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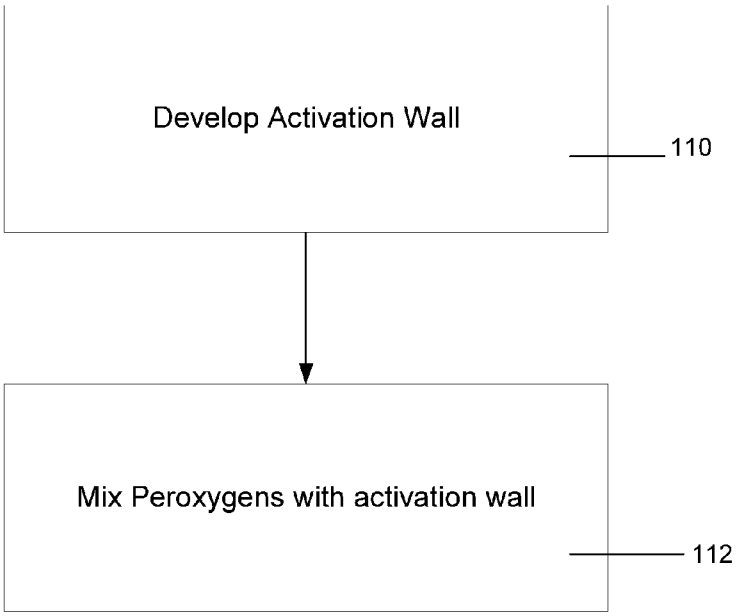

Figure 16

(57) Abstract: The disclosure is directed at a method and system of treating a contamined medium by injecting an inorganic supported metal substance to develop an activation wall proximate the contaminated medium; and passing peroxygens by the activation wall to develop a treatment substance for mixing with the contaminated medium to treat the hazardous organic compounds. The treatment substance is preferably a combination of per-oxyegns which are activated by an inorganic supported metal substance.

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SYSTEM AND METHOD FOR CHEMICAL OXIDATION OF ORGANIC COMPOUNDS USING NANO-METAL CATALYSTS TO ACTIVATE PEROXYGENS

FIELD OF THE DISCLOSURE

[0001] The present disclosure relates generally to treatment of a contaminated medium. More particularly, the present disclosure relates to chemical oxidation of organic compounds using nano-metal catalysts to activate peroxygens.

BACKGROUND OF THE DISCLOSURE

[0002] The future of the environment is a growing concern for society with many organizations and individuals looking at ways to preserve and protect the environment. One of these ways includes the treatment of contaminated mediums, such as land, water, or groundwater which has been contaminated by industrial factories.

[0003] More than two billion people depend on groundwater as a source of drinking water and therefore, it is a very valuable resource that should be protected. However, groundwater may be contaminated by many sources such as accidental spills, leaking underground storage tanks or municipal and industrial landfills leachate.

[0004] Different solutions have been attempted in the past, including soil excavation and pump-and-treat methods, however, there have proven costly and with limitations.

[0005] It is, therefore, desirable to provide a novel method and system for treatment of a contaminated medium.

SUMMARY OF THE DISCLOSURE

[0006] It is an object of the present disclosure to obviate or mitigate at least one disadvantage of previous systems for treating a contaminated medium.

[0007] In a first aspect, there is provided a method of treating hazardous organic compounds in a contaminated medium including injecting an inorganic supported metal substance to develop an activation wall proximate the contaminated medium; and passing peroxygens by the activation wall to develop a treatment substance for mixing with the contaminated medium to treat the hazardous organic compounds.

[0008] In another aspect, there is provided apparatus for treating hazardous organic compounds in a contaminated medium including peroxygens; and an inorganic supported metal substance.

[0009] Other aspects and features of the present disclosure will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the disclosure in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Embodiments of the present invention will now be described, by way of example only, with reference to the attached Figures, wherein:

Figure 1 is a schematic diagram of a system for treatment of a contaminated medium;

Figure 2 is a schematic diagram of the interaction between nano-particles and peroxygens;

Figure 3 is a chart showing experimental data from a first experiment for treating Tricholoroethene (TCE);

Figure 4 is a chart showing experimental data of concentration of TCE over time;

Figure 5 is a chart outlining experimental data of pH and Redox potential over molar ratio;

Figures 6 to 11 is a further chart outlining experimental data;

Figure 12 is a schematic diagram of a treatment substance;

Figure 13 is a schematic diagram of a setup for a second experiment;

Figures 14 to 15 are charts outlining data from a second experiment;

Figure 16 is a flowchart outlining a method of treating a contaminated medium in accordance with an embodiment; and

Figures 17a to 17f are charts outlining data from the experiments.

DETAILED DESCRIPTION

[0011] Generally, the present disclosure provides a method and system for treatment of a contaminated medium, such as the treatment of hazardous organic

compounds in a contaminated medium such as for the treatment, in situ or ex-situ, of water and wastewater from industrial plants.

[0012] In one embodiment, the method includes the introduction of a treatment substance which includes peroxygens and an inorganic supported metal substance, or inorganic supported nano-metal substance, to the contaminated medium to treat the hazardous compounds. The addition of the metal substance to the peroxygens causes a catalyzed reaction which produces a higher number of free radicals in comparison to known methods. The increased amount of free radicals may allow the reaction time or treatment time for the contaminated medium to be reduced.

[0013] Turning to Figure 1, a schematic diagram of a contaminated medium being treated is shown. A factory building 10, such as an industrial factory, is shown which includes an extraction well 12 located proximate the factory building 10. During normal operation, the factory building will produce contaminants which are typically stored in an underground storage tank (UST) 14. Over time, the UST 14 may start leaking some of these contaminants into the land near the factory building 10 thereby contaminating the ground or groundwater or the land surrounding the factory building 10. Once it is determined that there is a contaminated medium 16, treatment of this contaminated medium is required.

[0014] In one embodiment, a first well 18 is installed in order to inject peroxygens into the ground in order to assist in the treatment of the contaminated medium 16. The well 18 may be installed after it is determined that there is a contaminated medium, or the well 18 may be previously installed for other reasons and may be used for the injection process. A second well 20 is installed to allow for an inorganic supported metal substance, such as nano-metal particles to be injected as well. Alternatively, the inorganic supported metal substance may also be an inorganic nano-porous supported metal substance. As shown in Figure 1, the injection of the peroxygens causes the peroyxgens to move in the direction of arrows 22 while the injection of the metal substance causes the nano-metal particles to move in the direction of arrows 24. The injection of the nano-metal particles may also be seen as the creation of an activation wall 26.

[0015] Schematically, as shown at the bottom of Figure 1, the non-activated peroxygens 28 (or peroxides) interact with the activation wall 26 and become activated

peroxides 30 which then travel to a contaminated zone 32 to treat the contaminated zone (or contaminated medium 16) to remove the hazardous organic compounds within the contaminated medium.

[0016] After the contaminated medium is treated, the extraction well 12 may be used to extract the treated substances along with the peroygens and other matter. The extraction well 12 may also be used to evaluate the efficiency of the treatment.

[0017] Use of the nano-metal particles in the activation wall 26 increases the generation of free radicals which are used in the treatment process. The higher amount of free radicals results in a quicker treatment time which in some embodiments may be up to 100 times faster than known methods.

[0018] In operation, as schematically shown in Figure 16, an activation wall of an inorganic supported metal substance is developed 110 proximate the contaminated medium; and then peroxygens are passed by the activation wall 112 to develop a treatment substance for mixing with the contaminated medium to treat the hazardous organic compounds.

[0019] Turning to Figure 2, an exploded view of peroxygens interacting with an inorganic supported metal substance is shown. The non-catalyzed peroxygens 40, which may also be seen as non-activated peroxides, travel in the direction of arrows 42 and interact with the metal substance 44, seen as nano-metal particles, which are located on a surface of other particulates 46 such as sand grains. In a preferred embodiment, the nano-metal particles are nano-metal catalysts that are synthesized in a zero valent oxidation state and are supported by in-organic materials such as, but not limited to, metal additives or in-organic nano-porous media, or both. The addition of the in-organic material improves a subsurface migration potential of nano-metal catalysts and to enhance the calatalyzation efficiency towards peroxygens. After mixing with the metal substance 44, the peroxygens become activated peroxygens (reflected by arrows 48) and travel towards the contaminated medium 16 (of Figure 1) to treat the contaminated medium.

[0020] In an embodiment of the disclosure, the treatment substance is formed by combining iron based bimetallic nano-particles to peroxygens in order to activate the peroxygens. More specifically, in a preferred embodiment, bimetallic zero valent nano-particles (BZVNs) are combined with peroxygens. In a more preferred embodiment, the

treatment substance is either nano-Pd-Fe^0 or nano-Zn-Fe^0 combined with persulfate, nano-Co-Fe^0 combined with peroxymonosulfate or nano-Ag-Fe^0 combined with hydrogen peroxide.

[0021] In some embodiments, the nano-particles may be synthesized in order to change the nano-particles from an initial state to a bimetallic nano-particle state or to become a bimetallic nano-particle. This synthesis process causes the nano-particles to become bimetallic which improves or enhances the activation of the peroxygens when the two are mixed together thereby improving the treatment process.

[0022] In a preferred embodiment of this nano-particle synthesis, zero valent iron nano-particles were synthesized. One example of synthesizing zero valent iron nano-particles may be as follows:

[0023] A peristaltic pump (flow rate of 1.67 mL/min) was used to slowly drop $NaBH_4$ (0.25 M) onto the side of a Erlenmeyer flask containing $FeCl_3.6H_2O$ (0.045 M) to a volume ratio of 1:1 $NaBH_4$: $FeCl_3.6H_2O$ to produce the following reaction:

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0_{(s)\downarrow} + 3B(OH)_3 + 10.5H_2$$

[0024] This reaction occurred under nitrogen gas at ambient room (20 °C) temperature with vigorous mixing using a magnetic stirrer. The stock solutions of $NaBH_4$ and $FeCl_3.6H_2O$ were prepared with deoxygenated ultra-pure water. The precipitated iron was washed to remove excess cations and anions such as Cl^- and Na^+ (from $NaBH_4$ and $FeCl_3.6H_2O$) by centrifuging for 10 min at 15,000 rpm. The mass of the zero valent iron nano-particles produced was 2.57± 0.22 g/L of the mixture.

[0025] The process of depositing the second metal (Pd, Zn, Cr, Cu, Co, Cd, Ag, Mn, or Ni) on the zero valent iron surfaces was accomplished by acidifying the nano-particle surfaces with HCl (1 M) for a period of 60 seconds, followed by adding 1 % (wt/wt) [all the experiments were performed by adding 1 % load of the second metal except in one experiment in which a range of 0.1 % to 10 % was added] of the respective salts (e.g., $PdCl_2$) into the solution of zero valent iron nano-particles. The mixture was stirred for a minimum of two hours in zero headspace containers at ambient room temperature. The bimetallic nano-particles were washed by centrifugation and re-dispersed

in deoxygenated ultra-pure water. The reaction required to deposit the second metal on the zero valent iron surfaces is given by:

$$Pd^{2+} + Fe_{(s)}{}^{0} \rightarrow Pd^{0}_{\downarrow(s)} + Fe^{2+}$$

[0026] In one experiment, the interaction between the peroxygens and the inorganic supported metal substance was tested in order to verify the improvement in its use as a treatment substance. In the following description, ZVI stands for zero valent iron.

[0027] A comparison of the non-supported nano-metal catalyzed peroxygens with conventional treatment technologies were investigated. Six treatment methods were applied to treat Trichloroethene (TCE) (which was used in the experiment as a model compound of the hazardous organic compounds). Figure 3 is a chart outlining these test methods. The TCE was treated with nZVI-catalyzed persulfate, ZVI-catalyzed persulfate, Fe(II)-catalyzed persulfate, non-catalyzed persulfate, nano-ZVI and granular ZVI,. The kinetic study of the catalyzation ability of non-catalyzed persulfate and catalyzed persuflate with three different catalysts were investigated (as shown in the chart of Figure 4). The initial reaction rate for TCE oxidation by nZVI-catalyzed persulfate was very fast compared to ZVI-catalyzed persulfate, Fe(II)-catalyzed persulfate, and non-catalyzed persulfate.

[0028] In addition, pH and Redox potential of the nZVI/persulfate system (as shown in Figure 5) indicates that since nZVI is a relatively high reductive material, the nZVI catalyzed persulfate system yields a high oxidation condition even higher than the non-catalyzed persulfate due to the generation of the highly reactive free radicals such as the sulfate free radicals and the hydroxyl free radicals.

[0029] TCE treatment by bimetallic zero valent nano-particles (BZVN), such as supported nano-metal particles with in-organic materials (based on 1% (wt/wt) load of metal additives, was higher than that by the non-supported nano-metal particles. This is more clearly seen with respect to Figure 6. Thus, modifying the surfaces (such as via a synthesis process) of the nano-metal particles by adding palladium (or some other metals) results in an improvement in the treatment of TCE as the metal additives may cause a galvanic corrosion system on the surface of the nano-metal particles. In such a system, the metal additives act as catalysts (cathode) while the ZVI nano-particles act as an electron

donor (anode). Furthermore, it was observed that increasing the dosage of BZVN and persulfate causes an increase in the treatment efficiency (as shown in Figure 7).

[0030] Beside persulfate, two other peroxygens (peroxymonosulfate and hydrogen peroxide) were catalyzed by BZVN system in this experiment.

[0031] Peroxymonosulfate (HSO_5^-) was catalyzed by various BZVNs to treat TCE (based on 1% (wt/wt) load of the metal additives) at the molar ratio of 1/20/20 (Figure 8a) and 1/10/10 (Figure 8b) between TCE/peroxymonosulfate/nano-catalyst. In the reaction period of 20 seconds, > 99% of TCE was oxidized by using BZVN catalyzed peroxymonosulfate (with nine different BZVN) at the molar ratio of 1/20/20 between TCE/peroxymonosulfate/nano-catalyst compared to 72% by nano-Fe^0 catalyzed peroxymonosulfate, and < 4% TCE oxidation by non-catalyzed peroxymonosulfate.

[0032] At the molar ratio of 1/10/10 between TCE/peroxymonosulfate/nano-catalysts, TCE oxidation, in a 6 hour reaction period, was 14%, 71%, 92.1%, 93.7 %, 94.6 %, 95.8 %, 96.7%, 97.8%, 97.9%, 97.9%, and 98.6% for non-catalyzed peroxymonosulfate, nano-Fe^0 catalyzed peroxymonosulfate, nano-Ag-Fe^0 catalyzed peroxymonosulfate, nano-Cu-Fe^0 catalyzed peroxymonosulfate, nano-Zn-Fe^0 catalyzed peroxymonosulfate, nano-Cr-Fe^0 catalyzed peroxymonosulfate, nano-Ni-Fe^0 catalyzed peroxymonosulfate, nano-Cd-Fe^0 catalyzed peroxymonosulfate, nano-Mn-Fe^0 catalyzed peroxymonosulfate, nano-Pd-Fe^0 catalyzed peroxymonosulfate, and nano-Co-Fe^0 catalyzed peroxymonosulfate, respectively [Co-Fe^0 > Pd-Fe^0 = Mn-Fe^0 = Cd-Fe^0 > Ni-Fe^0 > Cr-Fe^0 > Zn-Fe^0 > Cu-Fe^0 > Ag-Fe^0]. Nano-Co-Fe^0 particles showed the best catalyzation efficiency toward peroxymonosulfate to treat TCE.

[0033] TCE oxidation by various dosages of nano-Fe^0 catalyzed H_2O_2, which may also be seen as the non-supported nano-metal particle, was investigated and results shown in Figure 9a. In general, the higher the dosage the higher the oxidation of TCE. For instance, at the molar ratio of 1/100/120 between TCE/H_2O_2/nano-Fe^0, the oxidation of TCE was > 90% in a 46 hour reaction period compared to ~ 50% TCE oxidation at the molar ratio of 1/20/20 between TCE/H_2O_2/nano-Fe^0. The mechanism of generating highly reactive free radicals in the H_2O_2/nano-Fe^0 system is given by:

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{+2} + 2H_2O \qquad (1)$$

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\bullet} + OH^{-} \qquad (2)$$

[0034] Nine different metals were deposited on the bare nano-Fe^0 (1% (wt/wt) load of metal additives) to enhance the catalyzation efficiency of nano-Fe^0 toward H_2O_2 to treat TCE. TCE oxidation by all the nine BZVN catalyzed H_2O_2 was higher than that by the bare nano-Fe^0 catalyzed H_2O_2 even at high molar ratio as 1/100/120 for TCE/ H_2O_2/ nano-Fe^0 as shown in Figure 9b. TCE oxidation in the reaction period of ~ 25 hours was 37%, 56%, 88%, 90%, 94%, 95%, 96%, 97%, 99%, and > 99% for non-catalyzed H_2O_2, nano-Fe^0 catalyzed H_2O_2, nano-Co-Fe^0 catalyzed H_2O_2, nano-Ni-Fe^0 catalyzed H_2O_2, nano-Cd-Fe^0 catalyzed H_2O_2, nano-Pd-Fe^0 catalyzed H_2O_2, nano-Mn-Fe^0 catalyzed H_2O_2, nano-Zn-Fe^0 catalyzed H_2O_2, nano-Cr-Fe^0 catalyzed H_2O_2, nano-Cu-Fe^0 catalyzed H_2O_2, and nano-Ag-Fe^0 catalyzed H_2O_2, respectively. Nano-Ag-Fe^0 particles were the most promising hydrogen peroxide catalysts.

[0035] The investigation of nano-Ag-Fe^0 particles was extended using various dosages of nano-Ag-Fe^0/ H_2O_2 to treat TCE as shown in Figure 9c. The oxidation of TCE in a three hour reaction period was 26%, 46%, 56%, 75%, 97%, and 97% for TCE/H_2O_2/nano-Ag-Fe^0 molar ratio of 1/0/20, 1/10/10, 1/20/20, 1/40/40, 1/80/80, and 1/100/100, respectively.

[0036] Generally, it was determined that BZVNs, seen as the supported nano-metal catalysts with in-organic materials were more promising catalysts for peroxygens (e.g., hydrogen peroxide, persulfate, and peroxymonosulfate) to treat TCE than the monometallic zero valent nano-particles (the non-supported nano-metal catalysts). For example, > 99% of TCE was treated in a 20 second reaction period by BZVN catalyzed peroxymonosulfate compared to 72% by nano-Fe^0 catalyzed peroxymonosulfate. In the investigation of nine different BZVNs, BZVNs have different ability to catalyze various oxidants. To illustrate, the highest TCE oxidation was achieved by nano-Pd-Fe^0 and nano-Zn-Fe^0 in the catalyzed persulfate system; nano-Co-Fe^0 and nano-Pd-Fe^0 in the catalyzed peroxymonosulfate system; and nano-Ag-Fe^0 in the catalyzed hydrogen peroxide system. In all the three oxidation systems, the higher the dosage the higher the oxidation of TCE. TCE oxidation by BZVN catalyzed peroxymonosulfate (at the molar ratio of 1:20:20 between TCE/oxidants/nano-catalysts) was higher than TCE oxidation by either BZVN catalyzed persulfate and BZVN catalyzed hydrogen peroxide systems.

[0037] Moreover, TCE treatment in the presence of six different geological materials (from various aquifers in North America) was treated successfully by BZVN catalyzed peroxygen. Figure 10 and 11 show TCE treatment by nano-Pd-Fe^0 catalyzed persulfate, nano-Zn-Fe^0 catalyzed persulfate systems, respectively.

[0038] In another experiment, in situ treatment of TCE using persulfate activated by a Nano-$PdFe^0$ activation wall was performed. A schematic set up of the experiment is shown with respect to Figure 13.

[0039] For the nano-particle Synthesis and characterization, Nano-Pd-Fe^0 particles were synthesized using a reduction method with sodium borohydride ($NaBH_4$) in which 1% wt/wt palladium was deposited onto the nano-Fe^0 surfaces. The average size of the synthesized nano-particles was 99 nm (± 30) as measured by high-resolution scanning electron microscopy (HR-SEM). The morphology of the synthesized nano-particles was cubic crystalline. Ferric oxyhydroxide (FeOOH) was observed on the surface of the fresh nano-particles using X-ray photoelectron spectroscopy (XPS).

[0040] For the collection and characterization of aquifer materials, uncontaminated core samples of aquifer materials were collected from a Canadian force base at Borden, Ontario. The aquifer materials were prepared by drying at 85 °C for at least 24 hours in an oven and then ground and passed through a 2-mm stainless steel sieve. Glass beads (soda-lime silica glass, 2 mm) were used in this study as the non-geological porous medium.

[0041] For the Experimental Design and Procedure, a plexiglas column (40 cm length x 3.8 cm inner diameter) was used to mimic the groundwater flow conditions. Each end of the column was filled with a multi-stage layer (1-2 cm thick) to retain the aquifer materials in the column. The multi-stage layer contains three stages of materials: a stainless steel sieve, glass wool, and finally glass beads. The column was filled with a geological porous medium in between two multi-stage layers. Next, 20 g of aquifer materials that had been contaminated by 0.0752 mL of pure TCE (99.8%), mixed with a solvent dye (Sudan IV), and allowed to sit for 48 hours in the dark at room temperature yielding 2% saturation, were placed in the middle of the column (13 cm from the inlet). The inlet of the column was connected with Teflon tubes that were attached to a peristaltic pump to regulate the water (or persulfate) inflow into the column.

[0042] A conceptual model for creating an activation wall of nano-Pd-Fe^0 particles to activate persulfate for the treatment of TCE-contaminated aquifer materials is presented in Figure 1. The laboratory experimental design of employing an activation wall approach in a one-dimensional sand packed column is presented in Figure 13. In the treatability test, Milli-Q water (18.2 MΩ cm^{-1}) was first injected through the inlet of the column, followed by the injection of a concentrated amount of nano-Pd-Fe^0 particles in a sampling port located 10 cm from the inlet to create an activation wall as shown in the laboratory experimental design. The slurry solution of nano-Pd-Fe^0 particles was injected manually using a syringe. Finally, persulfate was injected in the inlet, beginning the treatment period. All of the aqueous samples were collected from the outlet of the column. The samples were analyzed immediately after collection to avoid any time-induced changes.

[0043] The experiments were conducted under two different conditions. In each experiment or test, four parameters were varied: persulfate concentration, nano-iron concentration, flow rate, and treatment period.

[0044] In test 1, 598 mg of persulfate was injected into the inlet based on the calculated stoichiometry for treating the TCE source zone (110 mg of TCE).

$$3Na_2S_2O_8 + C_2HCl_3 + 4H_2O \rightarrow 2CO_2 + 9H^+ + 3Cl^- + 6Na^+ + 6SO_4^{2-}$$

[0045] Next, 70.1 mg of nano-Pd-Fe^0 particles, the amount needed to activate the persulfate (598 mg) based on the stoichiometry calculations, was injected into a sampling port of the column.

[0046] In test 2, the mass of persulfate used was almost 72 times greater than the stoichiometric amount needed to treat the TCE source zone. A lower injection flow rate was used (0.4 m/day instead of 1 m/day), and at least five pore volumes of Milli-Q water was injected prior the injection of persulfate (vs. one pore volume in test 1).

[0047] After the desired reaction period, the samples (0.7 mL) were collected from the outlet of the column and transferred into 2-mL vials for gas chromatography (GC) analysis. TCE was analyzed by a head-space solid phase micro-extraction (HS-SPME) method using an HP 6890 series GC equipped with a flame ionization detector (FID). The GC was connected to an auto sampler (Varian 8200).

[0048] The total iron, persulfate, and chloride were analyzed using a spectrophotometer (DR/2010, HACH). Persulfate anions were determined using known

methods with slight modifications. The total iron was determined using a standard method with 1,10-phenanthroline monohydrate. Chloride was determined by the mercuric thiocyanate method (HACH kits).

[0049] The aqueous pH, dissolved oxygen (DO), and electrical conductivity (EC) were determined using a pH/ISE meter, a DO meter, and conductivity meter, respectively.

[0050] After the experiment was set up, two treatability tests of TCE by Bimetallic Nano-particles/Persulfate were performed.

[0051] In test 1, the effluent dissolved-TCE concentration decreased with time when using either the non- or nano-activated persulfate systems (Figure 17a); however, the treatment process in both systems was not sufficient to reach the treatment goal, suggesting that the mass of persulfate or nano-Pd-Fe^0 particles should be much greater than the stoichiometric amounts for several possible reasons: (1) the contact time of persulfate with the TCE-contaminated layer was limited by the injection flow rate (1 m/day); (2) the ability of persulfate to treat TCE was limited by the presence of soil organic matter; and (3) the free radicals generated by the contact between persulfate and the activation wall of the nano-Pd-Fe^0 particles were scavenged by the soil organic matter and therefore unable to travel far from the generating point in the activation wall. .

[0052] The chloride released by the cleavage of the Cl-C bond in TCE molecules can also be used as an indicator of TCE treatment. In the effluent chloride concentration, a chloride peak was observed in the nano-Pd-Fe^0/persulfate system, whereas no chloride peak was observed in the non-activated persulfate system (Figures 17b and 17c), indicating that the activation wall of nano-Pd-Fe^0 particles enhances the treatment process of TCE source zone. The mass of the released chloride indicated of the treatment of ~ 9 % TCE. However, in the non-activated persulfate system, the effluent chloride concentration was similar to that of the chloride background concentration in the sand-packed column.

[0053] In the nano-activated persulfate system, the activation wall of nano-Pd-Fe^0 particles was deactivated after exposure to persulfate, However, after the deactivation of the nano-Pd-Fe^0 particles in the activation wall, the effluent chloride concentration was similar to the non-activated persulfate system.

[0054] In the nano-Pd-Fe^0 activated persulfate system, almost 35 % of the persulfate was consumed during the travel in the sand-packed column compared to ~ 10 %

persulfate consumption in the non-activated persulfate, indicating that ~ 25 % of the persulfate was consumed as a consequence of the interaction between persulfate and the activation wall of nano-Pd-Fe^0 particles. Thus, the consumption of persulfate was more than three orders of magnitude greater in the nano-Pd-Fe^0 activated persulfate system compared to the non-activated persulfate system. In the non-activated persulfate system, the organic matter and the native metals associated with aquifer materials can cause the decomposition of persulfate.

[0055] The effluent-dissolved oxygen concentration was almost identical in both the nano-Pd-Fe^0 activated persulfate and the non-activated persulfate systems (Figure 17d). Likewise, the effluent electrical conductivity (EC) concentration was also similar for both the nano-Pd-Fe^0 activated persulfate and the non-activated persulfate systems (Figure 17f).

[0056] The high buffering capacity of aquifer materials prevents pH from changing significantly in either system due to the dissolution of carbonate minerals such as calcite ($CaCO_3$) (Figure 17e).

[0057] In test 2, the effluent dissolved-TCE concentration was gradually decreased to below the method detection limit (1.6 µg/L); however, in the post-treatment period, the TCE concentration fluctuated above and below the method detection limit (as shown I Figure 14a).

[0058] Similarly to test 1, in the nano-Pd-Fe^0 activated persulfate system, a chloride peak was observed in the effluent chloride concentration, while no such peak was observed in the non-activated persulfate (as shown in Figures 14b and 14c), indicating that the TCE treatment was enhanced by employing the activation wall technique.

[0059] In the nano-Pd-Fe^0 activated persulfate system, the effluent persulfate concentration was similar to the influent persulfate concentration except in the first pore volume, in which 35 % of persulfate concentration was reduced, indicating that the activation wall of nano-Pd-Fe^0 decreased in the effluent persulfate concentration in the first pore volume. However, it is probable that after the deactivation of the nano-Pd-Fe^0 in the activation wall, the effluent persulfate concentration reached the influent persulfate concentration. Unlike test 1, as a result of using a high persulfate concentration (i.e., 30 g/L), the organic matter and the native metals in the aquifer materials cause an

insignificant decrease in the effluent persulfate concentration, as was found in the case of the non-activated persulfate system (as shown in Figures 14b and 14c).

[0060] The pH, DO, and EC were similar for the nano-Pd-Fe^0 activated persulfate and the non-activated persulfate systems. In test 2, the effluent dissolved oxygen concentration was significantly higher as a result of using a higher persulfate concentration than in test 1.

[0061] A mobility test of bimetallic nano-particles in non-geological porous medium was also performed. For the injection of nano-Fe^0 particles in a glass-bead-packed column, the effluent iron concentration was less than 6 % of the influent iron concentration; in contrast, this value was 100 % for the injection of nano-Pd-Fe^0 particles (as shown in Figure 15). Nano-Fe^0 particles are effectively filtered with glass beads because of the large size of the aggregated and agglomerated particles, whereas the nano-Pd-Fe^0 particles, which are less agglomerated, can be detected at the full iron concentration at the outlet. Three mechanisms are responsible of the filtration of nano-particles in porous media: Brownian diffusion, interception, and sedimentation. Brownian diffusion is the main process causing the retention of nano-particles in porous media. Therefore, it was determined that iron-based bimetallic nano-particles are mobile (with relatively poor mobility) in non-geological porous media.

[0062] Iron-based bimetallic nanoparticles have a much longer dispersion time in aqueous systems than iron-based monometallic nanoparticles. It was determined that the slurry solution of nano-Pd-Fe^0 particles was well dispersed in the solution, even after 6 weeks, whereas the dispersion of the slurry solution of nano-Fe^0 particles lasted for less than an hour. Nano-Fe^0 particles are rapidly aggregated and agglomerated due to the attractive forces between nanoparticles, such as the magnetic attractive force. As a result, the agglomerated nanoparticles are precipitated in aqueous systems by the gravitational force. In the case of nano-Pd-Fe^0 particles, the second metal deposited on the surfaces of nano-Fe^0 particles may enhance the repulsive forces, countering the attractive forces, as in the case of the polymer coated nano-Fe^0 particles.

[0063] Turning to Figure 12, a schematic diagram of a treatment substance for use in treating hazardous organic compounds is shown. The combination of peroxygens 100

with a bimetallic nZVI substance 102 produces the treatment substance 104 for use in treating a contaminated medium such as groundwater.

[0064] In another embodiment of the disclosure, there is provided a system and method of in situ chemical oxidation (ISCO) which may be defined as using chemical oxidizing agents to treat contaminated materials.

[0065] The above-described embodiments of the present invention are intended to be examples only. Alterations, modifications and variations may be effected to the particular embodiments by those of skill in the art without departing from the scope of the invention, which is defined solely by the claims appended hereto.

What is claimed is:

1. A method of treating hazardous organic compounds in a contaminated medium comprising:

injecting an inorganic supported metal substance to develop an activation wall proximate the contaminated medium; and

passing peroxygens by the activation wall to develop a treatment substance for mixing with the contaminated medium to treat the hazardous organic compounds.

2. The method of Claim 1 wherein the peroxygens are selected from a group consisting of persulfate, peroxymonosulfate, hydrogen peroxide, carbon peroxide or any catalyzed chemical oxidants.

3. The method of Claim 1 wherein the metal substance is nano-metal particles.

4. The method of Claim 3 wherein the nano-metal particles are in a zero valent oxidation state.

5. The method of Claim 4 wherein the nano-metal particles are selected from the group consisting of iron, zinc, silver, palladium, cobalt, platinum, manganese, cadmium,copper, gold, nickel, titanium and chromium.

6. The method of Claim 1 wherein the inorganic supported metal substance comprises metal additives or inorganic nano-porous media.

7. The method of Claim 6 wherein the metal additives are selected from a group consisting of gold, iron, zinc, silver, palladium, cobalt, platinum, manganese, cadmium, and chromium.

8. Apparatus for treating hazardous organic compounds in a contaminated medium comprising:

peroxygens; and

an inorganic supported metal substance.

9. The apparatus of Claim 8 wherein the inorganic supported metal substance are nano-scale zero valent iron particles (nZVI).

10. The apparatus of Claim 9 wherein the nZVI are bimetallic or multi-metallic nano-particles.

11. The apparatus of Claim 8 wherein the peroxygens are selected from a group consisting of persulfate, peroxymonosulfate, hydrogen peroxide, carbon peroxide or any catalyzed chemical oxidants

12. The apparatus of Claim 8 wherein the nano-metal supported metal substance are nano-metal particles.

13. The apparatus of Claim 12 wherein the nano-metal particles are selected from the group consisting of iron, zinc, silver, palladium, cobalt, platinum, manganese, cadmium, and chromium.

14. The apparatus of Claim 8 wherein the inorganic supported metal substance comprises metal additives or inorganic nano-porous media.

15. The apparatus of Claim 14 wherein the metal additives are selected from a group consisting of gold, iron, zinc, silver, palladium, cobalt, platinum, manganese, cadmium, and chromium.

16. The method of Claim 6 wherein the inorganic nano-porous media is nano-porous silica or nano-porous zeolite.

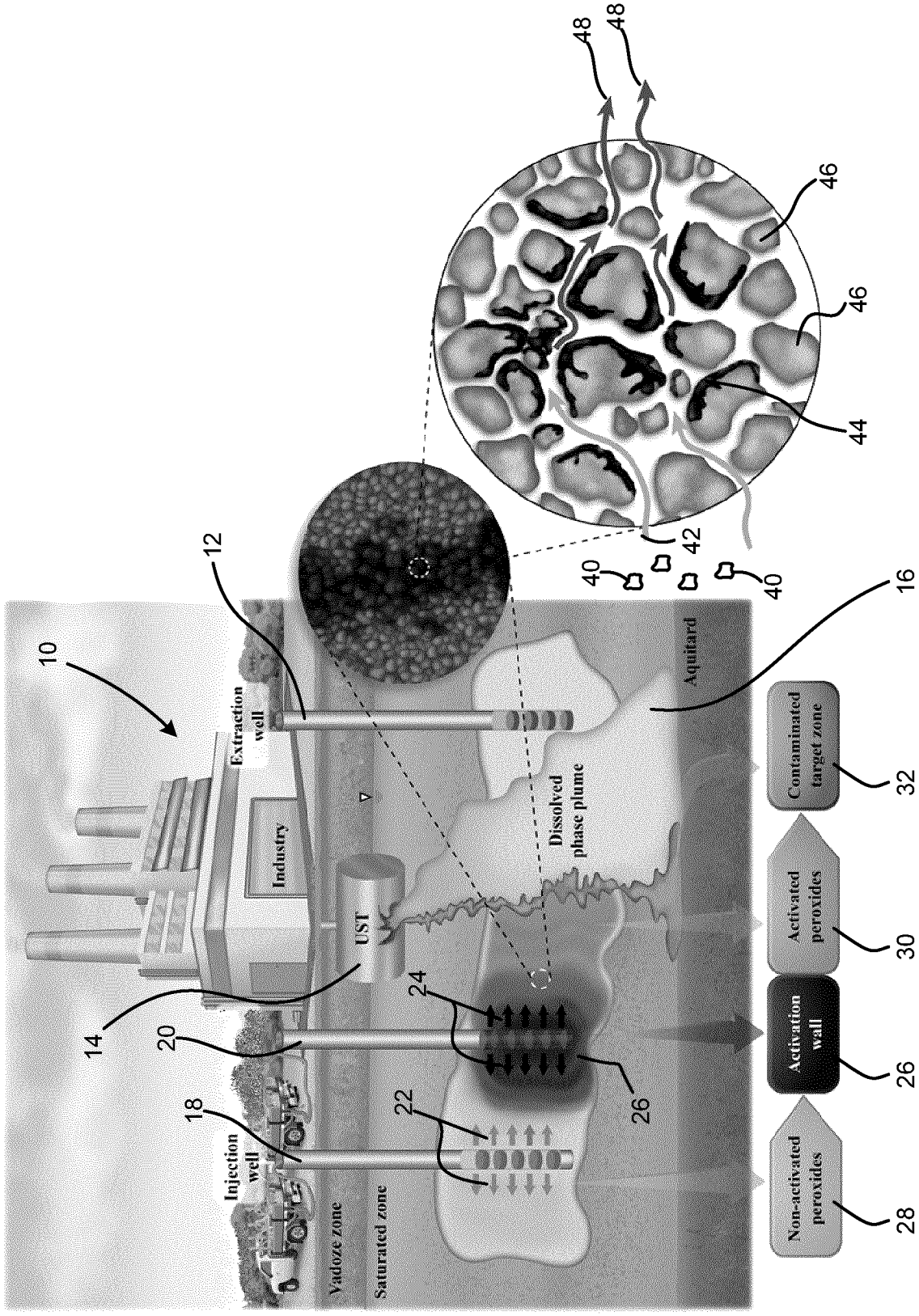


Figure 1

Figure 2

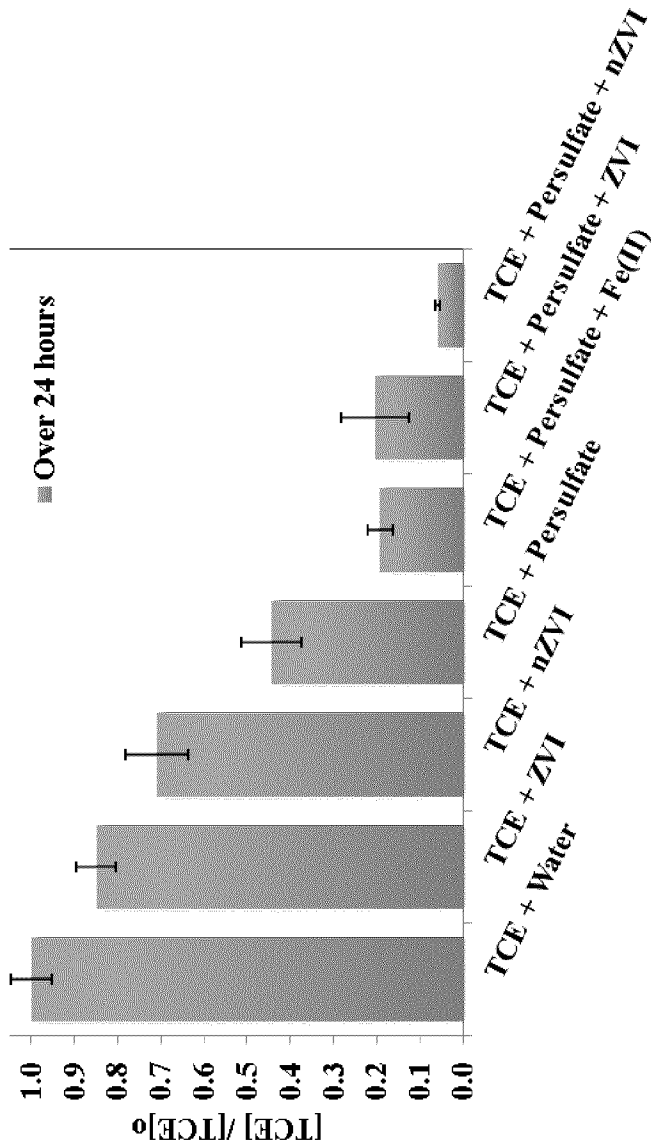

Over 24 hours
[TCE] /[TCE]o
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
TCE + Water
TCE + ZVI
TCE + nZVI
TCE + Persulfate
TCE + Persulfate + Fe(II)
TCE + Persulfate + ZVI
TCE + Persulfate + nZVI

Figure 3

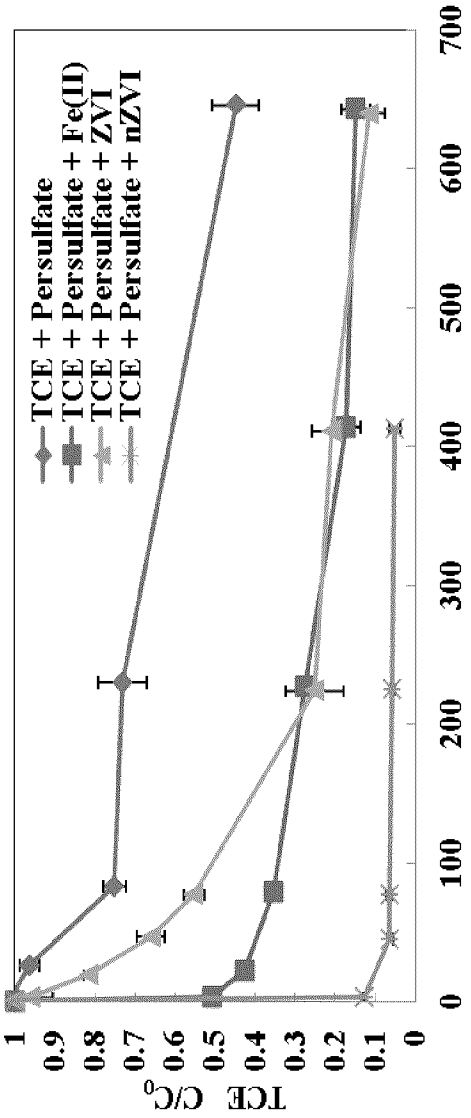

TCE + Persulfate
TCE + Persulfate + Fe(II)
TCE + Persulfate + ZVI
TCE + Persulfate + nZVI
TCE C/C0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
100
200
300
400
500
600
700
Time (min)

Figure 4

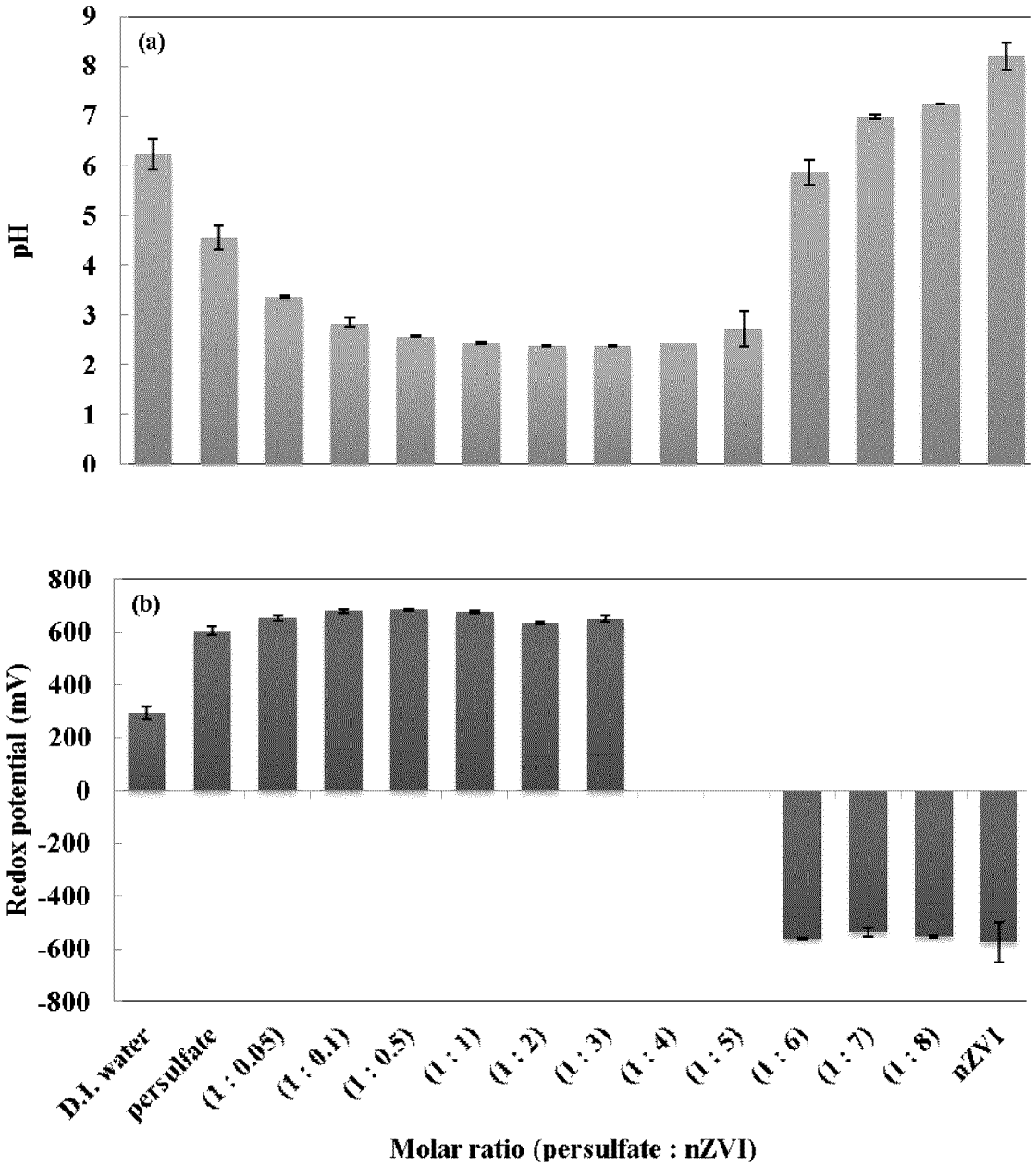

(a)
pH
9
8
7
6
5
4
3
2
1
0
(b)
Redox potential (mV)
800
600
400
200
0
-200
-400
-600
-800
D.I. water
persulfate
(1 : 0.05)
(1 : 0.1)
(1 : 0.5)
(1 : 1)
(1 : 2)
(1 : 3)
(1 : 4)
(1 : 5)
(1 : 6)
(1 : 7)
(1 : 8)
nZVI
Molar ratio (persulfate : nZVI)

Figure 5

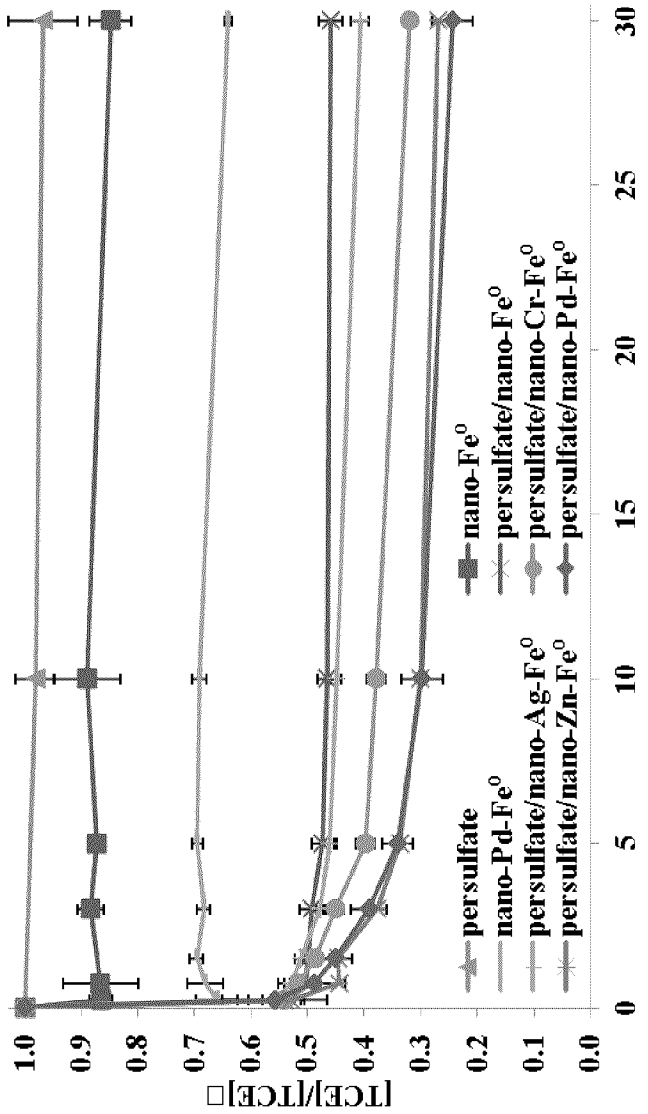

[TCE]/[TCE]□
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
5
10
15
20
25
30
min
persulfate
nano-Fe°
nano-Pd-Fe°
persulfate/nano-Fe°
persulfate/nano-Ag-Fe°
persulfate/nano-Cr-Fe°
persulfate/nano-Zn-Fe°
persulfate/nano-Pd-Fe°

Figure 6

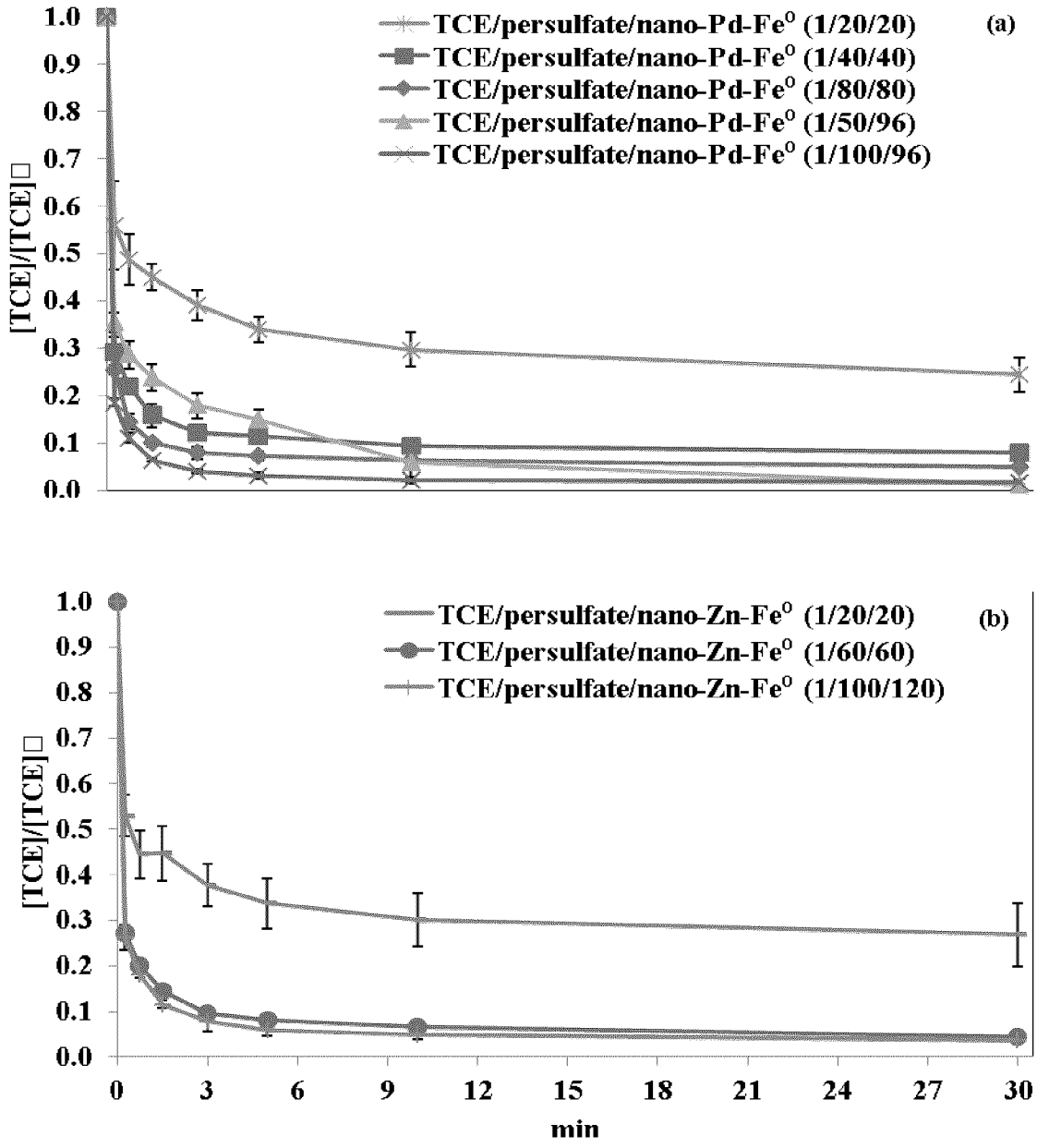

TCE/persulfate/nano-Pd-Fe^0 (1/20/20)
TCE/persulfate/nano-Pd-Fe^0 (1/40/40)
TCE/persulfate/nano-Pd-Fe^0 (1/80/80)
TCE/persulfate/nano-Pd-Fe^0 (1/50/96)
TCE/persulfate/nano-Pd-Fe^0 (1/100/96)
(a)
[TCE]/[TCE]□
TCE/persulfate/nano-Zn-Fe^0 (1/20/20)
TCE/persulfate/nano-Zn-Fe^0 (1/60/60)
TCE/persulfate/nano-Zn-Fe^0 (1/100/120)
(b)
[TCE]/[TCE]□
min

Figure 7

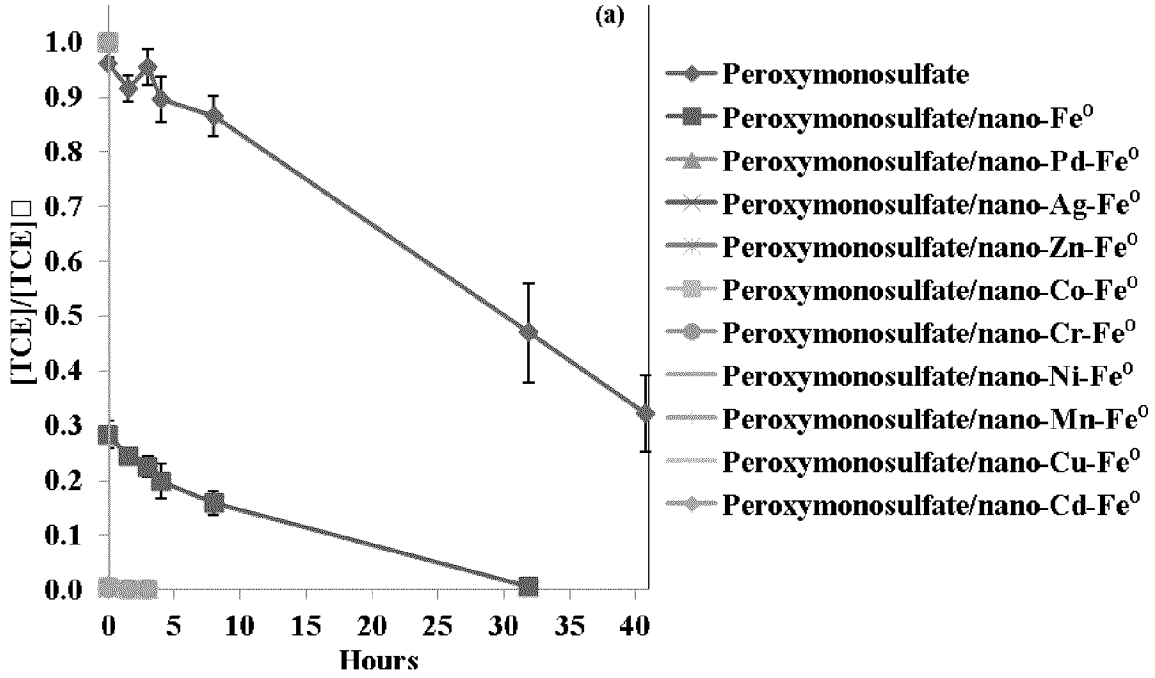


Figure 8a

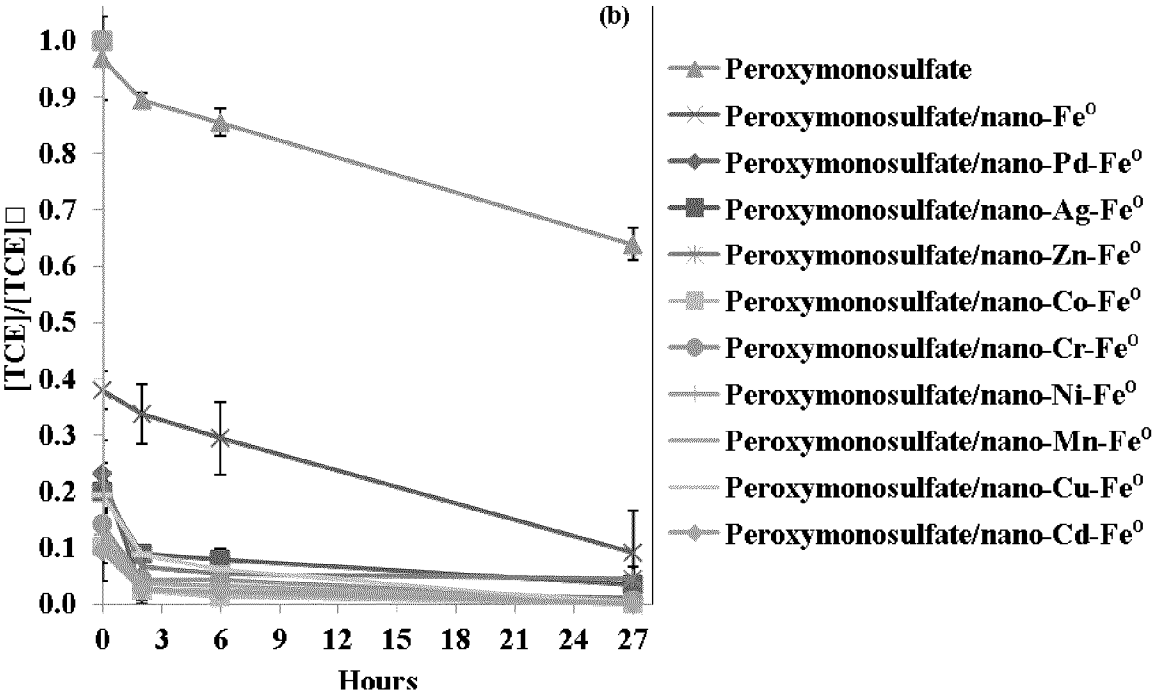


Figure 8b

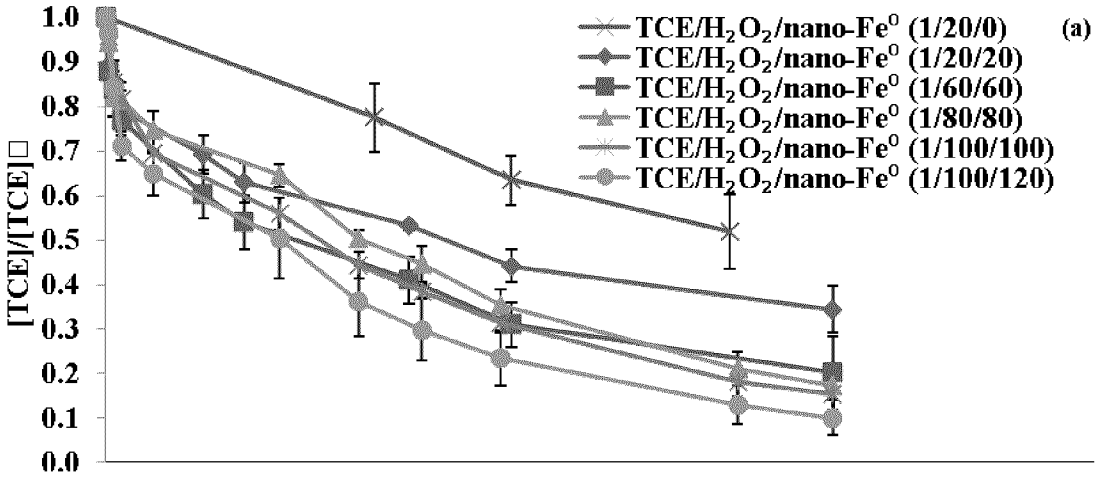


Figure 9a

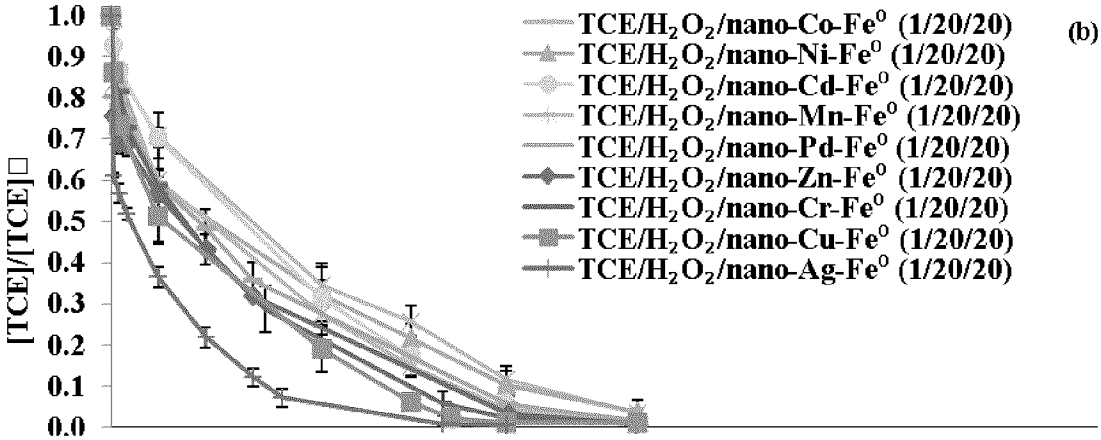


Figure 9b

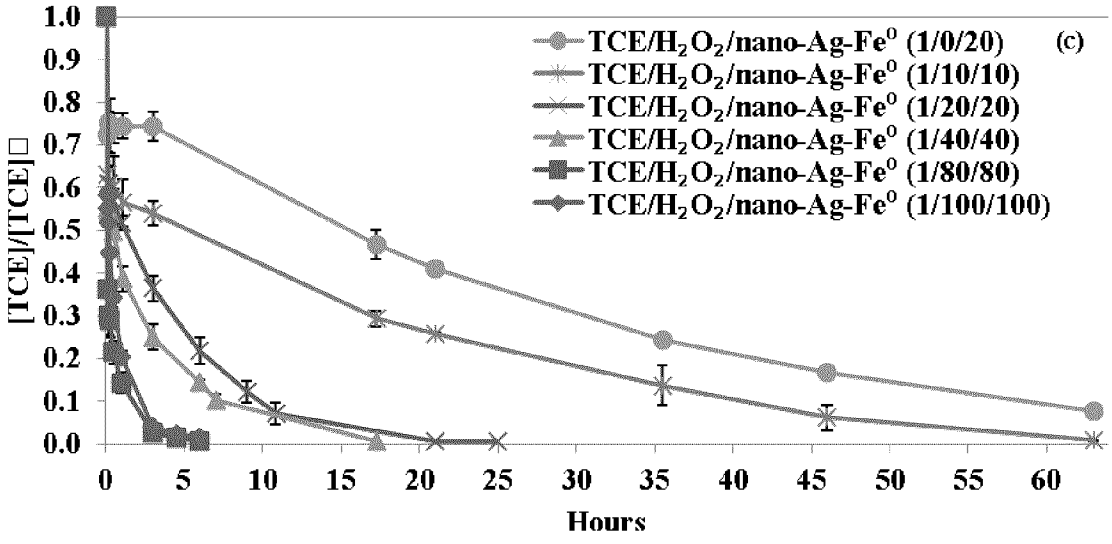


Figure 9c

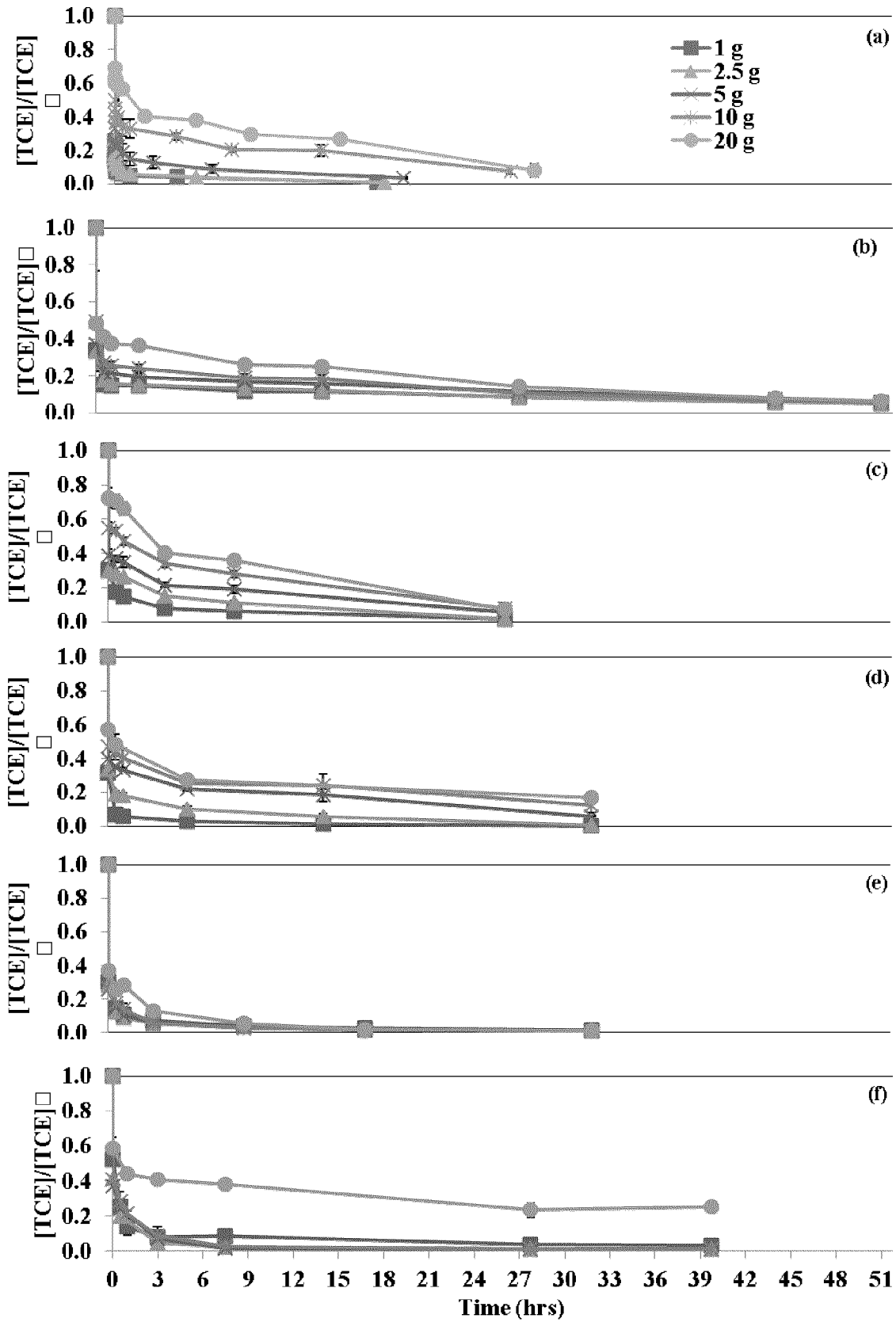

(a)
(b)
(c)
(d)
(e)
(f)
1 g
2.5 g
5 g
10 g
20 g
[TCE]/[TCE]□
1.0
0.8
0.6
0.4
0.2
0.0
0 3 6 9 12 15 18 21 24 27 30 33 36 39 42 45 48 51
Time (hrs)

Figure 10

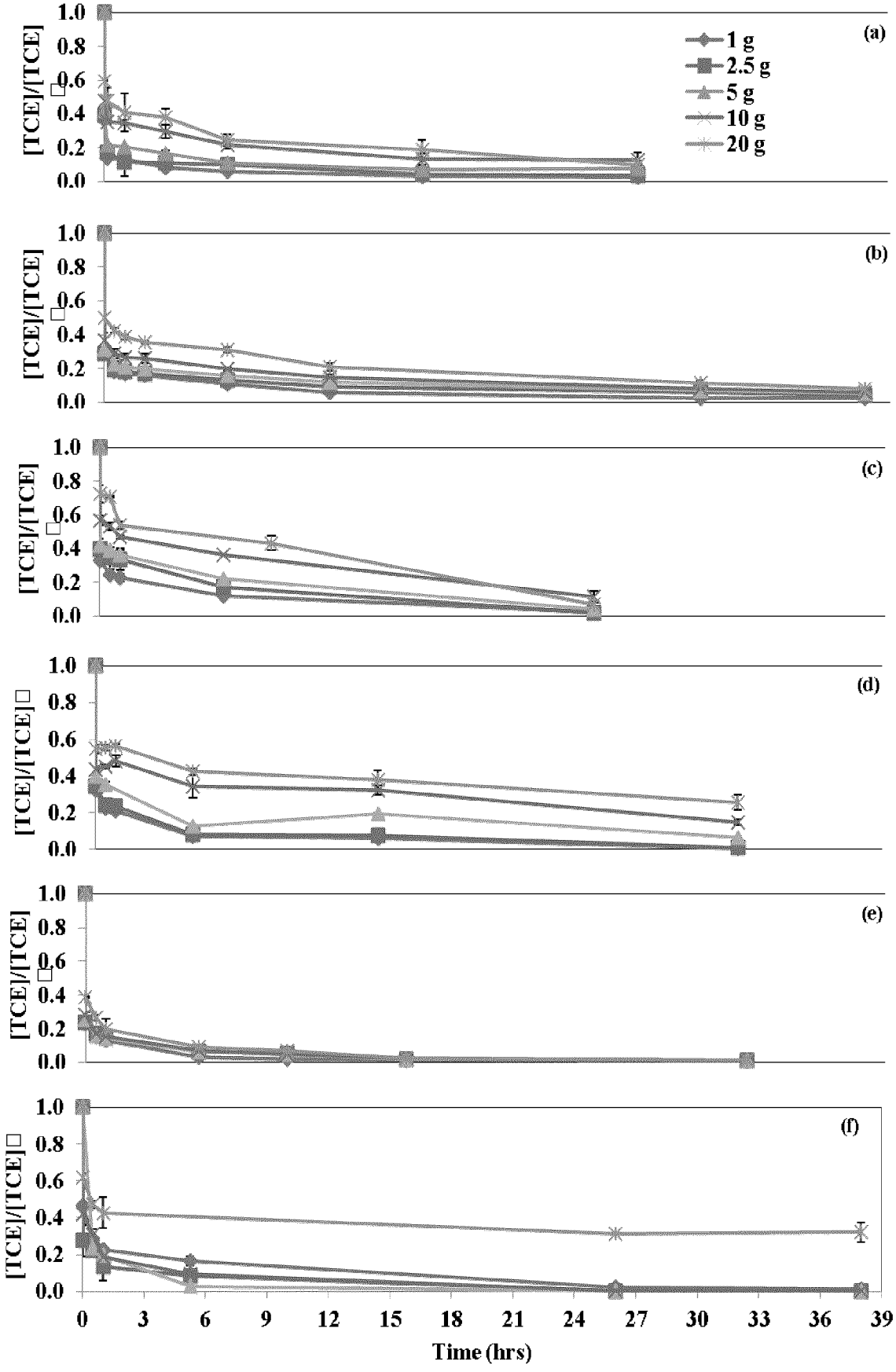

(a)
(b)
(c)
(d)
(e)
(f)
1 g
2.5 g
5 g
10 g
20 g
[TCE]/[TCE]□
1.0
0.8
0.6
0.4
0.2
0.0
0
3
6
9
12
15
18
21
24
27
30
33
36
39
Time (hrs)

Figure 11

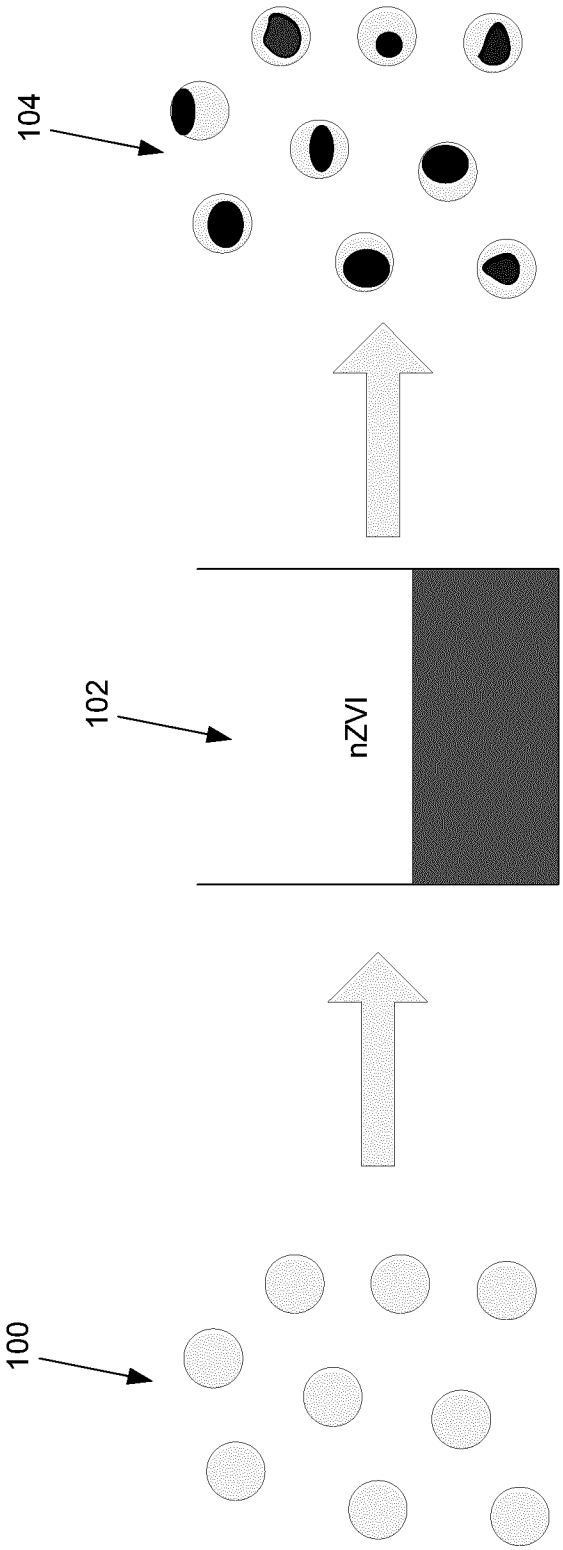
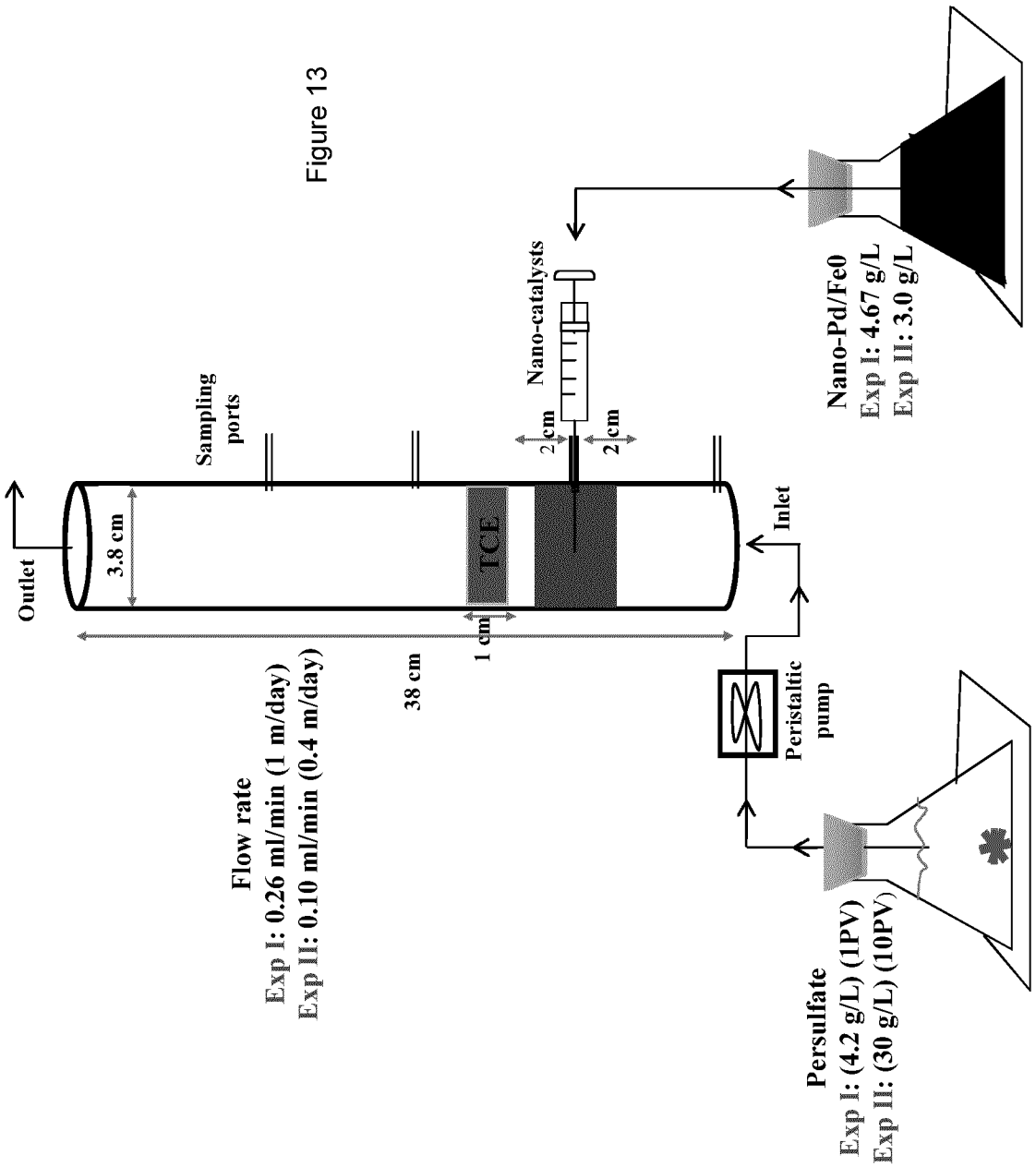


Figure 12

Figure 13


Outlet
3.8 cm
Sampling ports
TCE
Nano-catalysts
2 cm
2 cm
1 cm
38 cm
Inlet
Peristaltic pump
Nano-Pd/Fe0
Exp I: 4.67 g/L
Exp II: 3.0 g/L
Persulfate
Exp I: (4.2 g/L) (1PV)
Exp II: (30 g/L) (10PV)
Flow rate
Exp I: 0.26 ml/min (1 m/day)
Exp II: 0.10 ml/min (0.4 m/day)

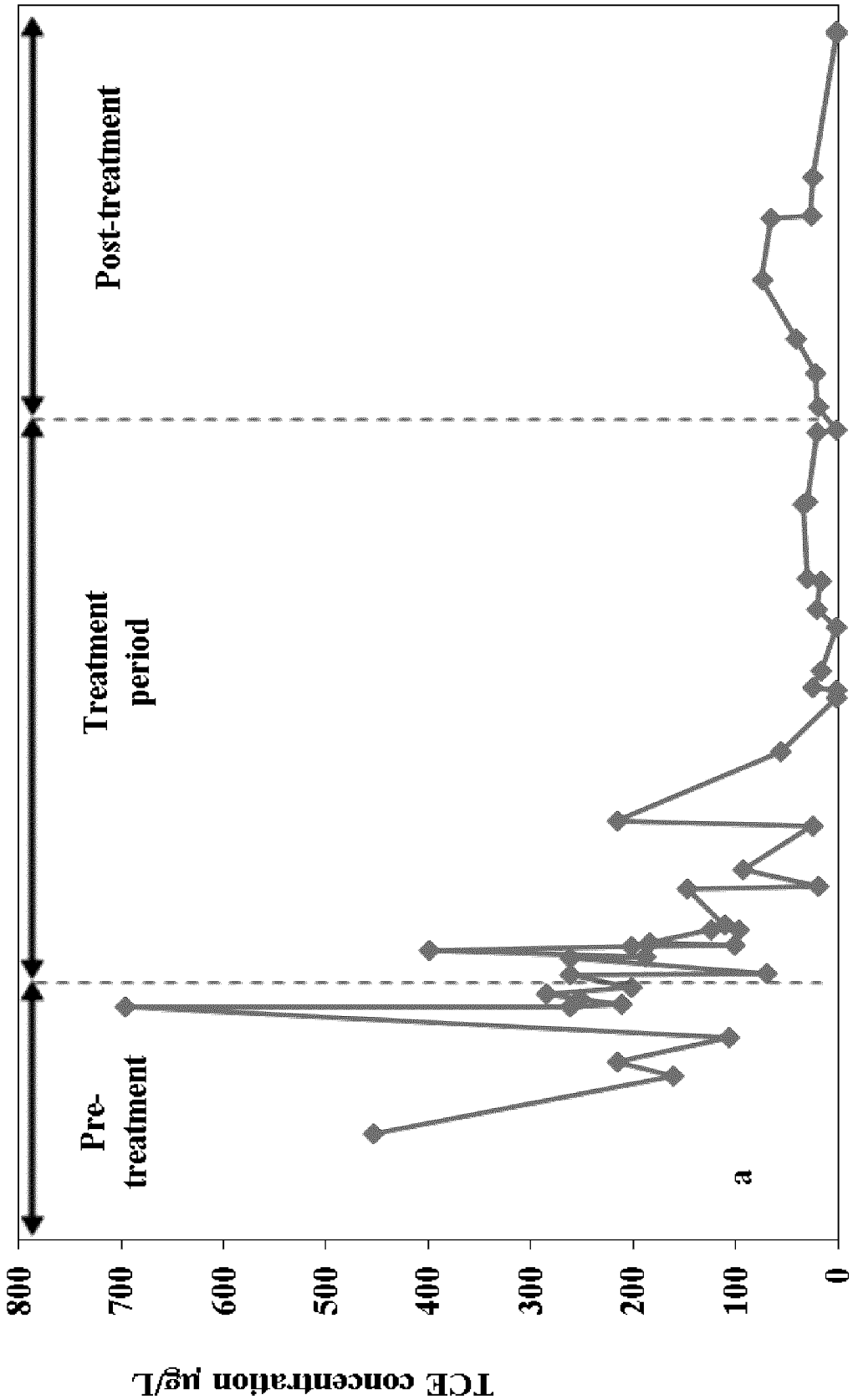

TCE concentration µg/L
800
700
600
500
400
300
200
100
0
Pre-treatment
Treatment period
Post-treatment
a

Figure 14a

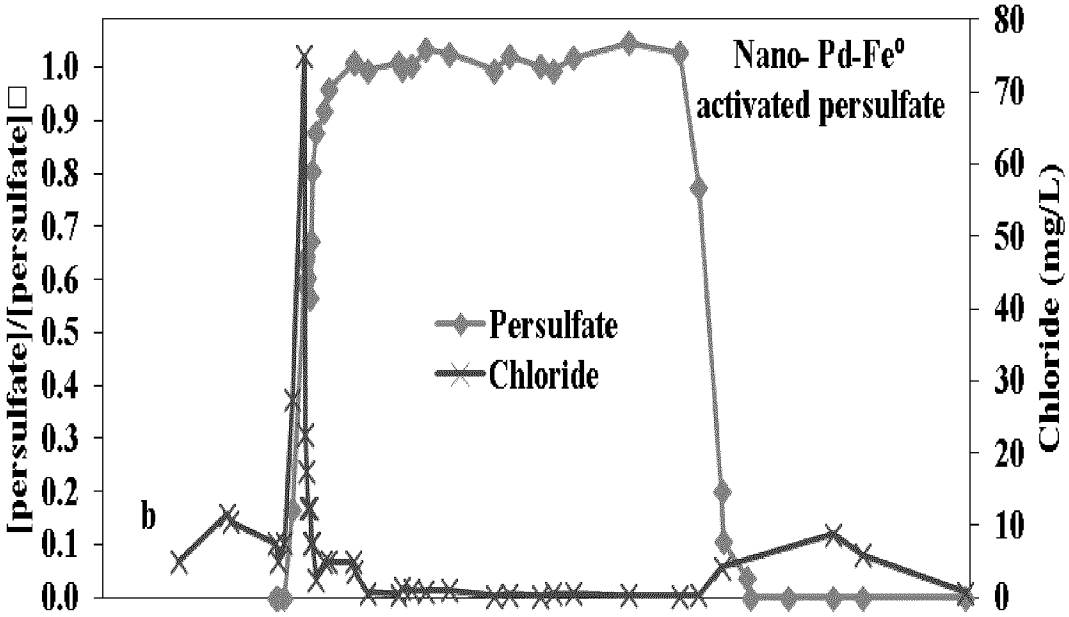


Figure 14b

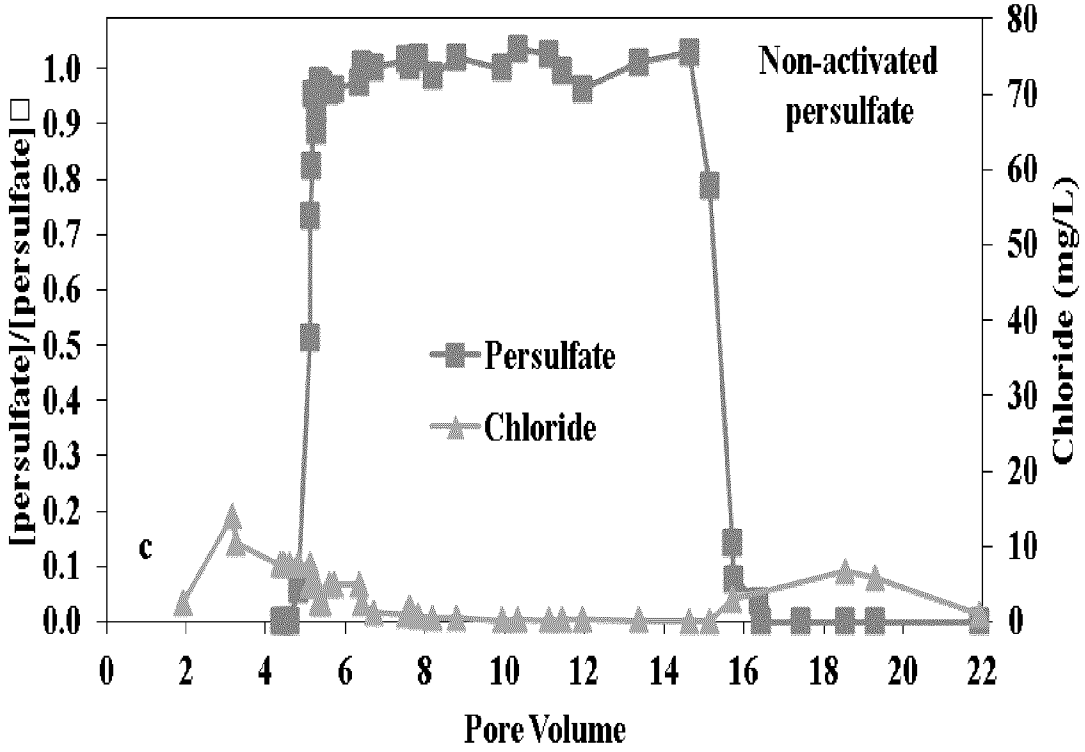


Figure 14c

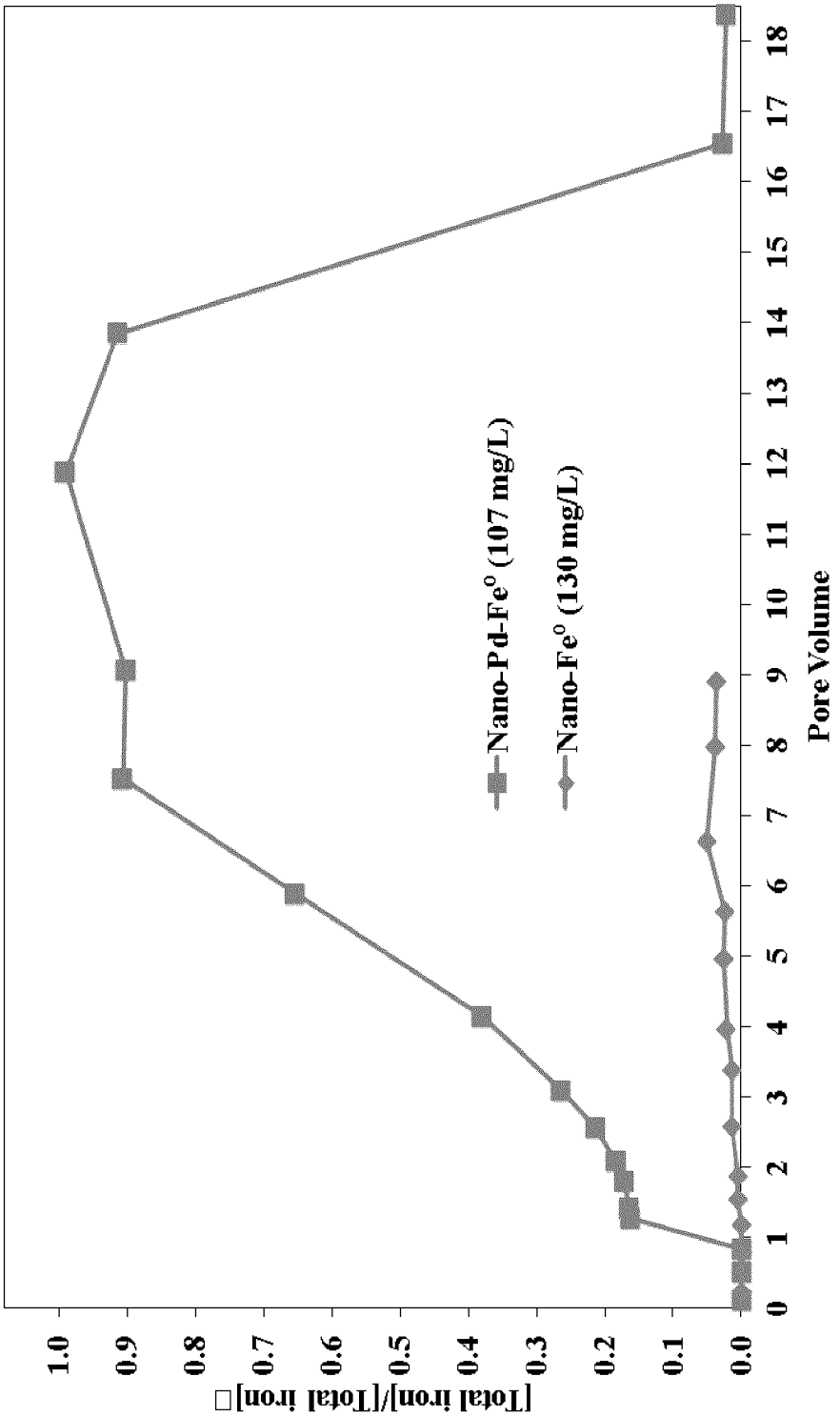

[Total iron]/[Total iron]□
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Pore Volume
Nano-Pd-Fe° (107 mg/L)
Nano-Fe° (130 mg/L)

Figure 15

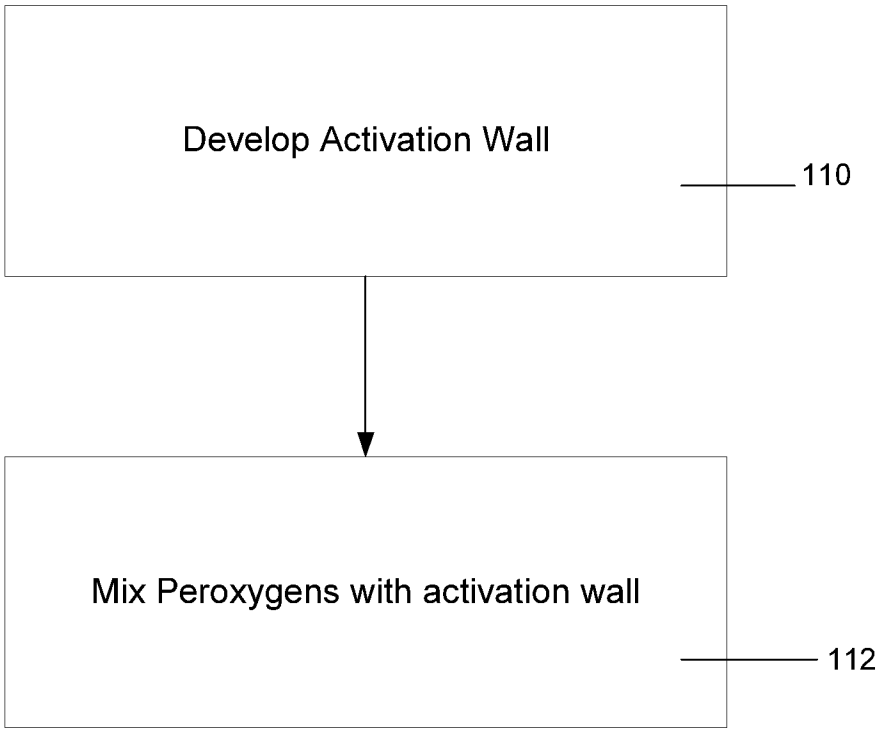

Develop Activation Wall
110
Mix Peroxygens with activation wall
112

Figure 16

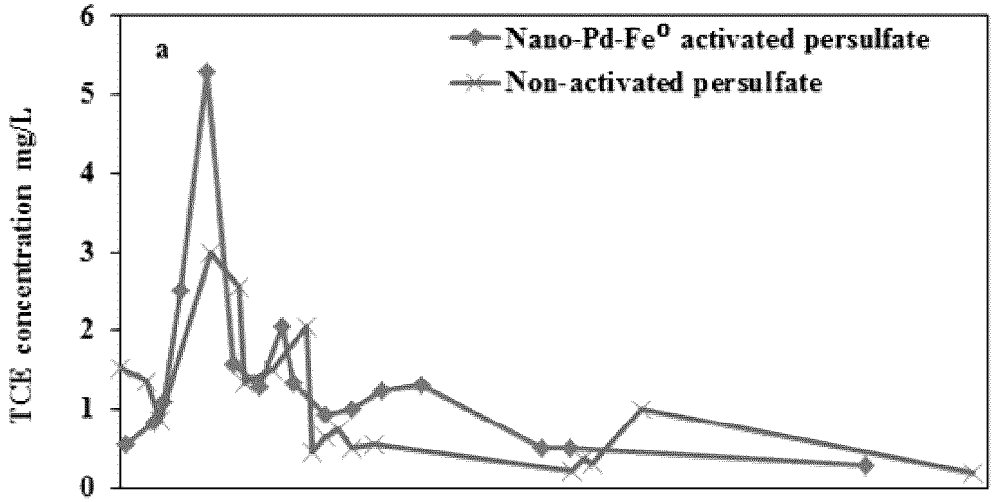


Figure 17a

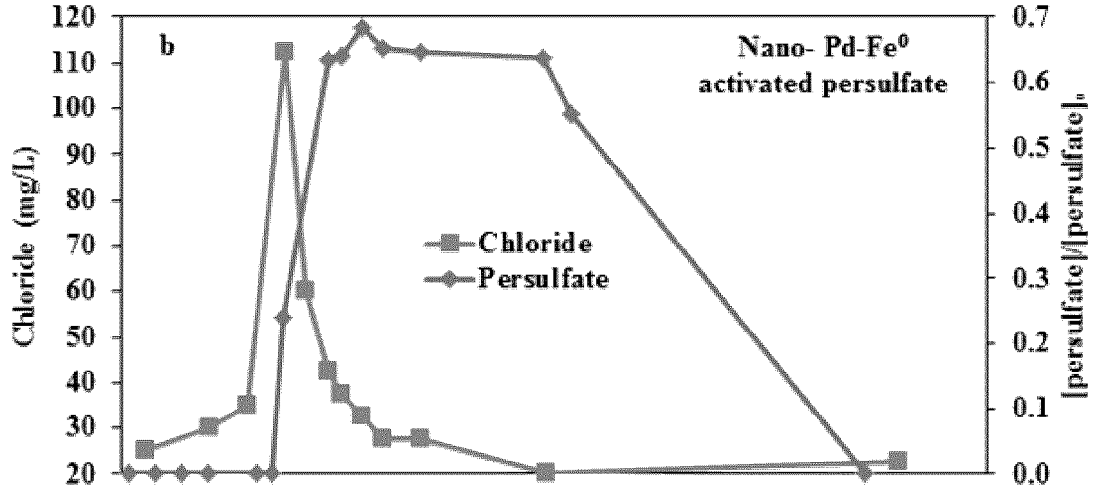


Figure 17b

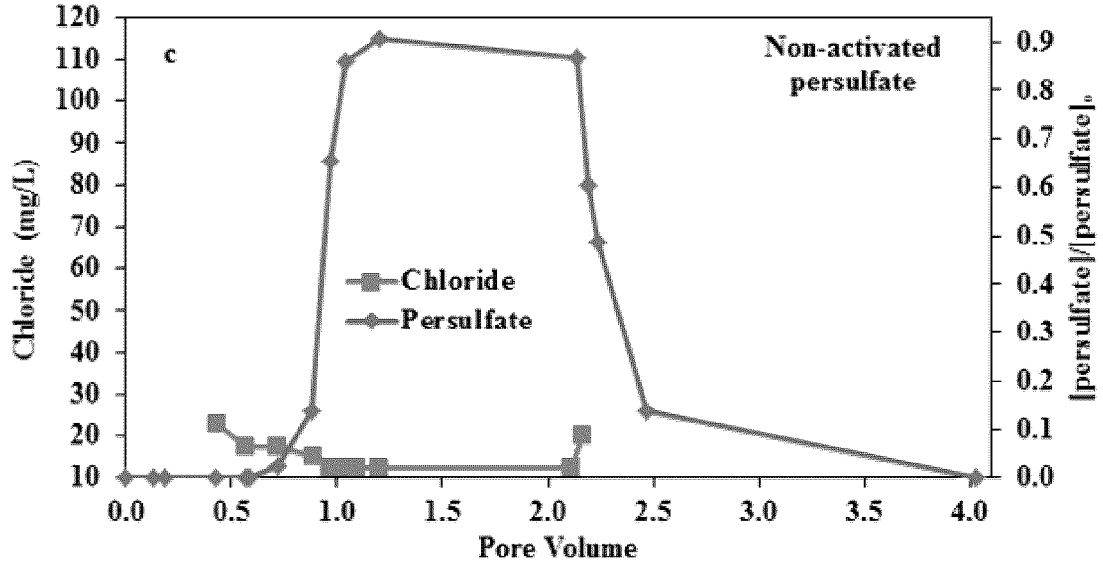


Figure 17c

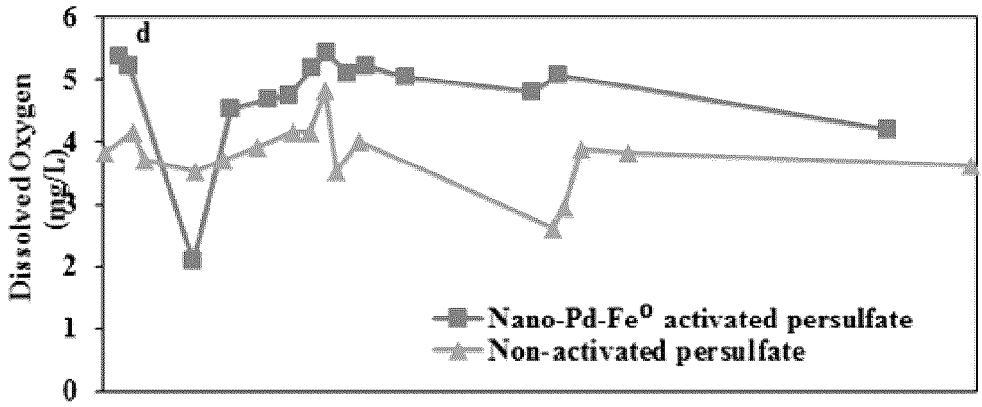


Figure 17d

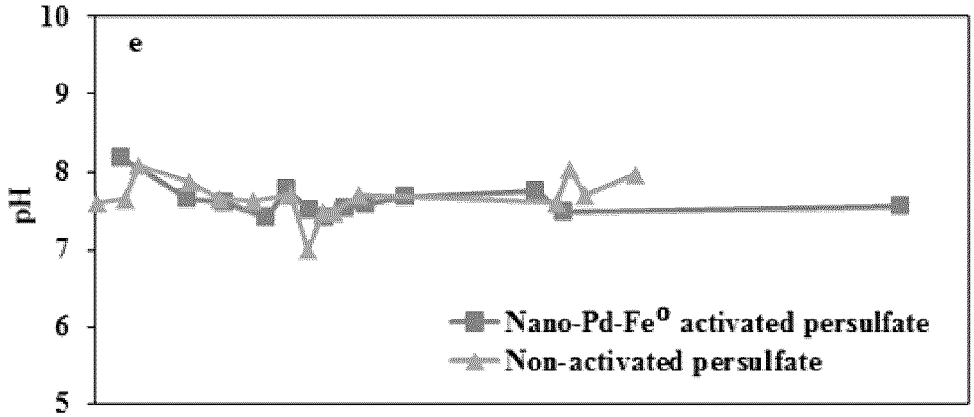


Figure 17e

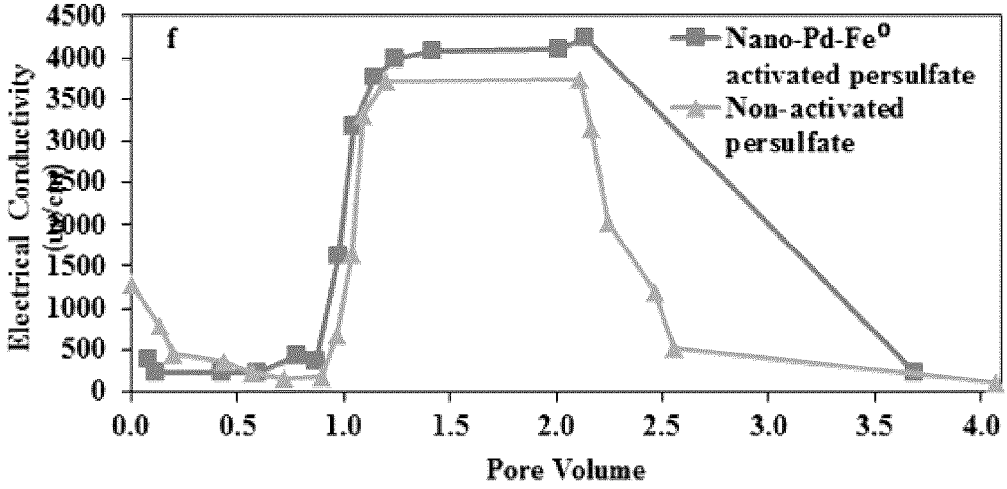


Figure 17f

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/050249

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***A62D 3/30*** (2007.01) , ***B09C 1/08*** (2006.01) , ***C02F 1/72*** (2006.01)
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)
IPC: ***A62D 3/30*** (2007.01) , ***B09C 1/08*** (2006.01) , ***C02F 1/72*** (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patent references cited-forward in relevant prior art identified using TotalPatent

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Intellect (Canadian Patents Database); Google Scholar; TotalPatent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2007/047946 A2 (Block et al) 26 April 2007 (26-04-2007); entire document	1 - 6, 8 - 9, 11 - 14, 16 1 - 16
X Y	US 2003/0134409 A1 (Mallouk et al) 17 July 2003 (17-07-2003); ¶0022 - 0024, 0026 - 0028, 0030, 0047 - 0048, 0053, 0057, Example 1; claims 23 - 27, 60, 73	7, 10, 15 1 - 16
A	US 7,887,880 B2 (Zhao et al) 15 February 2011 (15-02-2011); entire document	3 - 7, 9 - 10, 12 - 15
A	US 7,128, 841 B2 (Zhang) 31 October 2006 (31-10-2006); col. 1 - 6	3 - 7, 9 - 10, 12 - 15
A	BLOCK, PHILIP A., et al., "Novel Activation Technologies for Sodium Persulfate In Situ Chemical Oxidation", Proceedings of the Fourth International Conference on the Remediation of the Chlorinated and Recalcitrant Compounds (2004). Retrieved from the Internet: http://geo-log.eu/uploads/media/novelpersulfate_activation_technologies.pdf ; pp 1 - 8; entire document	1 - 16

[ ] Further documents are listed in the continuation of Box C.

[X] 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	Date of mailing of the international search report
29 June 2013 (29-06-2013)	04 July 2013 (04-07-2013)

Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 001-819-953-2476

Authorized officer
Ravi Philar (819) 953-3101

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2013/050249

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
WO2007047946A2	26 April 2007	AU2006304755A1	26 April 2007
		AU2006304755B2	07 July 2011
		BRPI0617476A2	26 July 2011
		CA2625080A1	26 April 2007
		EP1945317A2	23 July 2008
		EP1945317A4	22 August 2012
		US2008264876A1	30 October 2008
		US7785038B2	31 August 2010
		WO2007047946A3	30 April 2009
_US2003134409A1	17 July 2003	CA2455477A1	20 February 2003
		EP1432317A1	30 June 2004
		JP2005525210A	25 August 2005
		WO03013252A1	20 February 2003
US7887880B2	15 February 2011	US2008190865A1	14 August 2008
		WO2007001309A2	04 January 2007
		WO2007001309A3	14 June 2007
US7128841B2	31 October 2006	CA2559609A1	06 October 2005
		EP1723082A1	22 November 2006
		EP1723082A4	06 June 2007
		US2005199556A1	15 September 2005
		WO2005092802A1	06 October 2005