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प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित CHITOSAN REINFORCED MIXED OXYHYDROXIDE NANOCOMPOSITE FOR FLUORIDE AND ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 30th day of December 2016 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled CHITOSAN REINFORCED MIXED OXYHYDROXIDE NANOCOMPOSITE FOR FLUORIDE AND ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF as disclosed in the above mentioned application for the term of 20 years from the 30th day of December 2016 in accordance with the provisions of the Patents Act,1970.



अनुदान की तारीख : 23/12/2020 Date of Grant :



पेटेंट नियंत्रक Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, **30th day of December 2018** को और उसके पश्चात प्रत्येक वर्ष मे उसी दिन देय होगी। Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 30th day of December 2018 and on the same day in every year thereafter.

#### FORM 2

THE PATENTS ACT, 1970

## (**39 OF 1970**)

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The Patents Rules, 2003

COMPLETE SPECIFICATION

(Refer section 10 and rule 13)

TITLE OF THE INVENTION:

CHITOSAN REINFORCED MIXED OXYHYDROXIDE NANOCOMPOSITE FOR FLUORIDE AND ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF

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**3.** Preamble to the Description

## **COMPLETE SPECIFICATION**

The following specification describes the invention

#### **COMPLETE SPECIFICATION**

#### TITLE OF THE INVENTION

# CHITOSAN REINFORCED MIXED OXYHYDROXIDE NANOCOMPOSITE FOR 5 FLUORIDE AND ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF

#### **FIELD OF INVENTION**

The present invention relates to the field of water purification, specifically to the preparation and use of granular compositions. More specifically, it relates to the preparation of granular aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan (AIC) composites useful for water purification-related applications, especially for rapid removal of contaminants such as fluoride and arsenic from water without the use of electricity.

#### **BACKGROUND OF THE INVENTION**

Fluoride contamination in ground water is one of the most debilitating environmental issues facing the mankind, affecting over 160 million people globally. Fluorosis was identified in India in 1937. Affordable solution for effective removal of fluoride from drinking water has been long awaited. Adsorption on activated alumina, laterite and many other low cost materials, have been suggested, but all of them are limited by multiple issues such as poor adsorption capacity,
strong interference with common ions in water, reduced kinetics, potential leaching of hazardous ions, difficulties in recycling in reuse, etc. Because of these issues, many of the installed units become non-functional in rural areas.

In recent times, impressive number of active materials have been prepared for water related applications, especially for water purification. Amongst these materials, nanomaterials are increasingly playing a critical role in various aspects of water purification due to their enhanced capacity vis-à-vis existing adsorbents (Savage, N., Diallo, M., Duncan, J., Street, A., Sustich, R., (Ed), *Nanotechnology Applications for Clean Water*. William Andrew, New York, 2008 and the chapters therein; Anshup, Pradeep, T., Noble metal nanoparticles for water purification: A critical review. *Thin Solid Films*, 2009, 517, 6441).

30 Due to poor inherent binding ability and absence of long-range order associated with poor crystallinity, a large number of these materials are obtained in powder form. Hence, such

materials cannot be used as it is for water purification, due to several challenges associated with them, such as difficulties in particle separation, danger of particle leaching, and poor hydraulic conductivity. Such examples are well known in the literature and a few representative examples are cited here:

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- Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions, M.G. Sujana, G. Soma, N. Vasumathi, S. Anand, *Journal of Fluorine Chemistry*, 2009, 130, 749–754.
  - Enriched fluoride sorption using alumina/chitosan composite, N. Viswanathan, S. Meenakshi, J. Haz. Mater., 2010, 178, 226–232.
- Reduced graphene oxide-metal/metal oxide composites: Facile synthesis and application in water purification, T.S. Sreeprasad, S. M. Maliyekkal, K. P. Lisha, T. Pradeep, *J. Haz. Mater.*, 2011, 186, 1, 921–931.
  - Atomically precise silver clusters for efficient chlorocarbon degradation, M. S. Bootharaju, G. K. Deepesh, T. Udayabhaskararao and T. Pradeep, *J. Mater. Chem. A*, 2013, 611-620.

In actual water treatment system, adsorbents in granular form are required to pack in a column to remove contaminants from water. Hence, granulation of the powder materials is necessary, prior to their use as a filtration medium. There are number of granulation techniques available for the conversion of a powder medium to a granular form. A popular method is to use

- 20 organic/inorganic binders for preparing agglomerated particles followed by sintering or spray drying. Representative prior art is as follows:
  - (a) Agglomeration of alumina and binder as described in US Patent No. 7,449,030
  - (b) Water treatment composition comprising nanostructured materials as described in European (EP) Patent Application No. 1954634
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However, such approaches are less environment-friendly and uneconomical, as they lead to a loss of adsorption capacity because of the use of binders and high temperature processing.

Another general method for the conversion of a powder medium to granular form is to support the powder medium on a carrier composition. Conventionally, activated alumina, silica or iron oxides (in granular form) have been used. Examples are shown in Rautaray et al. in Indian patent application 1571/MUM/2008, PCT Application No. PCT/IB2011/002740 and

Our efforts in the past several years have shown that advanced materials can be created for effective removal of contaminants from water. Materials are prepared in water at room temperature and therefore cause no environmental toxicity due to solvents during their production and utilisation. Improved contaminants adsorption requires enhanced surface area and active functional groups, both of which have to provide with optimum stability to create granular 5 components. We have shown that, this can be achieved by biopolymer templating and creating AlOOH nanocrystallites with the biopolymer matrix. The AlOOH nanostructures create nanoscale boxes in which various nanoparticles can be embedded. For example, embedded silver nanoparticles release 50 ppb of Ag<sup>+</sup> ion into water constantly without their surface being covered with scales during the extended period of use (Biopolymer reinforced synthetic granular 10 nanocomposites for affordable point-of-use water purification, M. Udhaya Sankar, Sahaja Aigal, Amrita Chaudhary, Anshup, Shihabudheen M. Maliyekkal, A. Anil Kumar, Kamalesh Chaudhari and T. Pradeep, Proc. Natl. Acad. Sci., 2013, 110, 8459-8464). As a result, such materials are effective anti-microbial agents in real water.

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The biopolymer templating can also be used to create granular FeOOH, which can be used to provide arsenic free drinking water. The composite has a combined arsenite and arsenate adsorption capacity of 100 mg/g, therefore is helpful in creating water purification devices (Confined metastable 2-line ferrihydrite for affordable point-of-use arsenic free drinking water, Anil Kumar Avula, Anirban Som, Paolo Longo, Chennu Sudhakar, Radha Gobinda Bhuin, Soujit Sen Gupta, Anshup, Mohan Udhaya Sankar, Amrita Chaudhary, Ramesh Kumar and T. Pradeep, 20

Adv. Mater., 2017). Both AlOOH and FeOOH are known to show fluoride adsorption capacity as well. However, their effective capacities are limited.

In the light of the foregoing, there exists a need in the art to provide a composition that addresses the aforementioned problems and other disadvantages reflected in the prior art.

25 Both AlOOH and FeOOH, being two dimensional in nature can create nanocomposites and they may show enhanced uptake capacity. In the following we show that a composite of Al:Fe ratio of 1.5:1, prepared under specific conditions, provides an uptake capacity of 74.57 mg/g of fluoride in granular form enabling the creation of an effective water purifier in fluoride affected areas. The inherent strength of the material allows it to be packed in column and be stable under normal pH and conductivity of water. It shows iron and aluminium leaching below 30

the international water quality and below the United States Environmental Protection Agency (USEPA) norms.

#### SUMMARY OF THE INVENTION

The present invention, as described herein, relates to various water-related applications. Particularly, the invention demonstrates the utility of chitosan templated aluminum oxyhydroxide/2-line iron oxyhydroxide composite in water purification.

In one embodiment, the present invention demonstrates the utility of the composition as an active ingredient for water-related applications, such as removal of fluoride and arsenic from water with superior fluoride and arsenic adsorption capacity.

In other embodiment, the present invention demonstrates a method of granulation of diverse active ingredients, by gel-phase blending of chitosan templated nanocomposite with active ingredients, without binders.

In another embodiment, the present invention relates to the chitosan templated mixed oxide nanocomposite as a novel carrier composition for various types of materials. It can carry up to 50% of its own weight without significantly altering the strength of the granular composition. Carrier composition does not lose its stability in water, even if the material added to the carrier is water soluble. It provides a number of new opportunities with this composition: use of powder ingredient for water purification without limitation of poor hydraulic conductivity and no loss of active surface area due to unbound form of active ingredient.

In yet one embodiment, the present invention provides a method to prepare granular composition of diverse active ingredients by blending with a carrier composition and its subsequent use for water-related application, such as water purification.

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In yet other embodiment, the present invention demonstrates a method of preparation of an adsorbent composite with an active BET surface area of 170 m<sup>2</sup> g<sup>-1</sup>, which enhances the adsorption capacity.

In yet another embodiment, the present invention provides an adsorbent composite, which exhibits high adsorption kinetics and reduces any fluoride input at 10 ppm or above to below 1 ppm with suitable adsorbent dose.

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In yet other embodiment, the present invention provides an adsorbent composite which can be packed in column and be stable under normal pH and conductivity of water with minimal leaching of nanoparticles, making it an efficient adsorbent for water purification. Wherein, the active ingredient-carrier composition is not limited to water-related application, i.e. it can similarly be adopted for air-related application.

#### **BRIEF DESCRIPTION OF THE DRAWINGS** 5

Figure 1. Scanning electron micrograph of aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite in granular form (52 x 72 mesh) upon continuous exposure to fluoride contaminated water for about 3 months. a & b are of different magnifications.

Figure 2. X-ray diffraction pattern of the aluminum oxyhydroxide/2-line iron oxyhydroxidechitosan composite in powder form before exposing to fluoride solution (a), after exposing to 10 fluoride solution for 120 min (b).

Figure 3. High resolution transmission electron micrograph of aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite in powder form (a & b) before exposing to fluoride solution and (c & d) after exposing to fluoride solution for 120 min.

Figure 4. TEM-EDAX of (a) aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite in 15 powder form before exposing to fluoride solution. (b) Powdered aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite after exposing to fluoride solution for 120 min.

Figure 5. Scanning electron micrograph aluminum oxyhydroxide/2-line iron oxyhydroxidechitosan composite in powder form (a & b) before exposing to fluoride solution and (c & d) after exposing to fluoride solution for 120 min.

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Figure 6. Elemental X-ray images (SEM-EDAX) of (a) aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite in powder form before exposing to fluoride solution. (b) Powdered aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite after exposing to fluoride solution for 120 min.

Figure 7. Infrared spectra of as-synthesized aluminum oxyhydroxide-iron oxyhydroxide-25 chitosan composite before exposing to fluoride solution and after exposing to fluoride solution for 120 min. Some features are marked with vibrarional frequencies.

Figure 8. Residual fluoride concentration as a function of adsorbent dose (dosage study) with the composition reported in this invention tested for fluoride adsorption (initial concentration =

 $10\pm0.5$  ppm, volume = 100 mL synthetic challenge water, contact time = 120 min). 30

**Figure 9.** Residual fluoride concentration as a function of time (kinetic study) with the composition reported in this invention tested for fluoride adsorption (initial concentration =  $10\pm0.5$  ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).

Figure 10. Langmuir adsorption isotherm for fluoride ion adsorbed (mg/g). C<sub>e</sub>/q<sub>e</sub> (g/L) as a function of equilibrium concentration of fluoride ion (mg/L) left in the solution (initial adsorbent dose = 100 mg, volume = 100 mL deionized water, contact time = 120 min).

**Figure 11.** Residual fluoride concentration as a function of number of cycles (cycle saturation study) with the composition reported in this invention tested for fluoride adsorption (adsorbent dose used for all cycles of the pre-cycle = 100 mg, each cycle concentration =  $10\pm0.5$  ppm, each

- cycle volume = 100 mL synthetic challenge water, each cycle contact time = 120 min).
   Figure 12. Percentage fluoride removal as a function of pH with the composition reported in this invention tested for fluoride adsorption (initial adsorbent dose = 100 mg, initial concentration = 10±0.5 ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).
- Figure 13. Percentage fluoride removal in presence of various counter ions with the composition
  reported in this invention tested for fluoride adsorption (initial adsorbent dose = 100 mg, initial concentration = 10±0.5 ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).

**Figure 14.** XPS survey spectrum of (a) as synthesized aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite, and (b) composite after adsorbing fluoride ion.

20 **Figure 15.** XPS analysis of aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite in various regions of interest. Curve fitted (a) Fe 2p, (b) Al 2p, (c) C 1s and (d) O 1s regions of as it is material and those after adsorbing fluoride from solution.

**Figure 16.** Cartridge data of fluoride collected after each stage (a), after micro filter (MF) cartridge (A), after as synthesized aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite (B), and after the particle filter (C), (b) is the setup used for conducting cartridge

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composite (B), and after the particle filter (C). (b) is the setup used for conducting cartridge experiment.

**Figure 17.** Scanning electron micrograph of aluminum oxyhydroxide-iron oxyhydroxidechitosan composite in granular form ( $52 \times 72$  mesh) upon continuous exposure to arsenic contaminated water for about 3 months. a, b & c are of different magnifications. Figure 18. X-ray diffraction pattern of the aluminum oxyhydroxide/2-line iron oxyhydroxidechitosan composite in powder form before exposing to arsenic solution (a), after exposing to arsenic solution for 120 min (b).

Figure 19. High resolution transmission electron micrograph of aluminum oxyhydroxide-iron

oxyhydroxide-chitosan composite in powder form (a) before exposing to arsenic solution and (b) 5 after exposing to arsenic solution for 120 min.

Figure 20. TEM-EDAX of (a) aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite in powder form before exposing to arsenic solution. (b) Powdered aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite after exposing to arsenic solution for 120 min.

Figure 21. Scanning electron micrograph aluminum oxyhydroxide/2-line iron oxyhydroxide-10 chitosan composite in powder form (a, b & c) before exposing to arsenic solution and (d, e & f) after exposing to arsenic solution for 120 min.

Figure 22. Elemental X-ray images (SEM-EDAX) of (a) aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite in powder form before exposing to arsenic solution. (b)

Powdered aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite after exposing to 15 arsenic solution for 120 min.

Figure 23. Infrared spectra of as-synthesized aluminum oxyhydroxide-iron oxyhydroxidechitosan composite before exposing to arsenic solution and after exposing to arsenic solution for 120 min. The data was compared with standard As(V) precursor (Na<sub>2</sub>HAsO<sub>4</sub>.7H<sub>2</sub>O) and blank

chitosan before making template for the aluminum oxyhydroxide-iron oxyhydroxide-chitosan 20 composite. Some features are marked with vibrational frequencies.

Figure 24. Residual arsenic concentration as a function of adsorbent dose (dosage study, (a)) with the composition reported in this invention tested for arsenic adsorption (initial concentration =  $1\pm 0.1$  ppm, volume = 100 mL synthetic challenge water, contact time = 120 min). (b) is the magnified output data of (a) for better understanding.

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Figure 25. Residual arsenic concentration as a function of time (kinetic study, (a)) with the composition reported in this invention tested for arsenic adsorption (initial concentration =  $1\pm0.1$ ppm, volume = 100 mL synthetic challenge water, contact time = 120 min). (b) is the magnified output data of (a) for better understanding.

**Figure 26.** Langmuir adsorption isotherm for arsenic ion adsorbed (mg/g).  $C_e/q_e$  (g/L) as a function of equilibrium concentration of arsenic ion (mg/L) left in the solution (initial adsorbent dose = 100 mg, volume = 100 mL deionized water, contact time = 120 min).

Figure 27. Residual arsenic concentration as a function of number of cycles (cycle saturation study) with the composition reported in this invention tested for arsenic adsorption (adsorbent dose used for all cycles of the pre-cycle = 100 mg, each cycle concentration = 1±0.1 ppm, each cycle volume = 100 mL synthetic challenge water, each cycle contact time = 120 min).

**Figure 28.** Percentage arsenic removal as a function of pH with the composition reported in this invention tested for arsenic adsorption (initial adsorbent dose = 100 mg, initial concentration =  $1\pm0.1 \text{ ppm}$ , volume = 100 mL synthetic challenge water, contact time = 120 min).

- **Figure 29.** Percentage arsenic removal in presence of various counter ions with the composition reported in this invention tested for arsenic adsorption (initial adsorbent dose = 100 mg, initial concentration =  $1\pm0.1$  ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).
- Figure 30. XPS survey spectrum of (a) as synthesized aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite, and (b) composite after adsorbing arsenic ion.
   Figure 31. XPS analysis of aluminum oxyhydroxide-iron oxyhydroxide-chitosan composite in

various regions of interest. Curve fitted (a) Fe 2p, (b) Al 2p, (c) As 3d, (d) C 1s, (e) O 1s and (f) N 1s regions of as it is material and those after adsorbing arsenic from solution.

- 20 Referring to the drawings, the embodiments of the present invention are further described. The figures are not necessarily drawn to scale, and in some instances the drawings have been exaggerated or simplified for illustrative purposes only. One of ordinary skill in the art may appreciate the many possible applications and variations of the present invention based on the following examples of possible embodiments of the present invention.
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#### DETAILED DESCRIPTION OF THE INVENTION

The present invention can be understood readily with reference to the following detailed description of the invention and examples included therein.

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A method of preparation of granular composition of diverse active ingredients, which are usually in powder form, is described. Use of such granular composition is further demonstrated for a number of applications. In order to prepare the granular composition of powdered active ingredients, we have utilized unique granulation ability of chitosan templated aluminum oxyhydroxide/2-line iron oxyhydroxide composite. The strength of granular composition originates due to the inherent property of chitosan templated aluminum oxyhydroxide/2-line iron oxyhydroxide. This property is especially significant for aluminum oxyhydroxide and 2-line iron oxyhydroxide vis-à-vis other hydrous oxides prepared through similar route.

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The present invention demonstrates that matrix (chitosan templated aluminum oxyhydroxide/2-line iron oxyhydroxide) can be an active carrier in a few cases, such as for the removal of fluoride and arsenic from water. It is further demonstrated that the capability of the composition to remove fluoride from drinking water, with fluoride adsorption capacity far higher than for the compositions known in prior art.

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Aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite is prepared within the chitosan matrix. Chitosan is a biopolymer with several advantages such as being biodegradable, non-toxic and inexpensive. Another important benefit of using chitosan as matrix is that, it forms thread like structures. When aluminum oxyhydroxide/2-line iron oxyhydroxide nanocomposites are prepared inside the matrix, they bind strongly with the matrix, due to which they can easily be purified by the use of a membrane cloth filter.

The present disclosure relates to the preparation of granular composition of diverse active ingredients in powder form using aluminum oxyhydroxide/2-line iron oxyhydroxide composite dispersed in chitosan template as a fluoride and arsenic removal medium. In one aspect, the invention comprises of a granular composite of powder ingredient blended in aluminum oxyhydroxide/2-line iron oxyhydroxide nanoparticles on a chitosan template.

In other aspects, aluminum oxyhydroxide/2-line iron oxyhydroxide nanoparticles deposited on chitosan (prior to the step of drying of composition, i.e. when the moisture content is above 50%) is blended with nanoscale metal oxyhydroxide deposited on chitosan (with variable moisture content from 10-90%), wherein metal is chosen among titanium, zinc, manganese, iron, zirconium, lanthanum, cerium, silicon or a combination thereof.

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In various aspects, the composition is demonstrated to be a useful active ingredient in itself. In another aspect, the composition is utilized for the removal of contaminants from drinking water such as fluoride and arsenic.

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Aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite was synthesized as follows: About 2.16 g Na<sub>2</sub>SO<sub>4</sub> was added to 15 mL of 1 wt% chitosan solution in one step and

kept for 15 min incubation. Then 9 mL, 1 M aluminum sulfate was added followed by 2 h of incubation and addition of 6 mL, 1 M ferric hexachloride. The reaction mixture was kept under agitation for 1 h. Thereafter, aqueous 2 M NaOH was slowly added into the metal-chitosan solution with vigorous stirring to facilitate the precipitation of the metal-chitosan composites, till

5 the pH reached at 7. The final composition was further incubated for about 12 h, at ambient temperature to embed the synthesized nanoparticles in chitosan network. The resulting gel was washed with copious amounts of water to remove soluble salts and was dried at room temperature (28–30 °C). The resulting composite, namely, aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite, was insoluble in water and appeared like dark black shining crystallites. The dried composite was crushed to a powder form and used for fluoride adsorption. The yield was 1.2 g. The method of preparation of composite is water positive by two to three orders of magnitude; i.e., it produces 500 L of clean water for every 1 L of water consumed for its production.

The invention may be further described by the accompanied drawings.

15 Figure 1 depicts SEM image of the aluminum oxyhydroxide/2-line iron oxyhydroxidechitosan composite in the granular form (52 x 72 mesh) at various magnifications (1a, 1b), which has been exposed to running water for about 3 months. The composite exhibits excellent mechanical strength and does not degrade in water. Therefore, upon use for water purification, there were no fine particles leached into the water (which is a common phenomenon for a number of other adsorbents). This is especially important from the perspective of ensuring nanoparticles-free drinking water.

Figure 2 illustrates the X-ray diffraction pattern of aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite before and after adsorbing fluoride, respectively. The assynthesized composite and composite after adsorbing fluoride are amorphous in nature, proven by broadened peak shapes. The peak positions at 14.83°, 22.72°, 56.67° and 63.4° can be indexed as aluminum oxyhydroxide and peaks positions at 34.55° and 64.26° correspond to formation of 2-line iron oxyhydroxide, thereby proving that the composition disclosed herein, is a mixed oxide nanocomposite. After fluoride adsorption new peaks appear at 32.66°, 46.71° and 58.75° correspond to aluminum oxyfluoride.

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It is well-known that hydrous aluminum and iron oxides, as found in the Nature exhibit reasonable mechanical strength (as they occur in crystalline form). In case of aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite, it is highly amorphous (X-ray crystallographic data shown in Figure 2). Here, the role of chitosan is very crucial in improving the strength of aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite by binding with aluminum oxyhydroxide/2-line iron oxyhydroxide nanoparticles.

5 Figure 3 depicts HRTEM images of the aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite (Figure 3a and 3b) and the composite after adsorbing fluoride (Figure 3c and 3d). Aluminum oxyhydroxide and 2-line iron oxyhydroxide nanoparticles are not prominently visible in the large area image due to their small size; they could not be seen even at higher magnification due to their highly amorphous nature. It can be seen that aluminum oxyhydroxide/2-line iron oxyhydroxide nanoparticles are well-dispersed in the chitosan matrix. The metal oxyhydroxide nanoparticles are homogeneously sized. The thread like chitosan structure is not seen clearly due to the complete embedding of aluminum oxyhydroxide and 2-line iron oxyhydroxide nanoparticles. Upon closer observation, we can see that the nanoparticles are anchored onto chitosan nanoarchitecture. Outside the chitosan matrix, no nanoparticles were

15 present. This again confirms the composite formation, wherein aluminum oxyhydroxide/2-line iron oxyhydroxide nanocomposite is formed only inside the chitosan nanoarchitecture. This holds several advantages: (i) small and uniform sized nanoparticles are obtained, (ii) nanoparticles never leach out of the nanoarchitecture, thereby ensuring their safe use in water purification and (iii) nanoparticles do not undergo aggregation, even when high contaminant 20 concentration is loaded on the surface of nanoparticles.

Figure 4 depicts TEM-EDAX spectrum and elemental maps of aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite in powder form (Figure 4a) along with fluoride adsorbed composition (Figure 4b). For the purpose of this study, 1 g of adsorbent was shaken with 200 ppm, 1000 mL fluoride solution in de-ionized water. All the principal elements, including adsorbed fluorine are present in the spectrum. Elemental maps confirm that the distribution of fluoride is homogeneous and is extremely high. In the case of fluoride adsorbed composition, fluorine content in the composition is around 7.97%.

Figure 5 depicts SEM image of the aluminum oxyhydrxide/2-line iron oxyhydroxidechitosan composite in the powder form (Figure 5a and 5b) and composite after adsorbing fluoride (Figure 5c and 5d). There is no change in physical state of the material observed upon exposure to various fluoride concentrated solutions, which implies simple surface adsorption.

Figure 6 depicts SEM-EDAX spectrum and elemental maps of aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite in powder form (Figure 6a) along with fluoride adsorbed composition (Figure 6b). For the purpose of this study, 1 g of adsorbent was shaken with 200 ppm, 1000 mL fluoride solution in de-ionized water. All the principal elements including adsorbed fluorine are present in the spectrum. Elemental maps confirm that distribution of fluoride is homogeneous and extremely high. In case of the fluoride adsorbed composition, fluorine content in the composition is around 8.26%.

Figure 7 depicts the Fourier transform infrared (FTIR) spectrum of aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite along with the composite after adsorbing fluoride. The broad peak at 3435 cm<sup>-1</sup> could be attributed to the stretching of surface hydroxyl groups of aluminum oxyhydroxide and 2-line iron oxyhydroxide. After fluoride adsorption on the surface of composite, the band was shifted to 3445 cm<sup>-1</sup> and the peak broadened, indicating the interaction of fluoride ion with surface O–H groups. In addition to this, the band at 613 cm<sup>-1</sup> is assigned to the vibrational mode of AlO<sub>6</sub> while another two bands at 1112 and 1632 cm<sup>-1</sup> can be attributed to Al–OH stretching and bending vibrations in the boehmite lattice, which were shifted to 589 cm<sup>-1</sup>, 1153 cm<sup>-1</sup> and 1637 cm<sup>-1</sup>, respectively. A small band at 474 cm<sup>-1</sup>, which is a characteristic peak of low crystalline ferrihydrite (can be attributed to Fe-O) disappeared after fluoride adsorption. The removal mechanism is based on the ion-exchange between the surface active hydroxyl groups and the contaminant fluoride ions.

- 20 The concentration of fluoride in the effluent water, measured by the fluoride electrode, was consistently below 1 ppm, adhering to the World Health Organization (WHO) norms. This demonstrates that the active ingredient loaded in the aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan matrix is amply accessible by water, thereby ensuring that the composition can be utilized as an effective water purification composition.
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Figure 8 illustrates variation of residual fluoride concentration as a function of the adsorbent dose, for the composition disclosed here, where adsorbent dosage varies from 5-200 mg. An initial fluoride concentration of 10 ppm reaches below 1 ppm by using 100 mg.

Figure 9 depicts the residual fluoride concentration as a function of time, where the fluoride concentration reaches below the prescribed limits within 30 minutes, which indicates the
composition follows fast adsorption kinetics and needs only low contact time for water purification.

Fluoride adsorption isotherm of the as-synthesized composite was carried out in deionized water. As-synthesized composite adsorbs approximately 75 mg/g at an equilibrium fluoride concentration. Langmuir isotherm was plotted for fluoride adsorption (Figure 10) using the following expression.

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The linear form of Langmuir adsorption isotherm equation is as follows:

#### $C_e/q_e = C_e/q_{max} + 1/bq_{max}$

where,  $C_e$  (mg/L) is the equilibrium concentration of fluoride in the solution,  $q_e$  (mg/g) is the quantity of fluoride adsorbed and  $q_{max}$  (mg/g) is the monolayer adsorption capacity, and b (L/mg) is the Langmuir adsorption constant related to the free energy of adsorption and  $1/q_{max}$ and 1/bq<sub>max</sub> are the Langmuir constants.

Langmuir isotherm equation was used to estimate the maximum adsorption capacity of the adsorbent composition under the conditions: 298 K, pH 7.0, 120 min contact time and 1 g/L adsorbent dose while varying initial fluoride concentration from 1 to 200 mg/L. The values of the isotherm constants for fluoride adsorption are 0.008 and 0.007, respectively.

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For real time application in water purification, important water chemistry parameters such as pH value and coexisting anions can significantly interfere in the fluoride adsorption process. Figure 12 shows the variation of fluoride removal percentage with pH. It is evident that, the composition shows very high adsorption efficiency within the drinking water pH range (pH 6-8) making it an efficient adsorbent for fluoride removal. In presence of other competing ions such as chloride, sulphate, nitrate, silicate, sodium, potassium, calcium, magnesium, carbonate 20 and bicarbonate the fluoride removal percentage does not show any significant drop in performance (shown in Figure 13). The performance drops from 93% to around 80% in presence

of silicate, carbonate and bicarbonate ions.

From the XPS survey spectra of as-synthesized aluminum oxyhydroxide-iron 25 oxyhydroxide-chitosan composite and fluoride adsorbed composition (Figure 14), it is clearly seen that a sharp F 1s peak at 682.3 eV appears in the spectrum only after adsorption, confirming the adsorption of fluoride on the surface of the nanocomposite. Elements of our interest are compared and shown in Figure 15. The Fe 2p region of as-synthesized composition in powder form and fluoride adsorbed composition are shown in Figure 15a. Other than the main peaks,

presence of multiple peaks in the Fe 2p region are because of its surface and satellite peaks. 30 Figure 15b shows the Al 2p region of as-synthesized composition in powder form and fluoride characteristic peaks, changes were seen in other elements. The peak observed at 283.2 eV is close to the characteristic peak position for aliphatic carbon from the chitosan shown in Figure 15c. The peak position was shifted to 283.8 eV after fluoride adsorption. The peak at 529.3 eV is

adsorbed composition. Though we did not find any kind of change for Al(III) and Fe(III)

close to the characteristic peak position for bulk oxygen (O<sup>2-</sup>) (Figure 15d). This peak could be attributed to Al-O and Fe-O, which was shifted to 529.9 eV after fluoride adsorption. The peak appears at 530.9 eV mostly because of surface hydroxyl groups which are attached to Al and Fe. The peak position was shifted to 531.6 eV, with a decrease in the intensity for fluoride adsorbed composite. The peak at 533 eV is due to the adsorbed water on the surface of the composite, whose intensity increases after fluoride adsorption. This observation supports the fact that the active surface hydroxyl groups of the composite play a key role in fluoride removal mechanism, which was also inferred from the FTIR spectra.

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Table 1 shows the total organic carbon (TOC) leaching for chitosan, aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite before fluoride or arsenic adsorption and after fluoride or arsenic adsorption. For this study, 100 mg of material was spiked in 100 mL MQ water for 2h. Inorganic as well as organic carbon leaching from the as-it-is composite and fluoride or arsenic adsorbed composite are below the prescribed limits i.e. 4 ppm.

Sample No	Sample ID	TC (mg/L)	IC (mg/L)	TOC (mg/L)
1	MQ Water-Blank	0.341±0.09	0.222±0.02	0.119±0.06
2	Chitosan	7.170±0.004	6.370±0.032	0.800±0.028
3	Composite Before Fluoride or Arsenic adsorption	1.773±0.016	0.569±0.022	1.204±0.006
4	Composite After Fluoride adsorption	2.640±0.013	1.343±0.018	1.297±0.005
5	Composite After Arsenic adsorption	1.6544±0.009	2.045±0.027	0.3906±0.036

The toxicity characteristic leaching experiment (TCLP) for as synthesized material described in the prior art (aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite)

was done after fluoride or arsenic adsorption (the complete saturation) to ensure the adsorbed contaminants or embedded metal ions should not leach to the environment when they discarded. The data show that 3 ppb, 63 ppb and 2 ppb for Fe, Al and As, respectively, which are below the permissible limit of drinking water.

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The as synthesized aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite can be used to remove fluoride and arsenic from water to 0.3 ppm and 3 ppb with the input of 10 ppm and 1 ppm of fluoride and arsenic, receptively, when they present separately or even together in water. The permissible limit for fluoride and arsenic in drinking water is 1.5 ppm and 10 ppb, respectively.

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Method of preparing aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite is derived from preferred embodiments described in Indian Application No. 1529/CHE/2010 and Indian Application No. 486/CHE/2013. An aqueous organic polymer solution was taken with inorganic iron and aluminium salts such as  $Al_2(SO_4)_3$  and  $FeCl_3$ (hydrous or anhydrous) were precipitated using a suitable base such as NaOH. The organic polymer acts as a template, controls the size of particles of AlOOH and FeOOH formed and 15 gives mechanical strength to the composite after drying at room temperature.

The identification of the phase(s) of the as-prepared sample was carried out by X-ray powder diffraction (Bruker AXS, D8 Discover, USA) using Cu K $\alpha$  radiation at  $\lambda = 1.5418$  Å. Surface morphology, elemental analysis and elemental mapping studies were carried out using a scanning electron microscope (SEM) equipped with energy dispersive analysis of X-rays 20 (EDAX) (FEI Quanta 200). For this, sample was re-suspended in water by sonication for 10 min and drop casted on an indium tin oxide (ITO) conducting glass and was dried. High resolution transmission electron microscopy (HRTEM) images of the sample were obtained with JEM 3010 (JEOL, Japan). The samples prepared as above were spotted on amorphous carbon films supported on copper grids and dried at room temperature. X-ray photoelectron spectroscopic 25 (XPS) analysis was done using ESCA Probe TPD of Omicron Nanotechnology. Polychromatic Mg K $\alpha$  was used as the X-ray source (hv = 1253.6 eV). Spectra in the required binding energy range were collected and an average was taken. Beam induced damage of the sample was reduced by adjusting the X-ray flux. Binding energy was calibrated with respect to C 1s at 283.2

eV. Fluoride concentration in the water was measured by fluoride electrode. Leaching of iron 30

and aluminum in the water was detected using inductively coupled plasma mass spectrometry (NexION 300X ICP-MS, Perkin Elmer).

The as-synthesized adsorbent composite was tested for fluoride (in the form of sodium fluoride) and arsenic (in the form of sodium arsenate) removal from water.

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All the uptake capacity studies were done in a batch mode (in 250 mL polypropylene conical flasks). The working volume of the solutions were taken as 100 mL and required quantities of adsorbent were added. The flasks were kept for shaking at 207±5 rpm in an orbital shaker (Orbitek, India) at room temperature (25±2 °C). Samples were withdrawn at predetermined time intervals and analyzed for residual solute concentration. The water used for studies was either deionized water or synthetic challenge water (composition is mentioned herewith), and is mentioned in the respective figures.

#### **EXAMPLE 1**

## THE ROOM TEMPERATURE SYNTHESIS OF ALUMINUM OXYHYDROXIDE/2-15 LINE IRON OXYHYDROXIDE COMPOSITE EMBEDDED IN CHITOSAN TEMPLATE THROUGH A SIMPLE SOFT CHEMISTRY ROUTE:

The Al(III) precursor solution (such as aluminum sulfate) was mixed with chitosan (dispersed in 1% HCl solution) by one-shot addition with 10-15 min ultrasonication. Then the Fe(III) precursor solution (such as ferric chloride) was added in similar fashion. The mixture was then used immediately. Aqueous NaOH solution was added slowly into the metal-chitosan solution by vigorous stirring to facilitate the precipitation of the metal-chitosan composites. All these steps were carried out at a temperature of about 25±2 °C. Vigorous stirring was continued for 12 h. The precipitate was filtered, washed to remove any unwanted impurities, converted in the shape of flakes and dried at ambient conditions.

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#### **EXAMPLE 2**

## INCORPORATION OF VARIOUS METAL OXIDE/HYDROXIDE/OXYHYDROXIDE-CHITOSAN COMPOSITES WITHIN ALUMINUM OXYHYDROXIDE/2-LINE IRON OXYHYDROXIDE-CHITOSAN TEMPLATE:

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Precipitated aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite as in Example 1 was washed and filtered. Moisture content in the precipitate formed may vary from

50-90%. Subsequently, it was mixed with desired metal oxide/hydroxide/oxyhydroxide-chitosan composite prepared separately (as described in Indian Application Nos. 1529/CHE/2010, 947/CHE/2011, 4062/CHE/2011, 1521/CHE/2012). Metal was chosen from the following list: zinc, manganese, iron, aluminum, zirconium, lanthanum, cerium or silicon. The mixture was

5 prepared in an appropriate ratio, for example, with a dominant weight percentage for aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite (wt/wt). Thereafter, the precipitate was dried at ambient conditions.

#### EXAMPLE 3

# 10 INCORPORATION OF NANOPARTICLES WITHIN ALUMINUM OXYHYDROXIDE/2-LINE IRON OXYHYDROXIDE-CHITOSAN TEMPLATE:

Precipitated aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite as in Example 1 was washed and filtered. Moisture content in the precipitate form may vary from 50-90%. Subsequently, a nanoparticle dispersion (e.g. Al<sub>2</sub>O<sub>3</sub> nanoparticles dispersed in water) was

- 15 homogenized with aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite. The mixture was prepared in an appropriate ratio, preferably with a dominant weight percentage for aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite (wt/wt). Once the blending of nanoparticles in carrier composition was complete, the precipitate was dried at ambient conditions.
- 20

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It may be noted that the desired metal oxide/hydroxide/oxyhydroxide-chitosan composite can be loaded either in precipitated form or in dried powder form.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the claims.

#### **EXAMPLE 4**

## 30 THE UTILITY OF ALUMINUM OXYHYDROXIDE/2-LINE IRON OXYHYDROXIDE-CHITOSAN TEMPLATE AS A CARRIER OF VARIOUS ACTIVE INGREDIENTS:

The objective was that ingredient may be incorporated in such a proportion such that the mechanical strength of the aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite was not significantly altered, which may allow its use for water purification. The porous nature of the aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite allows the accessibility of water to such ingredients.

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For the purpose of illustration, a water insoluble composition was demonstrated. Reduced graphene oxide-MnO<sub>2</sub> composite (Indian Application No. 2563/CHE/2010) was mixed in varying proportions with aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite. Aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite in the precipitate form was washed and filtered. Moisture content in the precipitate form may vary from 50-90%. Subsequently, it was mixed with reduced graphene oxide-MnO<sub>2</sub> composite. The mixture was prepared in an appropriate ratio, for example, with a dominant weight percentage for aluminum oxyhydroxide/2-line iron oxyhydroxide-chitosan composite (wt/wt). Thereafter, the precipitate was dried at ambient condition.

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It may be noted that graphene oxide- $MnO_2$  composite is taken as a representative example of a number of water insoluble materials, for example but not limited to, water treatment compositions, metal nanoparticles and luminescent metal clusters.

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- WE CLAIM:
- 1. An adsorbent composition comprising biopolymer templated aluminum oxyhydroxide/2line iron oxyhydroxide granular nanocomposite, the said nanocomposite is prepared by the addition of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O and FeCl<sub>3</sub>.6H<sub>2</sub>O in water at a ratio of 1.5:1 at room
- 5 temperature with 12 h incubation time leading to the formation of AlOOH and FeOOH nanoparticles, wherein the adsorbent composition is granular and amorphous in nature, and removes fluoride and arsenic from water with a removal capacity of 75 mg/g and 109 mg/g, respectively.
  - 2. The adsorbent composition as claimed in claim 1, wherein the granular nanocomposite is insoluble and does not degrade in water.
  - 3. The adsorbent composition as claimed in claim 1, wherein the biopolymer is chitosan.
  - 4. The adsorbent composition as claimed in claim 1, wherein the biopolymer acts as a template and controls the particle size of AlOOH and FeOOH.
  - 5. The adsorbent composition as claimed in claim 1, wherein the biopolymer provides mechanical strength to the granular composition.
  - 6. The adsorbent composition as claimed in claim 1, wherein the ferric precursor is at least one selected from the group comprising ferric nitrate, ferric chloride, ferric sulfate or a combination thereof.
  - 7. The adsorbent composition as claimed in claim 1, wherein the aluminium precursor is at
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least one selected from the group comprising aluminium nitrate, aluminium chloride, aluminium sulfate or a combination thereof.

- 8. The adsorbent composition as claimed in claim 1, wherein the granular nanocomposite is prepared with at least one metal oxyhydroxide, where the metal is selected from the group consisting of zinc, titanium, zirconium, lanthanum, cerium, silicon or a combination thereof.
- 9. The adsorbent composition as claimed in 1, wherein the nanocomposite removes fluoride, arsenic and combination thereof from water below the permissible limits of 1.5 ppm and 10 ppb, respectively.

Dated at Chennai this December 14, 2020

Am Inger

Advocate & Patent Agent

Signature: U D. Moses Jeyakaran

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#### ABSTRACT

## CHITOSAN REINFORCED MIXED OXYHYDROXIDE NANOCOMPOSITE FOR FLUORIDE AND ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF

The present invention discloses an adsorbent composition of chitosan reinforced mixed oxide granular nanocomposite for water-related applications, specifically for water purification. The granular nanocomposite comprises active ingredients homogenized in the aggregated network of chitosan templated aluminum oxyhydroxide/2-line iron oxyhydroxide composite. The composition is versatile as any metal or non-metal ion (including transition metals and/or rare earth metals) can be used. The composition itself can be a water purifier, such as an adsorbent for fluoride and arsenic removal from water with excessively high fluoride and arsenic adsorption capacity.

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15 Figure 1 20 Signature: D. Moses Jeyakaran Advocate & Patent Agent 25 IN/PA — 369 30

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Figure 2

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## Figure 3

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Figure 5

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Figure 6



Figure 7

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Figure 8

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Figure 11

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Figure 12

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Figure 13

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Figure 14

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Fe 2p Al 2p а b 73.3 708.4 Intensity (a.u.) 721.4 After fluoride After fluoride 73.5 708.5 Before fluoride 721.6 ! Before fluoride 700 707 714 721 728 735 68 70 72 74 76 78 Binding energy (eV) 0 1s C1s С d 531.6 283.8 Intensity (a.u.) 529.9 After fluoride After fluoride 530.9 Before fluoride 529.3 283.2 Before fluoride 276 280 284 288 525 528 531 534 292 537 Binding energy (eV)

Figure 15

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## CHITOSAN REINFORCED MIXED OXYHYDROXIDE NANOCOMPOSITE FOR FLUORIDE AND ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF

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Figure 16

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## Figure 17

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Figure 18

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## Figure 19

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Figure 20

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Figure 21

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Figure 22

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Figure 23

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b а Input Ŧ Arsenic concentration (ppb) 3 -2 -Output Output 1-125 150 Ó Ó Dose (mg)

Figure 24

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b а Input Į Arsenic concentration (ppb) Output Output ò ò 140 160 180 Time (min.)

Figure 25

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1.0  $R^2 = 0.99794$ Max. adsorption capacity = 1/slope = 109.41 mg/g 0.8  $c_e/q_e$  (g/L) 0.6 0.4 0.2 0.0 20 40 60 80 100 0 c<sub>e</sub> (mg/L)

Figure 26

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Figure 27

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Figure 28

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Figure 29

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Figure 30

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76.3 Al 2p Fe 2p a b 709.6 After As(V) adsorption Intensity (counts) 722.7 After As(V) adsorption 76.4 709.5 Before As(V) adsorption 722.6 Before As(V) adsorption 72 82 720 70 74 76 78 80 84 704 708 712 716 724 728 732 Binding energy (eV) d As 3d C C 1s 287.0 46.9 After As(V) adsorption Intensity (counts) After As(V) adsorption 44.7 286.8 Standard As(V) Before adsorption Before As(V) adsorption 48 280 282 284 286 292 40 42 44 46 50 288 290 294 Binding energy (eV) 0 1s 531.3 е N 1s 399.7 f After As(V) adsorption After As(V) adsorption Intensity (counts) 529.8 399.6 531.2 Before As(V) adsorption Before As(V) adsorption 529. 534 402 404 525 528 531 396 398 400

Binding energy (eV)

Figure 31

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