



(51) International Patent Classification:

B01J 20/00 (2006.01) *C02F 1/00* (2006.01)

Chemistry, IIT Madras, IIT P.O. Chennai, 600036, CHENNAI 600036 (IN).

(21) International Application Number:

PCT/IN2017/050627

(74) Agent: **D MOSES JEYAKARAN**; Advocate, Trade-mark & Patent Attorney, #245/105 METTU STREET, AYANAVARAM, CHENNAI - 600 023 (IN).

(22) International Filing Date:

28 December 2017 (28.12.2017)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

201641044817 29 December 2016 (29.12.2016) IN

(71) Applicant: **INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT MADRAS)** [IN/IN]; The Dean, Industrial Consultancy & Sponsored Research [ICSR], Indian Institute of Technology Madras, IIT P.O. Chennai – 600 036, India, CHENNAI 600036 (IN).(72) Inventors: **PRADEEP, Thalappil**; Department of Chemistry, IIT Madras, IIT P.O. Chennai, 600036, CHENNAI 600036 (IN). **MUKHERJEE, Sritama**; Department of Chemistry, IIT Madras, IIT P.O. Chennai, 600036, CHENNAI 600036 (IN). **ANIL KUMAR, Avula**; Department of

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: METHOD FOR PREPARING CELLULOSE MICROSTRUCTURES-TEMPLATED NANOCOMPOSITES WITH ENHANCED ARSENIC REMOVAL CAPACITY AND A PURIFIER THEREOF

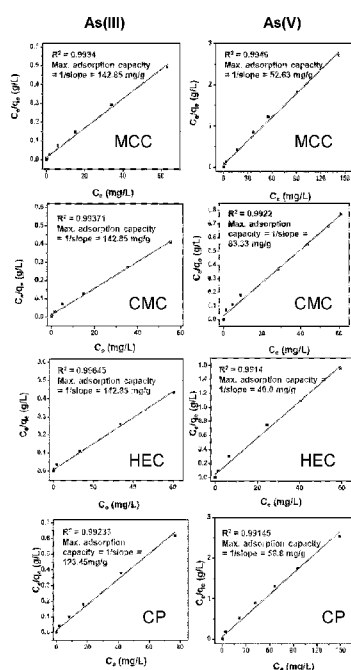


Figure 15

(57) Abstract: The present invention relates to the method of preparing microcrystalline cellulose based nanocomposites as adsorbents for water purification and related applications. The nanocomposite comprises an aggregated network of cellulose microcrystal and its derivatives templated 2-line iron oxyhydroxide. The granular nanocomposite acts as an active ingredient used for arsenic removal As(III) and As(V) from water with capacity greater than 98 mg/g, wherein the filtered water has an arsenic concentration below 10 parts per billion (ppb).

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*
- *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

DESCRIPTION

TITLE OF THE INVENTION

5 **METHOD FOR PREPARING CELLULOSE MICROSTRUCTURES-TEMPLATED NANOCOMPOSITES WITH ENHANCED ARSENIC REMOVAL CAPACITY AND A PURIFIER THEREOF**

FIELD OF THE INVENTION

10 The present invention relates to the field of water purification, specifically on the preparation of economical and sustainable granular composites useful for water purification-related applications, especially for rapid removal of contaminants from water without the use of electricity.

15 BACKGROUND OF THE INVENTION

Affordable and efficient water purification is one of the most desired objectives of the industrial world. Besides, development-induced demands, there are also geographical reasons or geological reasons for drinking water purification. Arsenic in drinking water is now a 102 year-old problem faced by 130 million people worldwide. Due to large scale microbial and chemical
20 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 groundwater from a depth of 30-100 meters results in water contaminated with arsenic in presence of arsenopyrite-containing layers (Bose, P.; Sharma, A., Role of Iron in Controlling Speciation and Mobilization of Arsenic in Subsurface Environment, Water Research, 2002, 36, 4916-4926). Presence of oxygen
25 increases arsenic dissolution in water and arsenic laden water becomes the source of drinking water in these regions. Even surface water is contaminated with arsenic, but to a lesser extent in this region. Creation of affordable materials to scavenge dissolved arsenic and delivering drinking water of international quality is a problem of advanced materials. Although, conventional materials have been used extensively for arsenic mitigation, nanomaterials are
30 emerging as important alternatives in this regard (Mohan, D.; Pittman, C. U.; Arsenic Removal from Water / Wastewater Using Adsorbents-A Critical Review, J. Haz. Mater., 2007, 142, 1-53).

The conventional belief is that nanostructuring enhances uptake of toxic species, as the surface area of the materials increase, and thereby uptake capacity per unit weight of the adsorbent.

Many publications have reported removal of arsenic by using biopolymer as starting
5 material. For example, biopolymer reinforced synthetic granular nanocomposites for affordable point-of-use water purification reported by Sankar et al., Proc. Natl. Acad. Sci., 2013, 110, 8459-8464. An important breakthrough in the development is the creation of metastable materials in the biomolecular confinement. The most important biomaterial used in this material is chitosan, derived from crustaceans. Although, the composite nanostructured materials using such
10 biopolymers do not release organic carbon into the process stream, there can be criticism on the use of such materials as they are animal-derived. It is in this context that plant derived polymers are considered as better templates. In a recent report, "Cellulose nanocrystal templated iron oxyhydroxide based adsorbent for arsenic removal from water and a device thereof" by T. Pradeep et al. 2016, have shown the utilization of nanocellulose for making such materials
15 (Indian Patent Application No. 201641027660).

Here, the present invention shows the creation of new materials with microcrystalline cellulose (MCC) and its variations (like carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC) and microcellulose of industrial grade (CP)) with comparable performance. The creation of such materials is essential for commercial applications as microcrystalline cellulose is one of
20 the cheapest sustainable biopolymeric materials available for templated synthesis.

MCC, which is a purified form with subunits of poly- α -cellobiose, derived from cellulose, by acid hydrolysis of cotton or wood-pulp, has great industrial interest because of its chemical inactivity, absence of toxicity and great hygroscopicity. Cellulose is a very important and fascinating biopolymer and an almost inexhaustible and renewable raw material. Most
25 cellulosic materials consist of crystalline and amorphous domains, in varying proportions, depending on both source and history. The physical properties of cellulose, as well as its chemical behavior and reactivity, are strongly influenced by the arrangement of the cellulose molecules with respect to each other and to the fiber axis. Increased sustainability and reduced impact on the eco-system enhances its importance, also considering the widespread public
30 acceptance of such materials (S. Ardizzone et al., Microcrystalline Cellulose Powders: Structure, Surface Features and Water Sorption Capability, Cellulose, 1999, 6, 57-69; D. Ciolacu et al.,

Amorphous cellulose-structure and characterization, Cellulose Chemistry and Technology, 2011, 45, 13-21).

The use of cellulose, its microcrystalline form as well as its derivatives is far more preferable in applications such as water purification than biopolymers like chitosan, which is derived from chitin extracted from animal shells. Recently, nanocrystalline cellulose (CNC) has also been used for making adsorbents with a conjecture that since it is in the nanoform, higher surface area and porosity would be inherent, giving high adsorption capacity (Indian Patent Application No. 201641027660). In addition to the use as adsorbents, nanostructured materials are considered superior also in the field of catalysis, drug delivery, semiconductors, photovoltaics and so on. But the present work shows better arsenic removal capacities of MCC and its variations. The increased capacity of microstructured materials over nanostructured materials is unconventional and non-obvious. Apart from being sustainable and high in abundance, environmentally less intensive processing of microcellulose makes it greener and economical as compared to CNC and chitosan. Furthermore, the Indian market price of MCC as raw material (food grade) is around Rs. 100 per kg while that of chitosan is Rs. 1500 per kg and neutral CNC costs in the range of Rs. 68,000-340,000 per kg. This clearly proves that with MCC we get 15 to 3000 times cheaper raw material making it a more desirable option for scaling up to industrial level, in view of the huge cost reduction and other benefits in terms of enhanced sustainability. So, we propose the use of MCC (and its variations)-templated 2-line iron oxyhydroxide nanocomposites for the removal of arsenic from water.

The 2-line iron oxyhydroxide is prepared within the MCC (and its variations (CMC, HEC and CP) matrices separately. Microcrystalline cellulose is a purified, partially depolymerized cellulose prepared by treating alpha-cellulose, obtained as a pulp from fibrous plant material, with mineral acids. The degree of polymerization is typically less than 400. Not more than 10% of the material has a particle size of less than 5 μm . It is fine, white or almost white, odorless and free flowing crystalline powder. It is sparingly soluble in water, ethanol, ether and dilute mineral acids (49th JECFA (1997), FAO Document Repository). Reaction of the microcrystalline cellulose proceeds with particular ease and speed. Derivatives like CMC and HEC can be formed which are also colloidal. These are entirely new materials with very different properties and potential applications. At high degrees of substitution (D.S.) derivatives of microcrystalline cellulose are substantially the same material as produced from conventional cellulose. (O. A.

Battista et al., Microcrystalline Cellulose, Ind. Eng. Chem., 1962, 9, 54). 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.

A number of materials have recently been prepared 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 are increasingly playing a critical role (Savage, N., et al., 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).

A number of 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 poor 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. 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. Some popular methods involve the use of organic/inorganic binders for preparing agglomerated particles followed by sintering or spray drying or support the powder medium on a carrier composition. A number of such examples are well known in the literature and a few representative examples are: T. Pradeep et al., J. Haz. Mater., 2011, 186, 1, 921-931; V. Chandra et al., ACS Nano, 2010, 4, 7, 3979-3986; M. S. Bootharaju et al., J. Mater. Chem. A, 2013, 611-620; Annamalai Leelavathi et al., Int. J. Nanosci., 2011, 4, 5, 839-843. Some of the patent applications related to biomaterials used for water purifications are: US Patent No. 7,449,030 describes agglomeration of alumina and binder therefore; European (EP) Patent Application No. 1954634 describes water treatment composition comprising nanostructured materials and Rautaray et al. in Indian patent application 1571/MUM/2008, PCT Application No. PCT/IB2011/002740 and EP Patent Application No. 1715947.

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 MCC and its variations-templated 2-line iron oxyhydroxide in various water-related applications. More specifically, the invention uses MCC and its variations templated 2-line iron oxyhydroxide as adsorbent in water purification devices, wherein the variations of microcrystalline cellulose are CMC, HEC and CP.

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 the preparation of granular form of diverse active ingredients, by gel-phase blending of MCC and its variations-templated 2-line iron oxyhydroxide as an active ingredient, without binders.

In another embodiment, the invention shows MCC and its variations-templated 2-line iron oxyhydroxide as a novel carrier composition for various types of materials. 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.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. Optical images of native microcrystalline cellulose powder and the 2-line ferrihydrite - microcrystalline cellulose powder composite.

Figure 2. Scanning electron micrograph of native microcrystalline cellulose. Figures a and b are of different magnifications.

Figure 3. Scanning electron micrograph of MCC-templated 2-line iron oxyhydroxide nanocomposite in granular form (52 x 72 mesh). Figures a, b and c are of different magnifications.

Figure 4. X-ray diffraction pattern of the native microcrystalline cellulose as it is (before binding with iron oxyhydroxide nanoparticles), in comparison to iron oxyhydroxide-microcrystalline

cellulose composite in powder form (a) before exposing to As solution, after exposing to (b) As(III) and (c) As(V) solutions for 120 min.

Figure 5. High resolution transmission electron micrograph of (a) the MCC-templated 2-line iron oxyhydroxide nanocomposite in powder form before exposing to As solution, after exposing to (b) As(III) and (c) As(V) solutions for 120 min.

Figure 6. TEM-EDAX of (a) MCC-templated 2-line iron oxyhydroxide nanocomposite in powder form before exposing to As solution, after exposing to (b) As(III) and (c) As(V) solutions for 120 min.

Figure 7. Scanning electron micrograph of (a) MCC-templated 2-line iron oxyhydroxide nanocomposite in powder form before exposing to As solution, after exposing to (b) As(III) and (c) As(V) solutions for 120 min.

Figure 8. Elemental X-ray images (SEM-EDAX) of (a) MCC-templated 2-line iron oxyhydroxide nanocomposite in powder form before exposing to As solution, after exposing to (b) As(III) and (c) As(V) solutions for 120 min.

Figure 9. XPS survey spectrum of (a) as synthesized MCC-templated 2-line iron oxyhydroxide nanocomposite, (b) composite after adsorbing As(III) and (c) As(V). As 3d region of the spectra are expanded in the inset.

Figure 10. XPS analysis of MCC-templated 2-line iron oxyhydroxide nanocomposite 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 11. Infrared features of microcrystalline cellulose, as-synthesized MCC-templated 2-line iron oxyhydroxide nanocomposite 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 12. Residual arsenic concentration as a function of adsorbent dose (dosage study) with the four compositions 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 13. Residual arsenic concentration as a function of time (kinetic study) with the four compositions 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 varied in minutes (min) as 1, 3, 5, 10, 15, 30, 45, 60, 75, 90, 105, 120, 150 and 180).

Figure 14. Residual arsenic concentration as a function of pH (4 to 10) with the four compositions 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).

5 **Figure 15.** 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 = 25 mg, volume = 25 mL deionized water, contact time = 120 min).

Figure 16. 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 = 25 mL synthetic challenge water, each cycle contact time = 120 min).

Figure 17. Raman features of microcrystalline cellulose, as-synthesized MCC-templated 2-line iron oxyhydroxide, standards As(III) salt and standard As(V) salt, in comparison to nanocomposite after exposing to As(III) and As(V) solutions for 120 min, respectively.

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.

25 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.

30

The present invention relates to a method of preparation of granular composition of diverse active ingredients, which are usually in powder form. Use of such granular composition is further demonstrated for a number of applications. In order to prepare the granular compositions of powder active ingredients, the present invention utilized unique granulation ability of MCC and its variations (carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC) and microcellulose of industrial grade (CP)) templated 2-line iron oxyhydroxide. The strength of granular composition originates due to the inherent property of MCC and its variations templated 2-line iron oxyhydroxide. This property is especially significant for 2-line iron oxyhydroxide vis-à-vis other hydrous oxides prepared through similar route. The nanocomposite can also be prepared from other biopolymers such as chitosan, banana silk and polymeric materials.

The present invention demonstrates that matrices like (MCC and its variations)-templated 2-line iron oxyhydroxide can be an active carrier in a 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 from drinking water, with arsenic adsorption capacity far higher than for the compositions known in prior art.

The present invention relates to the preparation of granular compositions of diverse active ingredients in powder form using 2-line iron oxyhydroxide dispersed in MCC (and its variations) as templates as arsenic removal medium. In one aspect, the invention comprises of a granular composite of powder ingredient blended in 2-line iron oxyhydroxide on MCC and its variations as templates.

In other aspects, 2-line iron oxyhydroxide deposited on MCC and its variations (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 MCC and its variations (with variable moisture content from 10-90%), wherein metal is chosen among aluminium, titanium, zinc, 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)). The composition are used as gravity fed product or as in-line purifier attached to pipeline water supply and also used for

domestic, industrial, public utility and for the purpose of arsenic removal. The input water is from any source including well water, river water, ground water, etc.

In a standard synthesis, the 2-line iron oxyhydroxide-cellulose nanocrystal composite was synthesized as follows: About 0.005 g MCC and its variations was dissolved in 10 mL, sonicated for about 10 min to make it a well dispersed homogeneous solution. This was precipitated at pH 9 using 0.2 M NaOH. After 5 min of incubation, 10 mL, 1 M ferric hexachloride was added. The mixture was brought to pH 8, using 2 M sodium hydroxide by slow addition. The final composition was further incubated for about 12 h, at ambient temperature to embed the synthesized nanoparticles in network of MCC and its variations. 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 composites, namely, 2-line iron oxyhydroxide-MCC and its variations composite, were insoluble in water and appeared like dark black shining crystals. The dried composite was crushed to a powder form and used for arsenic adsorption. The yield was 80 mg. Method of preparing of microcrystalline cellulose (MCC and its variations)-templated 2-line iron oxyhydroxide is derived from preferred embodiments described in Indian Patent Application No. 1529/CHE/2010 and Indian Patent Application No. 486/CHE/2013. The organic polymer acts as a template, controls the size of particles of FeOOH formed and gives mechanical strength to the composite after drying at room temperature. The as-synthesized adsorbent composite was tested for arsenic (in the form of sodium arsenate or sodium arsenite) removal from water.

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. BET surface areas of samples were recorded by Micromeritics-ASAP-2020-Surface-Area-and-Porosity-Analyzer-Software-V3.00H.

All the uptake capacity studies were done in a batch mode (in 250 mL polypropylene conical flasks). The working volumes of the solutions were taken as 25 mL or 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.

The invention may be further described by the accompanied figures.

Figure 1 (a and b) shows the optical image of the native MCC powder and of the MCC-templated 2-line iron oxyhydroxide, respectively on watch glass.

Figure 2 (a, b and c) shows SEM image of the native MCC at various magnifications. The fibre/rod like porous structures of MCC are visible at various magnifications.

Figure 3 shows SEM image of the MCC-templated 2-line iron oxyhydroxide nanocomposite in the granular form (52 x 72 mesh) at various magnification (a, b and c). The composite exhibits good mechanical strength and does not degrade in water.

Figure 4 shows the X-ray diffraction pattern of MCC (as it is), MCC-templated 2-line iron oxyhydroxide nanocomposite along with the composite after adsorbing As(III) and As(V), respectively. In case of MCC, presence of sharp features proves its crystalline nature, whereas as-synthesized composite, composite after adsorbing As(III), and composite after adsorbing As(V) are amorphous in nature, proven by broadened peak shapes. 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 MCC-templated 2-line iron oxyhydroxide nanocomposite, it is highly amorphous (X-ray crystallographic data shown in Figure 4). Here, the role of MCC is very crucial in improving the strength of 2-line iron oxyhydroxide-MCC composite by binding with 2-line iron oxyhydroxide nanoparticles.

Figure 5 (a, b and c) shows TEM images of the MCC-templated 2-line iron oxyhydroxide nanocomposite at 100 nm scale. 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 MCC matrix. The metal oxyhydroxide nanoparticles are homogeneously sized. The rod-like of MCC structure is not seen clearly due to the complete embedding of 2-line iron oxyhydroxide nanoparticles. Outside the MCC structure, no nanoparticles were present. This again confirms the composite formation, wherein 2-line iron oxyhydroxide nanoparticles are formed only inside the MCC nanoarchitecture. As small and uniform sized particles are obtained, some benefits can be assured like the nanoparticles never leach out of the architecture, thereby ensuring their safe use in water purification. Even when high contaminant concentration is loaded on the surface, nanoparticles do not undergo aggregation.

Figure 6 shows TEM-EDAX spectrum and elemental maps of MCC-templated 2-line iron oxyhydroxide nanocomposite 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, 150 mg of adsorbent was shaken with 200 ppm, 100 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 8.58%, whereas in case of As(V) adsorbed composition, it is around 3.01%. This affirms that performance of the composition is better for As(III) removal at higher concentrations and for As(V) at lower concentrations.

Figure 7 shows SEM image of the MCC-templated 2-line iron oxyhydroxide nanocomposite in the powder form (Figure 7a), composite after adsorbing As(III) (Figure 7b), and composite after adsorbing As(V) (Figure 7c). 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 8 shows SEM-EDAX spectrum and elemental maps of MCC-templated 2-line iron oxyhydroxide nanocomposite in powder form (Figure 8a) along with arsenic (As(III) and As(V)) adsorbed composition (Figure 8b and Figure 8c). For the purpose of this study, 150 mg of

adsorbent was shaken with 200 ppm, 100 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 5.31% whereas, in case of As(V) adsorbed composition, it is around 1.42%. This reaffirms 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 9 illustrates the XPS spectra of as-synthesized MCC-templated 2-line iron oxyhydroxide nanocomposite and arsenic adsorbed composition. Here, elements of our interest are compared and the deconvoluted spectra are shown in Figure 10 (a, b, c and d). The Fe 2p region of as-synthesized composition in powder form and arsenic adsorbed composition are shown in Figure 10a. Other than the main peaks, presence of multiple peaks in the Fe 2p region is because of its surface and satellite peaks. Although we did not find any kind of change for Fe(III) characteristic peaks, changes were seen in other elements. To understand the underlying phenomenon, we compared the adsorbed As(III) and As(V) materials with the corresponding standard As(III) and As(V) salts (Figure 10b). For standard As(III), As 3d region peak comes at 43.9 eV whereas standard As(V) shows peak at 44.5 eV. But we can see significant change in the peak position for both As(III) and As(V) in the adsorbed state. For As(III), As 3d peak was noted at 44.5 eV whereas As(V) gave a peak at 45.7 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). The peak observed at 284.8 eV is close to the characteristic peak position for aliphatic carbon from the microcrystalline cellulose shown in Figure 10c. The peak at 529.1 eV is close to the characteristic peak position for bulk oxygen (O^{2-}) (Figure 10d). The peak appears at 531.3 eV mostly because of surface hydroxyl groups which are attached to Fe. After As(III) and As(V), the corresponding peak shifts to 531.9 eV in both the cases. The contribution due to surface hydroxyl peaks (at 530.2 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.

Figure 11 shows the Fourier transform infrared (FTIR) spectrum of MCC (as it is), MCC-templated 2-line iron oxyhydroxide nanocomposite along with the As(III) and As(V) standards

as well as composite after adsorbing As(III) and As(V) as (i), (ii), (iii), (v), (iv) and (vi) respectively. Infrared spectroscopic investigation shows that the distinct MCC features at 3419 cm^{-1} due to -OH stretching, 2916 cm^{-1} due to C-H asymmetric stretching and tensile vibration in the pyranoid ring, 1384 cm^{-1} due to -OH bending and 1053 cm^{-1} corresponding to asymmetric C-O-C vibration (Ciolacu, D.; Ciolacu, F.; Popa, V. I. Amorphous cellulose-structure and characterization, Cellulose Chemistry and Technology, 2011, 45, 13-21) are shifted to 3430, 2920, 1387 and 1058 cm^{-1} , respectively indicating strong interaction with ferrihydrite particles. NaAsO₂ shows As-O stretching peaks at 785 and 1122 cm^{-1} (V, E. S. P. B.; Bencivenni, L.; Gingerich, K. A. Journal of Molecular Structure, 1983, 99, 23-29) which are red shifted to 790 and 1211 cm^{-1} after adsorption. Similarly, Na₂HAsO₄ shows peaks at 814 and 1109 cm^{-1} due to As-O stretching, which is also redshifted to 825 and 1163 cm^{-1} after interaction with the composite.

Figure 12 (a and b) represents the comparative performance of arsenic adsorbent compositions (with MCC, CMC, HEC and CP) as reported here for As(III) and As(V), separately. It is clearly observed that MCC-templated 2-line iron oxyhydroxide nanocomposite exhibits superior performance. 1 ± 0.1 ppm arsenic in synthetic challenge water was treated with different dosage of adsorbent ranging from 5 mg to 150 mg in 100 mL of challenge water.

Figure 13 (a and b) represents the comparative performance of arsenic adsorbent compositions (with MCC, CMC, HEC and CP) as reported here for As(III) and As(V), separately. 1 ± 0.1 ppm arsenic in synthetic challenge water was treated with 25 mg of adsorbent composition in 25 mL of synthetic challenge water to observe the adsorption kinetics and the study showed 10 ppb and 2.5 ppb of As(III) and As(V), respectively, just after 15 min of contact time.

Figure 14 (a and b) represents the comparative performance of arsenic adsorbent compositions (with MCC, CMC, HEC and CP) as reported here for As(III) and As(V), separately. 1 ± 0.1 ppm arsenic in synthetic challenge water was treated with 25 mg of adsorbent composition in 25 mL of synthetic challenge water to observe the performance in a wide range of $\text{pH} = 4$ to 10. It was observed that the adsorption performance of all the compositions remained unaffected by the pH environment.

Figure 15 (a, b, c, d, e, f, g, h) shows that arsenic adsorption isotherms of as-synthesized 2-line iron oxyhydroxide composites (with MCC, CMC, HEC and CP) were carried out in de-

ionized water. Langmuir isotherm was plotted for arsenic adsorption using the following linear equation:

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

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 25 mg per 25 mL adsorbent dose while varying initial arsenic concentration from 1 to 200 mg/L.

According to Langmuir isotherm equation, the maximum adsorption capacity obtained for the various cellulose templated 2-line iron oxyhydroxide composites are as follows:

- MCC-templated nanocomposite showed 143 mg/g for As(III) and 53 mg/g for As(V) giving 98 mg/g as average arsenic uptake.
- HEC-templated nanocomposite showed 143 mg/g for As(III) and 40 mg/g for As(V) giving 91 mg/g as average arsenic uptake.
- CMC-templated nanocomposite showed 143 mg/g for As(III) and 83 mg/g for As(V) giving 113 mg/g as average arsenic uptake.
- CP-templated nanocomposite showed 125 mg/g for As(III) and 59 mg/g for As(V) giving 92 mg/g as average arsenic uptake.

The concentration of arsenic in the effluent water, measured by inductively coupled plasma mass spectrometry (ICP-MS), was consistently below 10 ± 1 ppb, adhering to the World Health Organization (WHO) norms (Figure 8). This demonstrates that the active ingredient loaded in the 2-line iron oxyhydroxide-microcrystalline cellulose (and its variations) matrix is amply accessible by water, thereby ensuring that the composition can be utilized as an effective water purification composition.

Figure 17 shows the Raman spectrum of MCC-templated 2-line iron oxyhydroxide nanocomposite, As(III) and As(V) standards along with composite after adsorbing As(III) and As(V), respectively. Raman spectroscopic investigation shows that the distinct iron oxyhydroxide blended with MCC features in the region of 200 to 600 cm^{-1} . While the characteristic Raman peak of NaAsO_2 comes at 846 cm^{-1} and that of Na_2HAsO_4 comes at 837 cm^{-1} .

¹ and 876 cm⁻¹, the peak positions of adsorbed As(III) and As(V) on the composite were observed to be shifted to 816 cm⁻¹ and 842 cm⁻¹, respectively.

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 of As(III) and As(V) adsorption even when used with synthetic challenge water containing interfering ions like calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺), sodium (Na⁺), chloride (Cl⁻), carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), nitrate (NO₃⁻), silicate (SiO₃²⁻), sulfate (SO₄²⁻) and fluoride (F⁻).

The counter effect of above mentioned ions were tested separately for As(III) and As(V) adsorption (initial adsorbent dose = 25 mg, initial concentration = 1±0.1 ppm, volume = 25 mL synthetic challenge water, contact time = 120 min) at pH = 7 are present in Table 1 and Table 2, respectively.

Table 1

Sl. No.	Counter ions	Ion Input (ppm)	Input As(III) (ppb)	Output As(III) (ppb)
1.	Ca ²⁺	30	1000	22
2.	Mg ²⁺	15	1000	14
3.	K ⁺	5	1000	6
4.	Na ⁺	55	1000	7
5.	Cl ⁻	90	1000	8
6.	CO ₃ ²⁻	100	1000	12
7.	HCO ₃ ⁻	100	1000	16
8.	NO ₃ ⁻	2	1000	24
9.	SiO ₃ ²⁻	20	1000	44
10.	SO ₄ ²⁻	35	1000	35
11.	F ⁻	2	1000	21

Table 2

Sl. No.	Counter ions	Ion Input (ppm)	Input As(V) (ppb)	Output As(V) (ppb)
1.	Ca ²⁺	30	1000	0.7
2.	Mg ²⁺	15	1000	0.4
3.	K ⁺	5	1000	0.2
4.	Na ⁺	55	1000	0.3
5.	Cl ⁻	90	1000	0.2
6.	CO ₃ ²⁻	100	1000	20
7.	HCO ₃ ⁻	100	1000	14
8.	NO ₃ ⁻	2	1000	0.3
9.	SiO ₃ ²⁻	20	1000	11
10.	SO ₄ ²⁻	35	1000	0.5
11.	F ⁻	2	1000	0.5

The surface area of the native MCC powder and MCC-templated 2-line iron oxyhydroxide nanocomposite was determined using BET isotherm by N₂ adsorption at low temperature. The specific surface area of native MCC was 2.44 m² g⁻¹ (Ardizzone, S.; Dioguardi, F. S.; Mussini, T.; Mussini, P. R. Microcrystalline Cellulose Powders: Structure, Surface Features and Water Sorption Capability, Cellulose, 1999, 6, 57–69) while that of the composite was found to be 173.31 m² g⁻¹ with average pore size of 15.51 Å. This huge increase in surface area is attributed to nanoscale iron oxyhydroxide particles getting confined in the cellulose matrix and this high surface area is also responsible for superior arsenic removal performance by adsorption.

Uptake performance by native MCC powder was also observed for As(III) and As(V) to prove that 2-line iron oxyhydroxide plays major role in binding with arsenite and arsenate ions

and not the hydroxyl groups of cellulose species. It was found that for 1000 ppb input concentration of arsenite and arsenate given to 100 mL tap water, after a contact time of 2 h, the treated water had 818 ppb and 829 ppb of As(III) and As(V) leftover, respectively.

5 The total organic carbon (TOC) release from the components used in synthesizing the composites before and after arsenic uptake was observed and presented in Table 3. The acceptable United States Environmental Protection Agency (USEPA) limit for TOC in drinking water is 4 ppm.

Table 3

Sample ID	TOC (mg/L)
CMC before As adsorption	1.05
CMC after As(III) adsorption	0.50
CMC after As(V) adsorption	0.12
MCC before As adsorption	0.68
MCC after As(III) adsorption	0.26
MCC after As(V) adsorption	0.19
MCC raw material (as it is)	0.67
HEC before As adsorption	1.16
HEC after As(III) adsorption	1.27
HEC after As(V) adsorption	0.66
CP before As adsorption	1.56
CP after As(III) adsorption	0.36
CP after As(V) adsorption	3.09

10

The toxicity characteristic leaching protocol (TCLP) test has been conducted for the MCC-templated 2-line iron oxyhydroxide nanocomposite as per USEPA standard

protocol and the leaching was observed as 2.2 mg/L and 77 µg/L for arsenic and iron, respectively.

The physicochemical characteristics of influent natural water, all parameters are expressed in mg/L, except for pH and conductivity is given in table 4. ND – not detected.

Table 4

Parameters	Value
Total coliforms (CFU/mL)	1-2 x 10 ³
pH @ 25 °C	7.8
Conductivity (µS/cm)	640.0
Fluoride	0.57
Chloride	86.34
Nitrate	1.84
Sulfate	32.41
Silicate	15.87
Lithium	ND
Sodium	53.74
Ammonium	ND
Potassium	2.33
Magnesium	14.34
Calcium	28.72

EXAMPLE 1**MICROCRYSTALLINE CELLULOSE (MCC AND ITS VARIATIONS) TEMPLATED 2-LINE IRON OXYHYDROXIDE NANOCOMPOSITE SYNTHESIS AT AMBIENT REACTION CONDITIONS:**

5 The Fe(III) precursor solution such as ferric chloride (or the other ferric salts) was mixed with microcrystalline cellulose (and its variations) dispersed in water. The mixture was then stirred. Aqueous NaOH solution was added slowly into the metal-cellulose solution by vigorous stirring to facilitate the precipitation of the metal-cellulose composites. All these steps were carried out at a temperature of about 25 ± 2 °C. Vigorous stirring was continued for 12 h. The
10 precipitate was filtered, washed to remove unreacted reagents and excess base, and dried at ambient conditions.

EXAMPLE 2**INCORPORATION OF VARIOUS METAL OXIDE/HYDROXIDE/OXYHYDROXIDE-
15 MICROCRYSTALLINE CELLULOSE NANOCOMPOSITES WITHIN
MICROCRYSTALLINE CELLULOSE (MCC AND ITS VARIATIONS) TEMPLATED
2-LINE IRON OXYHYDROXIDE:**

Precipitated MCC-templated 2-line iron oxyhydroxide nanocomposite as in Example 1 was washed and filtered. Moisture content in the precipitate formed may vary from 50-90%.
20 Subsequently, it was mixed with desired metal oxide/hydroxide/oxyhydroxide-microcrystalline cellulose nanocomposite 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, iron, aluminum, zirconium, lanthanum, cerium or silicon. The mixture was prepared in an appropriate ratio, for example, with a dominant weight percentage for 2-line iron
25 oxyhydroxide-microcrystalline cellulose nanocomposite (wt/wt). Thereafter, the precipitate was dried at ambient conditions.

EXAMPLE 3**INCORPORATION OF NANOPARTICLES WITHIN MICROCRYSTALLINE
30 CELLULOSE (MCC AND ITS VARIATIONS) TEMPLATED 2-LINE IRON
OXYHYDROXIDE NANOCOMPOSITE:**

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

It may be noted that the desired metal oxide/hydroxide/oxyhydroxide-microcrystalline cellulose templated nanocomposite can be loaded either in precipitated form or in dried powder form.

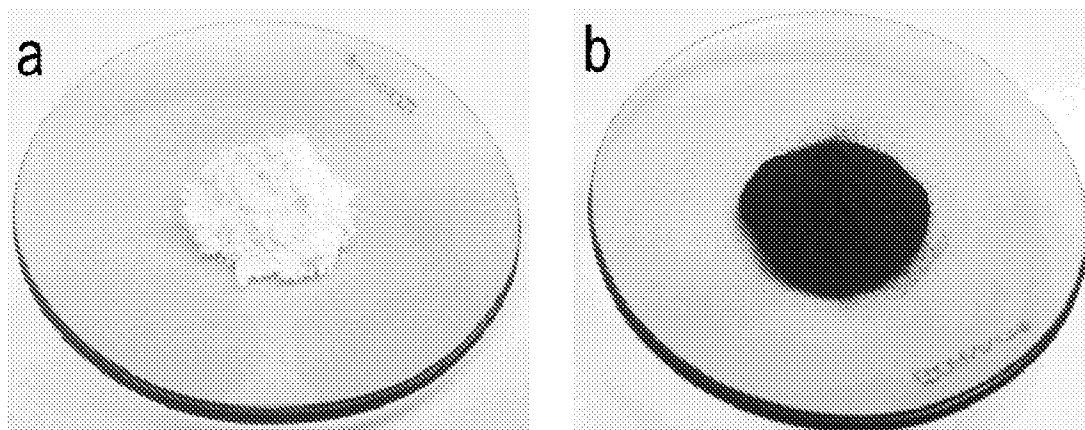
It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification 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.

We Claim:

1. A method of preparing microcrystalline cellulose (MCC and its variations) templated 2-line iron oxyhydroxide nanocomposites for the removal As(III) and As(V) from drinking water with capacity greater than 98 mg/g, prepared through the steps composed of
 - a. solubilizing microcellulose in water, after 10 min of sonication,
 - b. precipitating cellulose at pH = 9 using NaOH,
 - c. incubating cellulose with Fe(III) salt while stirring at pH < 2,
 - d. precipitating the iron-cellulose mixture at pH 8, followed by a continuous stirring of 12 h under ambient conditions (28-30 °C),
 - e. filtering and washing the gel formed with water until a clear filtrate was obtained,
 - f. drying the washed gel flakes and drying them at 65 °C for 12 h to get small chunks of composites, to be powdered before using for adsorption purpose.
2. The method as claimed in claim 1, wherein the cellulose microcrystals reinforce with oxyhydroxide nanostructure for removal of arsenic from drinking water, such that the filtered water has an arsenic concentration below 10 ppb.
3. The method as claimed in claim 1, wherein the nanocomposite is prepared with microcrystalline cellulose derivatives including carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC) and microcellulose of industrial grade (CP).
4. The method as claimed in claim 1, wherein nanocomposites are incubated under ambient conditions in the temperature range of 28-30 °C.
5. The method as claimed in claim 1, wherein the removal of arsenic takes place in a pH range of 4 to 10.
6. The method as claimed in claim 1, wherein the obtained nanocomposites are in granular forms.
7. The method as claimed in claim 1, wherein the nanocomposites is prepared with at least one metal oxyhydroxide, where metal is selected from the group of aluminium, titanium, zinc, iron, zirconium, lanthanum, cerium, silicon or a combination thereof.
8. The method as claimed in claim 1, wherein the nanocomposites is prepared with at least one biopolymer selected from the group of chitosan, banana silk and any polymeric materials.

9. The method as claimed in claim 1, wherein microcrystalline cellulose and its derivatives have hydroxyl groups and each microcellulose chain is of dimensions in the range of 10-60 μm .
10. The method as claimed in claim 1, wherein the ferric precursor is at least one selected from the group comprising Fe(II) or Fe(III) salts including chloride, sulphate or nitrate.
11. The method as claimed in claim 1, wherein the nanocomposites are used as gravity fed product or as in-line purifier attached to pipeline water supply.
12. The method as claimed in claim 1, wherein the input water is from any source including well water, river water, ground water.
13. The method as claimed in claim 1, wherein the material is used for domestic, industrial, public utility and for the purpose of arsenic removal.

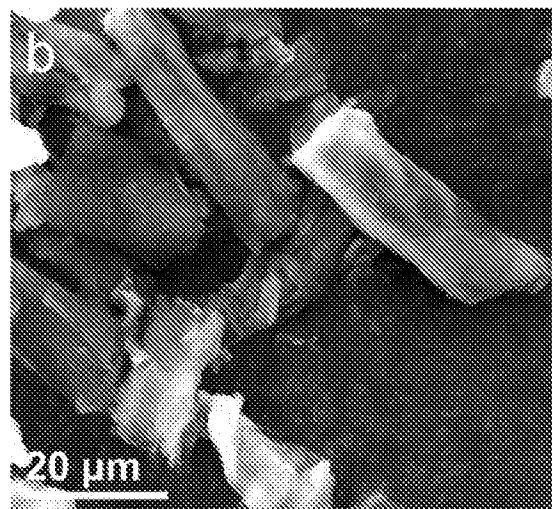
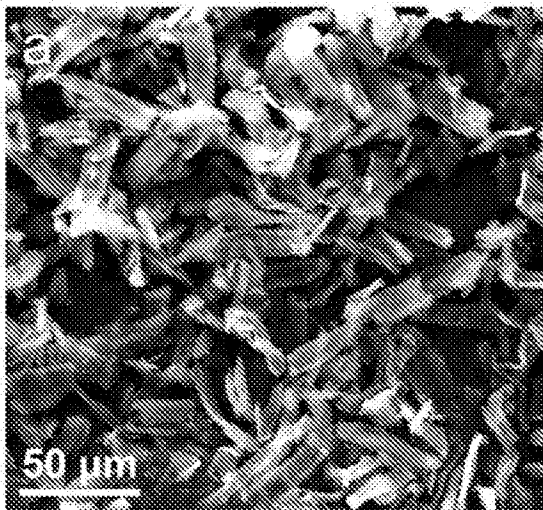
1/17

**Figure 1**

2/17

5

10



15

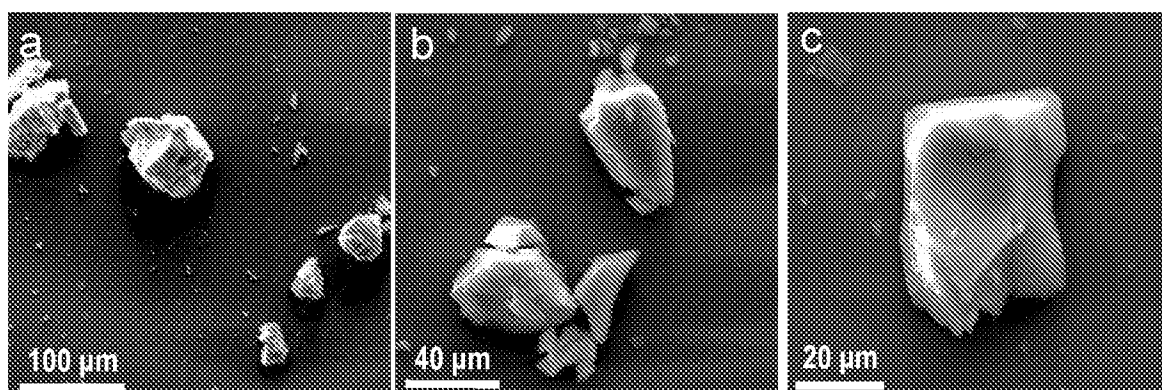
Figure 2

20

25

30

3/17

**Figure 3**

4/17

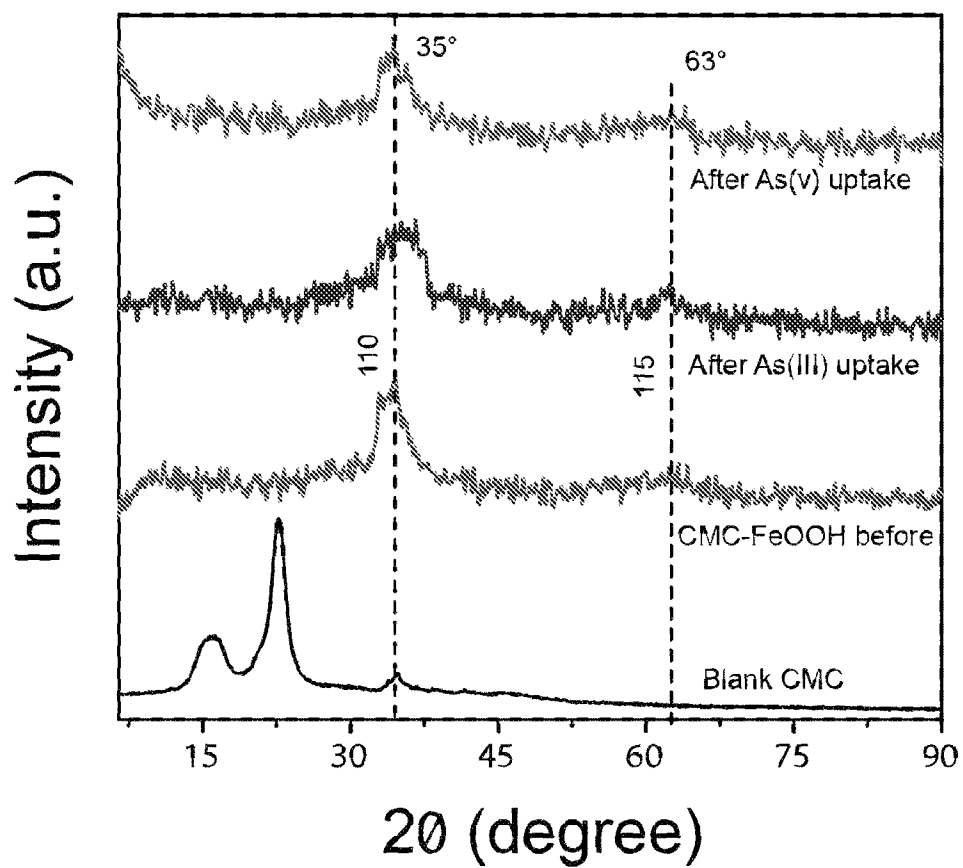
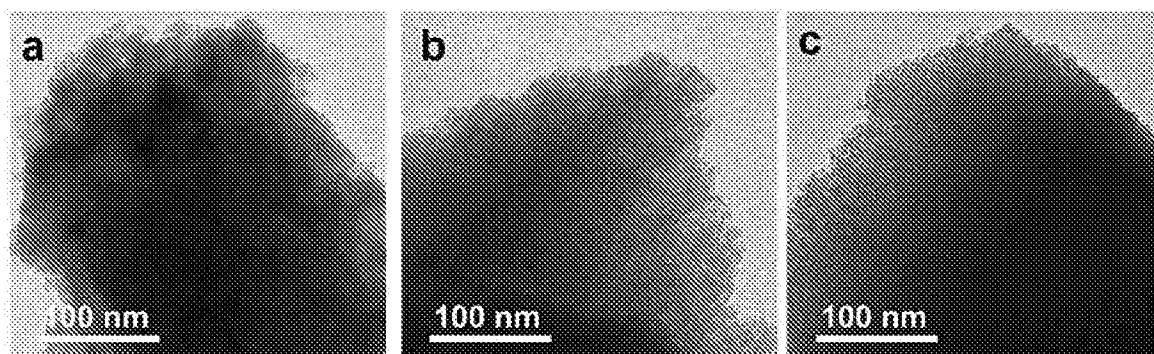


Figure 4

5/17

5

10



15

Figure 5

20

25

30

35

6/17

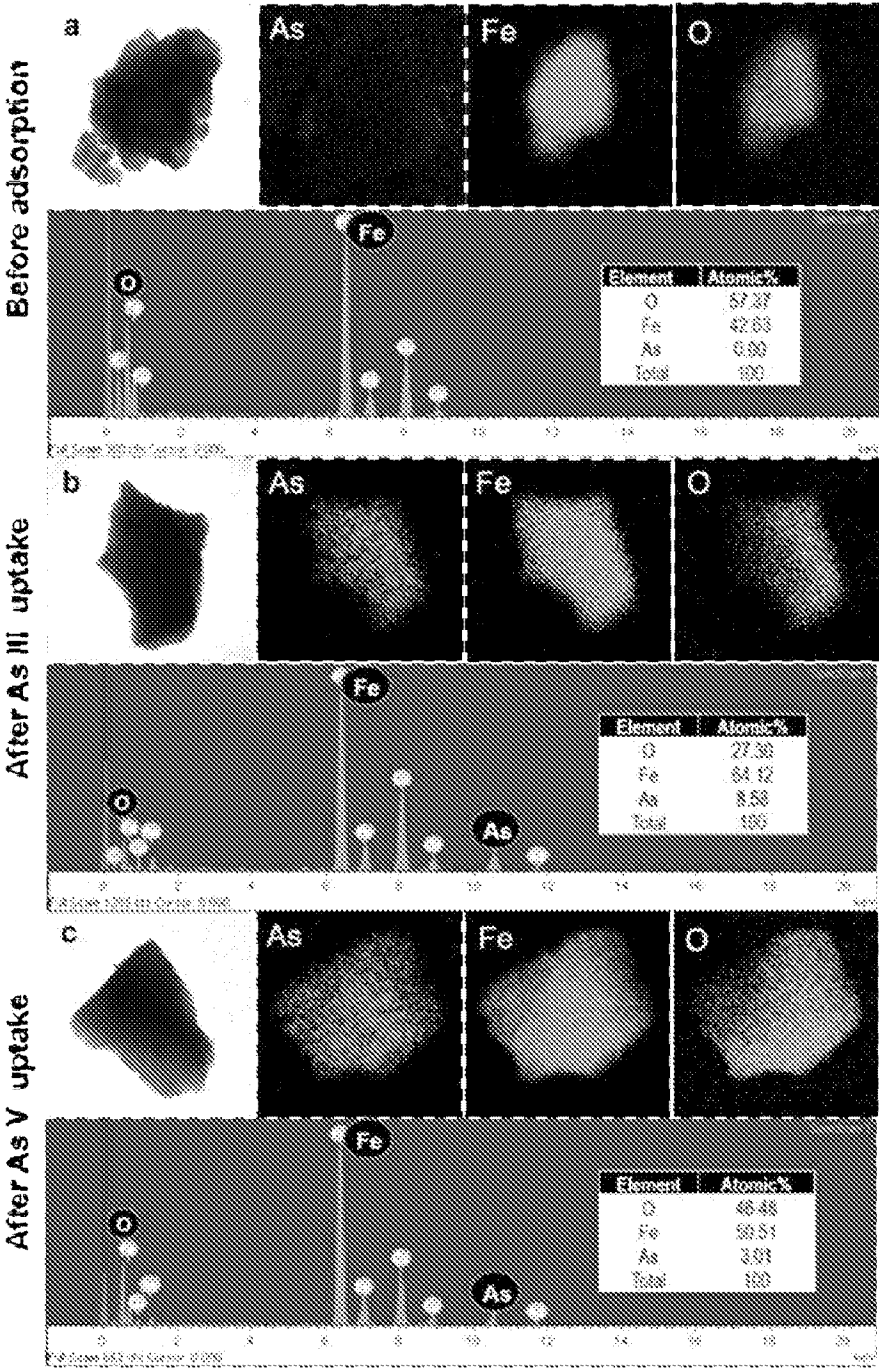
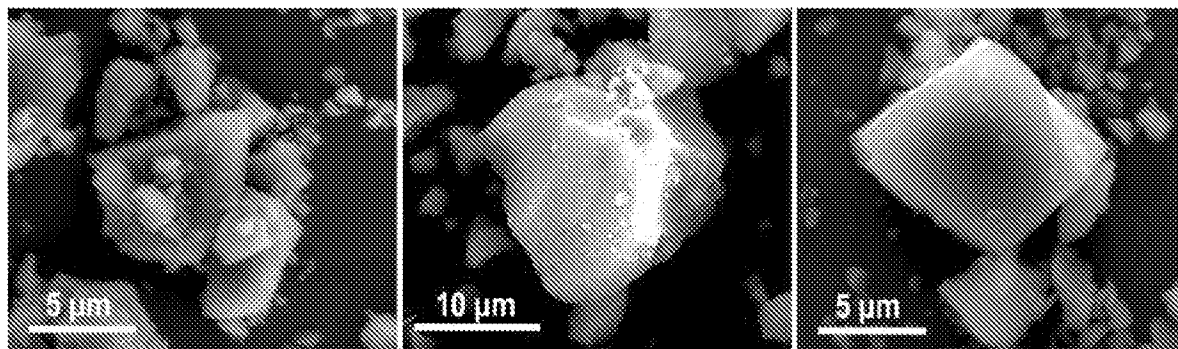


Figure 6

7/17

5



10

Figure 7

15

20

25

30

35

8/17

5

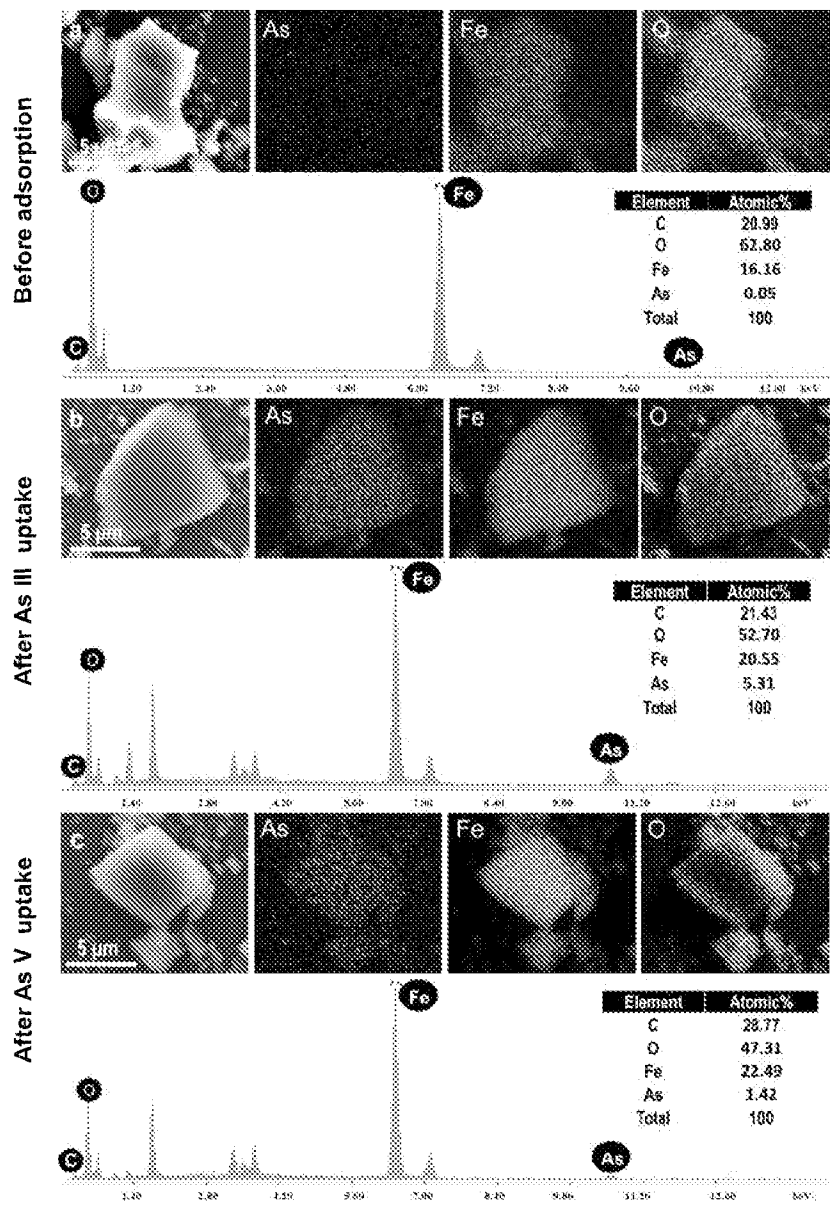


Figure 8

10

9/17

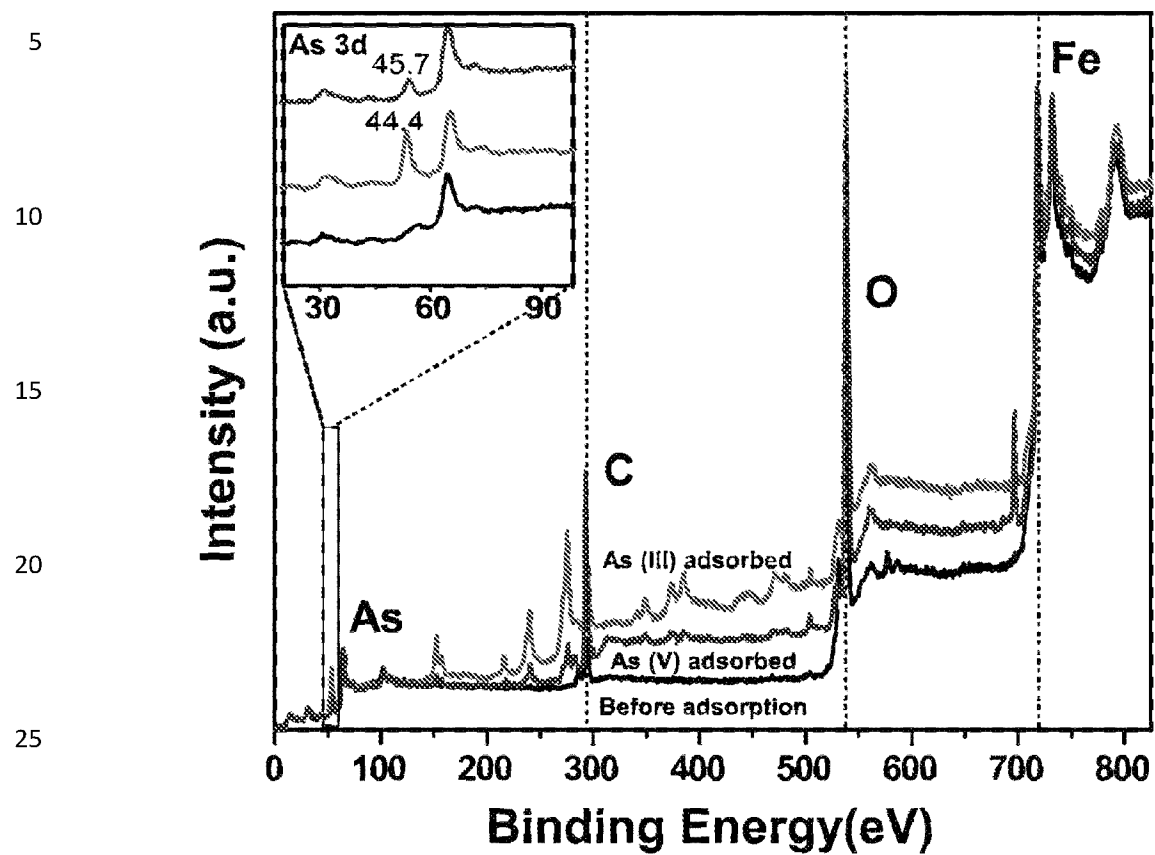


Figure 9

10/17

5

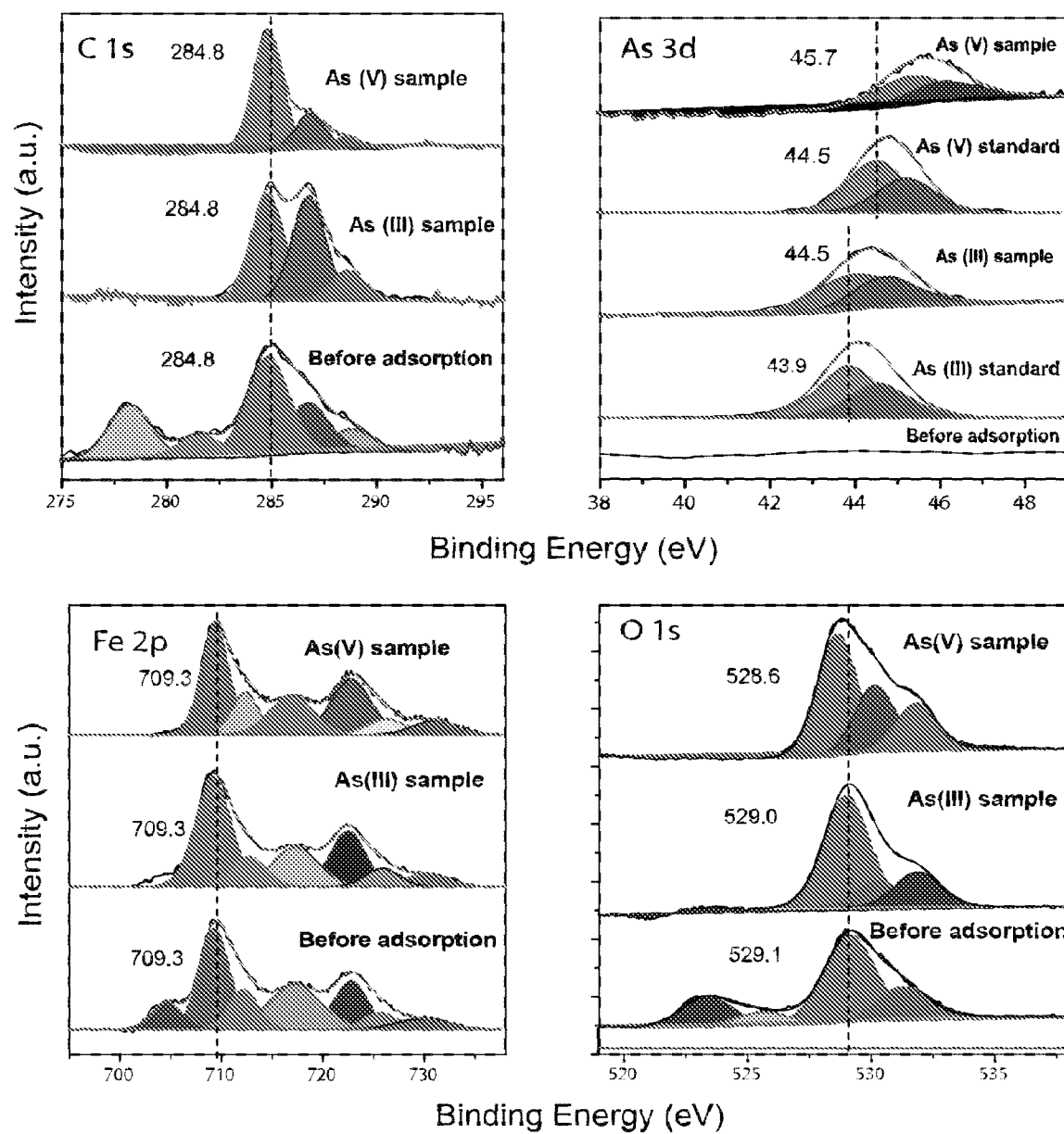


Figure 10

10

11/17

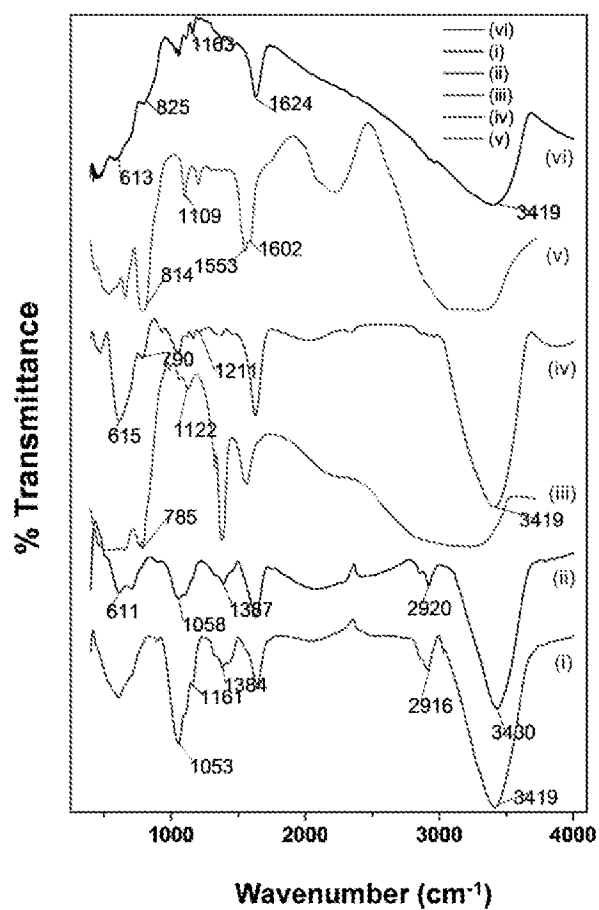
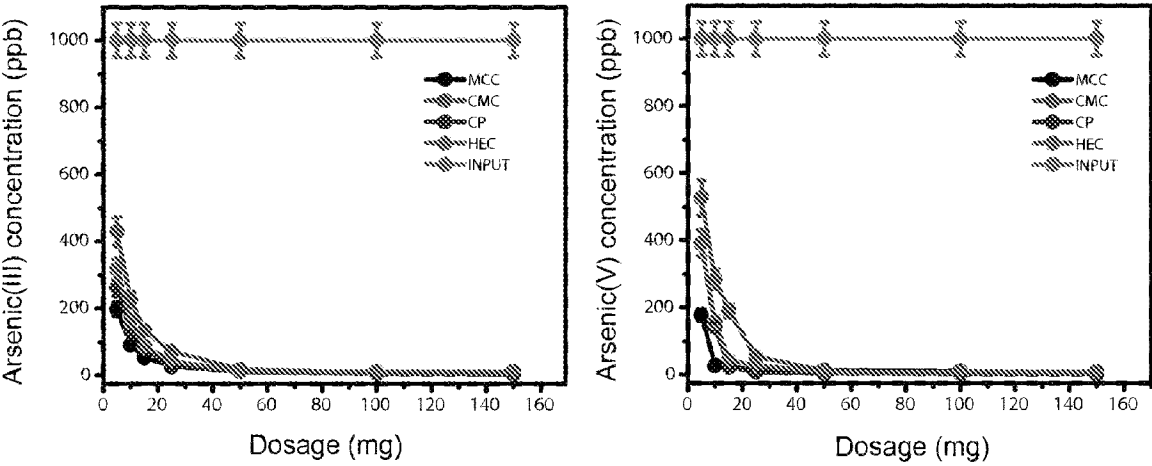


Figure 11

12/17

5



10

Figure 12

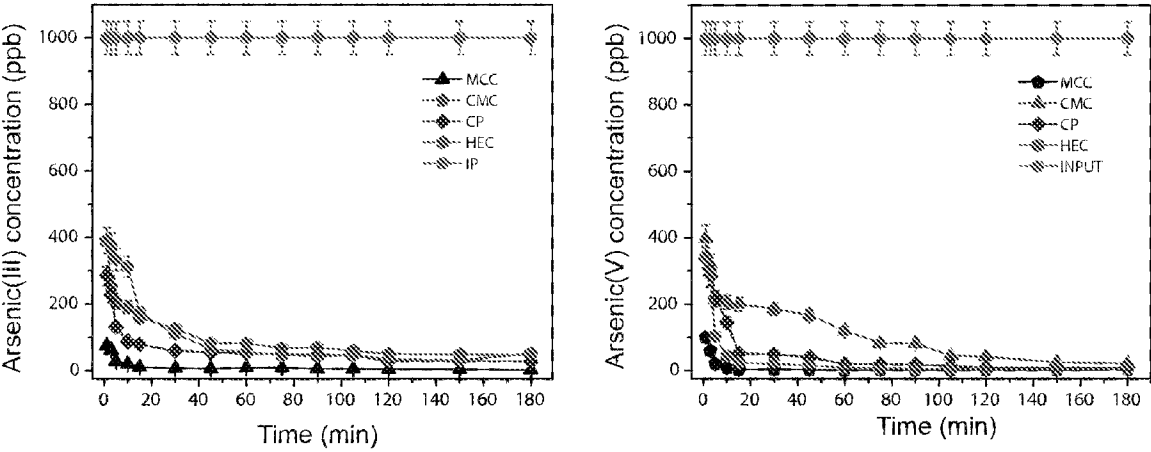
15

20

25

30

5



10

15

Figure 13

20

25

30

14/17

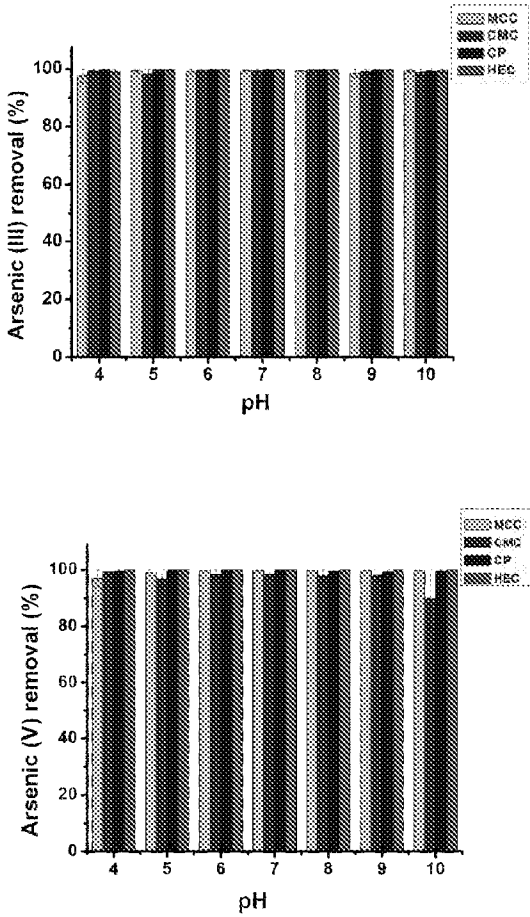


Figure 14

15/17

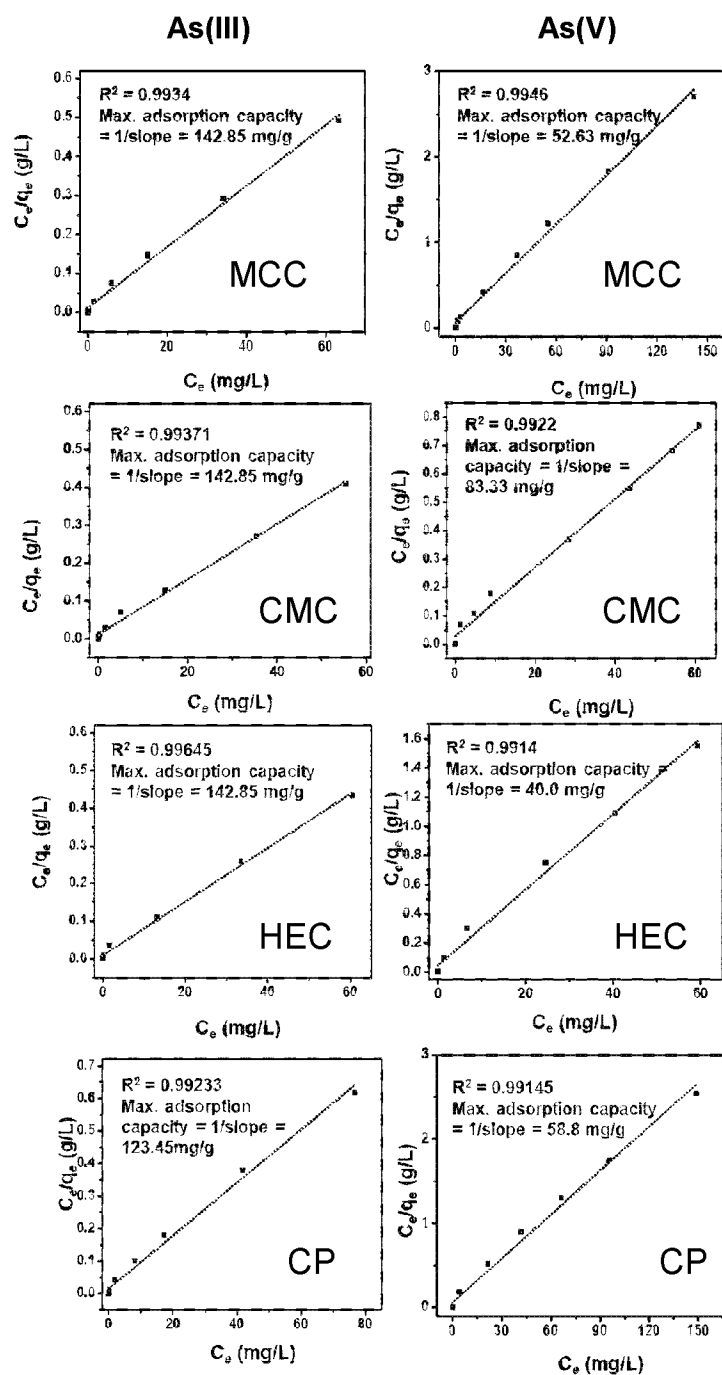


Figure 15

16/17

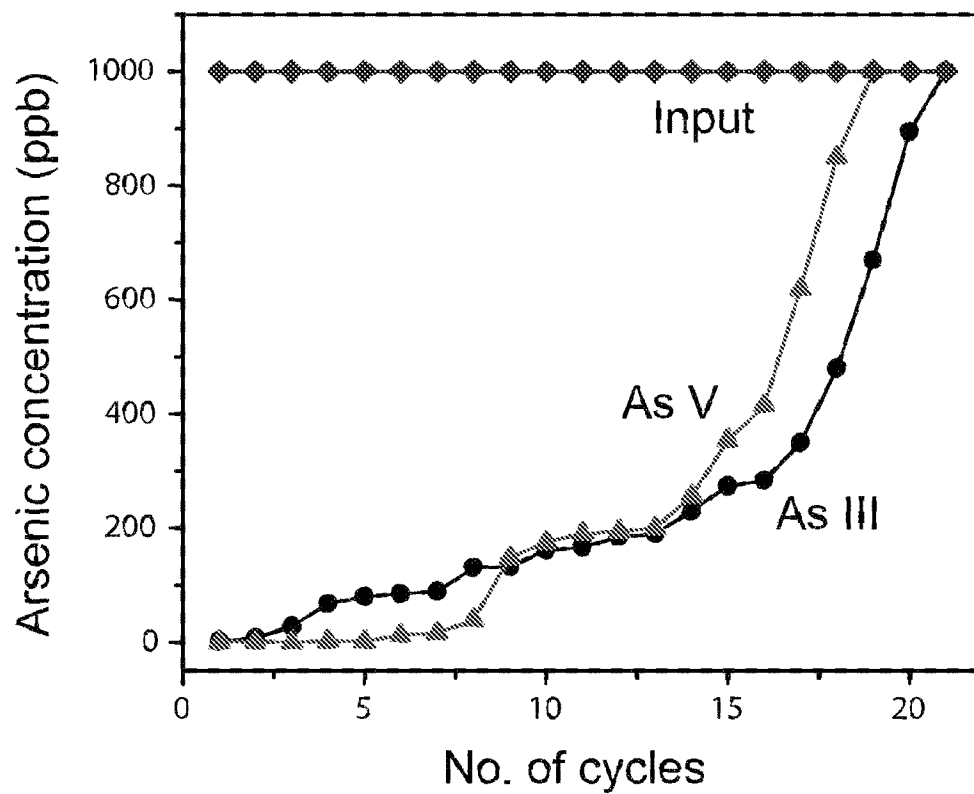
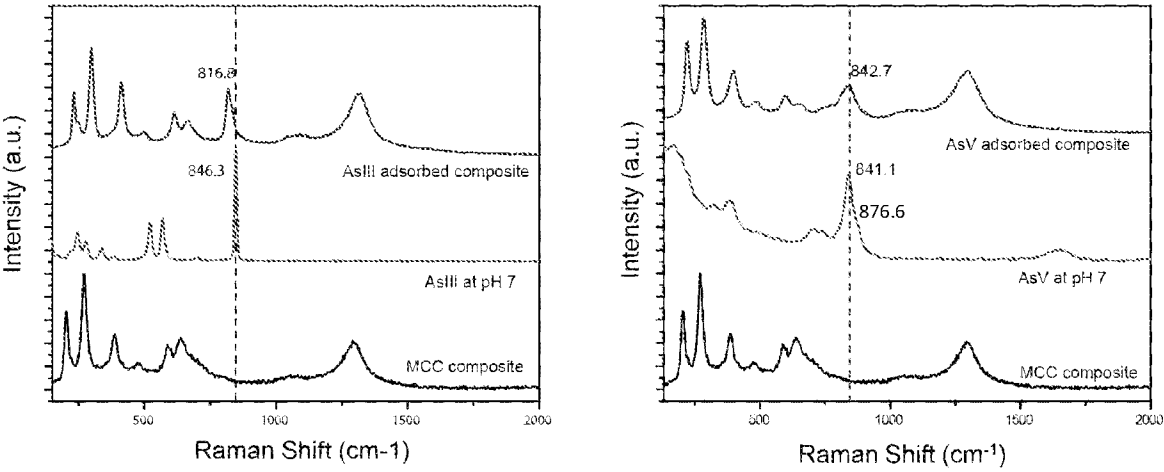


Figure 16

17/17

5



10

Figure 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2017/050627

A. CLASSIFICATION OF SUBJECT MATTER
B01J20/00,C02F1/00 Version=2018.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J, C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Patseer, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	IN 201641027660 A (INDIAN INSTITUTE OF TECHNOLOGY MADRAS) 26-08-2016 Claims 1-15; Abstract; Drawings 1-15; Examples 1-3 -----	1-13
Y	JP 2013133582 A (KAO CORP.) 08-07-2013 Claims 1-10; Abstract; Description Page 2, Comparative Example 1 -----	1-13
Y	WO 2011/151725 A2 (INDIAN INSTITUTE OF TECHNOLOGY MADRAS) 08-12-2011 Claims 1-52; Abstract; Examples 1-5	1-13

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search

10-04-2018

Date of mailing of the international search report

10-04-2018

Name and mailing address of the ISA/

Indian Patent Office
Plot No.32, Sector 14,Dwarka,New Delhi-110075
Facsimile No.

Authorized officer

Koushik Pal

Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2017/050627

Citation	Pub.Date	Family	Pub.Date
WO 2011/151725 A2	08-12-2011	US 2013168320 A1	04-07-2013
		JP 2013527118 A	27-06-2013
		CN 103179861 A	26-06-2013
		IN 1529CHE2010 A	07-08-2015