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पेटेंट प्रमाणपत्र
PATENT CERTIFICATE
(Rule 74 Of The Patents Rules)

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आवेदन सं. / Application No. : 201641027660
फाइल करने की तारीख / Date of Filing : 12/08/2016
पेटेंटी / Patentee : INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT Madras)

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 12th day of August 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 CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF as disclosed in the above mentioned application for the term of 20 years from the 12th day of August 2016 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 10/08/2020
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 12th day of August 2018 को और उसके पश्चात प्रत्येक वर्ष में उसी दिन देय होगी।

Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 12th day of August 2018 and on the same day in every year thereafter.

FORM 2
THE PATENTS ACT, 1970
(39 OF 1970)
&
The Patents Rules, 2003
COMPLETE SPECIFICATION
(Refer section 10 and rule 13)

TITLE OF THE INVENTION:

**CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED
ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**

2. APPLICANT:

(A) NAME: **INDIAN INSTITUTE OF TECHNOLOGY MADRAS**

(B) NATIONALITY: Indian

(C) ADDRESS: **INDIAN INSTITUTE OF TECHNOLOGY MADRAS**

IIT P.O. Chennai - 600 036

3. Preamble to the Description

COMPLETE SPECIFICATION

The following specification particularly describes the invention and the manner in which is to be performed.

COMPLETE SPECIFICATION

TITLE OF THE INVENTION

5 **CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED
ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**

FIELD OF THE INVENTION

10 The present invention relates to water based application, particularly in the field of water purification. More specifically, the invention relates to the use of granular compositions for rapid removal of contaminants from water without the use of electricity.

BACKGROUND OF THE INVENTION

15 Arsenic poisoning is said to be the largest mass poisoning in the history of humanity. Due to large scale microbial and chemical contamination, surface water is unsafe and groundwater is the most reliable and affordable way to provide safe water in several parts of the world. Accessing water from arsenopyrite-containing layer, from a depth of 30-100 meters, results in groundwater contaminated with arsenic. Presence of oxygen increases arsenic dissolution in
20 water and arsenic laden water becomes the source of drinking water. Even surface water is contaminated with arsenic, but to a lesser extent. Affordable technologies have been limited, which delay the introduction of sustainable solutions for arsenic mitigation. Due to this, even after 100 years of its detection, arsenic in drinking water continues to be a menace across the world, affecting over 130 million people.

25 Many publications have reported green and environmental solutions for arsenic mitigation. For example, Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater by Xuejun Guo., et al., Environ. Sci. Technol., 2005, 39, 6808-6818; and Removal of arsenic (V) by magnetic nanoparticle activated microfibrillated cellulose by Sanna Hokkanen, et al., Chem. Eng. J., 2015, 260, 886-894. However, the search for better,
30 affordable and sustainable materials for arsenic mitigation still continues.

 Biopolymers such as chitosan have been used to create green composites for arsenic removal (T. Pradeep, et al., Proc. Natl. Acad. Sci., 2013, 110, 8459-8464). Chitosan derived materials can be sensitive to many, as the biopolymer is derived from crustaceans, although no biopolymer in itself is released into the purified water. The purified water in a way is similar to a

natural water stream in which various life forms coexist. Despite such similarities, plant based materials are sought after as sustainable solutions both, from environmental and public acceptance perspectives.

Cellulose nanocrystal reinforced composites have been valuable materials, in general for diverse applications, even though their large scale production becomes a matter of concern, especially when demand increases abruptly.

Cellulose nanocrystal is a green plant derived alternative to nanocellulose crystal and have been an intensively explored material in various fields. Due to the presence of many covalent functional groups, creation of an organo-inorganic composite of desired functions is possible with this material. With the availability of such materials in abundance at an affordable cost, the animal based biopolymer composites may be replaced. Increased sustainability and reduced impact on the eco-system enhances the importance of such materials. Hence such materials would constitute the next generation adsorbents for arsenic remediation.

A number of materials have been prepared recently for water related applications, especially for water purification. These materials exhibit improved performance vis-à-vis existing compositions, thereby improving the efficiency of water purification. Amongst these materials, nanomaterials play a critical role in various aspects of water purification (Savage, N, et al., Nanotechnology Applications for Clean Water, 2008 and T Pradeep, et al., Thin Solid Films 2009, 517, 6441).

A number of these materials are obtained in fine powder form, presumably due to poor inherent binding ability, as well as due to the absence of long-range order associated with crystallinity. However, such materials cannot be used as it is for water purification, due to the difficulties in particle separation, danger of particle leaching, and poor hydraulic conductivity. A number of such examples are well known in the literature [T. Pradeep et al., J.Haz. Mater., 2011, 186, 1, 921-931; V. Chandra et al., ACS Nano, 2010, 4, 7, 3979-3986; T. Pradeep et al., J. Mater. Chem. A, 2013, 611-620; Udayabhaskararao et al., J. Nanosci., 2011, 4, 5, 839-843]

Hence, such powder materials require granulation prior to their use as a filtration medium. There are a number of techniques available for the conversion of a powder medium to a granular form. For example US Patent No. 7,449,030 and EPPatent Application No.1954634 describes a method for preparing agglomerated particles followed by sintering or spray drying by using organic/inorganic binders. 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 powder 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 European Patent Application No. EP1715947.

Researchers have looked at newer methods to synthesize iron oxide compositions in the laboratory and use them for water purification. Often, these compositions are prepared using water based routes below 100 °C. For example, Sol-gel mediated synthesis of Fe₂O₃ nanorods by K. Woo, et al., Adv. Mater., 2003, 15, 20, 1761-1764 and Granular ferric hydroxide-a new adsorbent for the removal of arsenic from natural water by W. Driehaus, et al., Water SRT-Aqua Aqua, 1998, 47, 1, 30-35., relates to iron oxide and its applications in water purification.

It may be understood from the references that a number of active ingredients cannot be used as it is due to their powdery nature. A representative example of such an ingredient is graphene. Using powder form for water related applications is prohibitive because it offers a very high pressure drop for water flow, thereby significantly reducing hydraulic conductivity.

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.

SUMMARY OF THE INVENTION

The present invention demonstrates the utility of cellulose nanocrystal (CNC) templated 2-line iron oxyhydroxide in various water-related applications. More specifically, the invention uses cellulose nanocrystal (CNC) templated 2-line iron oxyhydroxide as adsorbent in water purification devices.

In one embodiment, the present invention demonstrates the utility of the composition as an active ingredient for water-related applications, such as removal of arsenic from water with superior arsenic adsorption capacity vis-à-vis compositions reported in the prior art.

In other embodiment, the present invention provides a method for preparation of granular form of diverse active ingredients, by gel-phase blending of cellulose nanocrystal templated 2-line iron oxyhydroxide as an active ingredient, without binders.

In another embodiment, the invention shows cellulose nanocrystal templated 2-line iron oxyhydroxide 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.

Wherein the 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 such as 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 another 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 device. 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

Figure 1. Scanning electron micrograph of iron oxyhydroxide-cellulose nanocrystal composite in granular form (52 x 72 mesh) upon continuous exposure to water for about 3 months. A to C are of different magnifications.

Figure 2. X-ray diffraction pattern of the native cellulose nanocrystal as it is (before binding with iron oxyhydroxide nanoparticles), in comparison to iron oxyhydroxide-cellulose nanocrystal composite in powder form before exposing to As solution, after exposing to As (III) and As (V) solutions for 120 min.

Figure 3. High resolution transmission electron micrograph of (A) iron oxyhydroxide-cellulose nanocrystal composite in powder form before exposing to As solution. (B)&(C) Powdered iron oxyhydroxide-cellulose nanocrystal composite after exposing to As (III) and As (V) solutions for 120 min, respectively.

Figure 4. TEM-EDAX of (A) iron oxyhydroxide-cellulose nanocrystal composite in powder form before exposing to As solution. (B) &(C) Powdered iron oxyhydroxide-cellulose nanocrystal composite after exposing to As (III) and As (V) solutions for 120 min, respectively.

Figure 5. Scanning electron micrograph of (A) iron oxyhydroxide-cellulose nanocrystal composite in powder form before exposing to As solution. (B) &(C) Powdered iron oxyhydroxide-cellulose nanocrystal composite after exposing to As (III) and As (V) solutions for 120 min, respectively.

5 **Figure 6.** Elemental X-ray images (SEM-EDAX) of (A) iron oxyhydroxide-cellulose nanocrystal composite in powder form before exposing to As solution. (B) &(C) Powdered iron oxyhydroxide-cellulose nanocrystal composite after exposing to As (III) and As (V) solutions for 120 min, respectively.

Figure 7. Infrared features of (A) & (B) cellulose nanocrystal, as-synthesized iron oxyhydroxide-cellulose nanocrystal composite after exposing to As (III) and As (V) solutions for 120 min, in comparison to standard As (III) salt and standard As (V) salt, respectively.

Figure 8. Residual arsenic concentration as a function of adsorbent dose (dosage study) with the composition reported in this invention tested separately for As (III) and As (V) adsorption (initial concentration = 1 ± 0.1 ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).

Figure 9. Residual arsenic concentration as a function of time (kinetic study) with the composition reported in this invention tested separately for As (III) and As (V) adsorption (initial concentration = 1 ± 0.1 ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).

20 **Figure 10.** Langmuir isotherm for arsenite ion adsorbed (mg/g). C_e/q_e (g/L) as a function of equilibrium concentration of arsenite ion (mg/L) left in the solution (initial adsorbent dose = 32.5 mg, volume = 100 mL deionized water, contact time = 120 min).

Figure 11. Langmuir isotherm for arsenate ion adsorbed (mg/g). C_e/q_e (g/L) as a function of equilibrium concentration of arsenate ion (mg/L) left in the solution (initial adsorbent dose = 32.5 mg, volume = 100 mL deionized water, contact time = 120 min).

Figure 12. Residual arsenic concentration as a function of pH with the composition reported in this invention tested separately for As (III) and As (V) adsorption (initial adsorbent dose = 25

mg, initial concentration = 1 ± 0.1 ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).

Figure 13. XPS survey spectrum of (a) as synthesized iron oxyhydroxide-cellulose nanocrystal composite, (b) composite after adsorbing As (III) and (c) As (V). As 3d region of the spectra are expanded in the inset.

Figure 14. XPS analysis of iron oxyhydroxide-cellulose nanocrystal composite in various regions of interest. (A) Curve fitted Fe 2p, (B) As 3d, (C) C 1s and (D) O 1s regions of as it is material and those after adsorbing As (III) and As (V) from solution.

Figure 15. Residual arsenic concentration as a function of number of cycles (cycle saturation study) with the composition reported in this invention tested separately for As (III) and As (V) adsorption (adsorbent dose used for all cycles of the pre-cycle = 25 mg, each cycle concentration = 1 ± 0.1 ppm, each cycle volume = 100 mL synthetic challenge water, each cycle contact time = 120 min).

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.

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.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by the one having ordinary skill in the art to which this invention belongs, although any methods and materials, similar or equivalent to those described herein can be used in practice or in testing of the present invention. Example methods and materials are described below.

As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a metal" includes mixtures of two or more metals.

Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by the use of antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant, both in relation to the other endpoint and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

As used herein, the terms "optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

Each of the materials disclosed herein are either commercially available and/or the methods for production thereof are known to those of skill in the art.

In one aspect, the present invention demonstrates that matrix (cellulose nanocrystal-templated 2-line iron oxyhydroxide) can be an active carrier in few cases, such as for the removal of arsenic from water. It is further demonstrated that the capability of the composition to remove both forms of arsenic such as As (III) and As (V) from drinking water, with arsenic adsorption capacity far higher than for the compositions known in prior art.

In other aspect, the present invention shows preparation of 2-line iron oxyhydroxide within the cellulose nanocrystal matrix. Cellulose nanocrystal is a biopolymer with several advantages such as being biodegradable and inexpensive. Another important benefit of using cellulose nanocrystal as matrix is that, it forms rod-like or whisker-shaped particles (3-20 nm wide, 50-2000 nm long). When 2-line iron oxyhydroxide nanoparticles 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. Wherein the biopolymer material including, but not limited to cellulose nanocrystal, banana silk, nylon, cellulose nanofiber or a combination thereof.

In yet another aspect, the present invention relates to the preparation of granular composition of diverse active ingredients in powder form using 2-line iron oxyhydroxide

dispersed in cellulose nanocrystal template as an arsenic removal medium. In one aspect, the invention comprises of a granular composite of powder ingredient blended in 2-line iron oxyhydroxide on a cellulose nanocrystal template.

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

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 arsenite (As (III)) and arsenate (As (V)).

Method of preparing cellulose nanocrystal templated 2-line iron oxyhydroxide is derived from preferred embodiments described in Indian Application No. 1529/CHE/2010 and Indian Application No. 486/CHE/2013.

In a standard synthesis, the 2-line iron oxyhydroxide-cellulose nanocrystal composite was synthesized as follows: About 0.005 g cellulose nanocrystal was dissolved in 10 mL of de-ionized water, sonicated for about 10 min to make it well dispersed homogeneous solution. This was precipitated at pH 9 using 0.2 M NaOH. About 0.5 g Na_2SO_4 was added in one step. After 5 min of incubation, 10 mL of 1 M ferric hexachloride was added. The mixture was brought to pH 8, using 2M NaOH by slow addition. The final composition was further incubated for about 12 h, at ambient temperature to embed the synthesized nanoparticles in cellulose nanocrystal 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, 2-line iron oxyhydroxide-cellulose nanocrystal composite, was insoluble in water and appeared as dark black shining crystals. The dried composite was crushed to a powder form and used for arsenic adsorption. The yield was 1.0 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 synthesized 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 1 shows SEM image of the 2-line iron oxyhydroxide-cellulose nanocrystal composite in the granular form (52 x 72 mesh) at various magnification (1A, 1B and 1C), which has been exposed to running water for about 3 months.

Cellulose nanocrystal is a green plant derived alternative to synthetic polymer and have been an intensively explored material in various fields. Due to the presence of many covalent functional groups, creation of an organo-inorganic composite of desired functions is possible with this material. It is well-known that hydrous iron oxides, as found in the nature exhibit reasonable mechanical strength (as they occur in crystalline form). In case of 2-line iron oxyhydroxide-cellulose nanocrystal composite, it is highly amorphous (X-ray crystallographic data shown in Figure 2). Here, the role of cellulose nanocrystal is very crucial in improving the strength of 2-line iron oxyhydroxide-cellulose nanocrystal composite by binding with 2-line iron oxyhydroxide nanoparticles.

The material was kept in water and was found to be stable even after six months without any leaching of Fe. Stability of the composition is attributed to abundant -O and -OH functional groups of cellulose nanocrystal, which help in the formation of metastable amorphous metal oxyhydroxide and also ensure strong covalent binding of the nanoparticle surface to the template / matrix.

Figure 2 shows the X-ray diffraction (XRD) pattern of cellulose nanocrystal (as it is), 2-line iron oxyhydroxide-cellulose nanocrystal composite and composite after adsorbing As (III) and As (V), respectively. Presence of sharp features in case of cellulose nanocrystal proves its crystalline nature, whereas broad peak shapes observed for as-synthesized 2-line iron oxyhydroxide-cellulose nanocrystal composite and for composite after adsorbing As (III) and As (V) proves the amorphous nature of the composite. X-ray diffraction pattern of 2-line iron oxyhydroxide-cellulose nanocrystal shows the two line ferrihydrite phase (particle size < 2.1 nm) of the iron oxyhydroxide which matches with the Cambridge crystallographic database (CCD). As (III) and As (V) adsorption does not change the XRD profiles. No new phase was observed in XRD of the used materials which clearly shows the long term stability of invented composition in water.

A HRTEM image of the 2-line iron oxyhydroxide-cellulose nanocrystal composite is shown in Figure 3. 2-line iron oxyhydroxide nanoparticles are not prominently visible in the

large area image due to their small size, but they could not be seen even at higher magnification due to their highly amorphous nature. It can be seen that 2-line iron oxyhydroxide nanoparticles are well-dispersed in the cellulose nanocrystal matrix. The metal oxyhydroxide nanoparticles are homogeneously sized. The rod-like cellulose nanocrystal structure is not seen clearly due to the complete embedding of 2-line iron oxyhydroxide nanoparticles. Upon closer observation, the nanoparticles are anchored onto the cellulose nanocrystal nanoarchitecture. Outside the cellulose nanocrystal structure, no nanoparticles were present. This again confirms the composite formation, wherein 2-line iron oxyhydroxide nanoparticles are formed only inside the cellulose nanocrystal 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 concentration is loaded on the surface of nanoparticles.

TEM-EDAX spectrum and elemental maps of 2-line iron oxyhydroxide-cellulose nanocrystal composite in powder form (Figure 4A) along with arsenic (As (III) and As (V)) adsorbed composition (Figure 4B and Figure 4C). For the purpose of this study, 325 mg of adsorbent was shaken with 200 ppm of 250 mL arsenic solution in de-ionized water. All the principal elements, including adsorbed arsenic are present in the spectrum. Elemental maps confirm that the distribution of arsenic is homogeneous and is extremely high. In case of As (III) adsorbed composition, arsenic content in the composition is around 3.84%, whereas in case of As (V) adsorbed composition, it is around 1.78%. This is in consonance with the earlier result that performance of the composition is better for As (III) removal at higher concentrations and for As (V) at lower concentrations.

SEM image of the 2-line iron oxyhydroxide-cellulose nanocrystal composite in the powder form (Figure 5A), composite after adsorbing As (III) (Figure 5B), and composite after adsorbing As (V) (Figure 5C). There is no change in physical state of the material observed upon exposure to various arsenic concentrated solutions which implies a simple surface adsorption.

Figure 6 shows SEM-EDAX spectrum and elemental maps of 2-line iron oxyhydroxide-cellulose nanocrystal composite in powder form (Figure 6A) along with arsenic (As (III) and As (V)) adsorbed composition (Figure 6B and Figure 6C). For the purpose of this study, 325 mg of adsorbent was shaken with 200 ppm, 250 mL arsenic solution in de-ionized water. All the principal elements including adsorbed arsenic are present in the spectrum. Elemental maps

confirm that distribution of arsenic is homogeneous and extremely high. In case of As (III) adsorbed composition, arsenic content in the composition is around 1.30% whereas, in case of As (V) adsorbed composition, it is around 0.72%. This is in consonance with the earlier result that performance of the composition is better for As (III) removal at higher concentrations and for As (V) at lower concentrations.

Figure 7 shows the Fourier transform infrared (FTIR) spectrum of cellulose nanocrystal (as it is), 2-line iron oxyhydroxide-cellulose nanocrystal composite and composite after adsorbing As (III) and As (V), respectively. Presence of a peak at 1644 cm^{-1} confirms the adsorption of As (III) and at 1633 cm^{-1} confirms the adsorption of As (V) by the as-synthesized 2-line iron oxyhydroxide-cellulose nanocrystal composite.

Figure 8 represents the comparative performance of arsenic adsorbent composition as reported here for As (III) and As (V), respectively. It is clearly observed that 2-line iron oxyhydroxide-cellulose nanocrystal composite exhibits superior performance. 1 ± 0.1 ppm arsenic in synthetic challenge water treated with 250 mg/L adsorbent composition show 24 ppb (As (V)) and 55 ppb (As (III)) remaining after 120 min.

The concentration of arsenic in the effluent water, measured by inductively coupled plasma mass spectrometry (ICP-MS), was consistently below 10ppb, adhering to the WHO norms (Figure 8). This demonstrates that 2-line iron oxyhydroxide-cellulose nanocrystal matrix is amply accessible by water, thereby ensuring that the composition can be utilized as an effective water purification composition.

There are a number of unique advantages associated with the use of the composition as an active adsorbent: it does not show significant drop in the performance even when used with synthetic challenge water containing interfering ions. 1 ± 0.1 ppm arsenic in de-ionized water treated with 250 mg/L adsorbent composition shows 13 ppb (As (V)) and 40 ppb (As (III)), whereas 1 ± 0.1 ppm arsenic in synthetic challenge water treated with 250 mg/L adsorbent composition shows 24 ppb (As (V)) and 55 ppb (As (III)). Role of cellulose nanocrystal is further evident from the fact that 1 ± 0.1 ppm arsenic in synthetic challenge water treated with 250 mg/L adsorbent composition (prepared without cellulose nanocrystal) shows 312 ppb (As (V)) and 125 ppb (As (III)). This clearly establishes the importance of cellulose nanocrystal in the preparation of and effective composite.

The synthesized composition is tested against interfering ions in water is reported in Table 1. The counter ion effect of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and combination thereof on arsenic adsorption with the composition is tested separately for As (III) and As (V) adsorption (initial adsorbent dose = 25 mg, initial concentration = 1 ± 0.1 ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).

Table 1

Competitive ion	Ion concentration	Input As (III)	Adsorbed As (III)	Remaining As (III)
CO_3^{2-}	100 ppm	1000 ppb	895 ppb	105 ppb
HCO_3^-	100 ppm	1000 ppb	954 ppb	46 ppb
$\text{CO}_3^{2-} + \text{HCO}_3^-$	50 ppm + 50 ppm	1000 ppb	943 ppb	57 ppb
Competitive ion	Ion concentration	Input As (V)	Adsorbed As (V)	Remaining As (V)
CO_3^{2-}	100 ppm	1000 ppb	402 ppb	598 ppb
HCO_3^-	100 ppm	1000 ppb	920 ppb	80 ppb
$\text{CO}_3^{2-} + \text{HCO}_3^-$	50 ppm + 50 ppm	1000 ppb	439 ppb	561 ppb
Competitive ion	Ion concentration	Input As (III)+As (V)	Total As adsorbed	Total As remaining
$\text{CO}_3^{2-} + \text{HCO}_3^-$	50 ppm + 50 ppm	500 ppb + 500 ppb	691 ppb	309 ppb

Arsenic adsorption isotherm of as-synthesized composite was carried out in de-ionized water. As-synthesized composite adsorbs approximately 111 mg/g at an equilibrium As (III) concentration and 37 mg/g at an equilibrium As (V) concentration. Langmuir isotherm was plotted for arsenic adsorption (Figure 10 and Figure 11) using the following expression:

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 arsenic in the solution, q_e (mg/g) is the quantity of arsenic 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 $1/bq_{max}$ 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 0.325 g/L adsorbent dose while varying initial arsenic concentration from 1 to 200 mg/L. The values of the isotherm constants for As (III) adsorption are 0.009 and 0.008, respectively and for As (V) adsorption are 0.027 and 0.049, respectively.

XPS spectra of as-synthesized iron oxyhydroxide-cellulose nanocrystal composite and arsenic adsorbed composition are compared with elements of our interest shown in Figure 14. The Fe 2p region of as-synthesized composition in powder form and arsenic adsorbed composition are shown in Figure 14A. Other than the main peaks, presence of multiple peaks in the Fe 2p region is because of its surface and satellite peaks. Although, there is no change for Fe(III) characteristic peaks, changes were seen in other elements. To understand the underlining phenomenon, the adsorbed As (III) and As (V) materials were compared with the corresponding standard As (III) and As (V) salts (Figure 14 B). For standard As (III), As 3d region peak comes at 44.3 eV whereas standard As (V) shows peak at 44.9 eV. But significant change was observed in peak position for both As (III) and As (V) in the adsorbed state. For As (III), As 3d peak was noted at 45.0 eV whereas As (V) gave peak at 45.8 eV. Both the species moved to a higher binding energy state in comparison to standard native salts. By comparing the peak positions, it can be said that the nature of adsorbed As (III) resembles more to the free state As (V). Same phenomenon is observed for As (V) too. The peak observed at 295.0 eV is close to the characteristic peak position for aliphatic carbon from the cellulose nanocrystal shown in Figure 14C. The peak at 529.0 eV is close to the characteristic peak position for bulk oxygen (O_2^-) (Figure 14D). The peak appears at 531.0 eV mostly because of surface hydroxyl groups which are attached to Fe. Even though there is no significant change in the peak position, there is a change in relative contribution in the peak area for as it is composite, As (III) adsorbed composite as well as As (V) adsorbed composite. The contribution due to surface hydroxyl peaks (at 530.9 eV) has decreased and oxide (at 529.0 eV) has increased due to As (III) adsorption. This may be correlated to our experimental observation where higher adsorbing capacity of As

(III) in comparison to As (V) was seen. We suggest that As (III) are also bound with hydroxyl groups on the surface of the grains, and change them to a higher binding energy state. As a result, the peak at 530.9 eV comes down and the peak at 532 and 529.0 eV increase, the latter may have contribution from the adsorbed arsenate/arsenite also. The peak at 532 eV is attributed to covalent oxygen species in the matrix.

The TCLP (toxicity characterization leaching protocol) test has been conducted for the reported composition as per the USEPA standard protocol and the leaching was observed as 2 ppb and 24 ppb for arsenic and iron, respectively, from completely As (III) and As (V) saturated materials.

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 α radiation at $\lambda = 1.5418 \text{ \AA}$. 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 (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 (XPS) analysis was done using ESCA Probe TPD of Omicron Nanotechnology. Polychromatic Mg K α was used as the X-ray source ($h\nu = 1253.6 \text{ eV}$). 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 285.0 eV. Arsenic concentration in the water was detected using inductively coupled plasma mass spectrometry (NexION 300X ICP-MS, PerkinElmer) with appropriate standards.

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

The optimization of cellulose nanocrystal in the synthesized composition was tested separately for As (III) and As (V) adsorption, using varied concentration of cellulose nanocrystal in the composition shown in Table-2. Parameters: initial adsorbent dose = 25 mg, initial concentration = $1 \pm 0.1 \text{ ppm}$, volume = 100 mL synthetic challenge water, contact time = 120 min).

Table-2

Materials Synthesized	Size	Input As (III)	Adsorbed As (III)	Remaining As (III)
0.1 M NaOH CNCAs-1 Wt%	Powder	1000 ppb	939 ppb	61 ppb
0.1 M NaOH CNCAs-0.5 Wt%	Powder	1000 ppb	940 ppb	40 ppb
0.1 M NaOH CNCAs-0.1 Wt%	Powder	1000 ppb	947 ppb	53 ppb
0.5 M NaOH CNCAs-0.5 Wt%	Powder	1000 ppb	945 ppb	55 ppb
Materials Synthesized	Size	Input As (V)	Adsorbed As (V)	Remaining As (V)
0.1 M NaOH CNCAs-1 Wt%	Powder	1000 ppb	960 ppb	40 ppb
0.1 M NaOH CNCAs-0.5 Wt%	Powder	1000 ppb	978 ppb	13 ppb
0.1 M NaOH CNCAs-0.1 Wt%	Powder	1000 ppb	982 ppb	18 ppb
0.5 M NaOH CNCAs-0.5 Wt%	Powder	1000 ppb	976 ppb	24 ppb

The present invention also tested arsenic uptake capacity of the parent cellulose nanocrystal which was used to make the composition (Table-3). Cellulose nanocrystal at various pH conditions was tested separately for As (III) and As (V) adsorption (Parameters: initial adsorbent dose = 25 mg, initial concentration = 1 ± 0.1 ppm, volume = 100 mL synthetic challenge water, contact time = 120 min).

All the uptake capacity studies were done in a batch mode (in 250 mL polypropylene conical flasks). The working volume of the solutions was 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.

Table-3

Material	Input As (III)	Adsorbed As (III)	Remaining As (III)
CNC (as it is)	1000 ppb	120 ppb	880 ppb
CNC (pH 4)	1000 ppb	293 ppb	707 ppb
CNC (pH 10)	1000 ppb	149 ppb	851 ppb
Material	Input As (V)	Adsorbed As (V)	Remaining As (V)
CNC (as it is)	1000 ppb	83 ppb	917 ppb
CNC (pH 4)	1000 ppb	124 ppb	876 ppb
CNC (pH 10)	1000 ppb	94 ppb	906 ppb

EXAMPLE 1

5 THE ROOM TEMPERATURE SYNTHESIS OF 2-LINE IRON OXYHYDROXIDE EMBEDDED IN CELLULOSE NANOCRYSTAL TEMPLATE THROUGH A SIMPLE SOFT CHEMISTRY ROUTE:

The Fe(III) precursor solution (such as ferric chloride) was mixed with cellulose nanocrystal (dispersed in 0.1 M NaOH or 0.5 M NaOH or combination thereof) by one-shot
10 addition with 10-15 min ultrasonication. The mixture was then used immediately. Aqueous NaOH solution was added slowly into the metal-cellulose nanocrystal solution by vigorous stirring to facilitate the precipitation of the metal-cellulose nanocrystal 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
15 shape of flakes and dried at ambient conditions.

EXAMPLE 2

20 INCORPORATION OF VARIOUS METAL OXIDE/HYDROXIDE/OXYHYDROXIDE-CELLULOSE NANOCRYSTAL COMPOSITES WITHIN 2-LINE IRON OXYHYDROXIDE-CELLULOSE NANOCRYSTAL TEMPLATE:

Precipitated 2-line iron oxyhydroxide-cellulose nanocrystal 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-cellulose nanocrystal 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, aluminium, zirconium, lanthanum, cerium or silicon. The mixture was prepared in an appropriate ratio, for example, with a dominant weight percentage for 2-line iron oxyhydroxide -cellulose nanocrystal composite (wt/wt). Thereafter, the precipitate was dried at ambient conditions.

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EXAMPLE 3

INCORPORATION OF NANOPARTICLES WITHIN 2-LINE IRON OXYHYDROXIDE-CELLULOSE NANOCRYSTAL TEMPLATE

Precipitated 2-line iron oxyhydroxide-cellulose nanocrystal 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_2O_3 nanoparticles dispersed in water) was homogenized with 2-line iron oxyhydroxide-cellulose nanocrystal composite. The mixture was prepared in an appropriate ratio, preferably with a dominant weight percentage for 2-line iron oxyhydroxide-cellulose nanocrystal composite (wt/wt). Once the blending of nanoparticles in carrier composition was complete, the precipitate was dried at ambient conditions.

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It may be noted that the desired metal oxide/hydroxide/oxyhydroxide-cellulose nanocrystal 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.

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We Claim:**CLEAN COPY**

1. A method of preparing granular nanocomposite comprising cellulose nanocrystal templated 2-line iron oxyhydroxide with size less than 2.1 nm, wherein the granular nanocomposite is stable in water and packed into a purification system for removal of arsenic from water, such that the filtered water has an arsenic concentration below 10 parts per billion comprises of:
 - a. 0.005 g cellulose nanocrystal was dissolved in 10 mL of de-ionized water, sonicated for about 10 min and precipitated at pH 9 using 0.2 M NaOH
 - b. 0.5 g Na₂SO₄ was added in one step and after 5 min of incubation, 10 mL of 1 M metal precursor, ferric hexachloride was added
 - c. 2M NaOH was added slowly to bring the above mixture to pH 8 and
 - d. incubated for about 12 h, at ambient temperature to embed the synthesized nanoparticles in cellulose nanocrystal network.
2. The method as claimed in claim 1, wherein the granular composition contains functionalized form of cellulose nanocrystal.
3. The method as claimed in claim 1, wherein the metal precursor is ferric chloride, ferric nitrate, ferric sulphate, ferrous chloride, ferrous nitrate, ferrous sulphate, or a combination thereof.
4. The method as claimed in claim 1, wherein the arsenic adsorbed nanocomposite does not release arsenic back into clean water.
5. The method as claimed in claim 1, wherein the stability of 2-line iron oxyhydroxide in water is attributed to abundant -O and -OH functional groups of cellulose nanocrystal, which leads to the formation of metastable amorphous iron oxyhydroxide.
6. The method as claimed in claim 1, wherein the granular nanocrystal is impregnated with other metal oxide/ hydroxide/ oxyhydroxide – nanocrystal composites, the said metal is selected from the group of zinc, manganese, iron, aluminium, zirconium, lanthanum, cerium or silicon.
7. The method as claimed in claim 1, wherein the granular nanocomposite is utilized as an active ingredient for the removal of contaminants from water.
8. The method as claimed in claim 7, wherein the contaminants are arsenate, arsenite or a combination thereof.
9. The method as claimed in claim 1, wherein the granular nanocomposite adsorbs about 111 mg/g at an equilibrium As (III) concentration.

10. The method as claimed in claim 1, wherein the granular nanocomposite adsorbs about 37 mg/g at an equilibrium As (V) concentration.
11. The method as claimed in claim 1, wherein the nanocomposite is used as a gravity fed product or as in-line purifier attached to pipeline water supply.
12. The method as claimed in claim 1, wherein the nanocomposite packed into a purification system in the form of filtration candle, molded porous block, filter bed, column, packets, bags and sachet.
13. The method as claimed in claim 1, wherein the nanocomposite material is used along with other arsenic removing materials.
14. The method as claimed in claim 1, wherein the nanocomposite is used as a concentrator to remove arsenic from solutions which are aqueous, organic or a mixture as in industrial waste water.

Dated at Chennai this June 18, 2019

Signature: 

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

**CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED
ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE
THEREOF**

ABSTRACT

The present invention relates to cellulose nanocrystal-based composites as adsorbents and its method of preparation for water purification and related applications. The composite comprises an aggregated network of cellulose nanocrystal templated 2-line iron oxyhydroxide. The granular composite acts as an active ingredient used for arsenic removal from water. The said nanocomposite is packed into a purification system for removal of arsenic from water, such that the filtered water has an arsenic concentration below 10 parts per billion.

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ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**

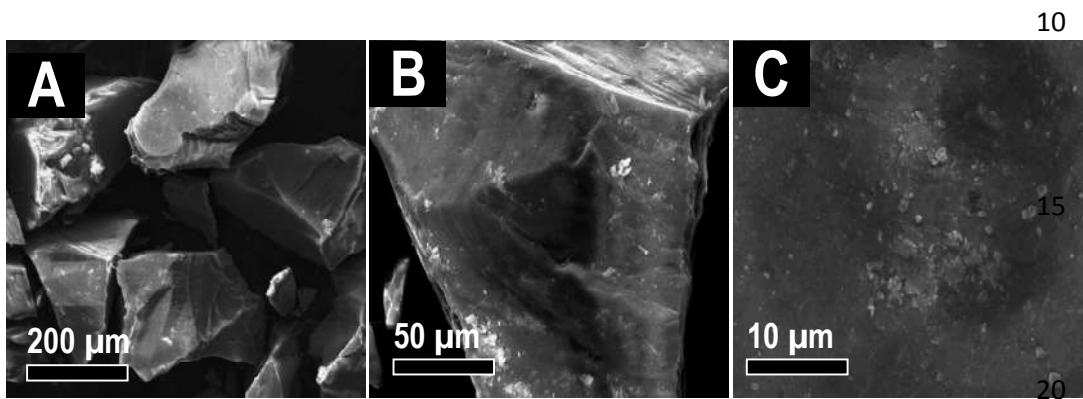


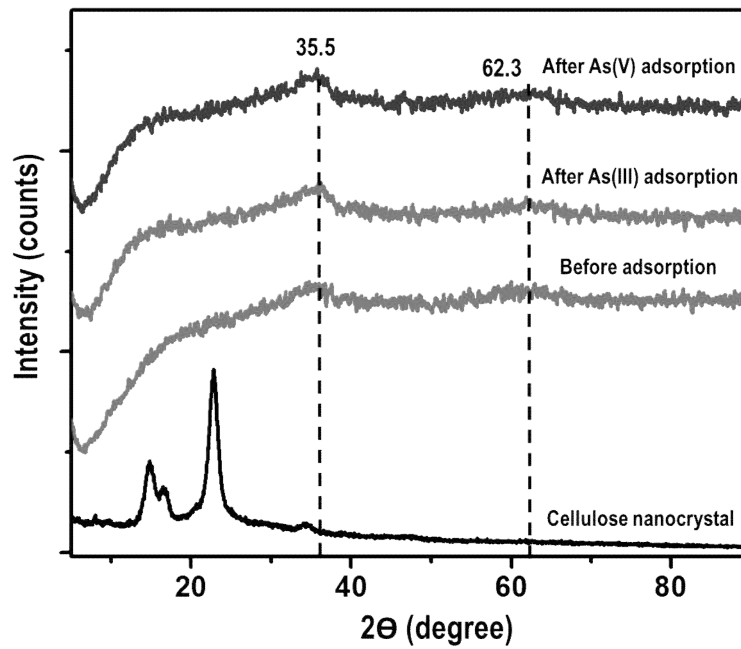
Figure 1

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Figure 2

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Advocate & Patent Agent
IN/PA — 369

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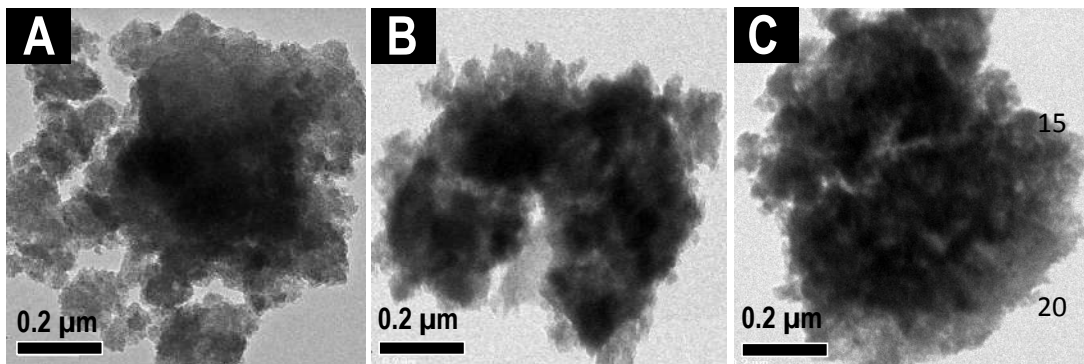
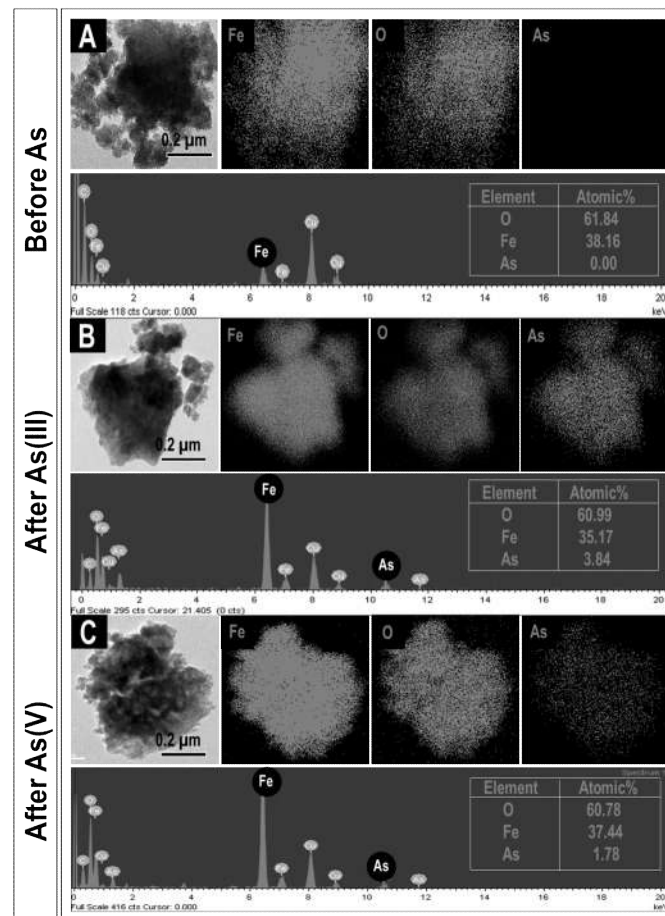


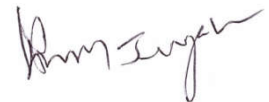
Figure 3

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Advocate & Patent Agent
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CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**Figure 4**

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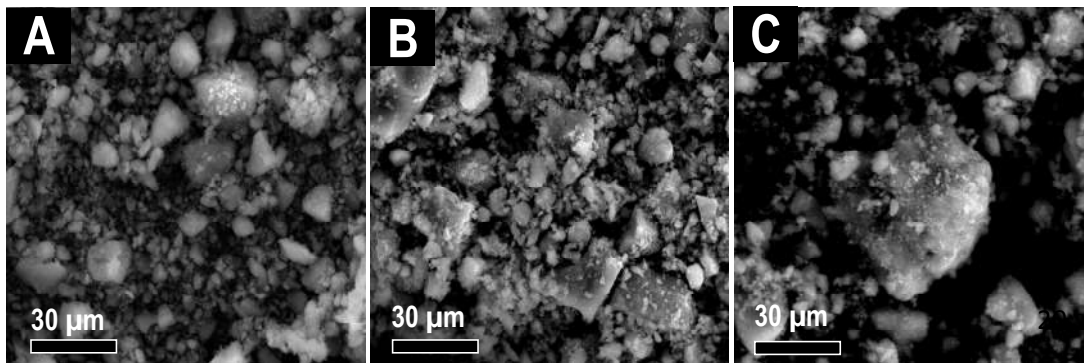
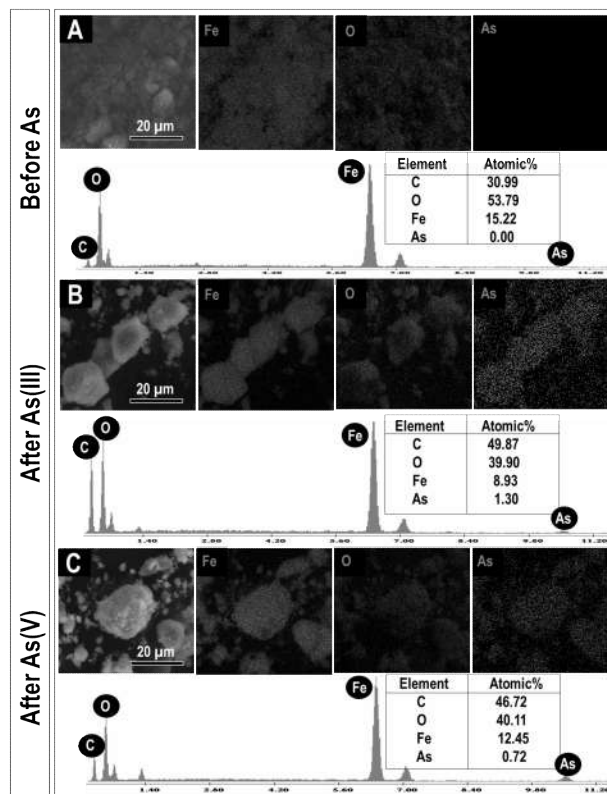


Figure 5

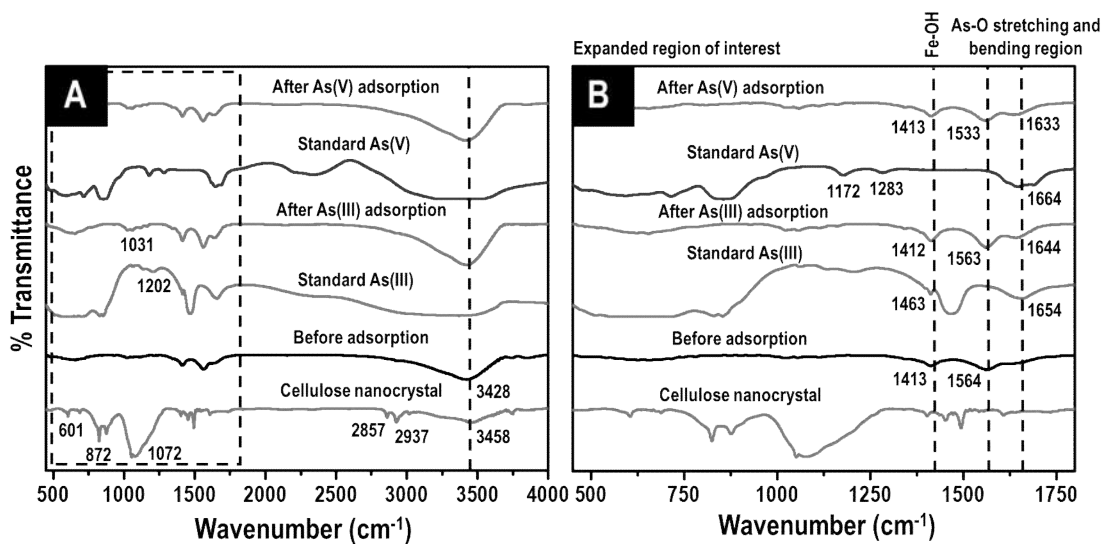
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CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**Figure 6**

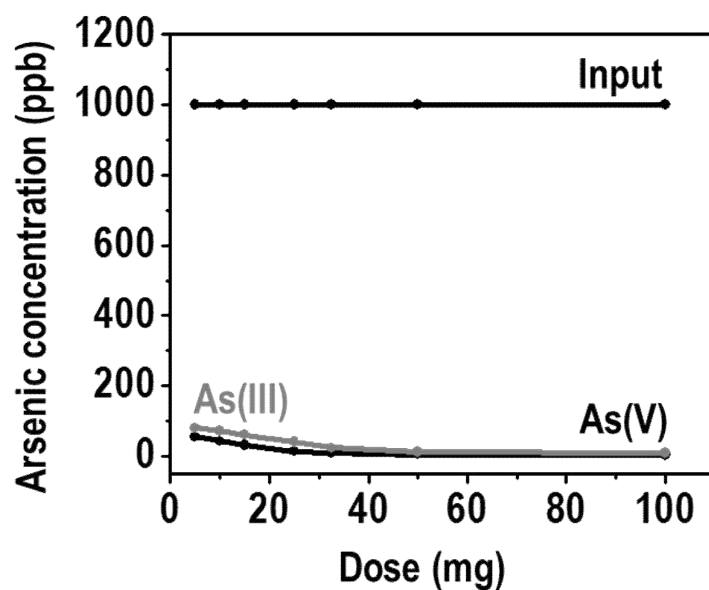
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Advocate & Patent Agent
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CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**Figure 7**

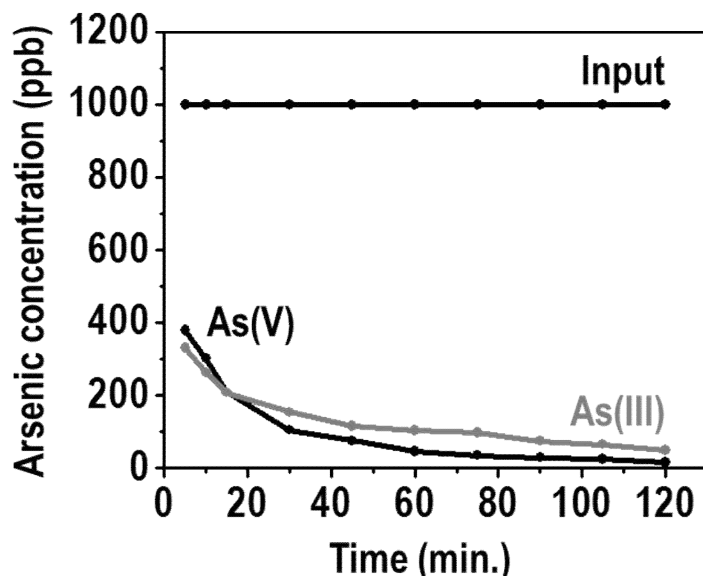
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Advocate & Patent Agent
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CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**Figure 8**

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D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**Figure 9**

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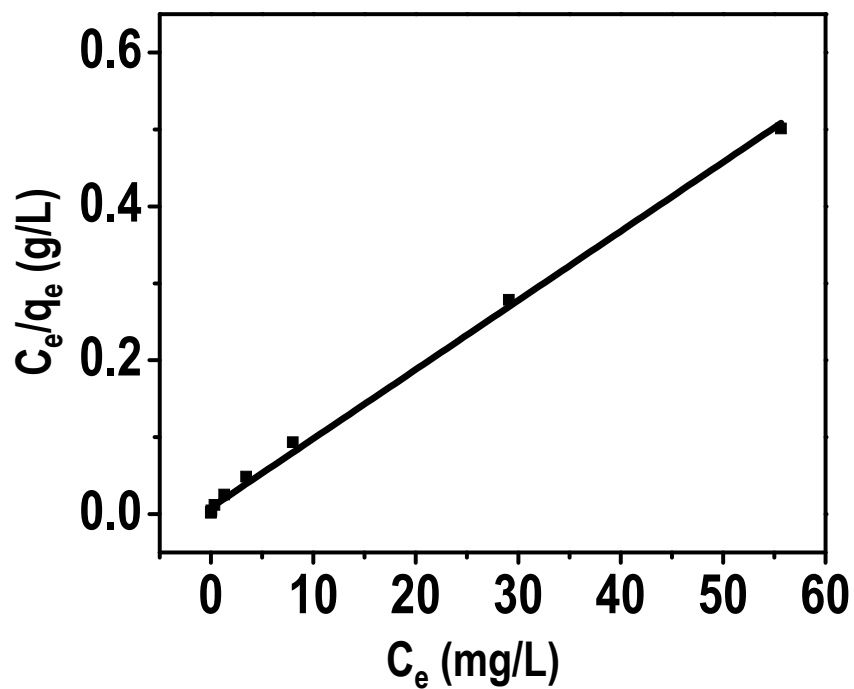
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Figure 10

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Advocate & Patent Agent
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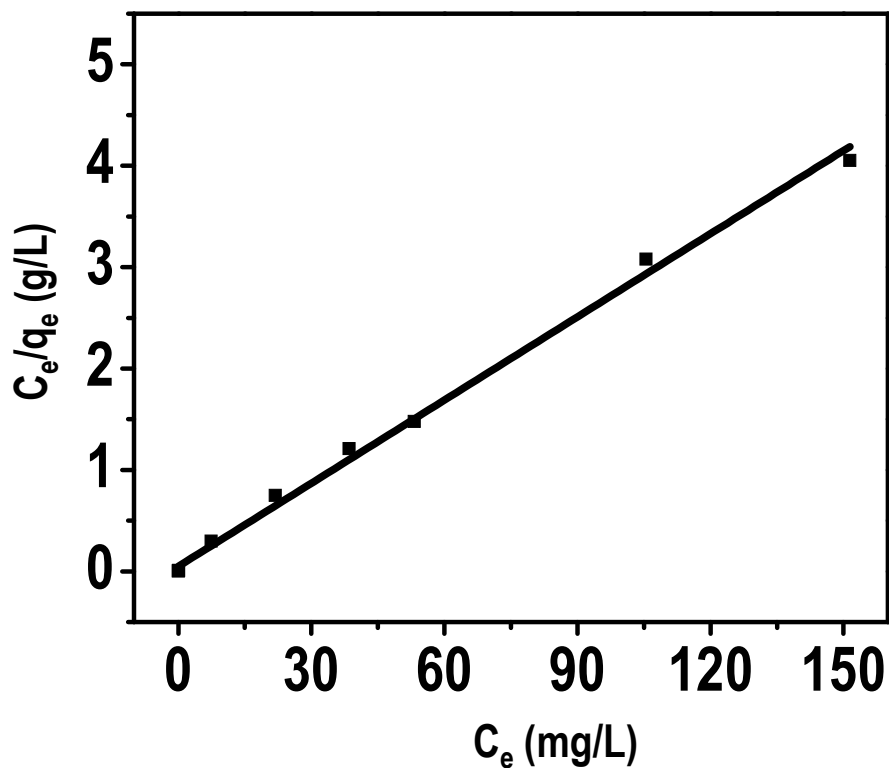
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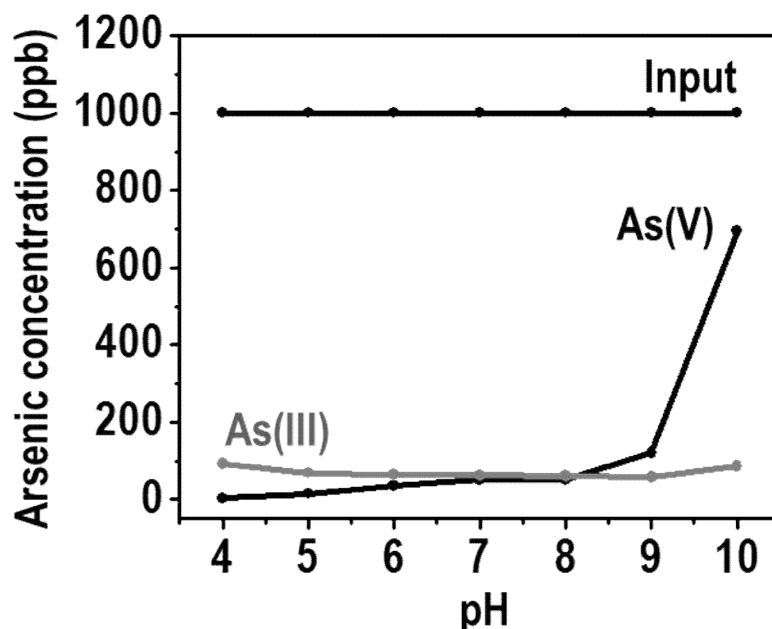
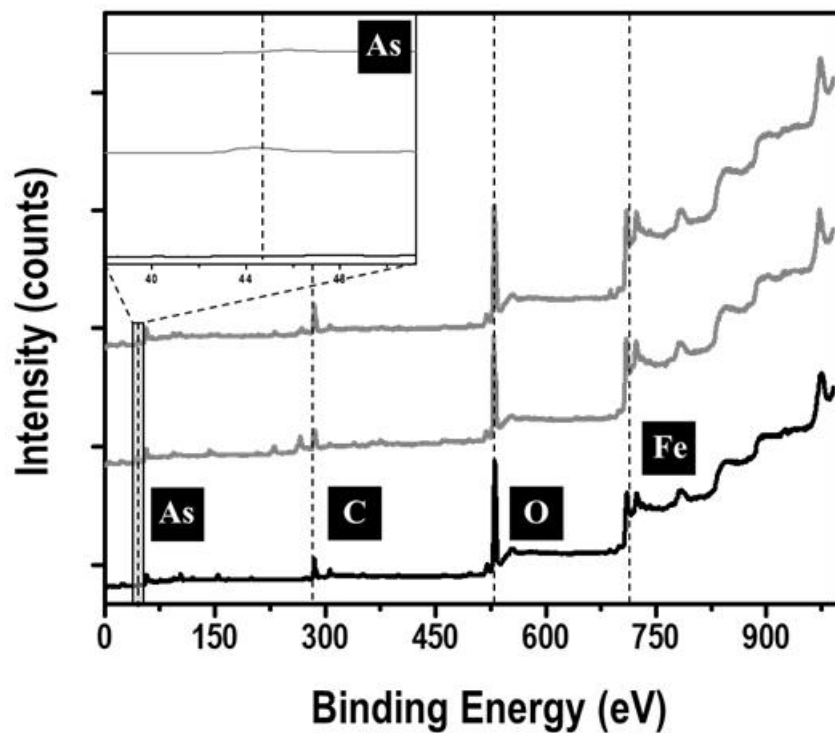
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Figure 12

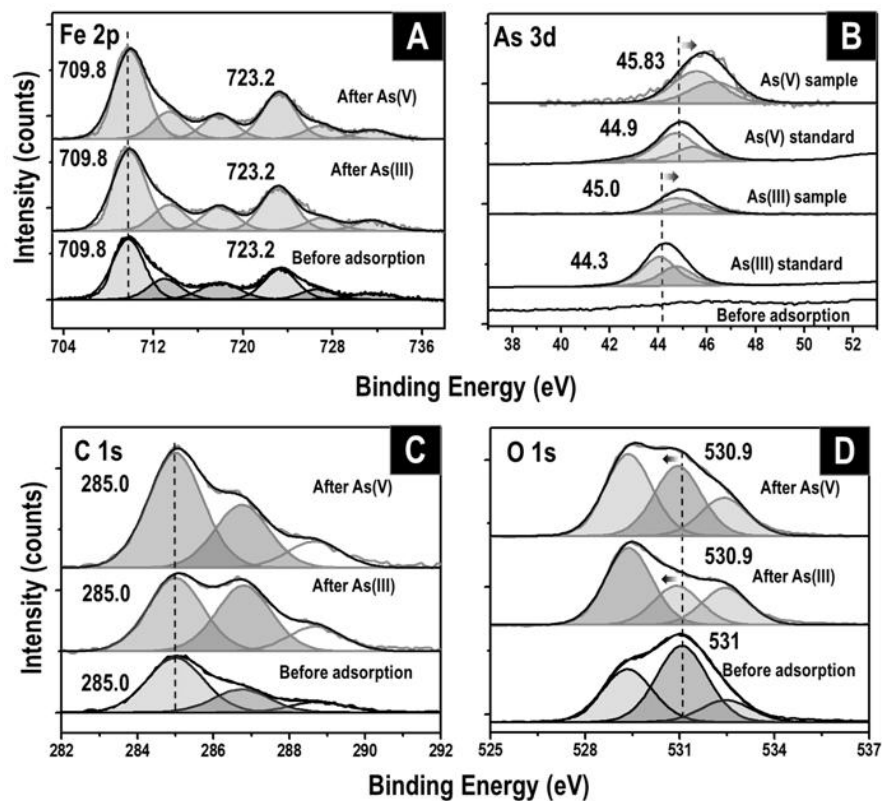
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CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**Figure 13**

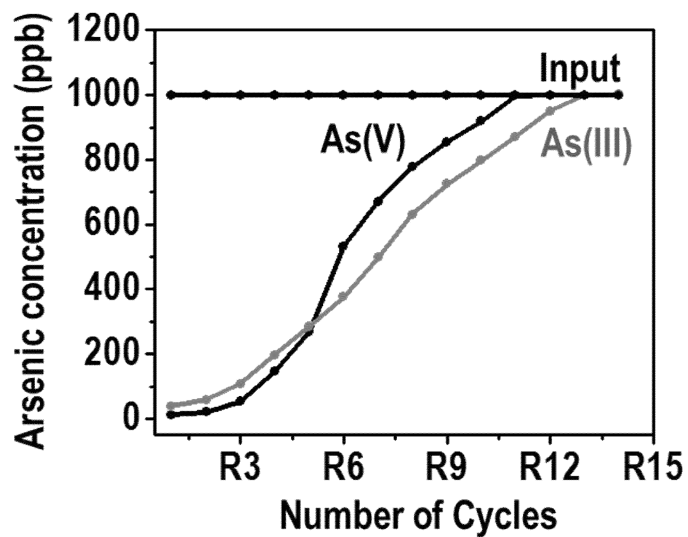
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Advocate & Patent Agent
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CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF**Figure 14**

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Advocate & Patent Agent
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**CELLULOSE NANOCRYSTAL TEMPLATED IRON OXYHYDROXIDE BASED
ADSORBENT FOR ARSENIC REMOVAL FROM WATER AND A DEVICE THEREOF****Figure 15**

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Advocate & Patent Agent
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