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(54) **Titre : OXYDE DE CERIUM (IV) AYANT D'EXCEPTIONNELLES PROPRIETES D'ELIMINATION DE L'ARSENIC**
(54) **Title: CERIUM (IV) OXIDE WITH EXCEPTIONAL ARSENIC REMOVAL PROPERTIES**

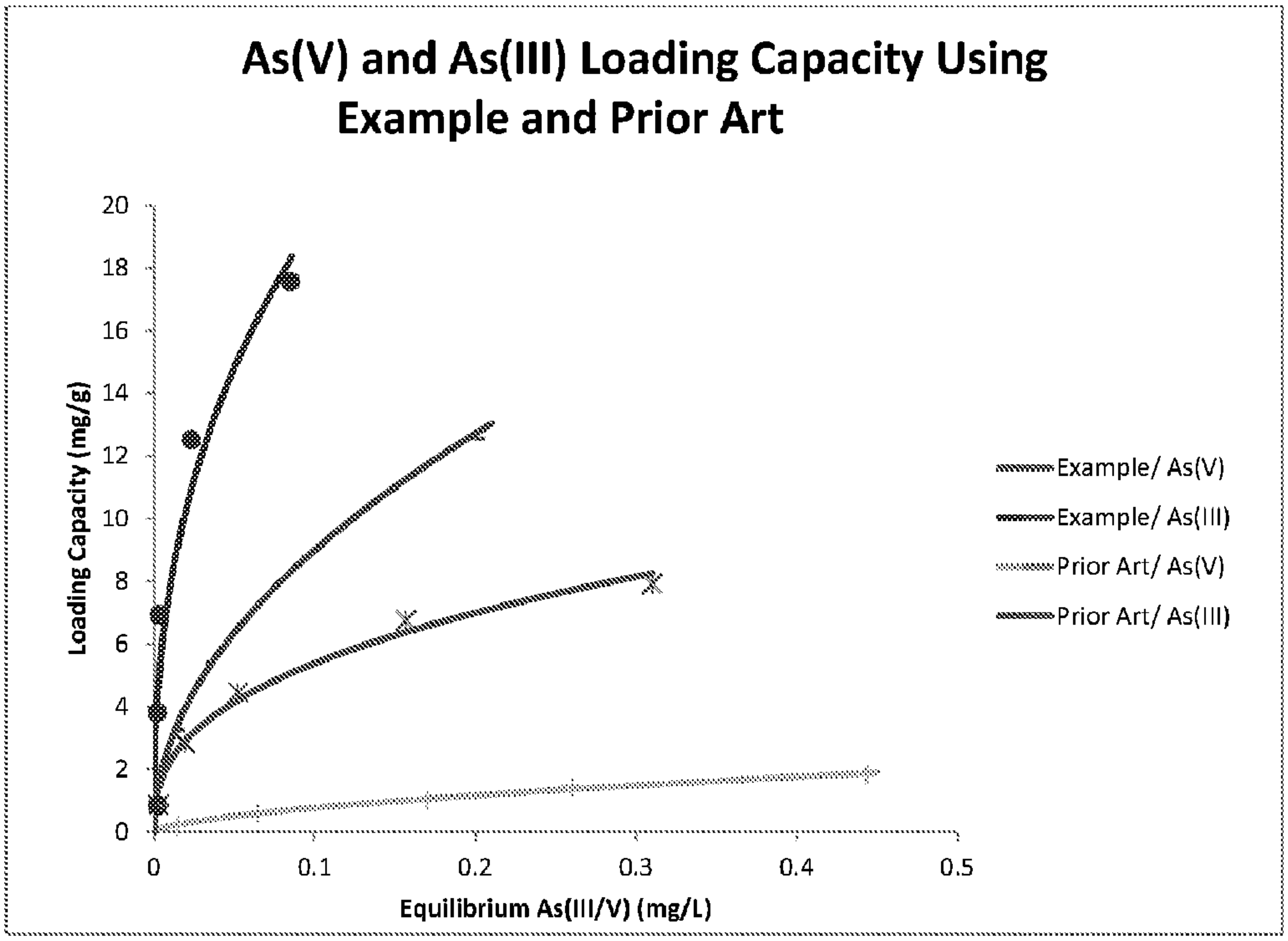

FIG. 9

(57) **Abrégé/Abstract:**

A cerium (IV) oxide composition having unexpectedly greater arsenic loading capacities than oxides of cerium (IV) of the prior art are disclosed. The arsenic loading capacities are greater at low level equilibrium levels of arsenic. The cerium (IV) oxide

(57) **Abrégé(suite)/Abstract(continued):**

composition is more effective at removing arsenite and arsenate. Moreover, the cerium (IV) oxide composition has a greater capacity for the previously more difficult to remove arsenite.

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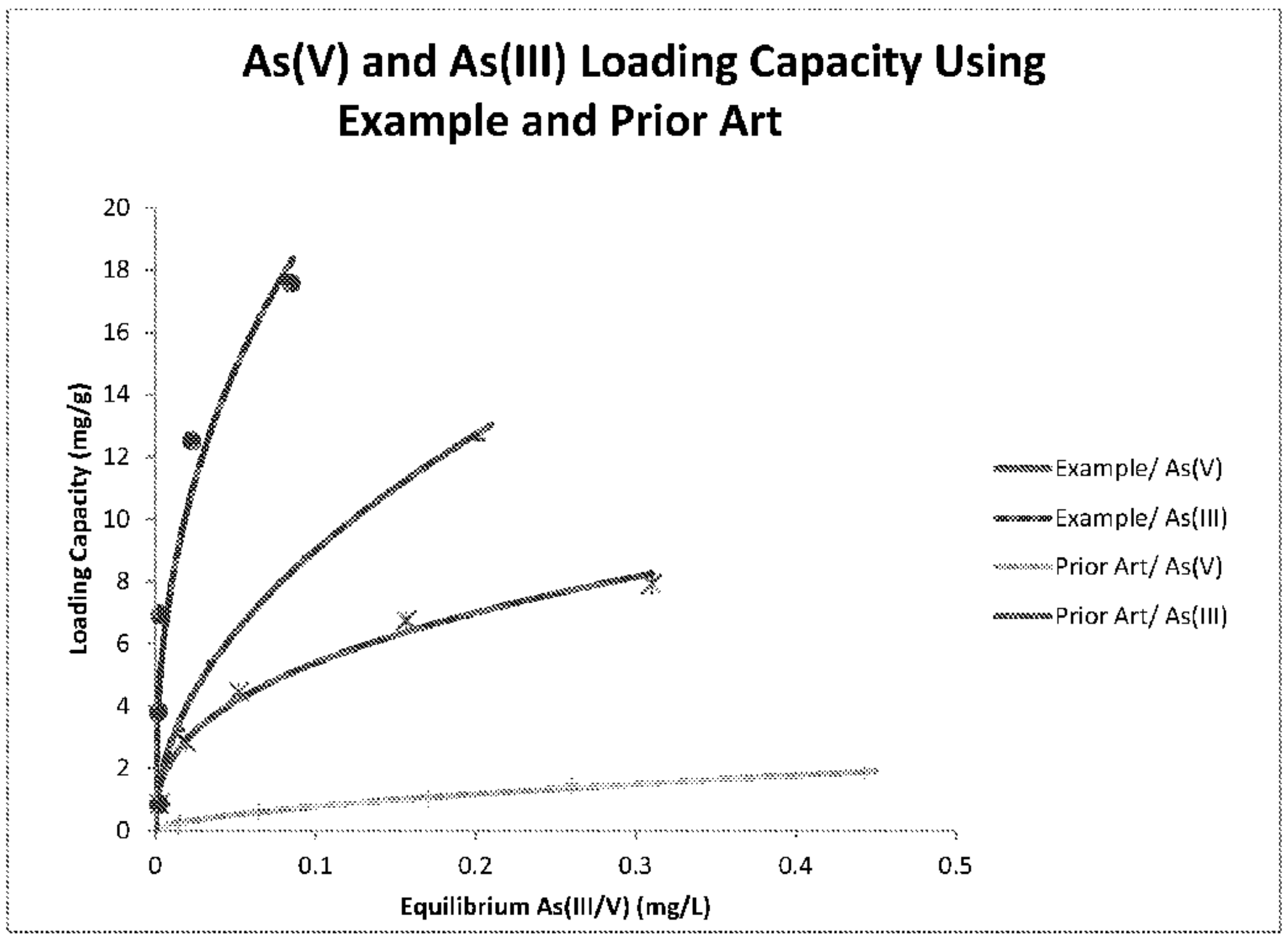


FIG. 9

(57) **Abstract**: A cerium (IV) oxide composition having unexpectedly greater arsenic loading capacities than oxides of cerium (IV) of the prior art are disclosed. The arsenic loading capacities are greater at low level equilibrium levels of arsenic. The cerium (IV) oxide composition is more effective at removing arsenite and arsenate. Moreover, the cerium (IV) oxide composition has a greater capacity for the previously more difficult to remove arsenite.

WO 2015/134981 A3

CERIUM (IV) OXIDE WITH EXCEPTIONAL ARSENIC REMOVAL PROPERTIES

CROSS REFERENCE TO RELATED APPLICATION

The present application claims the benefits of U.S. Provisional Application Serial No. 61/949,799 with a filing date of March 7, 2014, entitled "Ceric Oxide with Exceptional Target Material Removal Properties", which is incorporated in its entirety herein by this reference.

BACKGROUND

Arsenic is a toxic element that naturally occurs in a variety of combined forms. Its presence in natural waters may originate, for example, from geochemical reactions, industrial waste discharges and past and present agricultural uses of arsenic-containing pesticides. Because the presence of arsenic may have carcinogenic and other deleterious effects on living organisms, the U.S. Environmental Protection Agency (EPA) and the World Health Organization (WHO) have set the maximum contaminant level (MCL) for arsenic in drinking water at 10 parts per billion (ppb). Arsenic concentrations in wastewaters, ground waters, surface waters and geothermal waters frequently exceed this level. Thus, the current MCL and any future decreases, which may be to as low as 2 ppb, create the need for new techniques to economically and effectively remove arsenic from drinking water, well water and industrial waters or any other waters.

Arsenic occurs in four oxidation or valence states, i.e., -3, 0, +3, and +5. Under normal conditions arsenic is found dissolved in aqueous or aquatic systems in the +3 and +5 oxidation states, usually in the form of arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}). The effective removal of arsenic by coagulation techniques requires the arsenic to be in the arsenate form. Arsenite, in which the arsenic exists in the +3 oxidation state, is only partially removed by adsorption and coagulation techniques.

Various technologies have been used in the past to remove arsenic from aqueous systems. Examples of such techniques include adsorption on high surface area materials, such as alumina and activated carbon, ion exchange with anion exchange resins, co-precipitation and electro-dialysis. However, most technologies for arsenic removal are hindered by the difficulty of removing arsenic at very low levels and maintain an effective loading capacity. Additionally the amount of material necessary to remove arsenic at low levels can make the technology economically unfeasible. The more successful techniques that have been used in large municipal water supplies are not practical for residential applications because of space requirements and the need to use dangerous chemicals. The two most common techniques for residential water treatment have been reverse osmosis and solid filtration media such as activated alumina, iron oxide, and titanium oxide. The former method produces arsenic-containing waste streams that must be disposed of, and the latter requires the media to treat sufficiently large volumes of water in order to be economically viable.

The above facts coupled with the potential for the decrease in MCL to 10 ppb or less make it imperative that effective sorbents and/or reactants to remove arsenic from water and other aqueous systems be developed and used.

SUMMARY

This disclosure relates generally to cerium-containing compositions for removing arsenic contaminants from aqueous liquid streams. More specifically, this disclosure is particularly concerned with cerium-containing compositions for removing arsenic in the form of arsenite and arsenate from groundwater and drinking water. Typically, the cerium-containing composition is cerium oxide. More typically, the cerium-containing composition can be cerium (IV) oxide. The arsenite and arsenate can be present at parts per million or parts per billion or fractions of parts billion concentrations. The cerium-containing composition at high or very low treatment levels can remove the arsenite and arsenate from the aqueous liquid streams.

It has now been found that one or more of the arsenite and arsenate can be efficiently and effectively removed from water and other aqueous liquid feed stocks by treating the aqueous liquid stream containing one or more of the arsenite and arsenate with a cerium-containing composition. The cerium-containing composition generally comprises a cerium (IV) oxide composition (CeO_2). The cerium (IV) oxide composition can be in a crystalline form. Moreover, the cerium (IV) oxide composition can have a high surface area. Surprisingly, it has further been found that using cerium (IV) oxide composition (CeO_2) with particular characteristics as described below enables the sorption and removal of arsenic with higher removal capacities compared to traditional removal media, including cerium oxide lacking one or more of these particular characteristics. More specifically, it has further been found that using cerium (IV) oxide composition (CeO_2) with particular characteristics as described below enables the sorption and removal of one or more of arsenite and arsenate with higher removal capacities compared to traditional removal media, including cerium oxide lacking one or more of these particular characteristics.

The cerium (IV) oxide composition can be unsupported or supported. The supported cerium (IV) oxide composition can be deposited on a single support or deposited on multiple supports. The supports can be without limitation alumina, aluminosilicates, ion exchange resins, organic polymers, and clays. The cerium (IV) oxide composition can be deposited and/or mixed with a polymeric porous material. Moreover, it is believed that the cerium (IV) oxide composition surface exposure is enhanced when the cerium (IV) oxide composition is deposited and/or mixed with the polymeric porous material.

In accordance with some embodiments is a method of contacting a cerium (IV) oxide composition with an arsenic-containing aqueous stream. During the contacting of the cerium (IV) oxide with the arsenic-containing aqueous stream, one or more of the following is true: (i) the cerium (IV) oxide composition has a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV; (ii) the cerium (IV) oxide composition has a particle size D_{10} of more than about 0.5 μm and no more than about 7 μm; (iii) the cerium (IV) oxide composition has a particle size D_{50} of more than about 2 μm and no more than about 20 μm; (iv) the cerium (IV) oxide composition has a particle size D_{90} of more than about 12 μm and no more than about 50 μm; (v) the cerium (IV) oxide composition has a crystallite size of more than about 1 nm and no more than about 22 nm; and (vi) the cerium (IV) oxide composition has an acidic site concentration of more than about 0.0001 acidic sites/kg and no more than about 0.020 acidic sites/kg. The contacting of the cerium (IV) oxide composition with the arsenic-containing aqueous stream can remove some of the arsenic from the arsenic-containing stream.

In accordance with some embodiments is a method of contacting a cerium (IV) oxide composition with an arsenic-containing aqueous stream to remove a first level of arsenic from the arsenic-containing stream. The first level of arsenic can be greater than that removed by an oxide of cerium (IV) lacking one or more of: (i) a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV; (ii) a particle size D_{10} of more than about 0.5 μm and no more than about 7 μm; (iii) a particle size D_{50} of more than about 2 μm and no more than about 20 μm; (iv) a particle size D_{90} of more than about 12 μm and no more than about 50 μm; (v) a crystallite size of more than about 1 nm and no more than about 22 nm; and (vi) an acidic cite concentration of more than about 0.0001 acidic sites/kg and no more than about 0.020 acidic sites/kg.

In accordance with some embodiments is a method of contacting a cerium (IV) oxide composition with an arsenite-containing aqueous stream. During the contacting of the cerium (IV) oxide with the arsenic-containing aqueous stream, one or more of the following is true: (i) the cerium (IV) oxide composition has a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV; (ii) the cerium (IV) oxide composition has a particle size D_{10} of more than about 0.5 μm and no more than about 7 μm; (iii) the cerium (IV) oxide composition has a particle size D_{50} of more than about 2 μm and no more than about 20 μm; (iv) the cerium (IV) oxide composition has a particle size D_{90} of more than about 12 μm and no more than about 50 μm; (v) the cerium (IV) oxide composition has a crystallite size of more than about 1 nm and no more than about 22 nm; and (vi) the cerium (IV) oxide composition has an acidic site concentration of more than about 0.0001 sites/kg and no more than about 0.020 acidic sites/kg. The contacting of the cerium (IV) oxide composition with the arsenite-containing aqueous stream can remove some of the arsenite from the arsenite-containing aqueous stream.

In accordance with some embodiments is a method of contacting a cerium (IV) oxide composition with an arsenate-containing aqueous stream. During the contacting of the cerium (IV) oxide with the arsenate-containing aqueous stream, one or more of the following is true: (i) the cerium (IV) oxide composition has a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV; (ii) the cerium (IV) oxide composition has a particle size D_{10} of more than about 0.5 µm and no more than about 7 µm; (iii) the cerium (IV) oxide composition has a particle size D_{50} of more than about 2 µm and no more than about 20 µm; (iv) the cerium (IV) oxide composition has a particle size D_{90} of more than about 12 µm and no more than about 50 µm; (v) the cerium (IV) oxide composition has a crystallite size of more than about 1 nm and no more than about 22 nm; and (vi) the cerium (IV) oxide composition has an acidic site concentration of more than about 0.0001 sites/kg and no more than about 0.020 acidic sites/kg. The contacting of the cerium (IV) oxide composition with the arsenate-containing aqueous stream can remove some of the arsenate from the arsenate-containing aqueous stream.

In accordance with some embodiments is a method of introducing a cerium (IV) oxide composition into an aqueous stream having a first level of arsenic. During the introducing of the cerium (IV) oxide with the arsenate-containing aqueous stream, one or more of the following is true: (i) the cerium (IV) oxide composition has a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV; (ii) the cerium (IV) oxide composition has a particle size D10 of more than about 0.5 µm and no more than about 7 µm; (iii) the cerium (IV) oxide composition has a particle size D50 of more than about 2 µm and no more than about 20 µm; (iv) the cerium (IV) oxide composition has a particle size D90 of more than about 12 µm and no more than about 50 µm; (v) the cerium (IV) oxide composition has a crystallite size of more than about 1 nm and no more than about 22 nm; and (vi) the cerium (IV) oxide composition has an acidic site concentration of more than about 0.0001 sites/kg and no more than about 0.020 acidic sites/kg. After the introducing of the cerium (IV) oxide composition into the aqueous stream, the aqueous stream has a second level of arsenic, the first level of arsenic being greater than the second level of arsenic.

In accordance with some embodiments is a method of contacting a cerium (IV) oxide composition having from an acidic site concentration of more than about 0.0001 acidic sites/kg and no more than about 0.020 acidic sites/kg with an arsenic-containing aqueous stream. The contacting of the cerium (IV) oxide composition with the arsenic-containing aqueous stream can remove some of the arsenic from the arsenic-containing stream.

In accordance with some embodiments is a device. The device can have an inlet to receive an aqueous stream having a first level of arsenic, a contacting chamber in fluid communication with the inlet and containing a cerium (IV) oxide composition to contact the aqueous stream. Moreover, the aqueous stream has the first level of arsenic prior to the aqueous stream contacting the cerium (IV) oxide composition and a second level of arsenic after the contacting of the aqueous stream with the cerium (IV) oxide, the first level of arsenic is greater than the second level of arsenic. Furthermore, the device can have an outlet in fluid communication with the contacting chamber to output the aqueous stream having the second level of arsenic. Moreover, one or more of the following is true: (i) the cerium (IV) oxide composition has a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV; (ii) the cerium (IV) oxide composition has a particle size D10 of more than about 0.5 µm and no more than about 20 µm; (iii) the cerium (IV) oxide composition has a particle size D50 of more than about 2 µm and no more than about 20 µm; (iv) the cerium (IV) oxide composition has a particle size D90 of more than about 12 µm and no more than about 50 µm; (v) the cerium (IV) oxide composition has a crystallite size of more than about 1 nm and no more than about 22 nm; and (vi) the cerium (IV) oxide composition has an acidic site concentration of more than about 0.0001 acidic sites/kg and no more than about 0.020 acidic sites/kg.

In some embodiments, the arsenic-containing stream comprises one or more of arsenic (III) and arsenic (V).

In some embodiments, the cerium (IV) oxide composition removes about 125% more arsenic (III) per gram of CeO2 per µg/L of arsenic (III) in the arsenic-containing stream than an oxide of cerium (IV) and one or more of steps (i)-(vi) are false for the oxide of cerium (IV).

In some embodiments, the cerium (IV) oxide composition removes about 150% more arsenic (III) per gram of CeO2 per µg/L of arsenic (III) in the arsenic-containing stream than an oxide of cerium (IV) and wherein on or more of steps (i)-(vi) are false for the oxide of cerium (IV).

In some embodiments, the cerium (IV) oxide composition removes about 200% more arsenic (V) per gram of CeO2 per µg/L of arsenic (V) in the arsenic-containing stream than an oxide of cerium (IV) and wherein on or more of steps (i)-(vi) are false for the oxide of cerium (IV).

In some embodiments, the cerium (IV) oxide composition removes about 400% more arsenic (V) per gram of CeO2 per µg/L of arsenic (V) in the arsenic-containing stream than an oxide of cerium (IV) and wherein on or more of steps (i)-(vi) are false for the oxide of cerium (IV).

In some embodiments, the cerium (IV) oxide composition removes about 125% more arsenic (III) per µg/L of arsenic (III) in the arsenic-containing stream than an oxide of cerium (IV), and one or more of steps (i)-(vi) are false for the oxide of cerium (IV).

In some embodiments, the cerium (IV) oxide composition removes about 150% more arsenic (III) per µg/L of arsenic (III) in the arsenic-containing stream than an oxide of cerium (IV), and one or more of steps (i)-(vi) are false for the oxide of cerium (IV).

The cerium (IV) oxide composition can have a loading capacity for arsenite of from 2.1 to about 6.0 mg/g for an equilibrium arsenite concentration of from about 0.5 to about 5 ppb. This is in contrast to a loading capacity for arsenite for an oxide of cerium (IV) of the prior art which has an arsenite load capacity of from about 0.6 to about 2.0 mg/g over the same equilibrium arsenite concentration of from about 0.5 to 5 ppb.

Moreover, the cerium (IV) oxide composition can have a loading capacity for arsenate of from 0.1 to about 0.2 mg/g for an equilibrium arsenate concentration of from about 0.5 to about 2.5 ppb. This is in contrast to a loading capacity for arsenate for an oxide of cerium (IV) of the prior art which has an arsenate load capacity of from about 0.03 to about 0.08 mg/g over the same equilibrium arsenate concentration of from about 0.5 to 2.5 ppb.

In some embodiments, the cerium (IV) oxide composition removes about 200% more arsenic (V) per µg/L of arsenic (V) in the arsenic-containing stream than an oxide of cerium (IV), and one or more of steps (i)-(vi) are false for the oxide of cerium (IV).

In some embodiments, the cerium (IV) oxide composition removes about 400% more arsenic (V) per µg/L of arsenic (V) in the arsenic-containing stream than an oxide of cerium (IV), and one or more of steps (i)-(vi) are false for the oxide of cerium (IV).

In some embodiments, the arsenic-containing aqueous stream has a pH from about pH 4.5 to about 9.5 during the contacting of the cerium (IV) oxide and the arsenic-containing stream, the cerium (IV) oxide composition removes more arsenic per gram of CeO2 per µg/L of arsenic than an oxide of cerium (IV), and one or more of steps (i)-(vi) are false for the oxide of cerium (IV).

In some embodiments, step (i) can be true. In some embodiments where step (i) is true, one of steps (ii)-(vi) can be false and one or more of the others of steps (ii)-(vi) can be true. In some embodiments where step (i) is true, two of steps (ii)-(vi) can be false and one or more of the others of steps (ii)-(vi) can be true. In some embodiments where step (i) is true, three of steps (ii)-(vi) can be false and one or more of the others of steps (ii)-(vi) can be true. In some embodiments where step (i) is true, four of steps (ii)-(vi) can be false and the other of steps (ii)-(vi) can be true.

In some embodiments, step (ii) can be true. In some embodiments where step (ii) is true, one of steps (i) and (iii)-(vi) can be false and one or more of the others of steps (i) and (iii)-(vi) can be true. In some embodiments where step (ii) is true, two of steps (i) and (iii)-(vi) can be false and one or more of the others of steps (i) and (iii)-(vi) can be true. In some embodiments where step (ii) is true, three of steps (i) and (iii)-(vi) can be false and one or more of the others of steps (i) and (iii)-(vi) can be true. In some embodiments where step (ii) is true, four of steps (i) and (iii)-(vi) can be false and the other of steps (i) and (iii)-(vi) can be true.

In some embodiments, step (iii) can be true. In some embodiments where step (iii) is true, one of steps (i)-(ii) and (iv)-(vi) can be false and one or more of the other steps (i)-(ii) and (iv)-(vi) can be true. In some embodiments where step (iii) is true, two of steps (i)-(ii) and (iv)-(vi) can be false and one or more of the other steps (i)-(ii) and (iv)-(vi) can be true. In some embodiments where step (iii) is true, three of steps (i)-(ii) and (iv)-(vi) can be false and one or more of the other steps (i)-(ii) and (iv)-(vi) can be true. In some embodiments where step (iii) is true, four of steps (i)-(ii) and (iv)-(vi) can be false and the other of steps (i)-(ii) and (iv)-(vi) can be true.

In some embodiments, step (iv) can be true. In some embodiments where step (iv) is true, one of steps (i)-(iii) and (v)-(vi) can be false and one or more of the other steps (i)-(iii) and (v)-(vi) can be true. In some embodiments where step (iv) is true, two of steps (i)-(iii) and (v)-(vi) can be false and one or more of the other steps (i)-(iii) and (v)-(vi) can be true. In some embodiments where step (iv) is true, three of steps (i)-(iii) and (v)-(vi) can be false and one or more of the other steps (i)-(iii) and (v)-(vi) can be true. In some embodiments where step (iv) is true, four of steps (i)-(iii) and (v)-(vi) can be false and the other of steps (i)-(iii) and (v)-(vi) can be true.

In some embodiments, step (v) can be true. In some embodiments where step (v) is true, one of steps (i)-(iv) and (vi) can be false and one or more of the other steps (i)-(iv) and (vi) can be true. In some embodiments where step (v) is true, two of steps (i)-(iv) and (vi) can be false and one or more of the other steps (i)-(iv) and (vi) can be true. In some embodiments where step (v) is true, three of steps (i)-(iv) and (vi) can be false and one or more of the other steps (i)-(iv) and (vi) can be true. In some embodiments where step (v) is true, four of steps (i)-(iv) and (vi) can be false the other of steps (i)-(iv) and (vi) can be true.

In some embodiments, step (vi) can be true. In some embodiments where step (vi) is true, one of steps (i)-(v) can be false and one or more of the other steps (i)-(v) can be true. In some embodiments where step (vi) is true, and two of steps (i)-(v) are false and one or more of the other steps (i)-(v) are true. In some embodiments where step (vi) is true, hree of steps (i)-(v) can be false and one or more of the other steps (i)-(v) can be true. In some embodiments where step (vi) is true, four of steps (i)-(v) can false and the other of steps (i)-(v) can be true.

In some embodiments, the zeta potential at about pH 7 can be from about 7.5 to about 12.5 mV.

In some embodiments, the particle size D_{10} can be from about 1 to about 3 μm.

In some embodiments, the particle size D_{50} can be from about 7.5 to about 10.5 μm.

In some embodiments, the particle size D_{90} can be from about 20 to about 30 μm.

In some embodiments, the crystallite size can be from about 7.5 to about 12.5 nm.

In some embodiments, the cerium (IV) oxide composition can have from about 7.5 to about 9.5 wt% Ce $(IV)O_2$.

In some embodiments, the cerium (IV) oxide composition can have rare earth oxides other than Ce $(IV)O_2$. The cerium (IV) oxide composition can have one of no more than about 40, no more than about 25 and no more than about 10 wt% of the rare earth oxides other than cerium (IV) oxide composition.

These and other advantages will be apparent from the disclosure of the aspects, embodiments, and configurations contained herein.

As used herein, "at least one", "one or more", and "and/or" are open-ended expressions that are both conjunctive and disjunctive in operation. For example, each of the expressions "at least one of A, B and C", "at least one of A, B, or C", "one or more of A, B, and C", "one or more of A, B, or C" and "A, B, and/or C" means A alone, B alone, C alone, A and B together, A and C together, B and C together, or A, B and C together. When each one of A, B, and C in the above expressions refers to an element, such as X, Y, and Z, or class of elements, such as X_1-X_n, Y_1-Y_m, and Z_1-Z_o, the phrase is intended to refer to a single element selected from X, Y, and Z, a combination of elements selected from the same class (e.g., X_1 and X_2) as well as a combination of elements selected from two or more classes (e.g., Y_1 and Z_o).

It is to be noted that the term "a" or "an" entity refers to one or more of that entity. As such, the terms "a" (or "an"), "one or more" and "at least one" can be used interchangeably herein. It is also to be noted that the terms “comprising”, “including”, and “having” can be used interchangeably.

The term “means” as used herein shall be given its broadest possible interpretation in accordance with 35 U.S.C., Section 112, Paragraph 6. Accordingly, a claim incorporating the term “means” shall cover all structures, materials, or acts set forth herein, and all of the equivalents thereof. Further, the structures, materials or acts and the equivalents thereof shall include all those described in the summary of the invention, brief description of the drawings, detailed description, abstract, and claims themselves.

Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

All percentages and ratios are calculated by total composition weight, unless indicated otherwise.

It should be understood that every maximum numerical limitation given throughout this disclosure is deemed to include each and every lower numerical limitation as an alternative, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this disclosure is deemed to include each and every higher numerical limitation as an alternative, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this disclosure is deemed to include each and every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein. By way of example, the phrase from about 2 to about 4 includes the whole number and/or integer ranges from about 2 to about 3, from about 3 to about 4 and each possible range based on real (e.g., irrational and/or rational) numbers, such as from about 2.1 to about 4.9, from about 2.1 to about 3.4, and so on.

The preceding is a simplified summary of the disclosure to provide an understanding of some aspects of the disclosure. This summary is neither an extensive nor exhaustive overview of the disclosure and its various aspects, embodiments, and configurations. It is intended neither to identify key or critical elements of the disclosure nor to delineate the scope of the disclosure but to present selected concepts of the disclosure in a simplified form as an introduction to the more detailed description presented below. As will be appreciated, other aspects, embodiments, and configurations of the disclosure are possible utilizing, alone or in combination, one or more of the features set forth above or described in detail below. Also, while the disclosure is presented in terms of exemplary embodiments, it should be appreciated that individual aspects of the disclosure can be separately claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate embodiments of the disclosure and together with the general description of the disclosure given above and the detailed description given below, serve to explain the principles of the disclosure.

Fig. 1 is a plot of both arsenic (III) and (V) removal capacity against the initial arsenic concentration for a prior art oxide of cerium (IV);

Fig. 2 is a plot of both arsenic (III) and (V) removal capacity against the initial arsenic concentration for the cerium (IV) oxide composition of the Example;

Fig. 3 is a comparison plot of the percentage of both arsenic (III) and (V) removal against the initial arsenic concentration for a prior art oxide of cerium (IV) and the cerium (IV) oxide composition of the Example;

Fig. 4 is a comparison plot of both the arsenic (III) and (V) removal capacity against pH for a prior art oxide of cerium (IV) and the cerium (IV) oxide composition of the Example;

Fig. 5 is a comparison plot of the ratio of removed arsenic (III) and (V) against pH for a prior art oxide of cerium (IV) and the cerium (IV) oxide composition of the Example;

Fig. 6 is a plot of both the arsenic (III) and (V) removal against the initial arsenic concentration for the cerium (IV) oxide composition of the Example;

Fig. 7 is a plot of both the arsenic (III) and (V) removal against the initial arsenic concentration for a prior art oxide of cerium (IV);

Fig. 8 is a plot of the capacity ratio between the cerium (IV) oxide of the Example and a prior art oxide of cerium (IV) against the amount of arsenic in solution;

Fig. 9 is a comparison plot of the loading capacity of a prior art oxide of cerium (IV) and the cerium (IV) oxide composition of the Example for both arsenic (III) and (V) against the equilibrium arsenic (III/V) value;

Fig. 10 is a comparison plot of the inverse arsenic removal capacity of the cerium (IV) oxide of the Example and a prior art oxide of cerium (IV) against the equilibrium time for both arsenic (III) and (V);

Fig. 11 is a comparison plot of the fluoride removal capacity against the initial fluoride concentration for a prior art oxide of cerium (IV) and the cerium (IV) oxide composition of the Example;

Fig. 12 is a comparison plot of the ratio of removed fluoride against the initial fluoride concentration for a prior art oxide of cerium (IV) and the cerium (IV) oxide composition of the Example;

Fig. 13 is a comparison plot of the fluoride removal capacity against pH for a prior art oxide of cerium (IV) and the cerium (IV) oxide composition of the Example;

Fig. 14 is a comparison plot of the zeta potential of both the cerium (IV) oxide composition of the Example and a prior art oxide of cerium (IV) against pH; and

Fig. 15 is a comparison plot of the particle size distribution for both the cerium (IV) oxide composition of the Example and a prior art oxide of cerium (IV).

DETAILED DESCRIPTION

The process of the disclosure is primarily envisioned for removing one or more of arsenite and arsenate from an aqueous liquid stream using a cerium (IV) oxide (CeO_2) having particular properties. The aqueous liquid stream can be one or more of drinking water and groundwater that contains undesirable amounts of arsenic. Furthermore, the aqueous liquid stream can include without limitation well waters, surface waters (such as water from lakes, ponds and wetlands), agricultural waters, wastewater from industrial processes, and geothermal waters.

Generally, the cerium (IV) oxide composition can be used to treat any aqueous liquid stream containing arsenic. The cerium (IV) oxide composition of the present disclosure has a number of properties that are particularly advantageous for arsenic removal. Contacting of the cerium (IV) oxide composition with the aqueous liquid stream containing the arsenic can effectively reduce the arsenic level in the aqueous liquid stream. The initial level of arsenic in the aqueous liquid stream can be in the parts per million level, in the parts per billion level, or even in the less than 1 parts per billion level. Typically, the aqueous liquid stream includes no more than about 5 ppm, more typically no more than about 2.5 ppm, more typically no more than about 1 ppm, more typically no more than about 500 ppb, more typically no more than about 400 ppb, more typically no more than about 350 ppb, more typically no more than about 300 ppb, more typically no more than about 250 ppb, more typically no more than about 200 ppb, more typically no more than about 150 ppb, more typically no more than about 100 ppb, more typically no more than about 50 ppb, more typically no more than about 25 ppb, and even more typically no more than about 20 ppb of arsenic. The final arsenic level is substantially less than the initial arsenic level.

Typically, the contacting of the cerium (IV) oxide composition with the aqueous liquid stream can reduce the arsenic level in the aqueous liquid stream by more than about 75%. More typically, the contacting of the cerium (IV) oxide composition with the aqueous liquid stream can reduce the arsenic level in the aqueous liquid stream by more than about 80%, more typically more than about 85%, more typically more than about 90%, more typically more than about 95%, more typically more than about 97.5%, and even more typically more than about 99.5%.

The cerium (IV) oxide composition can have a zeta-potential, at pH 7, of more than about 1 mV. While not wanting to be bound by any theory it is believed that the zeta of the cerium (IV) oxide composition can affect the removal of the arsenic from an aqueous liquid stream. Typically, the cerium (IV) oxide composition has a zeta-potential, at pH 7, of more than about 5 mV. More typically, the zeta-potential, at pH 7, of the cerium (IV) oxide composition is more than about 10 mV. Generally, the cerium (IV) oxide composition has a zeta-potential of no more than about 30 mV. More generally, the zeta-potential of the cerium (IV) oxide composition is no more than about 20 mV or even more typically no more than about 15 mV. Commonly, at a pH of about 7, the cerium (IV) oxide composition has zeta-potential of no more than one of about 30 mV, about 20 mV and about 15 mV and a zeta-potential of more than one of about 1 mV, about 5 mV, and 10 mV. The zeta-potential of the cerium (IV) oxide composition at pH 7 usually ranges from about 7.5 to about 12.5 mV. It can be appreciated that the cerium (IV) oxide composition can have any one of the described zeta-potentials in combination with any one or more of the below isoelectric points, surface areas, average pore volumes, average pore sizes, particle sizes, crystalline sizes, and number of acidic sites.

Generally, the cerium (IV) oxide composition typically has an isoelectric point of more than about pH 7, more generally of more than about pH 8, and even more generally of more than about pH 9 but generally no more than about pH 12, more generally no more than about pH 11, and even more generally no more than about pH 10. The isoelectric point typically ranges from about pH 8.5 to about pH 10. While not wanting to be bound by any theory it is believed that the isoelectric point of the cerium (IV) oxide composition can affect the removal of arsenic an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described isolectric points in combination with any one or more of: the above zeta-potentials; and the below surface areas, average pore volumes, average pore sizes, particle sizes, crystalline sizes and number of acidic sites.

The cerium (IV) oxide composition can commonly have a surface area from about 30 to about 200 m^2/g, more commonly from about 60 to about 180 m^2/g, or even more typically from about 100 to about 150 m^2/g. Typically, the surface of the cerium (IV) oxide composition is from about 100 to about 150 m^2/g, more typically from about 110 to about 150 $m^2g/$. While not wanting to be bound by any theory it is believed that the surface area of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described surface areas in combination with any one or more of: the above zeta-potentials and isoelectric points; and the below average pore volumes, average pore sizes, particle sizes, crystalline sizes and number of acidic sites.

The cerium (IV) oxide composition typically has an average (mean, median, and mode) pore volume (as determined by N_2 adsorption) of more than about 0.01 cm^3/g, more typically of more than about 0.1 cm^3/g, and more typically of more than about 0.2 cm^3/g but typically no more than about 0.85 cm^3/g, more typically no more than about 0.8 cm^3/g, more typically no more than about 0.75 cm^3/g, more typically no more than about 0.65 cm^3/g, more typically no more than about 0.6 cm^3/g, more typically no more than about 0.55 cm^3/g, more typically no more than about 0.5 cm^3/g, and even more typically no more than about 0.45 cm^3/g. The pore volume can range from about 0.3 to about 0.4 cm^3/g, from more than about 0.4 to about 0.5 cm^3/g, or from more than about 0.5 to about 0.6 cm^3/g. While not wanting to be bound by any theory it is believed that the average pore volume of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described average pore volumes in combination with any one or more of: the above zeta-potentials, isoelectric points, and surface areas; and the below average pore sizes, particle sizes, crystalline sizes and number of acidic sites.

The cerium (IV) oxide composition generally has an average (mean, median, and mode) pore size (as determined by the BJH method) of more than about 0.5 nm, more generally of more than about 1 nm, and more generally of more than about 6 nm but generally no more than about 20 nm, more generally no more than about 15 nm, and even more generally no more than about 12 nm. The average pore size can range from about 0.5 to about 6.5 nm, from more than about 6.5 to about 13 nm, or from more than about 13 to about 20 nm. While not wanting to be bound by any theory it is believed that the average pore size of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described average pore sizes in combination with any one or more of: the above zeta-potentials, isoelectric points, surface areas and average pore volumes; and the below particle sizes, crystalline sizes and number of acidic sites.

The cerium (IV) oxide composition is usually in particulate form. Typically, the particulate cerium (IV) oxide composition has one or more of a particle size D_{10}, particle size D_{50} and particle D_{90}. While not wanting to be bound by any theory it is believed that the one or more of a particle size D_{10}, particle size D_{50} and particle D_{90}surface area of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described particle sizes D_{10}, D_{50} or D_{90} in combination with any one or more of: the above zeta-potentials, isoelectric points, surface areas, average pore volumes and average pore sizes; and the below crystalline sizes and number of acidic sites.

The particulate cerium (IV) oxide composition commonly has a particle size D_{10} from about 1 to about 3 µm. More commonly, the cerium (IV) oxide composition typically has a particle size D_{10} of more than about 0.05 µm, even more commonly of more than about 0.5 µm, and yet even more commonly of more than about 1 µm but more commonly no more than about 7 µm, even more commonly no more than about 5 µm, and yet even more commonly no more than about 3 µm. The particle size D_{10} typically ranges from about 1 to about 3 µm. While not wanting to be bound by any theory it is believed that the particle size D_{10} of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described D_{10} particle sizes in combination with any one or more of: the above zeta-potentials, isoelectric points, surface areas, average pore volumes and average pore sizes; and the below crystalline sizes and number of acidic sites.

Moreover, the cerium (IV) oxide composition generally has a particle size D_{50} of more than about 2 µm, more generally of more than about 4 µm, and more generally of at least about 5 µm but generally no more than about 20 µm, more generally no more than about 15 µm, and even more generally no more than about 12 µm. The particle size D_{50} usually ranges from about 7.5 to about 10.5 µm. While not wanting to be bound by any theory it is believed that the particle size D_{50} of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described D_{50} particle sizes in combination with any one or more of: the above zeta-potentials, isoelectric points, surface areas, average pore volumes and average pore sizes; and the below crystalline sizes and number of acidic sites.

The cerium (IV) oxide composition commonly has a particle size D_{90} of more than about 12 µm, more commonly of more than about 15 µm, and even more commonly of more than about 20 µm but commonly no more than about 50 µm, more commonly no more than about 40 µm, and even more commonly no more than about 30 µm. The particle size D_{90} generally ranges from about 20 to about 30 µm. While not wanting to be bound by any theory it is believed that the particle size D_{90} of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described D_{90} particle sizes in combination with any one or more of: the above zeta-potentials, isoelectric points, surface areas, average pore volumes and average pore sizes; and the below crystalline sizes and number of acidic sites.

The cerium (IV) oxide composition typically has a crystallite size of more than about 1 nm, more typically of more than about 4 nm, and even more typically of more than about 7.5 nm but typically no more than about 22 nm, more typically no more than about 17 nm, and even more typically no more than about 12.5 nm. The crystallite size commonly ranges from about 7.5 to about 12.5 nm. While not wanting to be bound by any theory it is believed that the crystallite size of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described crystalline sizes in combination with any one or more of the above zeta-potentials, isoelectric points, surface areas, average pore volumes, average pore sizes and particle sizes, and the below number of acidic sites.

Generally, the cerium (IV) oxide has no more than about 0.020 acidic sites/kg as measured by a zeta-potential titration. More generally, the cerium (IV) oxide has no more than about 0.015 acidic sites/kg, even more generally no more than about 0.010 acidic sites/kg, yet even more generally no more than about 0.005 acid sites/kg, and even yet more generally no more than about 0.001 acid sites/kg as measured by a zeta-potential titration. Even yet more generally, the cerium (IV) oxide has about 0 to about 0.001 acid sites/kg as measured by a zeta-potential titration. While not wanting to be bound by any theory it is believed that the number of acid sites/kg of the cerium (IV) oxide composition can affect the removal of arsenic from an aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition can have any one of the described number of acid sites in combination with any one or more of the above zeta-potentials, isoelectric points, surface areas, average pore volumes, average pore sizes and particle sizes.

The level of cerium (IV) oxide, $Ce(IV)O_2$ in the cerium (IV) oxide composition can vary. The cerium (IV) oxide composition typically comprises more than about 75 wt% $Ce(IV)O_2$, more typically more than about 85 wt% $Ce(IV)O_2$, even more typically more than about 90 wt% $Ce(IV)O_2$, or yet even more typically more than about 99.5 wt% $Ce(IV)O_2$.

The cerium (IV) oxide composition can contain rare earth oxides other than cerium (IV) oxide. Commonly, the rare earth oxides other than cerium (IV) oxide comprise no more than about 40 wt.%, more commonly no more than about 25 wt.%, and even more commonly no more than about 10 wt.% of the cerium (IV) oxide composition.

Usually, the cerium (IV) oxide composition can contain non-rare earth materials. Generally, the non-rare earth materials typically comprise no more than about 5 wt.%, more generally no more than about 2.5 wt.%, and even more generally no more than about 1 wt.% of the cerium (IV) oxide composition. In some embodiments, the cerium (IV) oxide composition can be free of any added non-rare materials. That is, the level of non-rare earth materials contained in the cerium (IV) oxide composition typically comprise naturally occurring “impurities” present in cerium oxide. Commonly, any one non-rare material contained in the cerium (IV) oxide composition is no more than about 4 wt%, more commonly no more than about 2.5 wt%, even more commonly no more than about 1 wt% and yet even more commonly no more than about 0.5 wt%.

It can be appreciated that the cerium (IV) oxide composition can have any one or more of the described wt% cerium(IV) oxide, wt% of rare earth oxides other than cerium (IV) oxide, and wt% of non-rare earth materials in combination with any one or more of the above zeta-potentials, isoelectric points, surface areas, average pore volumes, average pore sizes, particle sizes, crystalline sizes, and number of acid sites.

The capacity of the cerium (IV) oxide composition for arsenic can be high, even at low arsenic concentrations in the aqueous liquid stream. The contaminant arsenic removal capacity of the cerium (IV) oxide composition typically is more than about 2.5, more typically more than about 3, more typically more than about 3.5, more typically more than about 4, more typically more than about 4.5, more typically more than about 5, more typically more than about 5.5, more typically more than about 6, more typically more than about 6.5, more typically more than about 7, more typically more than about 7.5, more typically more than about 8, more typically more than about 8.5, more typically more than about 9, more typically more than about 9.5, more typically more than about 10, more typically more than about 10.5, more typically more than about 11, more typically more than about 11.5, more typically more than about 12, more typically more than about 12.5, and even more typically more than about 13 mg arsenic/g CeO_2, even when the arsenic concentration is no more than about 150 μg/L.

The cerium (IV) oxide composition typically has an arsenic adsorption capacity (mg/g)/final arsenic concentration in water (mg/g) ratio of more than about 100, more typically of more than about 250, more typically of more than about 500, more typically of more than about 750, more typically of more than about 1,000, more typically of more than about 1,250, more typically of more than about 1,500, more typically of more than about 1,750, more typically of more than about 2,000, more typically of more than about 2,250, more typically of more than about 2,500, more typically of more than about 2,750, more typically of more than about 3,000, more typically of more than about 3,250, more typically of more than about 3,500, more typically of more than about 3,750, and even more typically of more than about 4,000.

While not wishing to be bound by any theory, it is believed that the difference between one or more the zeta-potential, isoelectric point, surface area, an average (mean, median, and mode) pore volume (as determined by N_2 adsorption), an average (mean, median, and mode) pore size (as determined by the BJH method), D_{10} particle size, D_{50} particle size, D_{90} particle size, crystallite size and number of acidic sites/kg of the cerium (IV) oxide of the present disclosure and oxides of cerium of the prior art enables arsenic to better contact and/or sorb on the cerium (IV) oxide composition than the oxides of cerium (IV) of the prior art.

It can be appreciated the arsenic in the aqueous liquid stream typically dissolved in the aqueous liquid stream and usually exists in both the +3 and +5 oxidation states which respectively correspond to arsenite and arsenate. Techniques for removing arsenate exist and are quite effective, but removing the arsenite is a more difficult proposition because the present technologies for doing so are not greatly effective. It has now been found that substantially all of the dissolved arsenic can be easily removed by treating the aqueous liquid feed with cerium (IV) oxide and resulting in an arsenic-depleted treated aqueous liquid product.

In some embodiments, the arsenic-containing aqueous liquid stream is passed through an inlet into a vessel at a temperature and pressure, usually at ambient temperature and pressure, such that the water in the arsenic-containing aqueous liquid stream remains in the liquid state. In this vessel the arsenic-containing aqueous liquid stream is contacted with the cerium (IV) oxide composition. During the contacting of the cerium (IV) oxide composition with the arsenic of the arsenic -containing aqueous liquid stream, the arsenic one or more of sorbs and reacts with the cerium (IV) oxide composition. The one or more of sorbing and reacting of the cerium (IV) oxide composition with the arsenic removes the arsenic from the arsenic -containing aqueous liquid stream.

In some embodiments, the cerium (IV) oxide composition can be deposited on a support material. Furthermore, the cerium (IV) oxide can be deposited on one or more external and/or internal surfaces of the support material. It can be appreciated that persons of ordinary skill in the art generally refer to the internal surfaces of the support material as pores. The cerium (IV) oxide composition can be supported on the support material with or without a binder. In some embodiments, the cerium (IV) oxide composition can be applied to the support material using any conventional techniques such as slurry deposition.

In some embodiments, the cerium (IV) oxide composition is slurried with the arsenic-containing aqueous liquid stream. It can be appreciated that the cerium (IV) oxide composition and the arsenic -containing aqueous liquid stream are slurried they contact one another. While not wanting to be bound by any theory, it is believed that some, if not most or all of the arsenic in the arsenic-containing aqueous liquid stream is removed from the arsenic-containing aqueous liquid stream by the slurring and/or contacting of the cerium (IV) oxide composition with the arsenic-containing aqueous stream. Following the slurring and/or contacting of the cerium (IV) oxide with the arsenic -containing aqueous liquid stream, the slurry is filtered by any known solid liquid separation method. The term “some” refers to removing no more than about 50% of the arsenic contained in the arsenic-containing aqueous liquid stream. More generally, the term “some” refers to one or more of removing no more than about 10%, no more than about 20%, no more than about 30%, and no more than about 40% of the arsenic contained in the arsenic-containing aqueous liquid stream. The term “most” refers to removing more than about 50% but no more than about

100% of the arsenic contained in the arsenic-containing aqueous liquid stream. More commonly, the term “most” refers to one or more of removing more than about 60%, more than about 70%, more than about 90%, and more than about 90% but no more than 100% of the arsenic contained in the arsenic-containing aqueous liquid stream. The term “all” refers to removing about 100% of the arsenic contained in the arsenic-containing aqueous liquid stream. More generally, the term “all” refers to removing more than 98%, 99%, 99.5%, and 99.9% of the arsenic contained in the arsenic-containing aqueous liquid stream.

In some embodiments, the cerium (IV) oxide composition is in the form of a fixed bed. Moreover, the fixed bed of cerium (IV) oxide is normally comprises cerium (IV) oxide in the form of cerium (IV) oxide particles. The cerium (IV) oxide particles can have a shape and/or form that exposes a maximum cerium (IV) oxide particle surface area to the aqueous liquid stream with minimal back-pressure and the flow of the aqueous liquid stream through the fixed bed. However, if desired, the cerium (IV) oxide particles may be in the form of a shaped body such as beads, extrudates, porous polymeric structures or monoliths. In some embodiments, the cerium (IV) oxide composition can be supported as a layer and/or coating on such beads, extrudates, porous polymeric structures or monolith supports.

The contacting of the cerium (IV) oxide composition with the arsenic-containing aqueous liquid stream normally takes place at a temperature from about 4 to about 100 degrees Celsius, more normally from about 5 to about 40 degrees Celsius. Furthermore, the contacting of cerium (IV) oxide with the arsenic-containing aqueous liquid stream commonly takes place at a pH from about pH 1 to about pH11, more commonly from about pH 3 to about pH 9. The contacting of the cerium (IV) oxide composition with the arsenic-containing aqueous liquid stream generally occurs over a period of time of more than about 1 minute and no more than about 24 hours.

Some embodiments of the present disclosure include a device. The device can contain a cartridge and/or filter for treating an arsenic-containing aqueous stream. It can be appreciated that the arsenic-containing aqueous liquid stream can be a residential drinking water stream and/or source. The device can comprise one or more of a filtering and a cartridge device. Moreover, the device can comprise a container. One or more of the filtering and cartridge devices can be positioned in the container. The filter and cartridge devices can comprise an inlet attached to the source of the drinking water, a filter or cartridge containing the cerium (IV) oxide composition. The cerium (IV) oxide composition can be in the form of a fixed bed or a layer deposited on a substrate such as a porous polymeric structure or monolith. The device can have an outlet. In some embodiments, the cartridge and/or filter device can be configured to fit onto the faucet so that water exiting the faucet passes through the cartridge or filter device for dispensing. After the fixed bed in one of the cartridge or filter devices becomes saturated with arsenic, the cartridge or filter can be replaced with a new cartridge or filter of the same or similar design. The spent cartridge or filter is then disposed of in a legally approved manner.

In another embodiment, the process of the disclosure is used in community water treatment facilities to remove arsenic from drinking water before the water is distributed to local homes and businesses. For such use, the cerium (IV) oxide composition is typically present in large tanks in either slurry form or in a fixed bed so that relatively large amounts of arsenic containing water can be treated either in a continuous or batch mode. The water exiting or treated by the process typically has an arsenic concentration less than about 10 ppb, usually less than 5.0 ppb, and preferably less than 2.0 ppb.

The nature and objects of the disclosure are further illustrated by the following example, which is provided for illustrative purposes only and not to limit the disclosure as defined by the claims.

The following examples are provided to illustrate certain aspects, embodiments, and configurations of the disclosure and are not to be construed as limitations on the disclosure, as set forth in the appended claims. All parts and percentages are by weight unless otherwise specified.

Example

A cerium (IV) oxide composition was prepared by the following method. In a closed, stirred container a one liter of a 0.12 M cerium (IV) ammonium nitrate solution was prepared from cerium (IV) ammonium nitrate crystals dissolved in nitric acid and held at approximately 90°C for about 24 hours. In a separate container 200 ml of a 3M ammonium hydroxide solution was prepared and held at room temperature. Subsequently the two solutions were combined and stirred for approximately one hour. The resultant precipitate was filtered using Bückner funnel equipped with filter paper. The solids were then thoroughly washed in the Bückner using deionized water. Following the washing/filtering step, the wet hydrate was calcined in a muffle furnace at approximately 450°C for three hours to form the cerium (IV) oxide composition.

A cerium (IV) oxide composition used has a zeta-potential of approximately 9.5 mV at a pH of 7, an isoelectric point at about pH 9.1, a surface area between 110 and 150 m^2/g, a particle size D_{10} of approximately 2 μm, a particle size D_{50} of approximately 9 μm, a particle size D_{90} of approximately 25 μm, and a crystallite size of approximately 10 nm. As will be appreciated, crystallite sizes are measured by XRD or TEM and are the size of the individual crystals. The D_{xx} sizes are the size of the particles that are made-up of the individual crystallites and is measured by laser diffraction.

In order to test the arsenic adsorption characteristics of the cerium (IV) oxide composition the following equilibrium isotherm study was done. Test solutions containing arsenic in the form of arsenate or arsenite were prepared according to guidelines for NSF 53 Arsenic Removal water as specified in section 7.4.1.1.3 of NSF/ANSI 53 drinking water treatment units-health effects standards document. 20 milligrams of the cerium (IV) oxide composition, were placed in a sealed 500 milliliter polyethylene container and slurried with about 500 milliliters of the test solution containing arsenic at concentrations as described in Table 1. The resultant slurries were agitated by tumbling the containers for several hours. After agitation, the tap water was separated from the solids by filtration through a 0.45 micron syringe filter and sealed in 125 milliliter plastic sample bottles. The bottles were then sent to a certified drinking water analysis laboratory where the amount of arsenic in each liquid sample was determined by ICP mass spectroscopy. The results of these tests are set forth below in Tables 1 and 2.

Table 1

Initial arsenic(V) concentration before treatment with cerium (IV) oxide composition (µg/L)	Final arsenic(V) concentration after treatment with cerium (IV) oxide composition (µg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)
20	2.6	0.88
75	19.3	2.83
140	52	4.46
290	156.7	6.76
470	310	7.92

Table 2

Initial arsenic(III) concentration before treatment with cerium (IV) oxide composition (µg/L)	Final arsenic(III) concentration after treatment with cerium (IV) oxide composition (µg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)
19	2	0.86
77	2	3.81
140	3.1	6.94
270	23	12.52
440	85	17.57

In order to test the arsenic adsorption characteristics of the cerium (IV) oxide composition at different pH points the following study was done. Test solutions containing arsenic in the form of arsenate or arsenite were prepared at varying pH points according to guidelines for NSF 53 Arsenic Removal water as specified in section 7.4.1.1.3 of NSF/ANSI 53 drinking water treatment units-health effects standards document. 10 to 20 milligrams of the cerium (IV) oxide composition were placed in a sealed 500 milliliter polyethylene container and slurried with about 500 milliliters of the test solution at pH points as described in Tables 3 and 4. The resultant slurries were agitated by tumbling the containers for several hours. After agitation, the tap water was separated from the solids by filtration through a 0.2 micron syringe filter and sealed in 125 milliliter plastic sample bottles. The bottles were then sent to a certified drinking water analysis laboratory where the amount of arsenic in each liquid sample was determined by ICP mass spectroscopy. The results of these tests are set forth below in Tables 3 and 4.

Table 3

pH of water	Initial arsenic(V) concentration before treatment with cerium (IV) oxide composition (μg/L)	Final arsenic(V) concentration after treatment with cerium (IV) oxide composition (μg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)
2.45	140	7.5	3.27
4.50	150	11	6.91
6.50	140	8	7.10
8.52	140	16	6.18
9.54	140	84	2.80
10.56	33	22	0.54

Table 4

pH of water	Initial arsenic(III) concentration before treatment with cerium (IV) oxide composition (μg/L)	Final arsenic(III) concentration after treatment with cerium (IV) oxide composition (μg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)
2.43	130	45	4.27
4.42	130	8	6.02
6.43	130	7	6.21
8.38	130	8	6.17
9.54	130	9	6.06
10.71	69	11	2.92

In order to test the kinetics of arsenic adsorption of the said cerium (IV) oxide composition of the Example the following study was done. Test solutions containing arsenic (V) in the form of arsenate were prepared according to guidelines for NSF 53 Arsenic Removal water as specified in section 7.4.1.1.3 of NSF/ANSI 53 drinking water treatment units-health effects standards document. 10 milligrams of the cerium (IV) oxide composition of the Example, were placed in a sealed 500 milliliter polyethylene container and slurried with about 500 milliliters of the test solution at different pH points containing arsenic at concentrations as described in Tables 5 and 6. The resultant slurries were agitated by tumbling the containers for a set time given to each individual sample. After agitation, the tap water was separated from the solids by filtration through a 0.2 micron syringe filter and sealed in 125 milliliter plastic sample bottles. The bottles were then sent to a certified drinking water analysis laboratory where the amount of arsenic in each liquid sample was determined by ICP mass spectroscopy. The results of these tests are set forth below in Tables 5 and 6.

Table 5

Equilibrium Time (min)	Initial arsenic(V) concentration before treatment with cerium (IV) oxide composition (µg/L)	Final arsenic(V) concentration after treatment with cerium (IV) oxide composition (µg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)	Inverse of the arsenic removal capacity of cerium (IV) oxide composition (1/(mg As/g CeO_2))
18	100	38	3.13	26.32
34	100	27	3.76	37.04
77	100	18	4.18	55.56
139	100	11	4.54	90.91
228	100	6.9	4.66	144.93
475	100	4.1	4.99	243.90

Table 6

Equilibrium Time (min)	Initial arsenic(III) concentration before treatment with cerium (IV) oxide composition (µg/L)	Final arsenic(III) concentration after treatment with cerium (IV) oxide composition (µg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)	Inverse of the arsenic removal capacity of cerium (IV) oxide composition (1/(mg As/g CeO_2))
19	87	50	1.86	20
36	87	38	2.36	26.32
122	87	8	3.87	125
496	87	2	4.31	400.00

Test solutions containing Fluoride were prepared according to guidelines for NSF 53 Arsenic Removal water as specified in section 7.4.1.1.3 of NSF/ANSI 53 drinking water treatment units-health effects standards document. 500 milligrams of the cerium (IV) oxide composition of the Example were placed in a sealed 125 milliliter polyethylene container and slurried with about 50 milliliters of test solution with Fluoride concentrations as described in the Table. The resultant slurries were agitated by tumbling the containers for several hours. After agitation, the test solution was separated from the solids by filtration through a 0.45 micron syringe filter. The filtrate was sealed in 125 milliliter plastic sample bottles and sent to a certified drinking water analysis laboratory where the amount of arsenic in each filtrate was determined by ICP mass spectroscopy. The results of these tests are set forth below in Table 7.

Table 7

Initial Fluoride concentration before treatment with cerium (IV) oxide composition (mg/L)	Final Fluoride concentration after treatment with cerium (IV) oxide composition (mg/L)	Fluoride removal capacity of with cerium (IV) oxide composition (mg F/g CeO_2)
1.14	0.107	0.10
5.1	0.263	0.48
10.7	0.713	1.00
20.4	0.2533	1.80
48	15.600	3.21

Test solutions containing Fluoride were prepared according to guidelines for NSF 53 Arsenic Removal water as specified in section 7.4.1.1.3 of NSF/ANSI 53 drinking water treatment units-health effects standards document. 500 milligrams of the cerium (IV) oxide composition of the Example were placed in a sealed 125 milliliter polyethylene container and slurried with about 50 milliliters of test solution at different pH points as described in the Table. The resultant slurries were agitated by tumbling the containers for several hours. After agitation, the test solution was separated from the solids by filtration through a 0.45 micron syringe filter. The filtrate was sealed in 125 milliliter plastic sample bottles and sent to a certified drinking water analysis laboratory where the amount of arsenic in each filtrate was determined by ICP mass spectroscopy. The results of these tests are set forth below in Table 8.

Table 8

pH of Water	Final Fluoride concentration after treatment with cerium (IV) oxide composition (μg/L)	Fluoride removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)
2.53	0.167	6.82
4.53	1.300	6.45
6.47	2.227	5.10
8.63	3.133	4.22
9.46	9.200	6.06
10.5	6.050	0.95

Comparative Example

Test solutions containing arsenic(V) were prepared according to guidelines for NSF 53 Arsenic Removal water as specified in section 7.4.1.1.3 of NSF/ANSI 53 drinking water treatment units-health effects standards document. 20 milligrams of commercially available oxide of cerium (IV) (CeO_2 prepared by calcining $Ce_2(CO_3)_3 \cdot 6H_2O$ and having a

Zeta potential of about 16 mV at pH 7, an iso-electric point of about pH 8.8, a particle size D_{10} of about 4 um, particle size D_{50} of about 30 um, a particle size D_{90} of about 90 um, and a crystallite size of about 19 nm. in a muffle furnace for 2 hours), were placed in a sealed 500 milliliter polyethylene container and slurried with about 500 milliliters of an arsenic test solution at concentrations as described in Tables 1-8. The resultant slurries were agitated by tumbling the containers for several hours. After agitation, the test solution was separated from the solids by filtration through a 0.45 micron syringe filter. The filtrate was sealed in 125 milliliter plastic sample bottles and sent to a certified drinking water analysis laboratory where the amount of arsenic in each filtrate was determined by ICP mass spectroscopy. The results of these tests are set forth below in Tables 9-16.

Table 9

Initial Arsenic(V) concentration before treatment with an oxide of cerium (IV) of the prior art (μg/L)	Final Arsenic(V) concentration after treatment with an oxide of cerium (IV) of the prior art (μg/L)	Arsenic removal capacity of an oxide of cerium (IV) of the prior art (mg As/g CeO_2)
19	15	0.20
78	65	0.64
190	170	1.00
290	260	1.48
480	443	1.84

Table 10

Initial arsenic(III) concentration before treatment with an oxide of cerium (IV) of the prior art (μg/L)	Final arsenic(III) concentration after treatment with oxide of cerium (IV) of the prior art (μg/L)	Arsenic removal capacity of an oxide of cerium (III) of the prior art (mg As/g CeO_2)
20	2.9	0.85
79	13	3.25
140	32	5.42
270	92	8.78
450	200	12.54

Table 11

pH of water	Initial arsenic(V) concentration before treatment with cerium (IV) oxide composition (µg/L)	Final arsenic(V) concentration after treatment with cerium (IV) oxide composition (µg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)
2.45	140	39	5.15
4.50	150	12	6.89
6.50	140	46	4.75
8.52	140	110	1.50
9.54	140	127	0.67
10.56	33	25	0.38

Table 12

pH of water	Initial arsenic(III) concentration before treatment with cerium (IV) oxide composition (µg/L)	Final arsenic(III) concentration after treatment with cerium (IV) oxide composition (µg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)
2.43	130	22	5.23
4.42	130	5	6.29
6.43	130	14	5.73
8.38	130	35	4.61
9.54	130	61	3.50
10.71	69	36	1.66

Table 13

Equilibrium Time (min)	Initial arsenic(V) concentration before treatment with cerium (IV) oxide composition (µg/L)	Final arsenic(V) concentration after treatment with cerium (IV) oxide composition (µg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)	Inverse of the arsenic removal capacity of cerium (IV) oxide composition (1/(mg As/g CeO_2))
19	100	95	0.25	10.53
34	100	92	0.41	10.87
68	100	87	0.65	11.49
129	100	82	0.88	12.20
222	100	76	1.21	13.16
470	100	68	1.60	14.49

Table 14

Equilibrium Time (min)	Initial arsenic(III) concentration before treatment with cerium (IV) oxide composition (µg/L)	Final arsenic(III) concentration after treatment with cerium (IV) oxide composition (µg/L)	Arsenic removal capacity of cerium (IV) oxide composition (mg As/g CeO_2)	Inverse of the arsenic removal capacity of cerium (IV) oxide composition (1/(mg As/g CeO_2))
19	87	78	0.45	12.82
35	87	80	0.36	12.50
68	87	66	1.00	15.15
122	87	59	1.47	16.95
257	87	52	1.68	19.23
485	87	49	1.88	20.41

Table 15

Initial Fluoride concentration before treatment with cerium (IV) oxide composition (µg/L)	Final Fluoride concentration after treatment with cerium (IV) oxide composition (µg/L)	Fluoride removal capacity of cerium (IV) oxide composition (mg F/g CeO_2)
1.14	0.107	0.10
5.1	0.263	0.48
10.7	0.713	1.00
20.4	0.2533	1.80
48	15.600	3.21

Table 16

pH of Water	Final Fluoride concentration after treatment with with cerium (IV) oxide composition (μg/L)	Fluoride removal capacity of cerium (IV) oxide composition (mg F/g CeO_2)
2.53	0.167	6.82
4.53	1.300	6.45
6.47	2.227	5.10
8.63	3.133	4.22
9.46	9.200	6.06
10.5	6.050	0.95

The advantages of using the novel cerium (IV) oxide composition of this disclosure to the oxide of cerium (IV) of prior are obvious in the above tables and graphs. Superior arsenic removal capacities are evident at all final concentrations in water can be seen Figs. 1-10. Furthermore this exceptional arsenic adsorption capacity results in very low arsenic concentrations in the treated water as is demonstrated Figs. 1-10.

Figs.1-10 uniquely points out the drastic differences in the performance of the cerium (IV) oxide composition and the oxide of cerium (IV) of prior art (comparative Example) On the y-axis the As capacity divided by the Final As concentration is plotted in units of (mg As/g material) / (mg As/L solution).

Referring to Fig. 1, this Fig. shows the Arsenic (III) and (V) removal capacities of an oxide of cerium (IV) of the prior art (Comparative Example). The oxide of cerium (IV) of the prior art removal capacity of arsenic (III) is greater than the removal for arsenic (V). Additionally, the removal capacity of the oxide of cerium (IV) of the prior art for arsenic (III) decreases much slower than it does for arsenic (V) as the initial arsenic concentration increases.

Fig. 2 shows Arsenic (III) and (V) removal capacities of the cerium (IV) oxide composition of the Example. Compared to the oxide of cerium (IV) of the prior art (Comparative Example), the cerium (IV) oxide composition of the Example not only removes more arsenic at every initial concentration level, the removal capacity also decreases more slowly, compared to oxide of cerium (IV) of the prior art as the initial arsenic concentration increases. This is represented by the slopes of each of the lines in Figs. 1 and 2.

Referring to Fig. 3, this Fig. shows the percentage of arsenic (III) and (V) removal for both the oxide of cerium (IV) of the prior art (Comparative Example) and the cerium (IV) oxide composition of Example. In regards to arsenic (III), the cerium (IV) oxide composition (of the Example) removes a greater percentage of arsenic at every initial arsenic (III) concentration level than the oxide of cerium (IV) of prior art (comparative example). Similarly, in regards to arsenic

(V), the cerium (IV) oxide composition of the Example removes a substantially higher percentage of arsenic (V) at every initial arsenic (V) concentration level than the prior art oxide of cerium (IV). Additionally, for arsenic (III), the decrease in the percentage removed as initial arsenic concentration increases is less for the cerium (IV) oxide composition (of the Example) than the prior art oxide of cerium (IV) (Comparative Example).

Fig. 4 shows the removal capacity for both the cerium (IV) oxide composition (of the Example) and the oxide of cerium (IV) of the prior art (comparative example) as a function of pH. First, note that for both arsenic (III) and arsenic (V) at a pH of about pH 4, of the oxide of cerium (IV) of the prior art (Comparative Example) and the cerium (IV) oxide composition (of the Example) show essentially equal capacity. For a pH of less than about pH 4, the oxide of cerium (IV) (Comparative Example) has a greater capacity in regards to both arsenic (III) and arsenic (V). However, once pH reaches levels greater than about pH 4, the cerium (IV) oxide composition (of the Example) has a greater capacity in regards to both arsenic (III) and arsenic (V) than the oxide of cerium (IV) of the prior art (comparative example).

Fig. 5 shows the ratio of removed arsenic to the initial arsenic present as the pH level changes. First, note again that for both arsenic (III) and arsenic (V) at a pH of about 4, oxide of cerium (IV) (Comparative Example) and the cerium (IV) oxide composition (Example) show essentially equal capacity. For a pH of less than about pH 4, the cerium (IV) oxide composition (of the Example) has the highest ration as to arsenic (V), but the lowest as to arsenic (III). However, at a pH of greater than about 4, the cerium (IV) oxide composition (of the Example) has a ratio of removed arsenic (III) that remains consistently over 0.9. In regards to arsenic (V), the cerium (IV) oxide composition (of the Example) has a ratio of approximately 0.9 until a pH of about pH 9, when the ratio steeply declines to about 0.4. The oxide of cerium (IV) of the prior art (Comparative Example), on the other hand, shows the ratio of arsenic (V) declining sharply starting about pH of about pH 4, while the ratio of removed arsenic (III), while not declining as sharply, also declines starting at about pH of about pH 4.

Referring to Fig. 6, this Fig. shows the amount of removed arsenic (III) and (V) for the cerium (IV) oxide composition of Example. The cerium (IV) oxide composition of the Example is able to remove arsenic (III) at much higher quantities at every initial arsenic concentration value, and also the ability to remove arsenic also declines at a slower rate with respect to both arsenic (III) and (V) as compared to the oxide of cerium (IV) of the prior art (Comparative Example).

Fig. 7 shows the amount of removed arsenic (III) and (V) for the oxide of cerium (IV) of the prior art (Comparative Example). While the oxide of cerium (IV) of the prior art (Comparative Example) still removes arsenic (III) much more effectively than arsenic (V), the oxide of cerium (IV) of the prior art is less effective at removing both arsenic (III) and (V) as compared to the cerium (IV) oxide composition (of the Example). Comparing Fig. 7 with Fig. 6, the cerium (IV) oxide composition (of the Example) removes a greater amount of each of arsenic (III) and (V) at every initial concentration level, and the capacity to remove arsenic (III) and (V) decreases at a slower rate as the initial arsenic concentration increases.

Fig. 8 shows the capacity ratio of the cerium (IV) oxide (of the Example) to the oxide of cerium (IV) of the prior art (Comparative Example) for arsenic (III) and (V) removal capacity. For both arsenic (III) and (V), the removal capacity ratio declines steeply between 0 and about 5 ppb of arsenic in solution. For arsenic concentrations above 5 ppb, the decline is much slower, and is essentially linear between about 10 and about 50 ppb. For arsenic (III) concentrations below about 10 ppb, the ratio between the cerium (IV) oxide composition (of the Example) and the oxide of cerium (IV) of the prior art (the Comparative Example) is between approximately 2.8 and 3.8, and even at about 50 ppb the ratio is still approximately 2.4. For arsenic (V) concentrations below about 10 ppb, the ratio between the cerium (IV) oxide composition (of the Example) and the oxide of cerium (IV) of the prior art (Comparative Example) is between approximately 1.6 and 3.1, and even at about 50 ppb the ratio is still approximately 1.1. Thus, the cerium (IV) oxide (of the Example) has a higher capacity than the oxide of cerium (IV) of the prior art for both arsenic (III) and (V) at every arsenic concentration up to at least 50 ppb.

Referring to Fig. 9, this Fig. shows the removal capacity of the cerium (IV) oxide of the composition (of the Example) and the oxide of cerium (IV) of the prior art (Comparative Example) for both arsenic (III) and (V) with respect to the equilibrium of arsenic (III/V). The cerium (IV) oxide composition outperforms the oxide of cerium (IV) of the prior art with respect to both arsenic (III) and (V). With respect to arsenic (III), the cerium (IV) oxide composition shows a steep increase, reaching a removal capacity of about 17 at an equilibrium value of about 0.9. In contrast, the oxide of cerium (IV) of the prior art shows a less steep increase, reaching a removal capacity of only about 13, which it does not reach until an equilibrium value of about 0.2. With respect to arsenic (V), the cerium (IV) oxide composition shows a less steep curve, reaching a removal capacity of about 8 at an equilibrium value of about 0.3. By contrast, the oxide of cerium (IV) of the prior art (Comparative Example) shows a relatively flat curve, only reaching a removal capacity of about 2 at an equilibrium value of about 0.45.

Fig. 10 shows the inverse of the removal capacity as a function of time for the cerium (IV) oxide composition of the Example and the Comparative Example. The cerium (IV) oxide composition of the Example shows an inverse arsenic removal capacity that is substantially higher for both arsenic (III) and (V) than that for the Comparative Example.

Fig. 11 shows the removal of fluoride as a function of initial fluoride concentration for the cerium (IV) oxide composition of the Example and the Comparative Example. The cerium (IV) oxide composition of the Example removes fluoride less effectively than the Comparative

Example for every level of initial fluoride concentration, despite the fact that the cerium (IV) oxide of the Example displays substantially superior arsenic (III) and (V) removal.

Fig. 12 shows the ratio of fluoride removal as a function of initial fluoride concentration for both the cerium (IV) oxide composition of the Example and the Comparative Example. Again, despite showing a substantially superior ability to remove arsenic (III) and (V), the ratio of fluoride removed by the cerium (IV) oxide composition of the Example is lower than that removed by the Comparative Example.

Fig. 13 shows the fluoride removal as a function of pH for both the cerium (IV) oxide composition of the Example and the Comparative Example. The removal ability as a function of pH is less effective for the cerium (IV) oxide composition of the Example than the Comparative Example at every pH level except for pH of about 10. Again, this is despite the fact that the cerium (IV) oxide composition of the Example shows improved results in arsenic (III) and (V) removal as a function of pH for most pH levels.

Fig. 14 shows the zeta potential for both the Example and the Comparative Example as a function of pH. The zeta potential of the cerium (IV) oxide composition of the Example is higher from a pH of about 4 until a pH of about 8.5. For a pH of above about 8.5, the Comparative Example has a larger zeta potential.

Fig. 15 shows the particle size distribution for both the Example and the Comparative Example. The particle size distribution of the Example is much less uniform than that of the Comparative Example, and the cerium (IV) oxide composition of the Example also has a smaller average particle size than the Comparative Example.

The arsenic (III) and arsenic (V) removal data as depicted in Tables 1-6 for the cerium (IV) oxide composition and Tables 9-14 and Figs. 1-10 for the oxide of cerium (IV) of the prior art, the cerium (IV) composition has expected properties towards arsenic (III) and arsenic (IV). In other words, a person of ordinary skill in the art of rare earths and/or water treatment chemistry would not expect the cerium (IV) oxide composition of the present disclosure to remove arsenic from an aqueous stream differently than the oxide of cerium (IV) of the prior art. Furthermore, the cerium (IV) oxide composition remove fluoride from an aqueous differently than the oxide of cerium (IV) of the prior art, as depicted in Tables 7,8, 15 and 16 and Figs.11-13 The cerium (IV) oxide composition has surprising and unexpected removal capacities for arsenite and arsenate, particularly at low levels arsenite and arsenate in aqueous stream.

Another way to think of this is as the distribution coefficient (K). K= [As] in solid/[As] in solution. As can be seen from Tables 17 and 18, if the cerium (IV) oxide composition and the oxide of cerium (IV) have the same capacity, 1) the cerium (IV) oxide composition can treat a significantly lower concentration of As and 2) the final concentration obtained with the cerium

(IV) oxide composition will be drastically lower than in that obtained with the oxide of cerium (IV) of the prior art, as shown in Tables 17 and 18.

At nearly the same initial concentration, the final concentration and capacity are strikingly different. Also when the data is normalized to capacity, the initial and final concentrations are strikingly different.

Table 17

Removal Media	Removal Media Amount	Initial Concentration of Arsenic (ppb)	Final Concentration of Arsenic (ppb)	Removal Media Loading Capacity (mg/g)
Cerium (IV) Oxide Composition	20 mg	100	~3	~5.2
Oxide of Cerium (IV) of the Prior Art	20 mg	100	~70	~2.6

Table 18

Removal Media	Removal Media Amount	Initial Concentration of Arsenic (ppb)	Final Concentration of Arsenic (ppb)	Removal Media Loading Capacity (mg/g)
Cerium (IV) Oxide Composition	20 mg	45	~0.5	~2.2
Oxide of Cerium (IV) of the Prior Art	20 mg	100	~70	~2.6

Therefore, by applying the cerium ((IV) oxide composition of this disclosure to arsenic removal, a) exceptional amounts of arsenic can be removed by a relatively low amount of cerium (IV) oxide composition due to its high arsenic capacity and b) very low arsenic content water can be produced due to its superior arsenic removal capacity at low final arsenic concentrations.

Not wishing to be bound by any theory, the aforementioned examples illustrate that the cerium (IV) oxide composition embodied in the present disclosure provides for much better arsenic removal performance owing to its unique material characteristics. Without the unique characteristics of the cerium (IV) oxide composition embodied in the present disclosure, it is believed that arsenate or arsenite may not easily be able to come into contact with maximum number of active sites on the surface of the cerium (IV) oxide composition.

A number of variations and modifications of the disclosure can be used. It would be possible to provide for some features of the disclosure without providing others.

The present disclosure, in various aspects, embodiments, and configurations, includes components, methods, processes, systems and/or apparatus substantially as depicted and described herein, including various aspects, embodiments, configurations, subcombinations, and subsets thereof. Those of skill in the art will understand how to make and use the various aspects, aspects, embodiments, and configurations, after understanding the present disclosure. The present disclosure, in various aspects, embodiments, and configurations, includes providing devices and processes in the absence of items not depicted and/or described herein or in various aspects, embodiments, and configurations hereof, including in the absence of such items as may have been used in previous devices or processes, e.g., for improving performance, achieving ease and\or reducing cost of implementation.

The foregoing discussion of the disclosure has been presented for purposes of illustration and description. The foregoing is not intended to limit the disclosure to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the disclosure are grouped together in one or more, aspects, embodiments, and configurations for the purpose of streamlining the disclosure. The features of the aspects, embodiments, and configurations of the disclosure may be combined in alternate aspects, embodiments, and configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the claimed disclosure requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed aspects, embodiments, and configurations. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate preferred embodiment of the disclosure.

Moreover, though the description of the disclosure has included description of one or more aspects, embodiments, or configurations and certain variations and modifications, other variations, combinations, and modifications are within the scope of the disclosure, e.g., as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative aspects, embodiments, and configurations to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

CLAIMS

What is claimed is:

1. A method, comprising:

contacting a cerium (IV) oxide composition with an arsenic-containing aqueous stream, wherein one or more of the following (i) through (vi) is true:

(i) the cerium (IV) oxide composition has a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV;

(ii) the cerium (IV) oxide composition has a particle size D_{10} of more than about 0.5 μm and no more than about 7 μm;

(iii) the cerium (IV) oxide composition has a particle size D_{50} of more than about 2 μm and no more than about 20 μm;

(iv) the cerium (IV) oxide composition has a particle size D_{90} of more than about 12 μm and no more than about 50 μm;

(v) the cerium (IV) oxide composition has a crystallite size of more than about 1 nm and no more than about 22 nm; and

(vi) the cerium (IV) oxide composition has an acidic site concentration of more than about 0.0001 acidic sites/kg and no more than about 0.020 acidic sites/kg; and

wherein the contacting of the cerium (IV) oxide composition with the arsenic-containing aqueous stream removes some of the arsenic from the biological contaminant-containing aqueous stream.

2. The method of claim 1, wherein the arsenic comprises one or both of arsenite and arsenate.

3. The method of claim 2, wherein one or more of following are true:

(I) wherein the cerium (IV) oxide composition removes about 125% more arsenic (III) per gram of CeO2 per μg/L of arsenic (III) in the arsenic-containing stream than an oxide of cerium (IV);

(II) wherein the cerium (IV) oxide composition removes about 150% more arsenic (III) per gram of CeO2 per μg/L of arsenic (III) in the arsenic-containing stream than an oxide of cerium (IV);

(III) wherein the cerium (IV) oxide composition removes about 200% more arsenic (V) per gram of CeO2 per μg/L of arsenic (V) in the arsenic-containing stream than an oxide of cerium (IV);

(IV) wherein the cerium (IV) oxide composition removes about 400% more arsenic (V) per gram of CeO2 per μg/L of arsenic (V) in the arsenic-containing stream than an oxide of cerium (IV) and wherein one or more of (i), (ii), (iii), (iv), (v) and (vi) are false for the oxide of cerium (IV).

4. The method of claim 2, wherein one or more of the following are true;

(A) wherein the cerium (IV) oxide composition removes about 125% more arsenic (III) per µg/L of arsenic (III) in the arsenic-containing stream than an oxide of cerium (IV);

(B) wherein the cerium (IV) oxide composition removes about 150% more arsenic (III) per µg/L of arsenic (III) in the arsenic-containing stream than an oxide of cerium (IV);

(C) wherein the cerium (IV) oxide composition removes about 200% more arsenic (V) per µg/L of arsenic (V) in the arsenic-containing stream than an oxide of cerium (IV);

(D) wherein the cerium (IV) oxide composition removes about 400% more arsenic (V) per µg/L of arsenic (V) in the arsenic-containing stream than an oxide of cerium (IV);

(E) wherein the arsenic-containing aqueous stream has a pH from about pH 4.5 to about 9.5 during the contacting of the cerium (IV) oxide and the arsenic-containing, wherein the cerium (IV) oxide composition removes more arsenic per gram of CeO_2 than an oxide of cerium (IV) oxide and

wherein one or more of (i), (ii), (iii), (iv), (v) and (vi) are false for the oxide of cerium (IV).

5. The method of claim 2, wherein the cerium (IV) oxide composition has a loading capacity for arsenite of from 2.1 to about 6.0 mg/g for an equilibrium arsenite concentration of from about 0.5 to about 5 ppb and wherein the cerium (IV) oxide composition has a loading capacity for arsenate of from 0.1 to about 0.2 mg/g for an equilibrium arsenate concentration of from about 0.5 to about 2.5 ppb.

6. The method of claim 1, wherein one of the following is true:

(a) wherein one of (i) through (vi) is true and the other five of (i) through (vi) are false;

(b) wherein two of (i) through (vi) are true and the other four of (i) through (vi) are false;

(c) wherein three of (i) through (vi) are true and the other three of (i) through (vi) are false;

(d) wherein four of (i) through (vi) are true and the other two of (i) through (vi) are false;

(e) wherein five of (i) through (vi) are true and the other one of (i) through (vi) is false; and

(f) wherein all six of (i) through (vi) are true.

7. The method of claim 1, wherein one or more of the following is true:

(a) wherein the zeta potential at about pH 7 is from about 7.5 to about 12.5 mV;

(b) wherein the particle size D_{10} is from about 1 to about 3 µm;

(c) wherein the particle size D_{50} is from about 7.5 to about 10.5 µm;

(d) wherein the particle size D_{90} is from about 20 to about 30 μm;

(e) wherein the crystallite size is from about 7.5 to about 12. 5 nm; and

(f) wherein the number of acid sites is no more than about 0.02 acidic sites/kg.

8. The method of claim 1, wherein the cerium (IV) oxide composition comprises rare earth oxides other than Ce $(IV)O_2$ and wherein the rare earth oxides other than Ce $(IV)O_2$ comprise one of no more than about 40, no more than about 25 and no more than about 10 wt% of the cerium (IV) oxide composition.

9. The method of claim 1, wherein the cerium (IV) oxide lacks any added non-rare earth materials comprising one or more silcon, titanium and zirconium.

10. The method of claim 1, wherein the cerium (IV) oxide composition has a loading capacity for arsenite of from 2.1 to about 6.0 mg/g for an equilibrium arsenite concentration of from about 0.5 to about 5 ppb.

11. The method of claim 1, wherein the cerium (IV) oxide composition has a loading capacity for arsenate of from 0.1 to about 0.2 mg/g for an equilibrium arsenate concentration of from about 0.5 to about 2.5 ppb.

12. A device, comprising:

an inlet to receive

an aqueous stream having a first level of arsenic;

a contacting chamber, in fluid communication with the inlet and containing a cerium (IV) oxide composition to contact the aqueous stream, wherein one or more of the following (i)-(vi) is true:

(i) the cerium (IV) oxide composition has a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV;

(ii) the cerium (IV) oxide composition has a particle size D_{10} of more than about 0.5 μm and no more than about 7 μm;

(iii) the cerium (IV) oxide composition has a particle size D_{50} of more than about 2 μm and no more than about 20 μm;

(iv) the cerium (IV) oxide composition has a particle size D_{90} of more than about 12 μm and no more than about 50 μm;

(v) the cerium (IV) oxide composition has a crystallite size of more than about 1 nm and no more than about 22 nm; and

(vi) the cerium (IV) oxide composition has an acidic site concentration of more than about 0.0001 acidic sites/kg and no more than about 0.020 acidic sites/kg; and wherein the aqueous stream has the first level of arsenic prior to the of the aqueous stream contacting the cerium (IV) oxide composition and a second level of arsenic after the contacting of the aqueous stream with the cerium (IV) oxide, wherein the first level of arsenic is greater than the second level of arsenic, and

an outlet in fluid communication with the contacting chamber to output the aqueous stream having the second level arsenic.

13. The device of claim 12, wherein the arsenic comprises arsenite.

14. The device of claim 12, wherein the arsenic comprises arsenate.

15. The device of claim 12, wherein one of the following is true:

(I) wherein one of (i) through (vi) is true and the other five of (i) through (vi) are false;

(II) wherein two of (i) through (vi) are true and the other four of (i) through (vi) are false;

(III) wherein three of (i) through (vi) are true and the other three of (i) through (vi) are false;

(IV) wherein four of (i) through (vi) are true and the other two of (i) through (vi) are false;

(V) wherein five of (i) through (vi) are true and the other one of (i) through (vi) is false; and

(VI) wherein all six of (i) through (vi) are true.

16. The device of claim 12, wherein one or more of the following is true:

(a) wherein the zeta potential at about pH 7 is from about 7.5 to about 12.5 mV;

(b) wherein the particle size D_{10} is from about 1 to about 3 µm;

(c) wherein the particle size D_{50} is from about 7.5 to about 10.5 µm;

(d) wherein the particle size D_{90} is from about 20 to about 30 µm;

(e) wherein the crystallite size is from about 7.5 to about 12. 5 nm; and

(f) wherein the number of acid sites is no more than about 0.02 acidic sites/kg.

17. The device of claim 12, wherein the cerium (IV) oxide composition removes more arsenic per gram of CeO_2 than an oxide of cerium (IV) and wherein one or more of (i), (ii), (iii), (iv), (v) and (vi) are false for the oxide of cerium (IV).

18. A composition, comprising:

a cerium (IV) oxide composition having sorbed arsenic, wherein one or more of the following (i) through (vi) is true:

(i) the cerium (IV) oxide composition has, prior to the biological contaminant being sorbed, a zeta potential at about pH 7 of no more than about 30 mV and of more than about 1 mV;

(ii) the cerium (IV) oxide composition has a particle size D_{10} of more than about 0.5 µm and no more than about 7 µm;

(iii) the cerium (IV) oxide composition has a particle size D_{50} of more than about 2 µm and no more than about 20 µm;

(iv) the cerium (IV) oxide composition has a particle size D_{90} of more than about 12 µm and no more than about 50 µm;

(v) the cerium (IV) oxide composition has a crystallite size of more than about 1 nm and no more than about 22 nm; and

(vi) the cerium (IV) oxide composition has, prior to the biological contaminant being sorbed, an acidic site concentration of more than about 0.0001 acidic sites/kg and no more than about 0.020 acidic sites/kg.

19. The composition of claim 18, wherein the sorbed arsenic comprises one or more of arsenite and arsenate and wherein one of the following is true:

(I) wherein one of (i) through (vi) is true and the other five of (i) through (vi) are false;

(II) wherein two of (i) through (vi) are true and the other four of (i) through (vi)are false;

(III) wherein three of (i) through (vi) are true and the other three od (i) through (vi) are false;

(IV) wherein four of (i) through (vi) are true and the other two of (i) through (vi) are false;

(V) wherein five of (i) through (vi) are true and the other one of (i) through (vi) is false; and

(VI) wherein all six of (i) through (vi) are true.

20. The composition of claim 18, wherein the sorbed arsenic comprises one or more of arsentite and arsenate and wherein one or more of the following is true:

(a) the zeta potential at about pH 7 is from about 7.5 to about 12.5 mV;

(b) the particle size D_{10} is from about 1 to about 3 µm;

(c) the particle size D_{50} is from about 7.5 to about 10.5 µm;

(d) the particle size D_{90} is from about 20 to about 30 µm;

(e) the crystallite size is from about 7.5 to about 12. 5 nm; and

(f) the number of acid sites is wherein the number of acid sites is no more than about 0.02 acidic sites/kg.

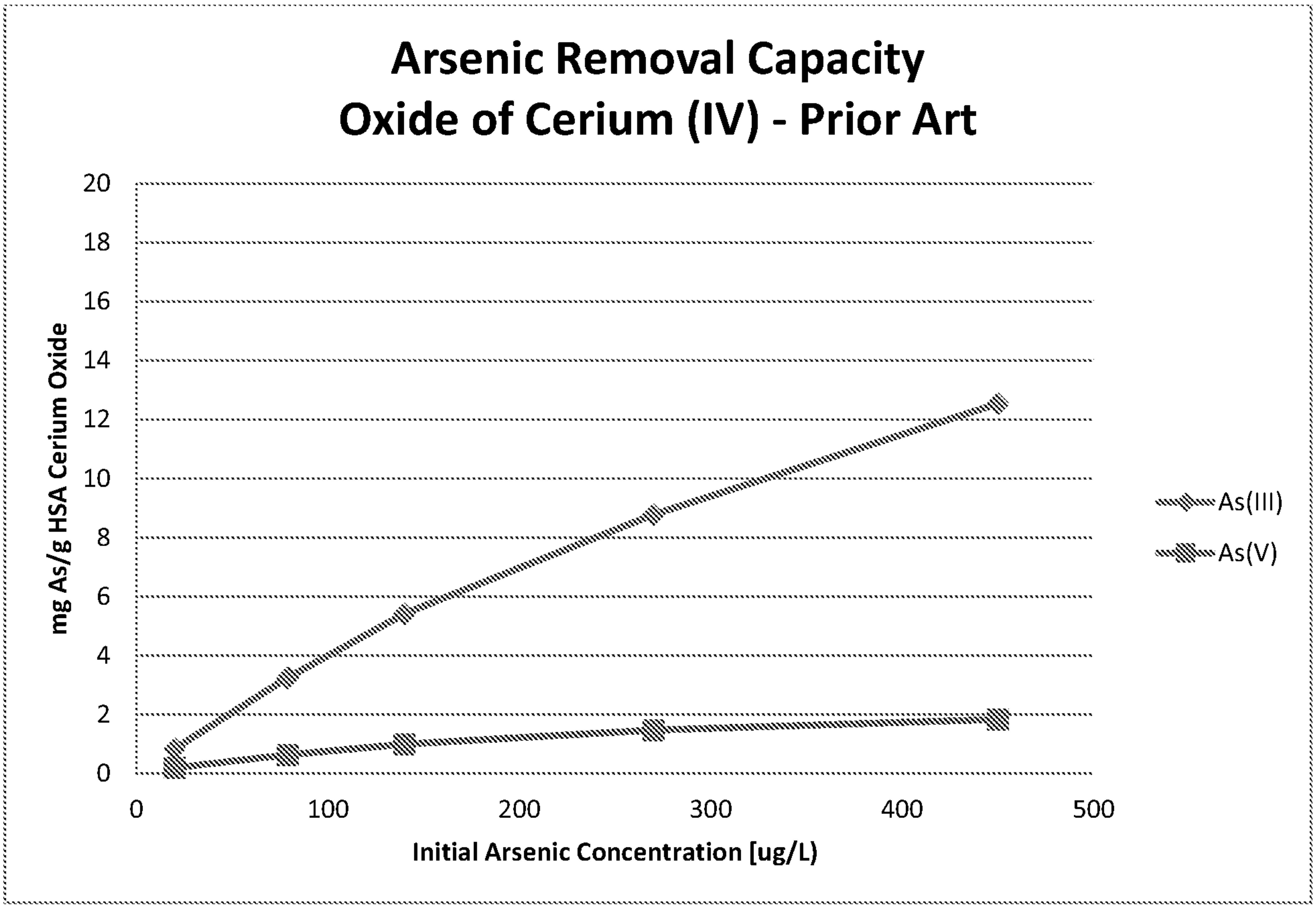

Arsenic Removal Capacity
Oxide of Cerium (IV) - Prior Art
mg As/g HSA Cerium Oxide
20
18
16
14
12
10
8
6
4
2
0
0
100
200
300
400
500
Initial Arsenic Concentration [ug/L]
As(III)
As(V)

FIG. 1

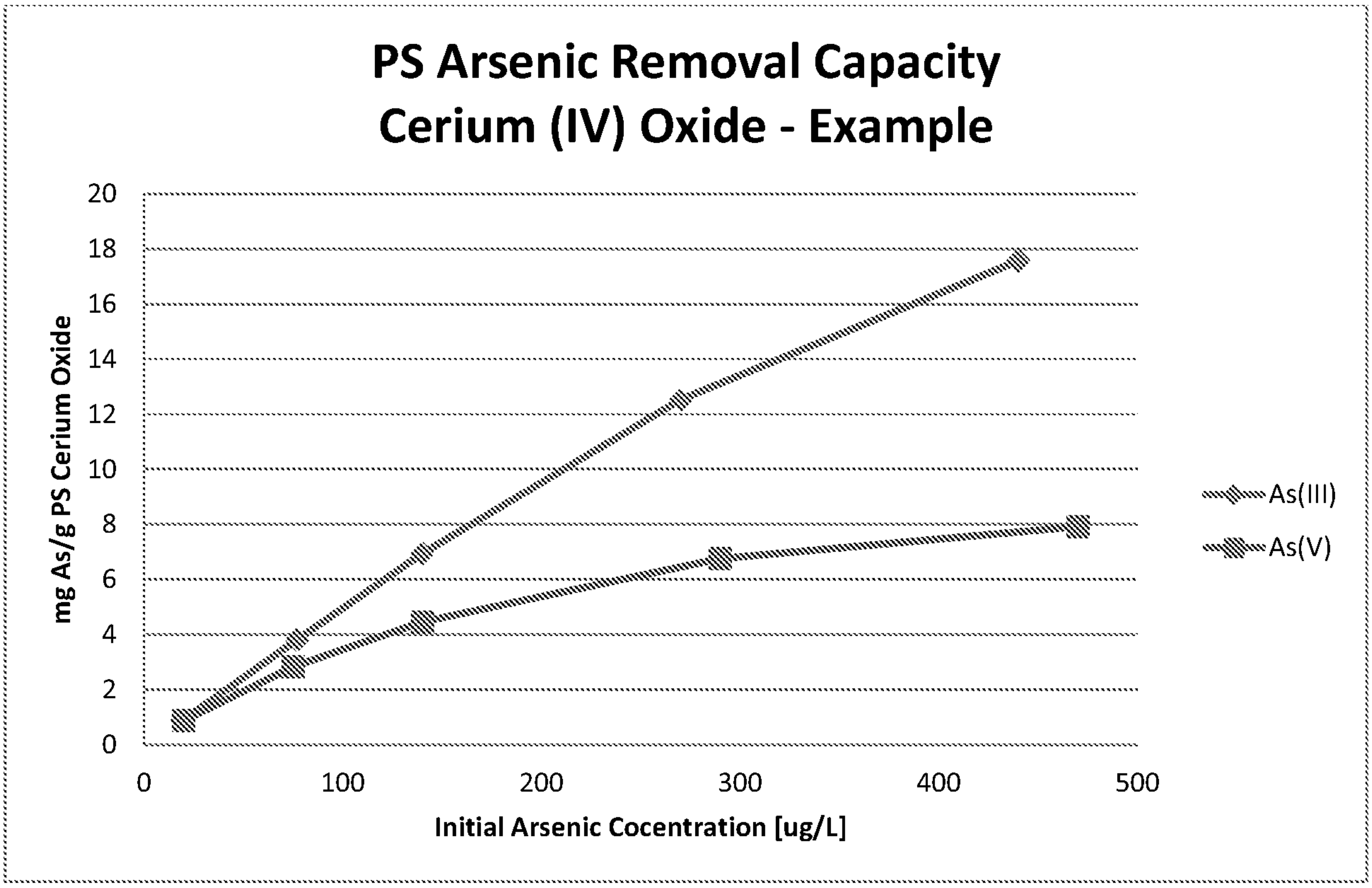

PS Arsenic Removal Capacity
Cerium (IV) Oxide - Example
mg As/g PS Cerium Oxide
0
2
4
6
8
10
12
14
16
18
20
0
100
200
300
400
500
Initial Arsenic Cocentration [ug/L]
As(III)
As(V)

FIG. 2

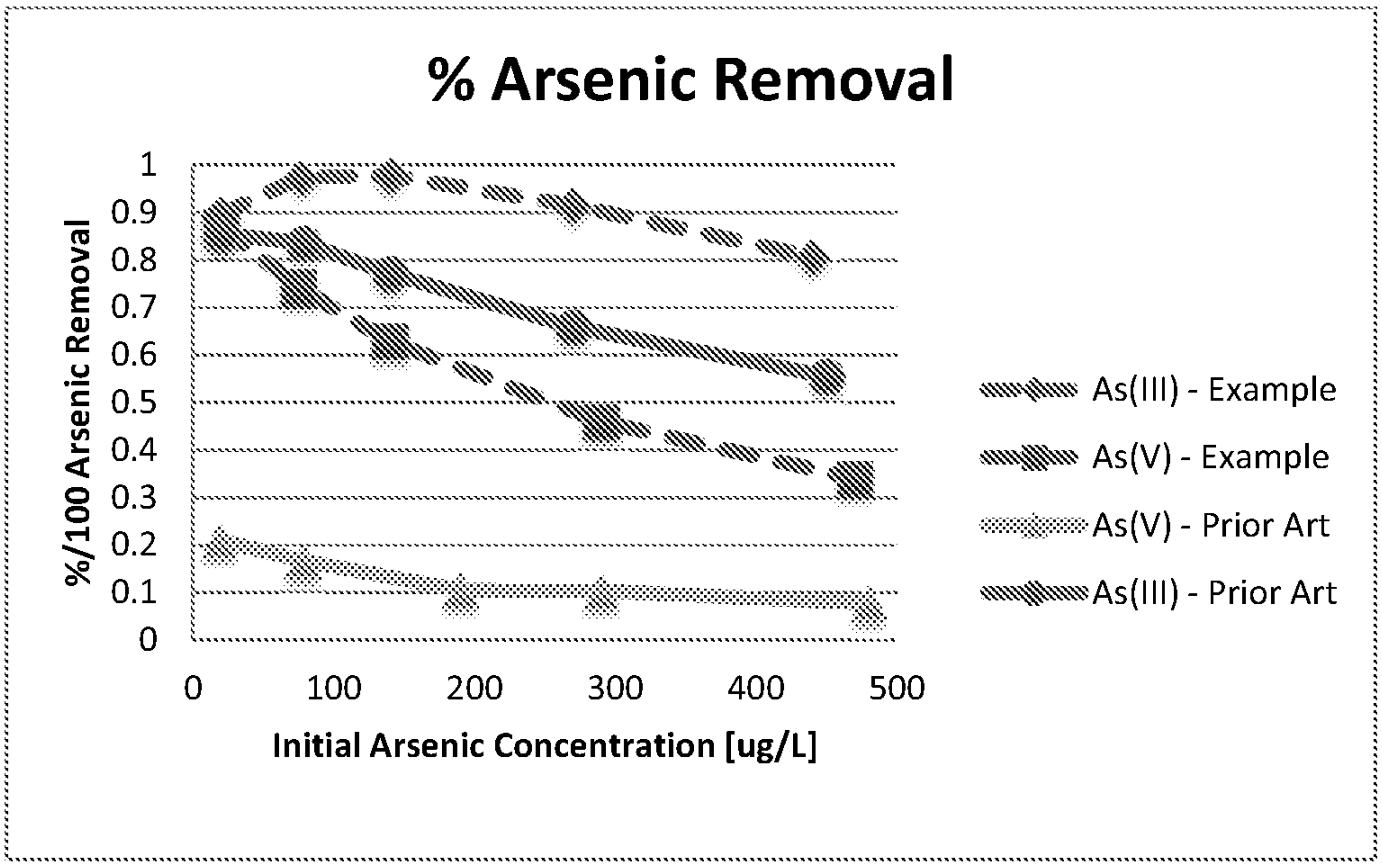

% Arsenic Removal
%/100 Arsenic Removal
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
100
200
300
400
500
Initial Arsenic Concentration [ug/L]
As(III) - Example
As(V) - Example
As(V) - Prior Art
As(III) - Prior Art

FIG. 3

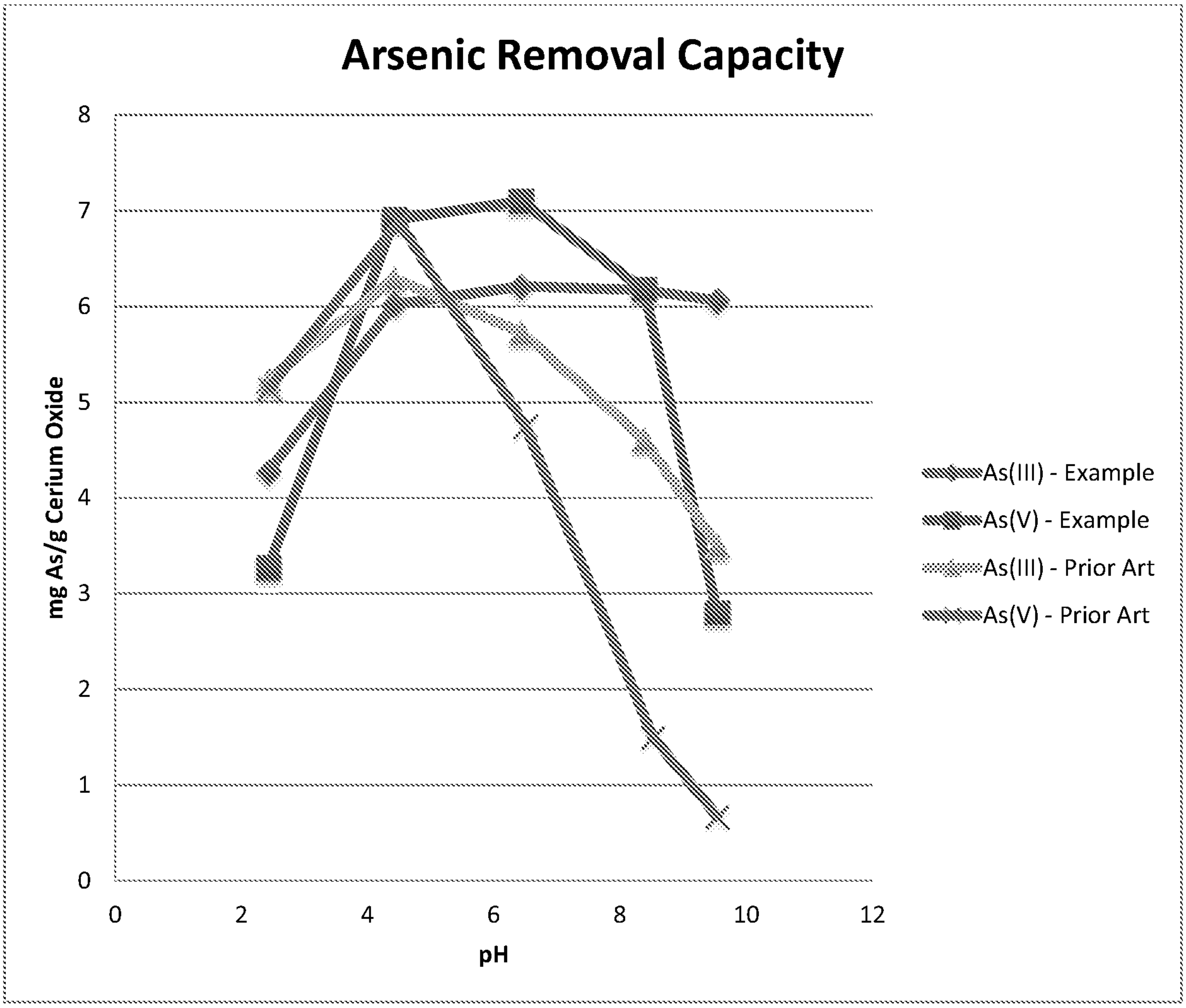

Arsenic Removal Capacity
mg As/g Cerium Oxide
pH
0
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
As(III) - Example
As(V) - Example
As(III) - Prior Art
As(V) - Prior Art

FIG. 4

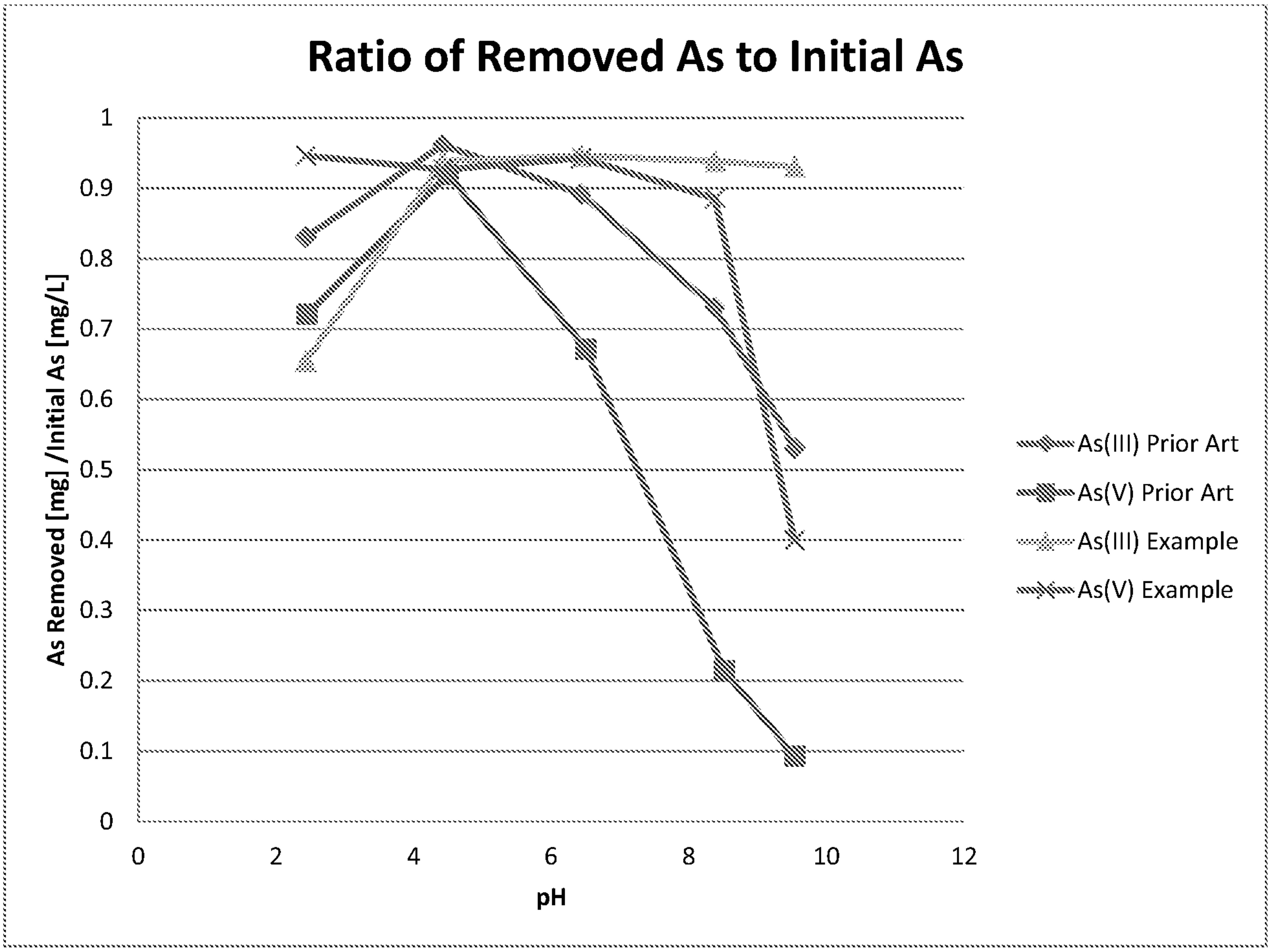

Ratio of Removed As to Initial As
As Removed [mg] /Initial As [mg/L]
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10
12
pH
As(III) Prior Art
As(V) Prior Art
As(III) Example
As(V) Example

FIG. 5

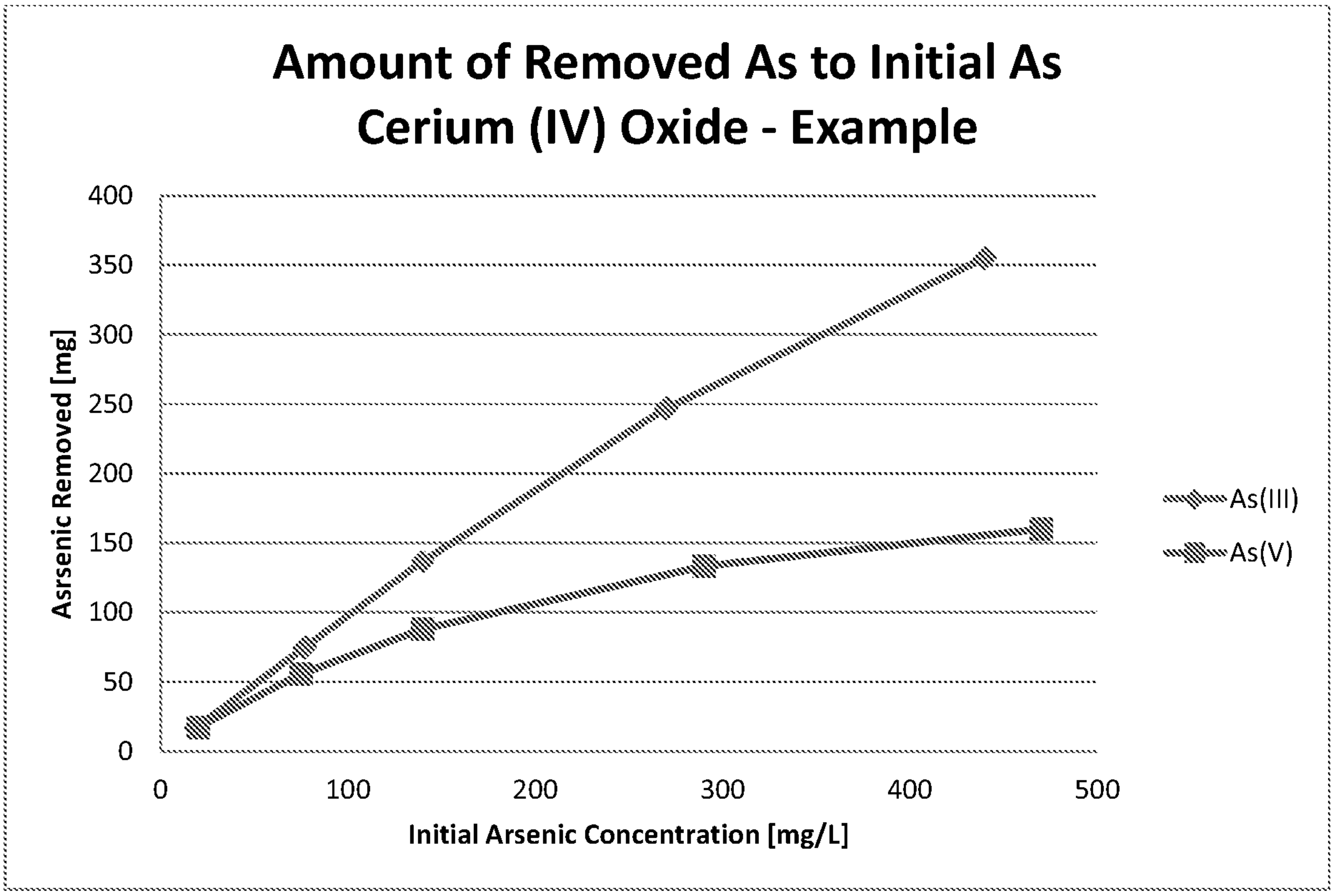

Amount of Removed As to Initial As
Cerium (IV) Oxide - Example
Asrsenic Removed [mg]
400
350
300
250
200
150
100
50
0
0
100
200
300
400
500
Initial Arsenic Concentration [mg/L]
As(III)
As(V)

FIG. 6

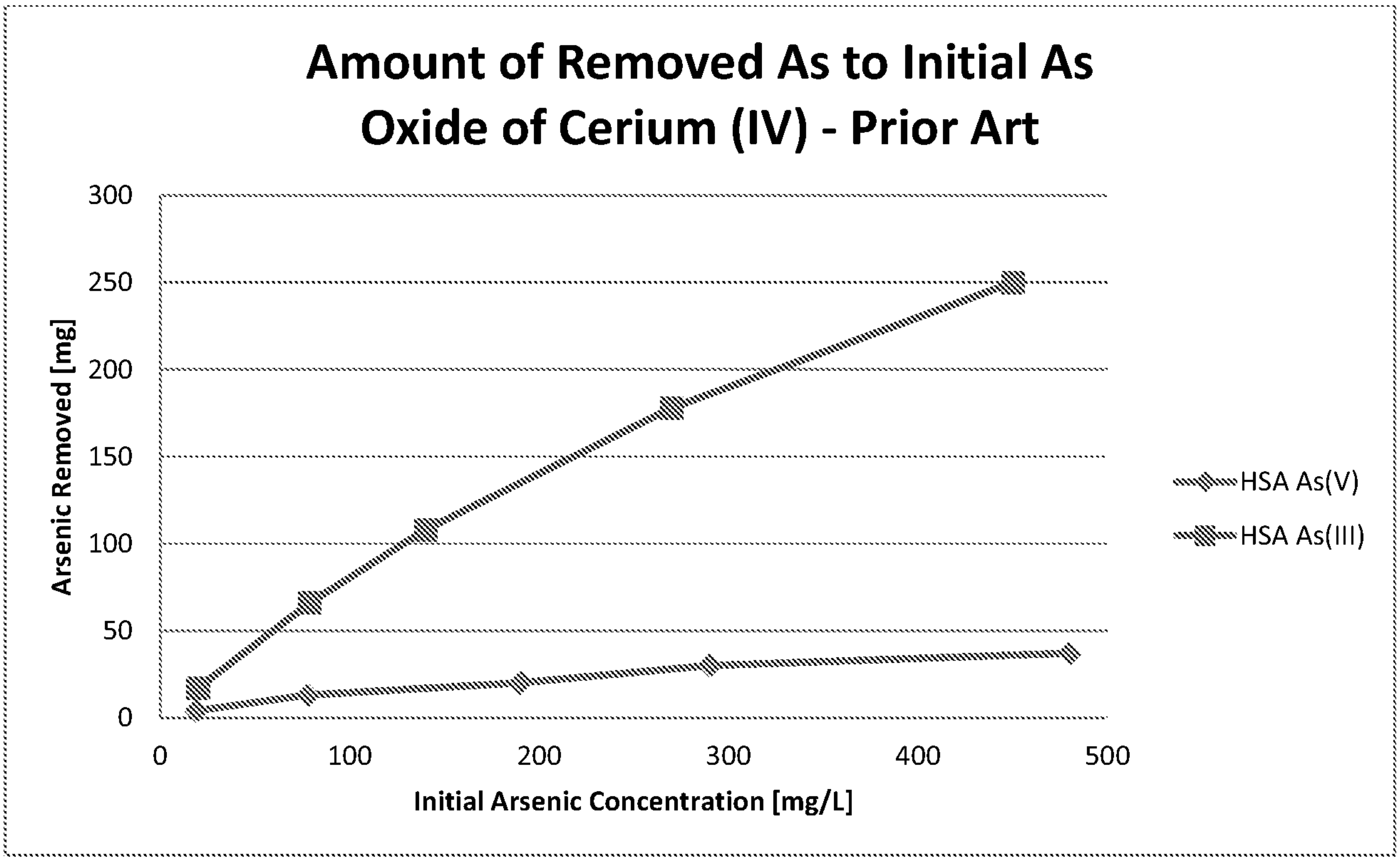

Amount of Removed As to Initial As
Oxide of Cerium (IV) - Prior Art
Arsenic Removed [mg]
300
250
200
150
100
50
0
0
100
200
300
400
500
Initial Arsenic Concentration [mg/L]
HSA As(V)
HSA As(III)

FIG. 7

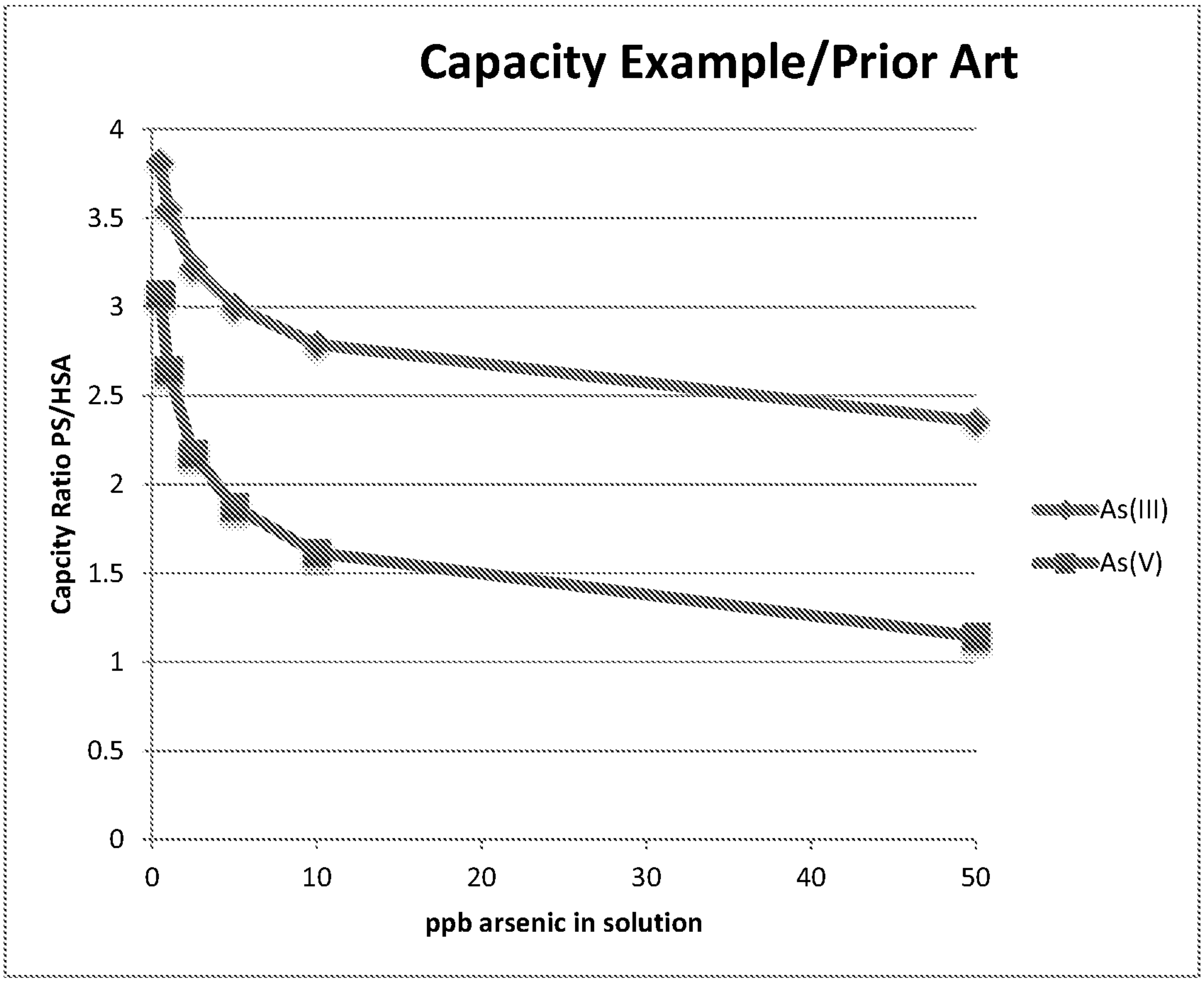

Capacity Example/Prior Art
Capcity Ratio PS/HSA
4
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
50
ppb arsenic in solution
As(III)
As(V)

FIG. 8

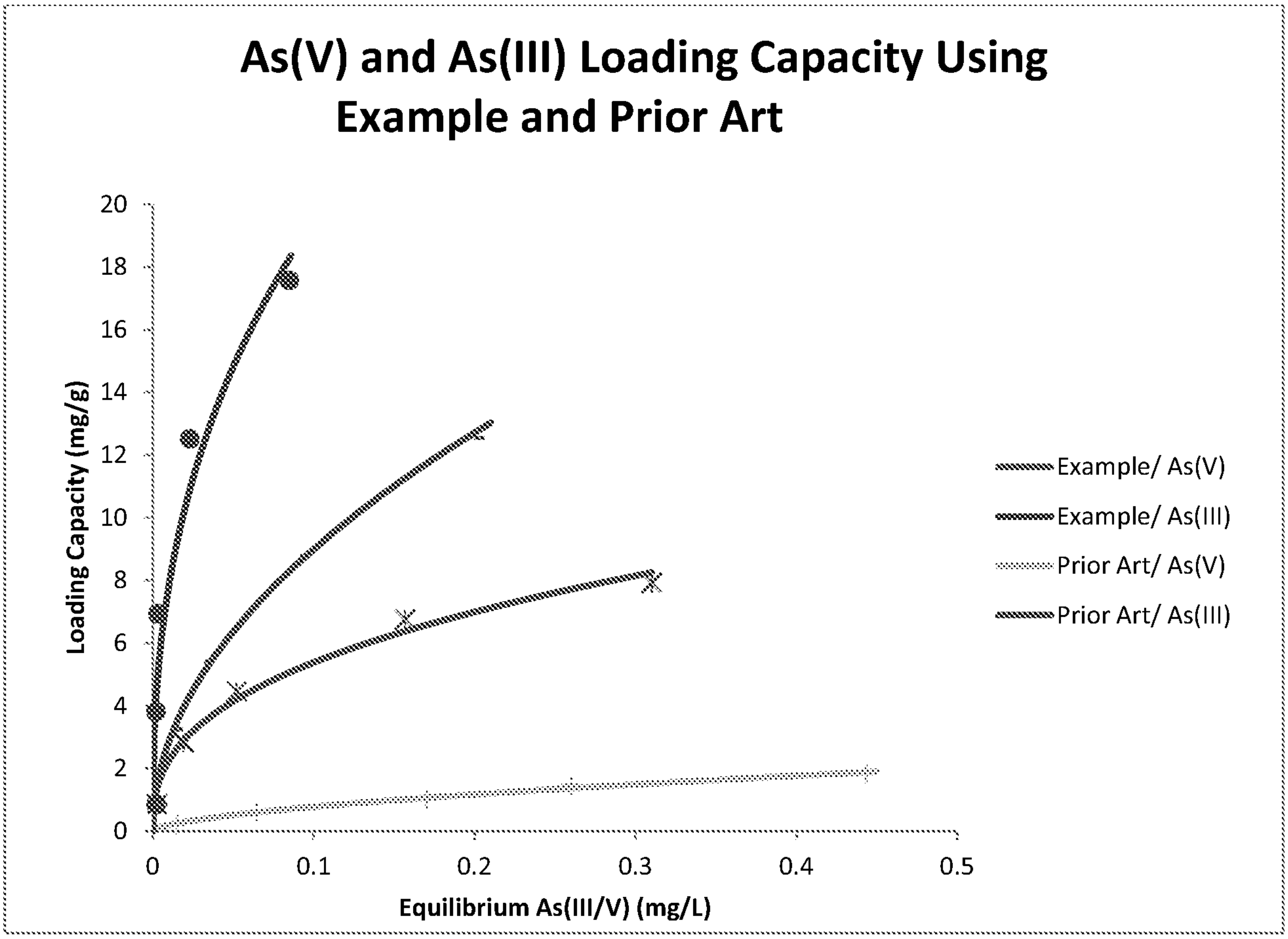

As(V) and As(III) Loading Capacity Using Example and Prior Art
Loading Capacity (mg/g)
20
18
16
14
12
10
8
6
4
2
0
0
0.1
0.2
0.3
0.4
0.5
Equilibrium As(III/V) (mg/L)
Example/ As(V)
Example/ As(III)
Prior Art/ As(V)
Prior Art/ As(III)

FIG. 9

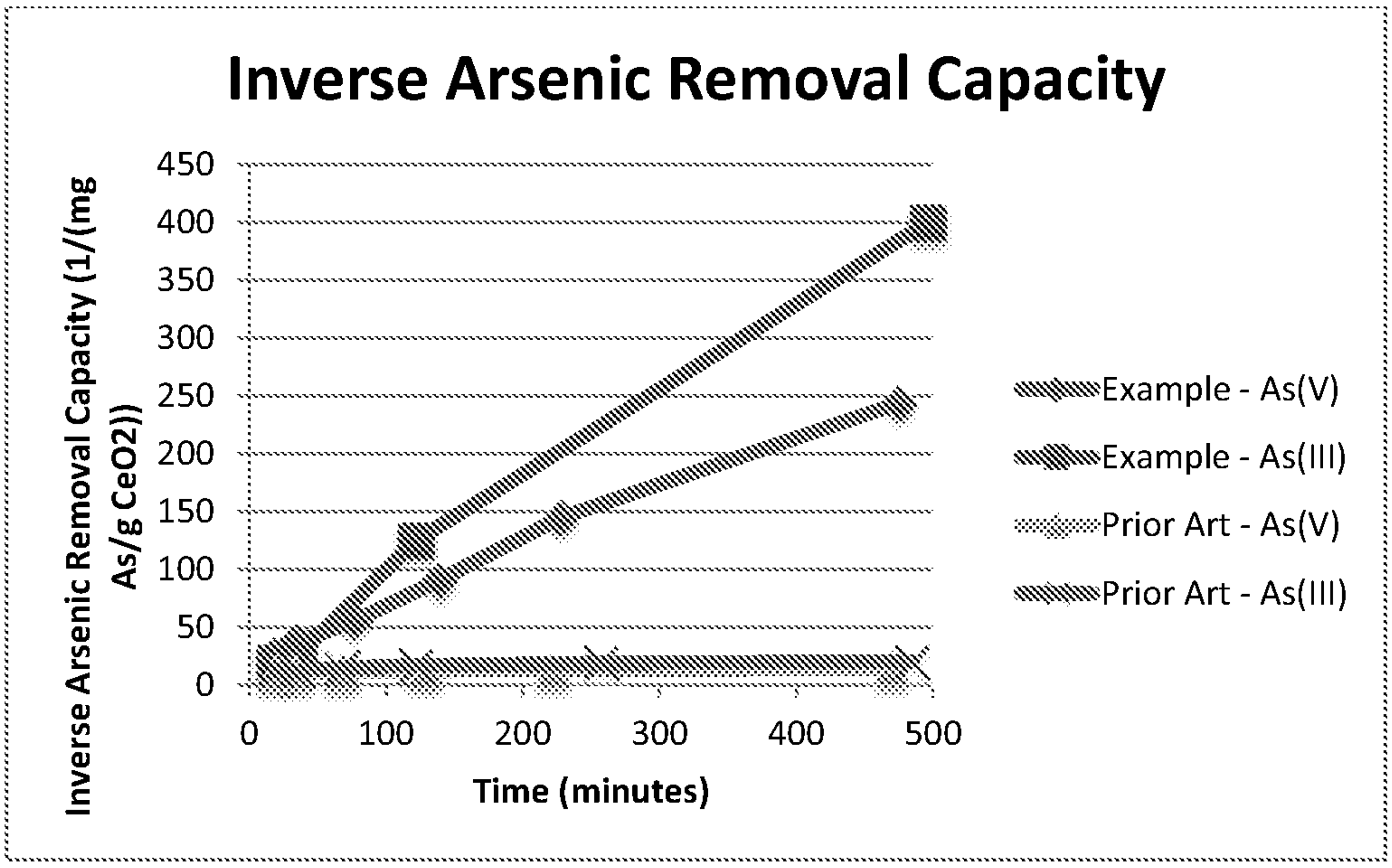

Inverse Arsenic Removal Capacity
Inverse Arsenic Removal Capacity (1/(mg As/g CeO2))
450
400
350
300
250
200
150
100
50
0
0
100
200
300
400
500
Time (minutes)
Example - As(V)
Example - As(III)
Prior Art - As(V)
Prior Art - As(III)

FIG. 10

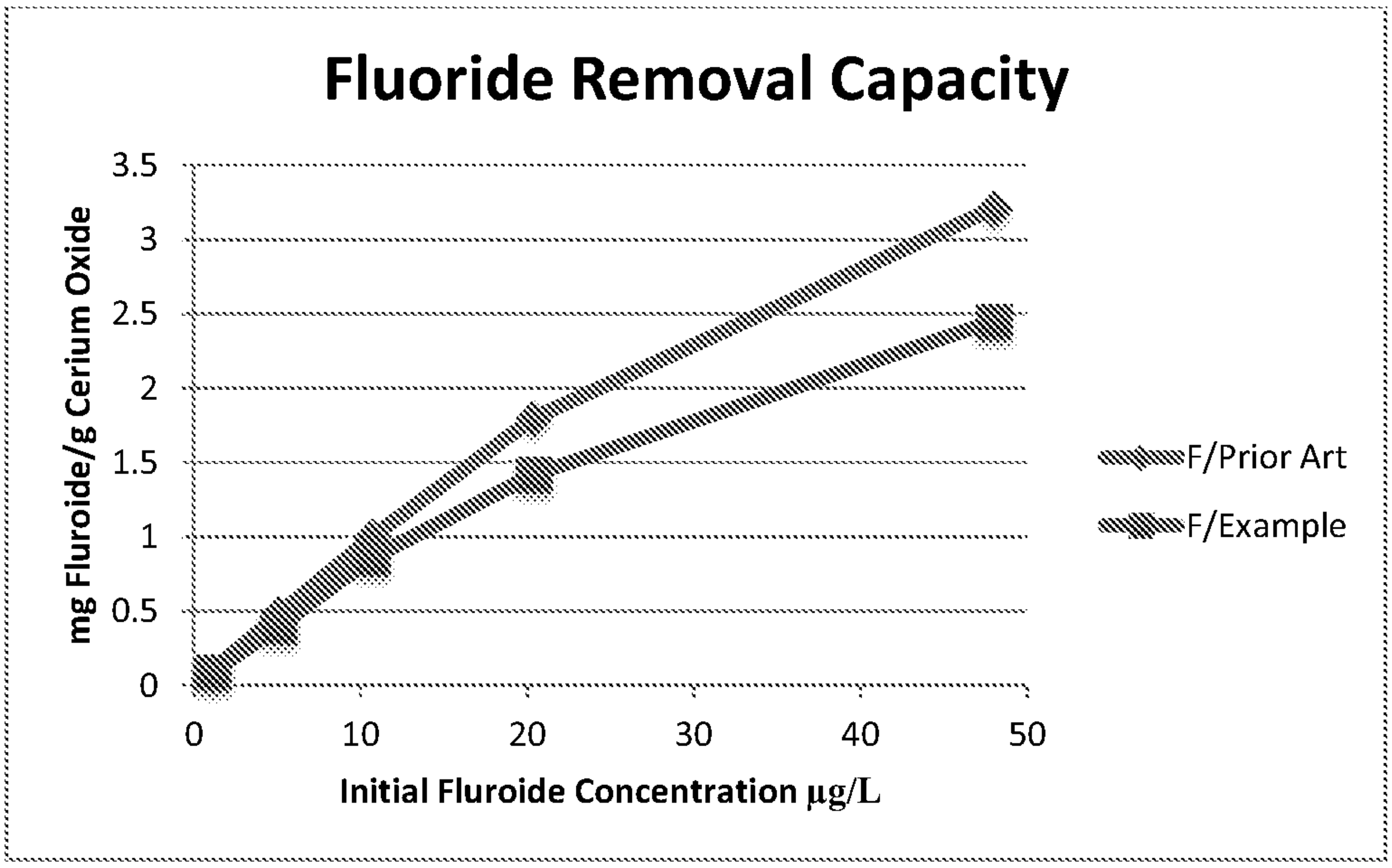

Fluoride Removal Capacity
mg Fluroide/g Cerium Oxide
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
50
Initial Fluroide Concentration µg/L
F/Prior Art
F/Example

FIG. 11

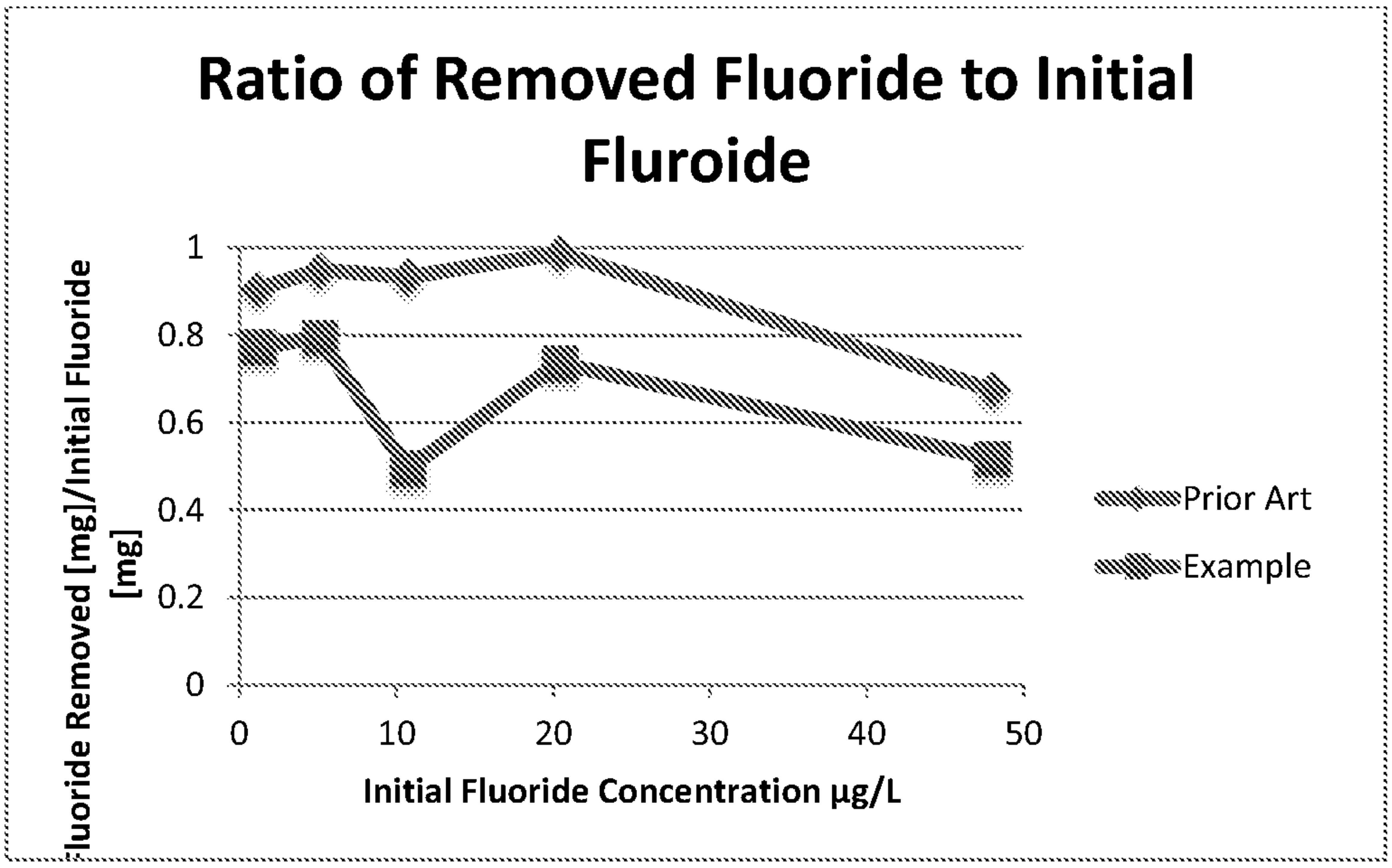

Ratio of Removed Fluoride to Initial Fluroide
luoride Removed [mg]/Initial Fluoride [mg]
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
Initial Fluoride Concentration µg/L
Prior Art
Example

FIG. 12

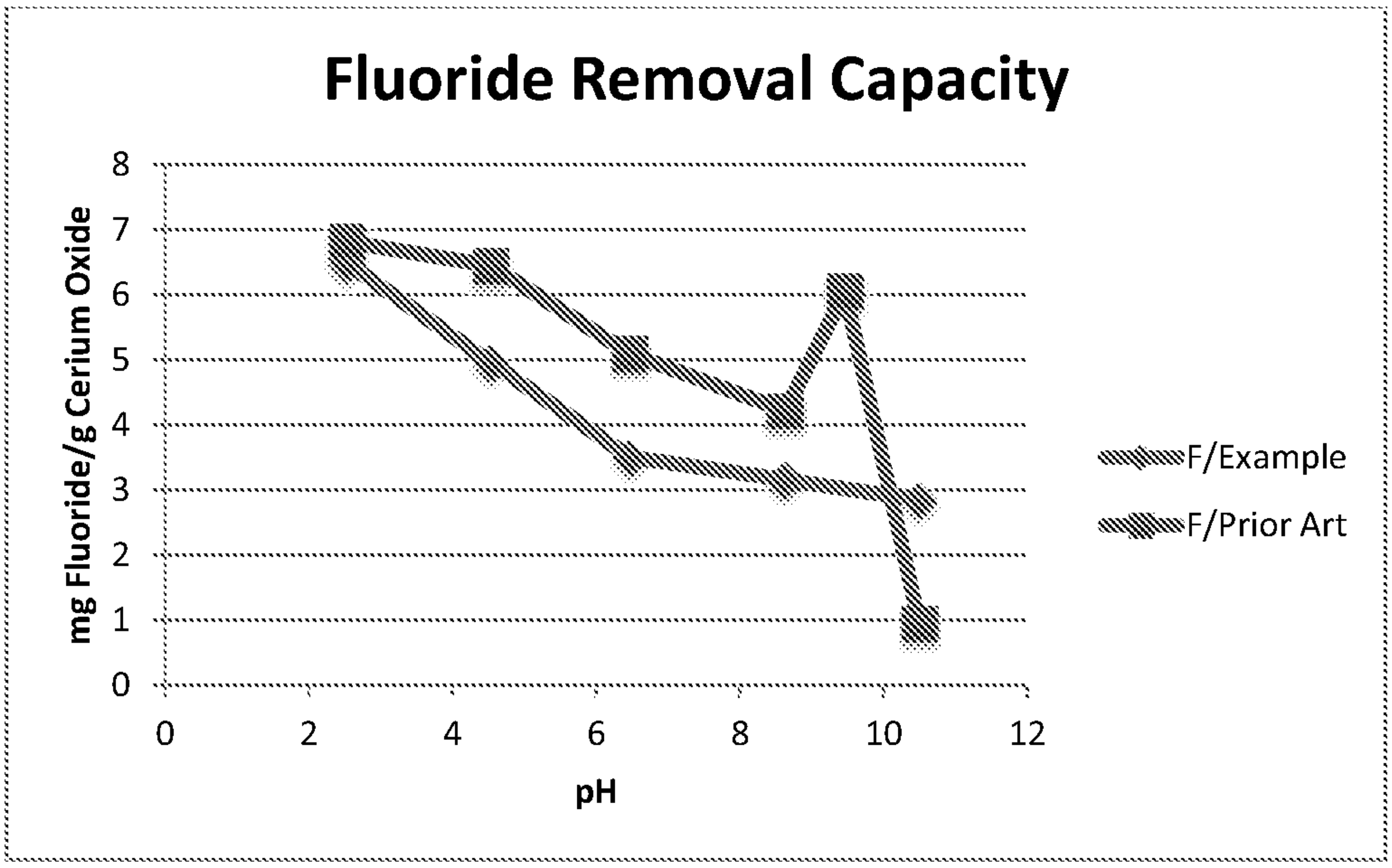

Fluoride Removal Capacity
mg Fluoride/g Cerium Oxide
8
7
6
5
4
3
2
1
0
0
2
4
6
8
10
12
pH
F/Example
F/Prior Art

FIG. 13

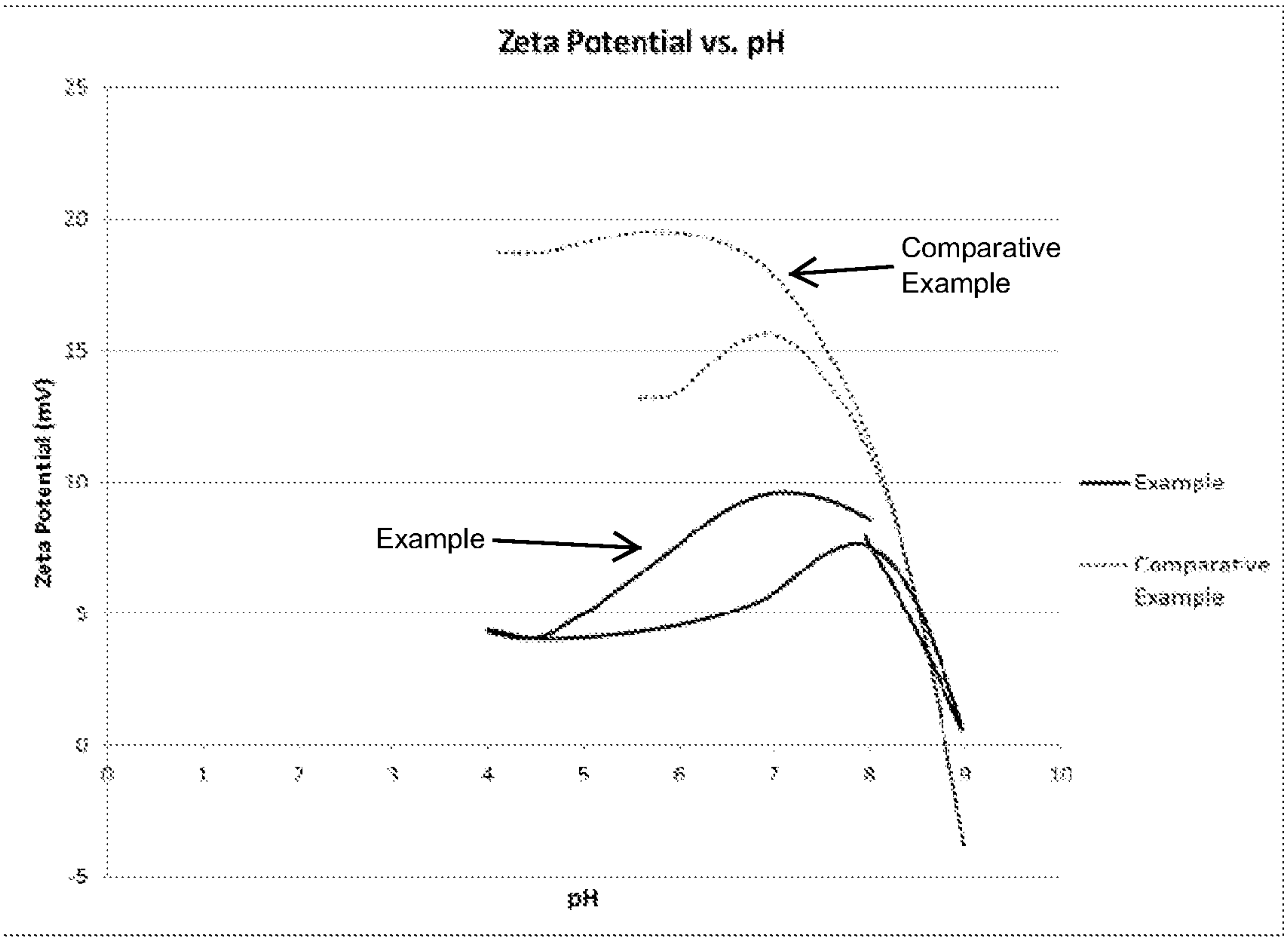

Zeta Potential vs. pH
Zeta Potential (mV)
25
20
15
10
5
0
-5
0
1
2
3
4
5
6
7
8
9
10
pH
Comparative Example
Example
Example
Comparative Example

FIG. 14

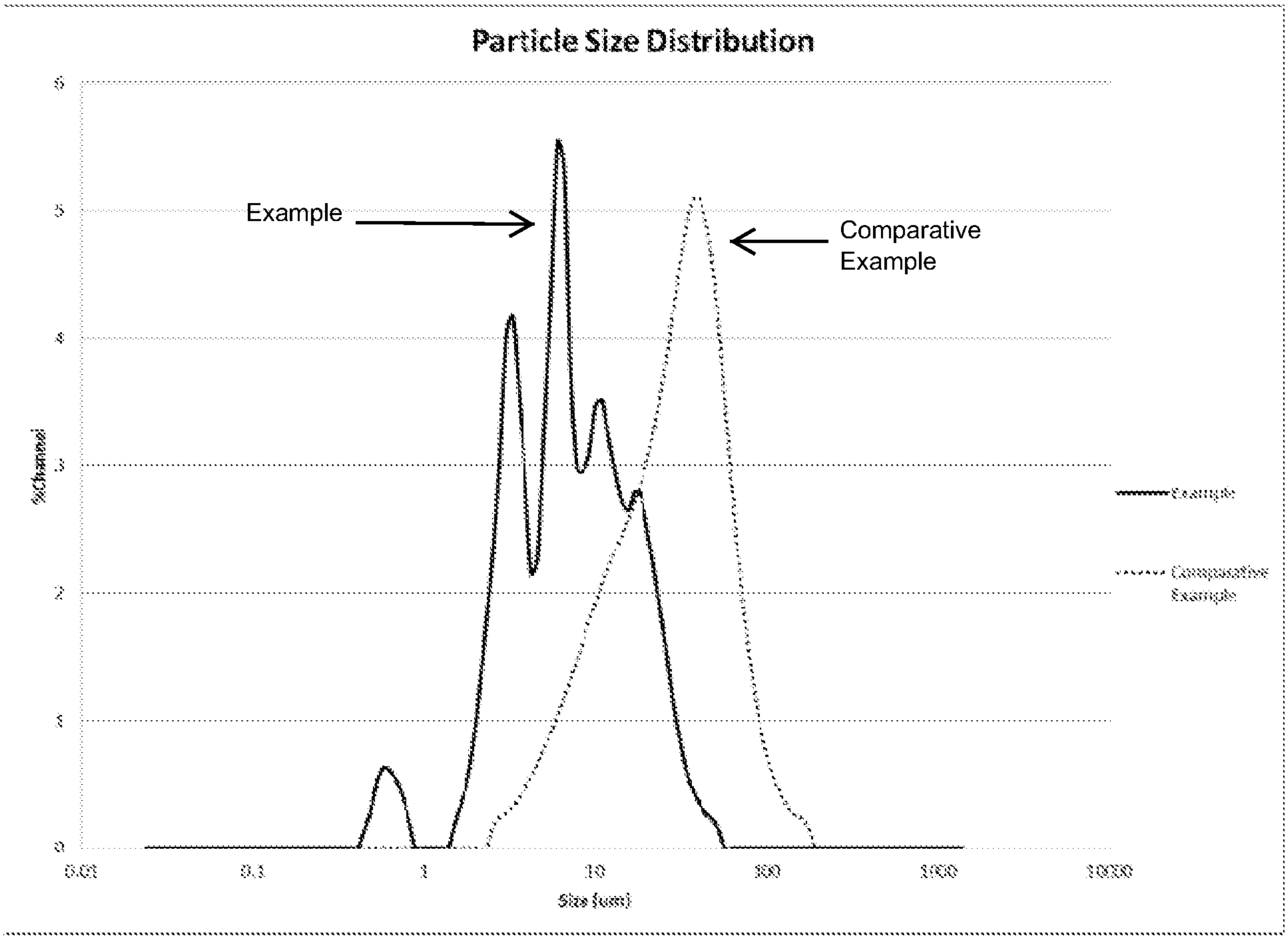
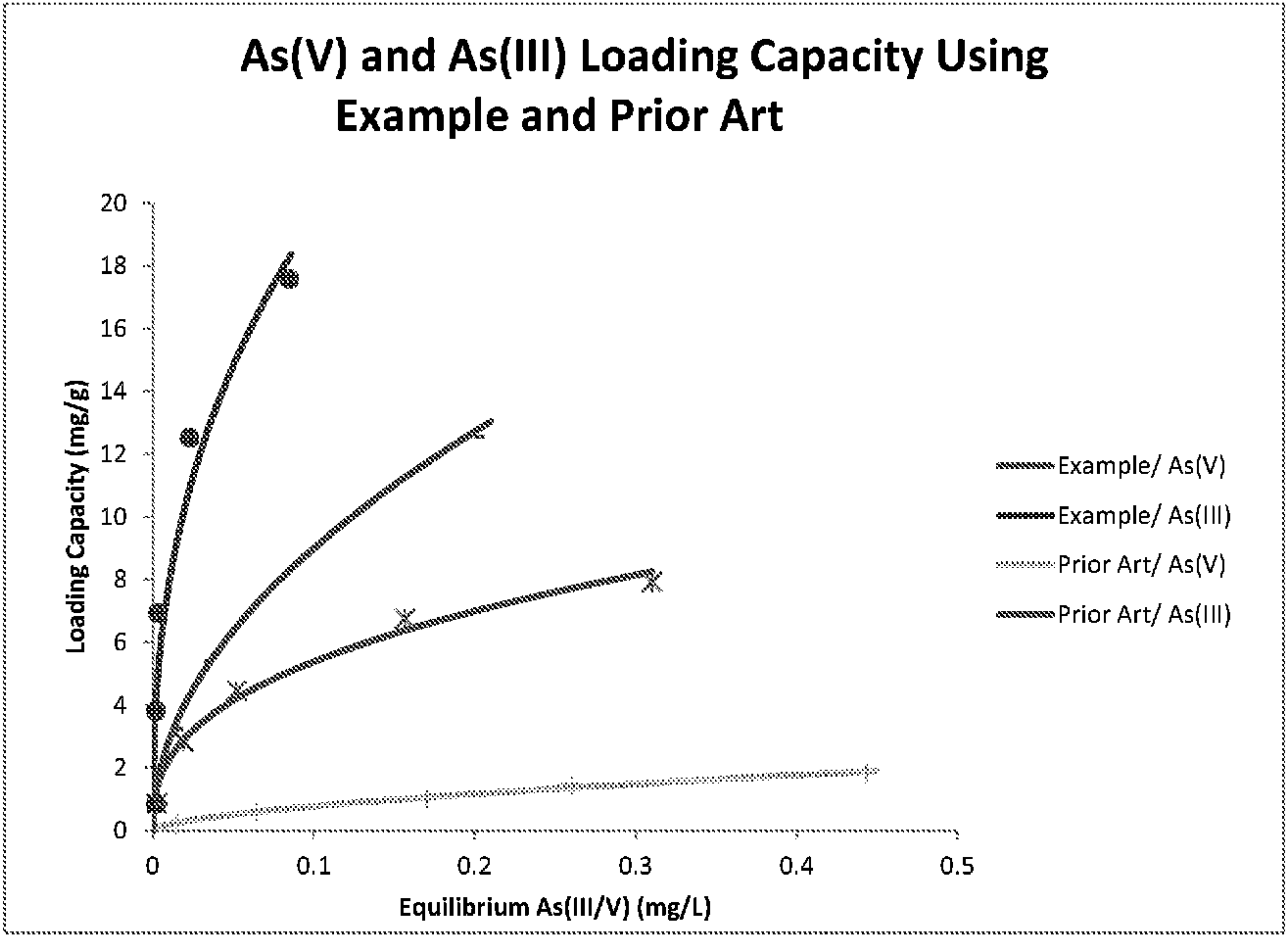

Particle Size Distribution
Example
Comparative Example
%Channel
0
1
2
3
4
5
6
0.01
0.1
1
10
100
1000
10000
Size (um)
Example
Comparative Example

FIG. 15



As(V) and As(III) Loading Capacity Using Example and Prior Art
Loading Capacity (mg/g)
20
18
16
14
12
10
8
6
4
2
0
0
0.1
0.2
0.3
0.4
0.5
Equilibrium As(III/V) (mg/L)
Example/ As(V)
Example/ As(III)
Prior Art/ As(V)
Prior Art/ As(III)

FIG. 9