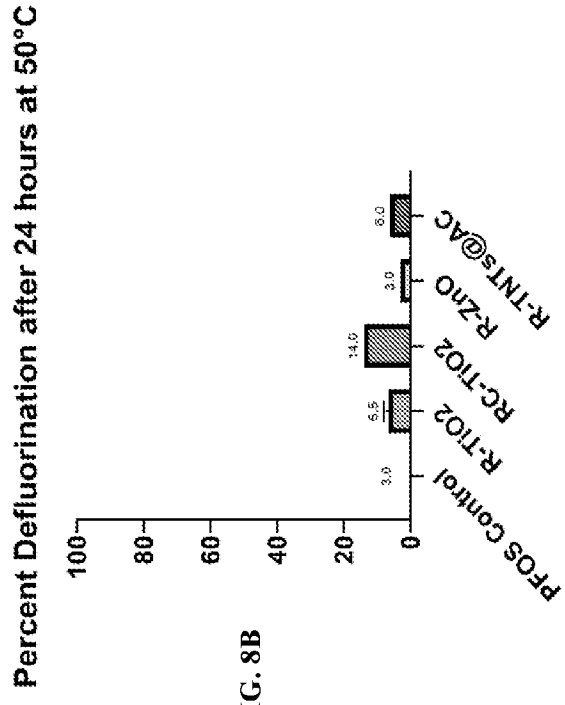

FIG. 8B

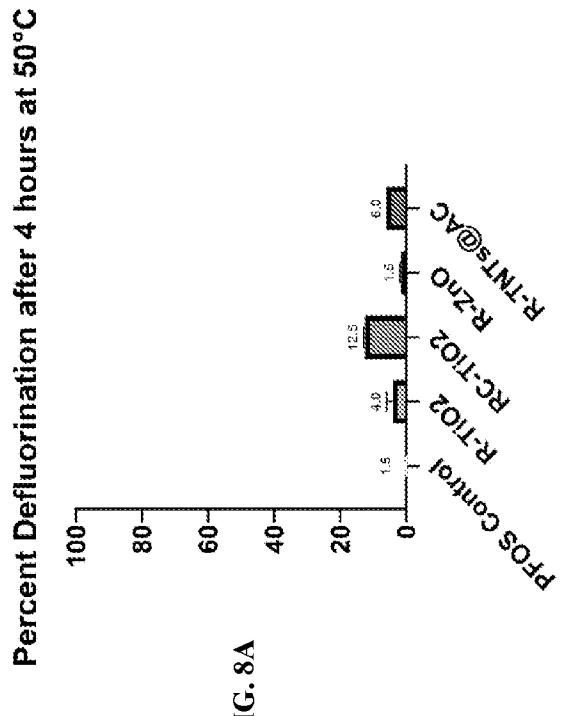

FIG. 8A

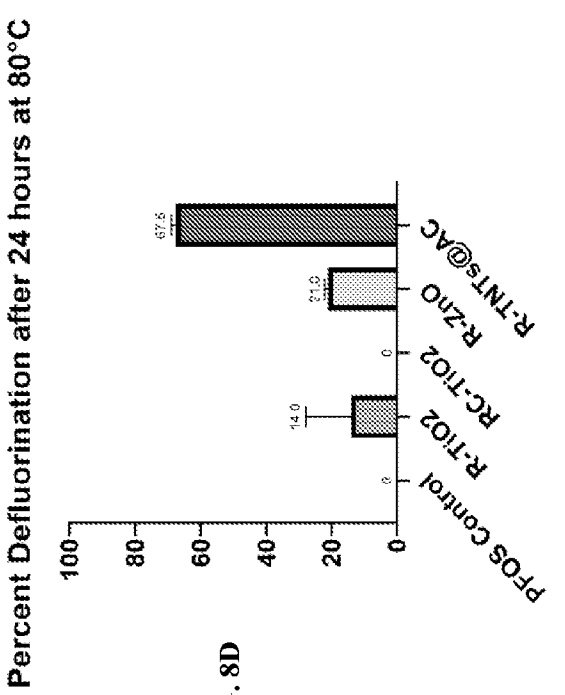

FIG. 8D

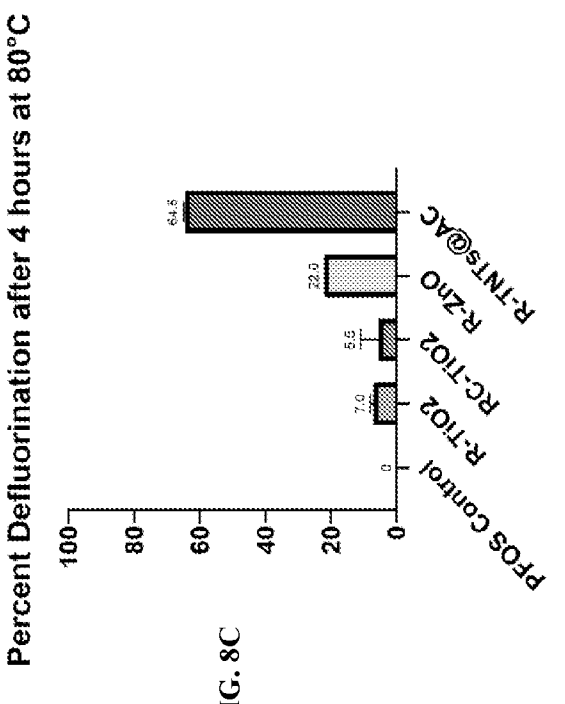

FIG. 8C

Sample	Retention Time (min)	Amount (ppb)	Defluorination (%)
ZnO-1	4.397	88.5082	68.52
ZnO-2	4.200	39.7003	30.74
TiO_2-1	4.510	26.7325	20.79
TiO_2-2	4.500	40.0910	31.04
TNTs@AC-1	4.427	27.3006	21.14
TNTs@AC-2	4.397	65.8007	50.94

TABLE 1. Raw data of three types of reduced TMO (Conditions: 1 g/L r-TMO, 25 mL 200 ppb PFOS, pH 7±0.1, 80 °C, dark, 24-hr reaction duration)

FIG. 9

Sample	Retention Time (min)	Amount (ppb)	Defluorination (%)
ZnO-1	4.397	88.5082	68.52
ZnO-2	4.200	39.7003	30.74
TiO_2-1	4.510	26.7325	20.79
TiO_2-2	4.500	40.0910	31.04
TNTs@AC-1	4.427	27.3006	21.14
TNTs@AC-2	4.397	65.8007	50.94

TABLE 2. Raw data of three types of r-TMO (Conditions: 2 g/L r-TMO, 25 mL 200 ppb PFOS, pH 7±0.1, 80 °C, dark, 24-hr duration

FIG. 10

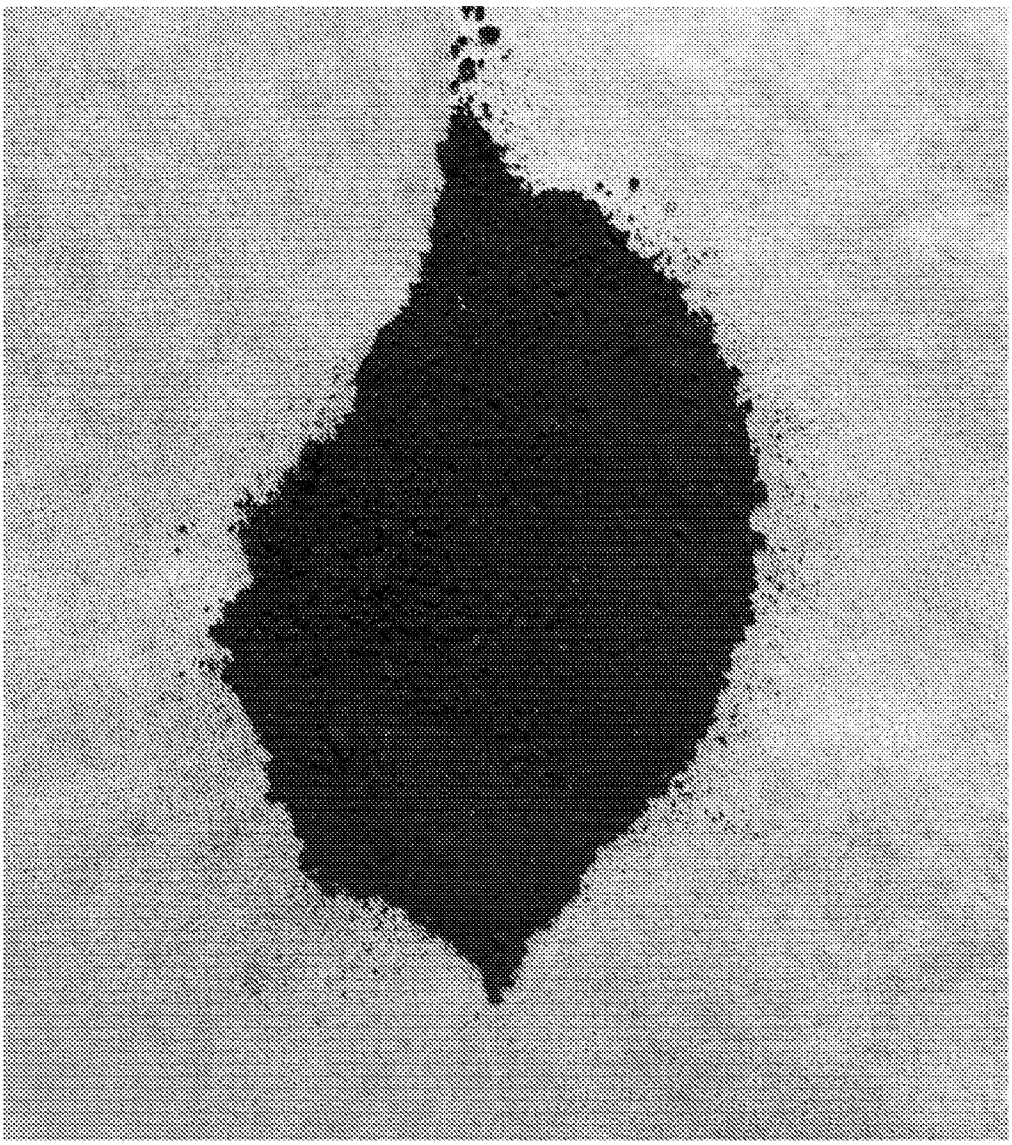

FIG. 11

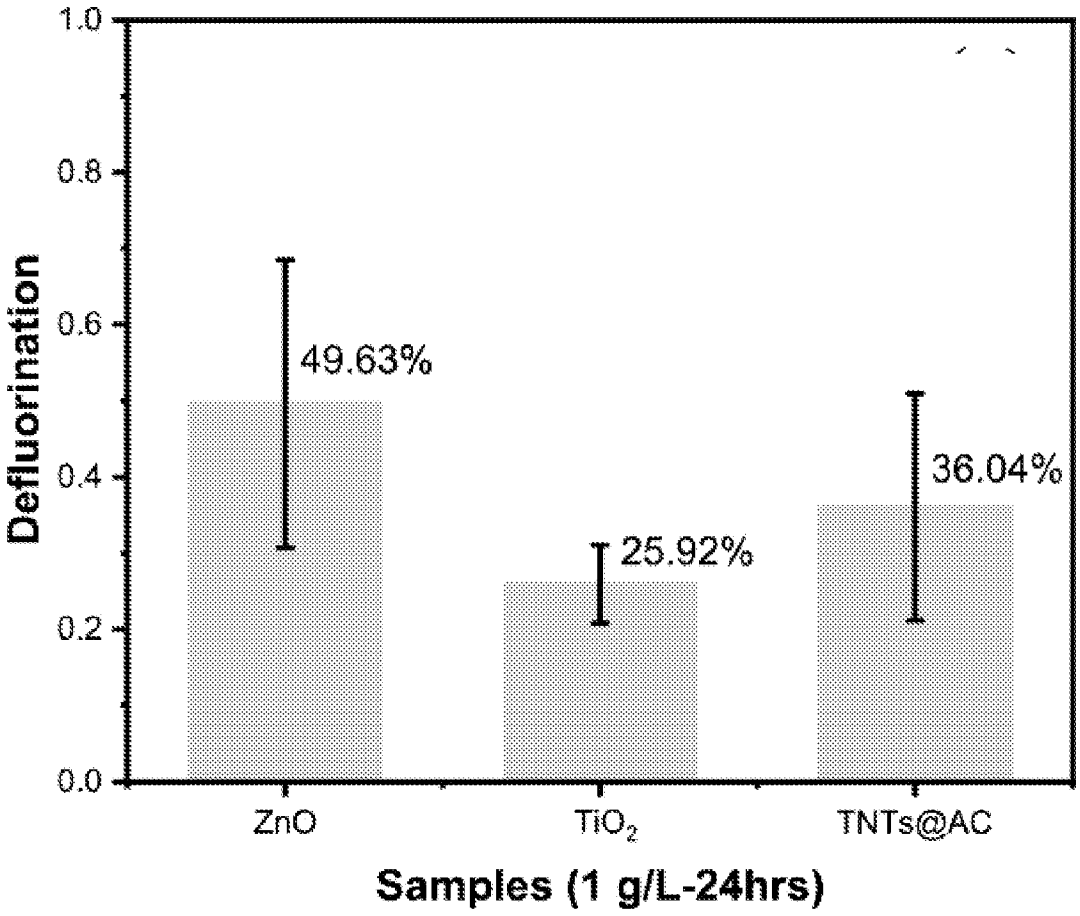
1.0
0.8
0.6
0.4
0.2
0.0
Defluorination
49.63%
25.92%
36.04%
ZnO
TiO2
TNTs@AC
Samples (1 g/L-24hrs)

FIG. 12

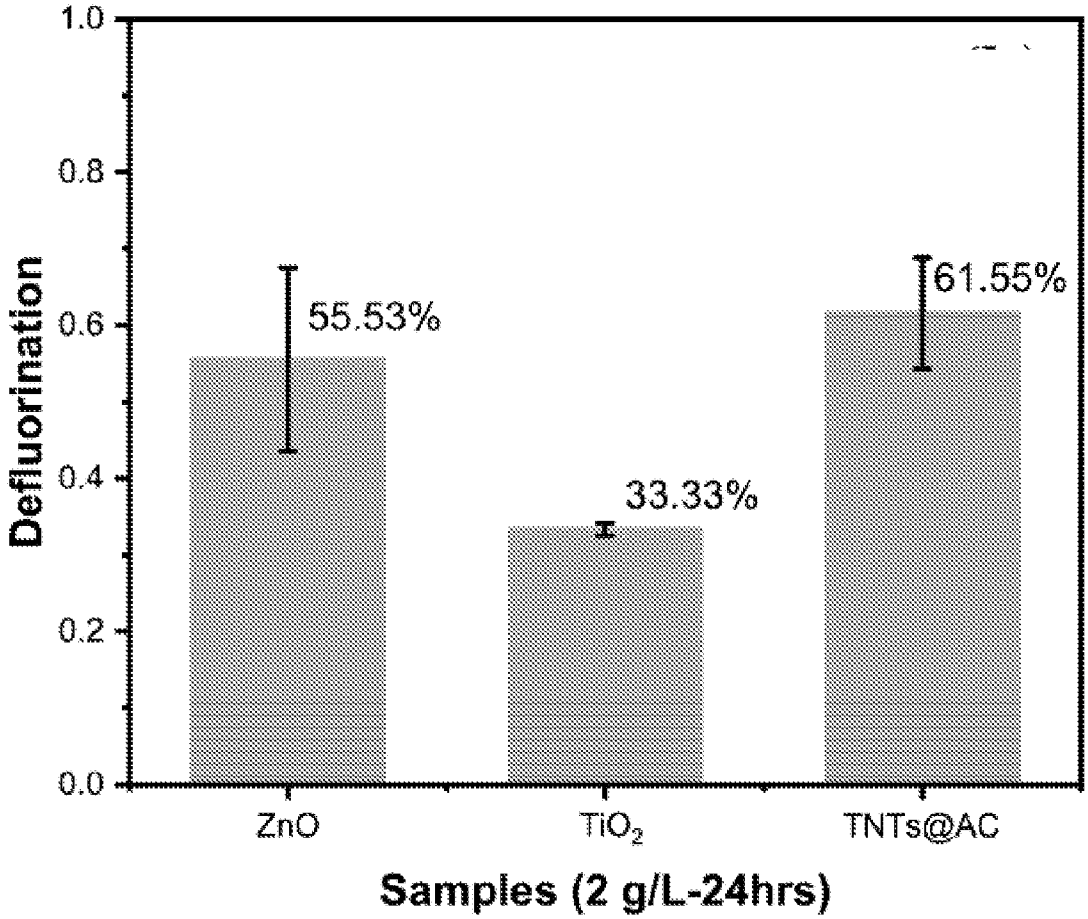
1.0
0.8
0.6
0.4
0.2
0.0
Defluorination
55.53%
33.33%
61.55%
ZnO
TiO2
TNTs@AC
Samples (2 g/L-24hrs)

FIG. 13