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PATENT CERTIFICATE
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पेटेंट सं. / Patent No. : 300346
आवेदन सं. / Application No. : 2433/CHE/2010
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पेटेंटी / Patentee : INDIAN INSTITUTE OF TECHNOLOGY

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित A METHOD OF PREPARING SELF-ASSEMBLED MANGANESE-ZINC OXIDE NANOSHEET GRANULAR COMPOSITE FOR PATHOGENS AND HEAVY METALS FREE WATER नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 23rd day of August 2010 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 A METHOD OF PREPARING SELF-ASSEMBLED MANGANESE-ZINC OXIDE NANOSHEET GRANULAR COMPOSITE FOR PATHOGENS AND HEAVY METALS FREE WATER as disclosed in the above mentioned application for the term of 20 years from the 23rd day of August 2010 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 28/08/2018
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

OKSupta

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 23rd day of August 2012 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 23rd day of August 2012 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:

**A SINGLE COMPONENT METHOD AND A DEVICE FOR PATHOGENS AND
HEAVY METALS FREE WATER**

2. APPLICANT:

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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

A SINGLE COMPONENT METHOD AND A DEVICE FOR PATHOGENS AND HEAVY METALS FREE WATER

FIELD OF INVENTION:

This invention relates to the preparation of Mn-Zn composite metal oxide formed by the assembly of MnZnO nanosheets of thickness <15 nm and its application for water treatment. More specifically, the novel composition is used for the removal of bacteria, viruses and heavy metals such as mercury and arsenic from contaminated water. The as-prepared material was also supported on various matrices such as chitosan, cellulose, carbon, rice husk and alumina. Application of the material as a filter medium in removing bacteria, virus, mercury and arsenic from water has been demonstrated.

PRIOR ART:

Water is one of the vital natural resources for sustaining all forms of life on Earth. Though more than two-thirds of the Earth's surface is covered with water, the decline in fresh water quality and quantity has become a common problem in many countries due to various reasons, including urbanization, industrialization and unscientific use of the available resources. Water contamination, be it biological or chemical has emerged as one of the serious pollution problems worldwide and contributes to major proportion of the public health problems. The presence of biological contaminants like bacteria, viruses and protozoa in water are the primary cause of diarrhea, dysentery, gastroenteritis, typhoid, cholera, jaundice, polio and other water-borne diseases.

In 2006, waterborne diseases were estimated to cause 1.8 million deaths each year while about 1.1 billion people lacked access to clean drinking water. The death due to water borne diseases is 3.1% of all deaths and 3.7% of all DALY's (disability adjusted life years). A vast majority of diarrheal disease in the world (88%) is attributable to unsafe water, sanitation and hygiene (World Health Report 2002, reducing risks, promoting healthy life, World Health Organization, Geneva (Chapter 4)). Apart from these biological contaminants, a number of other contaminants have been found in groundwater and surface water across the world. This includes pesticides, fluoride, nitrate, sulfate, phosphate and heavy metals such as arsenic, lead, mercury, chromium. In many places, concentrations of these pollutants are much above the drinking water standards and often water is not suitable even for irrigation and industrial activities. Considering the

widespread occurrence and associated health effects of various biological and chemical contaminants in drinking water, it is important to remove these contaminants from water before consumption in order to control the health hazards due to waterborne diseases.

The current practices for removing water contaminants include boiling, membrane processes, ion-exchange, sorption, chemical oxidation, and UV treatment. Adsorption onto a solid surface is a preferred choice for many end users because of its simplicity, ease of operation and lower cost. However, selection of the right material and its composition is most important for the effective removal of the contaminants from water. Chemical such as chlorine (and other members of halogen family) is a highly efficient disinfectant to kill disease-causing bacteria but it reacts with organic compounds to form toxins called halogenated organics (e.g., trihalomethanes), some of which are highly toxic and have been linked to a wide range of human health maladies. The addition of some chemicals may impart unpleasant taste and odor to water. In addition to these secondary problems, chemical agents like chlorine are also reported to be not suitable for removing some protozoa and viruses. Apart from the functional drawbacks, introducing a chemical addition step increases the complexity and reduces the overall viability of operation, especially in small scale house-hold treatment units. Recently several reports appeared in the print media on the uncontrolled leak of chlorine gas in the environment. This led to health problems for several people (<http://timesofindia.indiatimes.com/City/Bhubaneswar/Chlorine-leak-in-Berhampur-affects-over-40-/articleshow/6076368.cms> and <http://tribune.com.pk/story/27917/scores-in-hospital-after-mumbai-gas-leak/>). Considering all these, it is necessary to look at new approaches for addressing water contamination problem in environmentally friendly way.

Recently, nanomaterials are gaining attention as adsorbents for removing various pollutants, including biological and chemical pollutants from water. Unusual properties arise in nanoscale materials when compared with their bulk counterparts due to larger surface area, greater density of reactive sites on the particle surfaces, and/or higher intrinsic reactivity of the reactive surface sites (Savage, N., Diallo, M.S. Nanomaterials and water purification: Opportunities and challenges. *J. Nanopart. Res.*, **2005**, 7, 331). These unique properties of nanomaterials are highly promising in water purification process and as a result, researchers have focused on nanotechnology for an efficient, cost effective and eco-friendly method to decontaminate water (Dhermendra, K.T., Behari, J., Sen, P., Application of nanoparticles in waste water treatment. *World Appl. Sci J.*, **2008**, 3, 417; Pradeep, T., Anshup, Noble metal nanoparticles for water purification: A critical review. *Thin Solid Films*, **2009**, 517, 6441–6478).

In our earlier work, we removed various contaminants from drinking water: organic contaminants such as pesticides (T. Pradeep, A. Sreekumar Nair, Indian Patent 200767 and PCT Application PCT/IN05/0002), inorganic contaminants such as mercury (T. Pradeep, Lisha K. P., Anshup, Indian Patent Application 169/CHE/2009) and biological contaminants such as E-coli (T. Pradeep, Prashant Jain, Indian Patent 20070608) and fluoride (T. Pradeep, S. M. Maliyekkal, Anshup, Indian Patent Application 2089/CHE/2009; T. Pradeep, S. M. Maliyekkal, Anshup, M. Udhaya Sankar, Indian Patent Application 1529/CHE/2010). As a continuation of our research activities on nanomaterials for environmental remediation and applications, we found a novel nanoscale composite metal oxide composition for decontaminating pathogens like, bacteria, viruses, and heavy metals like mercury and arsenic.

Mixed oxides have been of research interest for environmental remediation due to their improved physical and chemical properties. As far as environmental applications are concerned, they are important because many of them are known to show improved performance compared to their individual reference oxides. Besides, such oxides also perform multiple roles simultaneously. Recent research by Zang et al. showed that Mn-Fe binary metal oxide is superior in removing As (III) compared to manganese oxide and iron oxide (G Zhang, J Qu, H Liu, R Liu, and R, Wu. Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal, *Wat. Res.*, **2007**, 41, 1921-1928). This material is claimed to have combined the oxidation property of manganese dioxide and the high adsorption features to As (V) of iron oxides. Kamimura et al. showed that addition of Fe₂O₃ into CeO₂ enhances the ability of pure CeO₂ for the production of 3-pentanone from 1-propanol. They assumed that both the redox ability and the basicity of the catalyst play important roles in the reaction process. (Y Kamimura, S Sato, R Takahashi, T. Sodesawa, T, Akashi. Synthesis of 3-pentanone from 1-propanol over CeO₂–Fe₂O₃ catalysts. *App. Catalysis A: General*, **2003**, 252(2), 399-410). An Fe–Ce bimetal adsorbent investigated by Zhang et al. showed a significantly higher As (V) adsorption capacity than the referenced Ce and Fe oxides (CeO₂ and Fe₃O₄) prepared by the same procedure. (Y Zhang, M Yang, X.M Dou, H He, and D.S Wang, Arsenate Adsorption on an Fe–Ce Bimetal Oxide Adsorbent: Role of Surface Properties, *Environ. Sci. Technol.*, **2005**, 39(18), 7246–7253.). These studies and studies similar to this clearly show the importance of composite oxides composition for environmental remediation.

Prior art on Mn and Zn based oxides for anti-microbial activity:

1. J. Sawai, Quantitative evaluation of antibacterial activities of metallic oxide powders (ZnO, MgO and CaO), *J. Microbiol Meth*, **2003**, 54(2),177-182

2. Song Jin, Paul H. Fallgren, Jeffrey M. Morris, Qi Chen. Removal of bacteria and viruses from waters using layered double hydroxide nanocomposites, *Science and Technology of Advanced Materials*, **2007**, 67–70
3. Al-Nakib Chowdhury, Md. Shafiul Azam, Md. Aktaruzzamana and Abdur Rahim, Oxidative and antibacterial activity of Mn₃O₄, *J. Hazard Mater*, **2009**, 172(2-3), 1229-1235
4. I. Perelshtein, G. Applerot, N. Perkash, E. Wehrschetz-Sigl, A. Hasmann, G. M. Guebitz and A. Gedanken, Antibacterial Properties of an In Situ Generated and Simultaneously Deposited Nanocrystalline ZnO on Fabrics, *ACS Appl. Mater. Interfaces*, **2009**, 1 (2), 361–366
5. Nadanathangam Vigneshwaran, Sampath Kumar, A A Kathe, P V Varadarajan and Virendra Prasad, Functional finishing of cotton fabrics using zinc oxide–soluble starch nanocomposites, *Nanotechnology*, **2006**, 17, 5087–5095
6. Lingling Zhang, Yunhong Jiang, Yulong Ding, Malcolm Povey and David York, Investigation into the antibacterial behaviour of suspensions of ZnO nanoparticles (ZnO nanofluids), *J. of Nanoparticle Research*, 2007, 9, 479-489
7. Lingling Zhang, Yunhong Jiang, Yulong Ding, Nikolaos Daskalakis, Lars Jeuken, Malcolm Povey, Alex J. O'Neill and David W. York, Mechanistic investigation into antibacterial behaviour of suspensions of ZnO nanoparticles against E. coli, *Journal of Nanoparticle Research*, **2009**, 12, 5, 1625-1636

Prior art on Mn and Zn based oxides for heavy metal removal:

1. Arsenic Removal with Agglomerated Nanoparticle Media, Paul Westerhoff, *WERC and AWWA*, **2006**
2. Dinesh Mohan, Charles U. Pittman, Jr., Arsenic removal from water/wastewater using adsorbents—A critical review, *Journal of Hazardous Materials*, **2007**, 142, 1-2, 1-53
3. Véronique Lenoble, Christelle Laclautre, Bernard Serpaud, Véronique Deluchat, Jean-Claude Bollinger, As(V) retention and As(III) simultaneous oxidation and removal on a MnO₂-loaded polystyrene resin, *Sci Total Environ*, **2004**, 326, 1-3, 197-207
4. Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: From nanopowders to aggregated nanoparticle media, Kiril Hristovski, Andrew Baumgardner, Paul Westerhoff, *Journal of Hazardous Materials*, **2007**, 147, 1-2, 265-274
5. Bruce A. Manning, Scott E. Fendorf, Benjamin Bostick, and Donald L. Suarez, Arsenic(III) Oxidation and Arsenic(V) Adsorption Reactions on Synthetic Birnessite, *Environ. Sci. Technol.*, 2002, 36 (5), 976-981
6. H. Chen, J. He, Facile synthesis of monodisperse manganese oxide nanostructures and their application in water treatment, *J. Phys. Chem. C*, **2008**, 112 (45), 17540–17545.

7. H. Chen, M. Wang, D. Xiao, D. Clifford, Water treatment composition comprising nanostructured materials, United States Patent 7655148

8. K.P. Lisha, Shihabudheen M. Maliyekkal and T. Pradeep, Manganese dioxide nanowhiskers: A potential adsorbent for the removal of Hg(II) from water, *Chem. Engg. J.*, **2010**, 160, 432 - 439

A major concern associated with the use of ZnO for water purification is the release of Zn^{2+} in water. ZnO can hydrolyze in water releasing Zn^{2+} ions and/or, depending on the pH, form zincanates $[Zn(OH)_3^-]$ as a result of the amphoteric properties of Zn^{2+} . Zn concentration in water is reported to be 2.4 ppm (I. Perelshtein, G. Applerot, N. Perkas, E. Wehrschetz-Sigl, A. Hasmann, G. M. Guebitz and A. Gedanken, Antibacterial Properties of an In Situ Generated and Simultaneously Deposited Nanocrystalline ZnO on Fabrics, *ACS Appl. Mater. Interfaces*, **2009**, 1 (2), 361–366). While this is below WHO limit for Zn^{2+} in water, the continuous leaching leads to dissolution of adsorbent media over a period of time.

DESCRIPTION OF THE INVENTION:

The present invention describes a novel synthetic method for preparing Mn-Zn composite oxide and its application as an antibacterial and antiviral composition and also as a filter medium for removing heavy metals. The as-synthesized composite -metal oxide crystals have flower-like structure with size about 500 nm. Each flower-like microstructure is constructed with assemblage of number of nanosheets of Mn-Zn oxide of thickness < 15 nm. The material is characterized by a number of microscopic and spectroscopic techniques. The present invention also demonstrates the immobilization of the said materials on suitable matrices and their application as filter media for removing the said contaminants from drinking water. The following examples are provided to illustrate the present invention. However, the examples should not be construed as limiting the scope of the invention.

Example 1

This example describes the synthesis of self-assembled Mn-Zn composite oxide. For this, 40 ml of 0.1 M of zinc acetate and 40 ml of 0.1 M of manganese acetate were added to 60 ml of ethanol and stirred for 10 min. Subsequently, NaOH (0.1 M) was added to this mixture drop by drop till the pH reached nearly neutral and stirred for another 15 min. A white precipitate floated on the reactor which upon heating the solution for 10 min at $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ changes color from white to pale brown and settles down slowly. The settled precipitate was separated, washed and dried at $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ overnight, crushed and stored in glass bottle for further characterization and adsorption studies.

Example 2

Mn-Zn composite oxide was loaded on chitosan through two solution phase methods. In the first method, a known quantity of Mn-Zn composite oxide powder (Example 1) was re-dispersed in distilled water and the dispersion was slowly added to chitosan solution (chitosan dissolved in 2.5 - 5% acetic acid) under thorough stirring. Subsequently, the pH of the mixture was brought to neutral by means of an alkali. The composite material formed was separated, washed and dried. In the second method, Mn-Zn composite oxide gel (Example 1) formed just after precipitation was filtered, washed and re-suspended in distilled water and mixed with chitosan solution (dissolved in 2.5 - 5% acetic acid) as described earlier. The pH of the mixture was then increased by adding alkali drop by drop under stirring. The hybrid material formed was separated, washed and dried at $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$.

Example 3

In order to support Mn-Zn composite oxide on cellulose fibers, Mn-Zn composite oxide is grown on the surface of cellulose. Manganese and zinc salt solution with ethanol are mixed with cellulose and stirred overnight. The pH of the mixture was then increased by adding alkali drop by drop under stirring followed by heating at $70\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$. Then the composite material formed was separated, washed with de-ionized water and dried at $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. Dried material is used directly as granule or as powder after crushing.

Example 4

In order to support Mn-Zn composite oxide on activated alumina, one of the two methods can be used. In the first method, Mn-Zn composite oxide is grown on the surface of activated alumina. Manganese and zinc salt solution with ethanol are mixed with activated alumina and stirred overnight. The pH of the mixture was then increased by adding alkali drop by drop under stirring followed by heating at $70\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$. Then the composite material formed was separated, washed with de-ionized water and dried at $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. Dried material is used directly as granule or as powder after crushing.

In the second method, Mn-Zn composite oxide powder (Example 1) is re-dispersed in water. Subsequently, activated alumina is added to the dispersion, either in powder form or granular form. The mixture is stirred overnight. Then the composite material formed was separated, washed with deionized water and dried at $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$.

Example 5

In another example, activated alumina is replaced by activated silica.

Example 6

In another example, activated alumina is replaced by rice husk ash.

Example 7

In another example, activated alumina is replaced by activated carbon.

Example 8

In another example, a mixture of support is used for immobilization of Mn-Zn nanosheets. For example, a mixture of cellulose and chitosan is used. In a typical approach, Mn-Zn composite oxide is precipitated in the presence of cellulose and chitosan in acetic acid solution. As the pH of the mixture increases, Mn-Zn composite oxide and chitosan precipitate out of the solution. The composite material is then washed, dried and heated at $70\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$.

Example 9

In another example, Mn is replaced by Al by use of an aluminum salt such as aluminum nitrate in the reaction.

Example 10

In another example, Mn is replaced by Fe(II) by use of an iron(II) salt such as iron(II) nitrate in the reaction.

Example 11

In another example, Mn is replaced by Fe(III) by use of an iron(III) salt such as iron(III) nitrate in the reaction.

Material characterization

The identification of the phase(s) of the as-prepared samples and samples exposed to contaminants were 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, the sample prepared as mentioned above was re-suspended in water by means of ultra-sonication for 10 minutes and drop casted on an indium tin oxide (ITO) conducting glass and dried. High resolution Transmission Electron Microscopy (HRTEM) images of the sample were obtained with JEOL 3010. The samples prepared as above were spotted on amorphous carbon films supported on copper grids and dried in ambience.

Adsorption studies

Bacteria and virus removal

Bacteria and virus removal capacity of nanomaterial and nanomaterial in supported form (as powder and as beads) were investigated following US NSF drinking purifier standards. As per the US NSF drinking water purifier performance standards, the challenge water for bacteria and virus removal claim should contain 1×10^5 CFU/ml and 1×10^3 PFU/ml, respectively. The bacterium culture to be used for testing is Escherichia coli and the removal should be above 99.9999%. The virus culture to be used for testing is Bacteriophage MS2 and the removal should be above 99.99 %.

Materials used were sterilized initially for batch study. The bacterial culture was initially inoculated to physiological saline water. The input concentration of E-coli was maintained as 3×10^5 CFU/ml. Different doses of material were added to these and stirred. The material was separated from the solution at predetermined time intervals. The residual colonies in the solution were counted using successive dilution technique. 1 ml of sample was mixed with sterile agar medium and plated at 37 °C for 36 hours. After 36 hours, the plates were tested for number of viable bacterial cells present in a culture.

The interior region of ceramic candle (water purification cartridge, pore size: 1-5 micron, flow rate: 1 liter/h) was filled with the supported nanomaterial for column study. Input water having E. coli concentration of 5×10^8 CFU/ml which is 5,000 times higher than as suggested by US NSF was fed through column. Samples of the effluent were collected periodically and concentration of E-coli in effluent was quantified to analyze the performance of supported nanomaterial. Similarly virus concentration is 4,000 times higher than as suggested by US NSF (typical concentrations used: 4×10^6 - 2×10^7 PFU/ml) was used and the performance of material was analyzed. The concentration of Mn and Zn in the output water was analysed using ICP-OES.

Heavy metal removal

The uptake capacity of the as-prepared material for heavy metals such as Hg (II) was tested. All the Hg (II) uptake studies were done in a batch reactor (250 mL conical flask). The working volume of the solution was taken as 100 mL and required quantities of adsorbent were added. The flasks were kept for shaking at 160 ± 5 rpm in an orbital shaker (Riviera, India) at room temperature (30 ± 2 °C). Samples were withdrawn at predetermined time intervals and analyzed for residual solute (Pb, As and Cd) concentrations using appropriate technique. Equilibrium and kinetic studies were performed at studied at nearly neutral pH (6.5 ± 0.2) and at room temperature. Effect of adsorbent dose was investigated at a pH

of 6.5 ± 0.1 and solute concentration of 10 mg/L. Effect of pH on adsorption was also carried out by varying the pH over wide range. The pH of the samples was adjusted using dilute NaOH or HCl solution. Residual mercury analysis was conducted using R6G-based spectrophotometric technique (T.V. Ramakrishna, G. Aravamudan, M. Vijayakumar, *Anal. Chim. Acta*, 1976, 84, 369).

A batch study to check the removal capacity of arsenic was also conducted. The working volume of the solution was taken as 10 mL and different quantity of adsorbents were added. The flasks were kept for shaking at 160 ± 5 rpm in an orbital shaker (Riviera, India) at room temperature (30 ± 2 °C). Samples were withdrawn at predetermined time intervals and analyzed using ICP-OES.

DESCRIPTION WITH REFERENCE TO DRAWINGS AND TABULATED DATA

Characterization of the material and adsorption studies

The system was characterized with various techniques such as powder X-ray Dffraction (XRD), Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM).

Figure 1. The XRD patterns of Mn-Zn composite oxide and Hg (II) adsorbed on Mn-Zn composite oxide.

Figure 1 shows the XRD pattern of the as-synthesized material before and after mercury exposure. The XRD spectrum of pristine sample clearly shows the existence of more than one phase of Mn-Zn oxide. The intense peaks observed can be attributed to ZnMnO (labeled as '+') (JH Li, DZ Shen, JY Zhang, DX. Zhao, BS. Li, YM Lu, YC Liu, XW Fan, *Magnetism origin of Mn-doped ZnO nanoclusters, J.Magn.Magn. Mat.* **2006**, 302, 118–12.1) and the weaker peaks can be attributed to the presence of ZnMn₂O₄ (labeled as 'o') (JCPDF-71-2499). No peaks corresponding to MnO_x or ZnO were observed. Upon exposure to Hg (II), a little change in XRD pattern was observed and all the weaker peaks corresponding to ZnMn₂O₄ have vanished.

Figures 2 to 4. SEM, EDAX analysis of Mn-Zn composite oxide and Hg (II) reacted Mn-Zn composite oxide.

The SEM and EDAX analysis were performed before and after Hg (II) adsorption. As seen in SEM images, all crystals have flower-like structure with size about 500 nm and resembles to that of natural corals. It can also be deduced from the SEM images, that each microstructure is constructed of a number of nanosheets and they align themselves to form flower-like structure. Sheet-like particles might have formed by the assemblage of monoclinic units in three directions, but growth in normal direction to the

sheets was found to be the slowest. Simultaneously, the sheets clustered together to form a flower-like structure. The samples after exposure to Hg (II) showed some morphological change with closer arrangement of nanosheets compared to the pristine sample. The elemental mapping and EDAX spectrum shows uniform distribution of the principal elements Mn, Zn and O in the sample. The EDAX spectrum of the sample after Hg (II) adsorption showed its presence in the sample along with the principal elements, indicating that Hg (II) is adsorbed on the sample.

Figure 5. The HRTEM micrographs and EDAX spectrum of Mn-Zn composite oxide and Hg (II) reacted Mn-Zn composite oxide.

HRTEM images of the sample before and after Hg (II) ion exposure were taken. Similar to SEM images, a flower like morphology was observed and some change in the morphology was also observed after Hg (II) adsorption. The expanded image of a single particle shows that the material is crystalline and it is consistent with XRD data. The d- spacing (0.29 Å and 0.42 Å) values observed were slightly different from those of reference oxides. Such changes in lattice parameters could be due to the substitution of Mn in ZnO.

Figure 6. Effect of pH on mercury (II) removal

The pH of feed water plays a significant role in most of the adsorption by a metal oxide medium as it influences the distribution of solute species as well as the surface properties of the adsorbents. This study was conducted to find the effect of pH on Hg (II) adsorption by Mn-Zn composite oxide and the data is shown in Figure 6. It is evident from the figure that Hg (II) adsorption by Mn-Zn composite oxide is not significantly affected by the pH variations. However, the adsorption of Hg (II) is more favored at higher pH values (pH>5). In order to better assess the binding ability of Mn-Zn composite oxide at various solution pH, the K_d values were calculated and plotted against the pH. It is reported that higher the K_d value, better is the binding ability to the target pollutant. In general, the K_d values of $>10^3$ mL/g are considered good, and those above $>10^4$ mL/g are outstanding (Yantasee, W., Warner, C.L., Sangvanich, T., Addleman, R.S., Carter, T.G., Wiacek, R.J., Fryxell, G.E., Timchalk, C., Warner, M.G. Removal of Heavy Metals from Aqueous Systems with Thiol Functionalized Superparamagnetic Nanoparticles. *Environ. Sci. Technol.* **2007**, 41, 5114-5119). From the results it is clear that Mn-Zn composite oxide is an excellent candidate for removing Hg (II) from water at a wide range of pH, which makes the system more useful in various field conditions.

Figure 7. Effect of adsorbent dose on Hg (II) removal by Mn-Zn composite oxide

The effect of adsorbent dose on the extent of Hg (II) removal by Mn-Zn composite oxide was investigated. Adsorbent dose was varied over a range of 5 to 100 mg. The results obtained from these studies are depicted in Figure 7. As expected, adsorption of Hg (II) increases with increase in adsorbent dose up to a certain value. At higher adsorbent dose, there is more number of adsorption sites available, which increases the uptake. When the adsorbent dose was further increased, the proportionate increase in Hg (II) adsorption was not observed. This may be due to the unsaturated adsorption sites and increased particulate interaction and thus leading to agglomeration of the particles. A similar trend was reported by Rao et al. (2009) for Hg (II) removal from aqueous solution using activated carbon prepared from agricultural by-product/waste (Rao, M.M., Reddy, D.H.K.K., Venkateswarlu, P., Seshiah, K., Removal of mercury from aqueous solutions using activated carbon prepared from agricultural by-product/waste, *J. Environ. Manage.*, **2009**, 90, 634-643). From the K_d Vs adsorbent dose plots, it is evident that K_d value increases with increase in adsorbent dose, implying the heterogeneous nature of the surface. For a homogeneous surface, the K_d values at a given pH should not change with adsorbent dose. It is also evident from the K_d value that, maximum binding ability of Mn-Zn composite oxide is at higher dose and reduces with decrease in adsorbent dose for a fixed concentration of the Hg(II). At low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites and results in decreasing K_d values.

Figure 8. Equilibrium data on heavy metal removal by Mn-Zn composite oxide.

Adsorption capacity of an adsorbent is one of the basic parameters required for the design of any batch or fixed bed adsorption system. The equilibrium adsorption studies of Hg(II) by Mn-Zn composite oxide was carried out at 30 ± 2 °C and varying the initial Hg(II) concentration. As evident from the data (Figure 8), Hg(II) uptake capacity of Mn-Zn composite oxide increases with increase in initial Hg(II) concentration and the equilibrium data fitted reasonably well with Freundlich model. The mathematical representations of the Freundlich model are given below:

$$q_e = K_F C_e^{1/n}$$

The maximum uptake capacity predicted by the model is 117 g/L. The model predicted value and the experimentally obtained uptake capacity values shows that the as synthesized material is excellent in removing Hg(II) compared to reference oxide reported for Hg(II) uptake (Mishra, S.P., Dubey, S.S., D. Tiwari, Inorganic particulates in removal of heavy metal toxic ions IX. Rapid and efficient removal of Hg(II) by hydrous manganese and tin oxides, *J. Colloid Interface Sci.* **2004**, 279 61-67; Chen, H., He, J.,

Facile synthesis of monodisperse manganese oxide nanostructures and their application in water treatment, *J. Phys. Chem. C.* **2008**, 112, 17540-17545).

Figure 9-10. Effect of adsorbent (Mn-Zn composite oxide) doses on arsenic removal.

Adsorption capacity for the removal of arsenic was carried out using different dose of adsorbent. 10 ml of 95 ppm (Figure 9) arsenate and 11 ppm (Figure 10) arsenite solution was treated with 20,40,60,80 and 100 mg of supported material. Adsorption of arsenic (III and V) increases with increase in adsorbent dose up to a certain value. At higher adsorbent dose, there is more number of adsorption sites available, which increases the uptake, however, capacity decreases with increase in dose quantity.

Figure 11. Effect of adsorbent (Mn-Zn composite oxide) doses on bacteria removal.

Adsorbent dose optimization studies were carried out to quantify the amount of Mn-Zn composite oxide required to completely removing bacteria from water. Reference adsorbents like ZnO and MnO₂ were also tested to compare the performance. The results show that that Mn-Zn oxide is superior in bacterial removal compared to ZnO and MnO₂ (reference oxides) (Figure 11). With the Mn-Zn composite oxide, the concentration of Mn and Zn in the output water was <50 ppb and <250 ppb respectively.

Figure 12. Kinetics of Mn-Zn composite oxide and various other adsorbents for bacterial removal

This study was carried out to understand the contact time required to completely remove the bacteria with a specific amount of Mn-Zn composite oxide. A comparative study was also performed with reference oxides, like ZnO and MnO₂. The study revealed that 500 mg of material is required to completely remove initial bacterial concentration of 3X10⁵ CFU/ml. The study also reveals that removal kinetics is faster in the case of Mn-Zn composite oxide compared to ZnO and MnO₂.

Table 1

Virus removal capacity of supported nanomaterial (Mn-Zn composite oxide) in the powder form was studied. One liter of water of virus concentration 2.6x10⁷ PFU/ml was passed through column. Effluents were collected and concentration of virus had been quantified following US NSF standards at 500 ml and 1000 ml. It has been observed that 100 % of virus is removed when the material is used in the powdered form.

Table: 2

This study was carried out to see virus (MS2) removal capacity of supported nanomaterial in the form of beads. Virus concentration of 6x10⁶ was passed through column and effluent was collected at 800 ml and

1600 ml. Quantification of virus concentration showed 100% and 99.46% removal at 800 ml and 1.6 liter, respectively.

Table: 3

Bacteria removal capacity on supported nanomaterial in the powder form was carried out using E-coli of concentration 8×10^8 CFU/ml. Effluents collected at 600 ml and 1200 ml was quantified and it is found that a removal efficiency of 99.99% is achieved.

Table: 4

This study was carried out to see virus (MS2) removal capacity of supported nanomaterial in the form of beads using E-coli of concentration 5×10^7 CFU/ml. Effluent was collected at 1 L, 2.2 L and 3.3 L and concentration of E-coli was quantified following US NSF standards. It was observed that removal of E-coli for the effluent collected at 1, 2.2 and 3.3 liters is 100%, 100% and 99.99%, respectively.

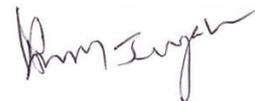
We Claim:

1. An adsorbent composition based on composite oxide consisting of manganese and zinc, having particles of less than <500 nm size each of which composed of plates of thickness < 15 nm, wherein the adsorbent composition is used for the removal of micro-organisms, heavy metals from water separately or jointly.
2. A method of preparing an adsorbent composition based on composite oxide consisting of manganese and zinc wherein the preparation method is based on eco-friendly steps comprising of
 - (a) preparing a composite of metal precursor and the template, wherein the metal ion is complexed with the template;
 - (b) hydrolyzing the mixture prepared as in step (a), wherein the metal precursor is precipitated on the template through the slow addition of an alkali by which the pH of the solution is brought in the range of 7 to 14;
 - (c) recovering the precipitated material from step (b) by filtration wherein the template also enhances the settling ability of the floe;
 - (d) converting the semi-solid filtered material from step (c) to a specific shape with or without use of binder;
 - (e) drying the material of a specific shape from step (d) to remove the moisture content at temperatures below 100 °C by methods such as oven drying.
3. An adsorbent composition as claimed in claim 1, wherein the adsorbent composition utilized for the removal of micro-organisms such as bacteria and virus, heavy metals such as mercury and arsenic from drinking water wherein
 - (a) the adsorbent is used in the batch set-up by mixing it with contaminated water or a column setup by passing the contaminated water through an adsorbent bed containing the granular adsorbent in the packed form;
 - (b) the pH of the contaminated water is varied between 4 to 9;
 - (c) the total dissolved salt content of contaminated water is varied up to 1000 ppm;
 - (d) the concentration of phosphate, sulfate and bicarbonate is individually varied up to 250 ppm.
4. An adsorbent composition as claimed in claim 1, wherein the size of as-prepared 3D architecture is varied in the range of 10 to 500 nm by varying the experimental parameters.
5. An adsorbent composition as claimed in claim 1, wherein the thickness of nanosheets is varied in the range of 10 to 100 nm by varying the experimental parameters.
6. An adsorbent composition as claimed in claim 2, wherein the templates includes but not limited to cellulose, chitosan, banana silk, activated alumina, activated carbon, charcoal, rice husk, sawdust and sand is used individually or in combination, with varying ratios.

7. An adsorbent composition as claimed in claim 2, wherein the template is a derivative of cellulose, chitosan, banana silk, activated alumina, activated carbon, charcoal, rice husk, sawdust or surface functionalized forms of the same.
8. An adsorbent composition as claimed in claim 2, wherein the template is used in solid form or in dissolved form.
9. An adsorbent composition as claimed in claim 2, wherein the metal precursor is selected from a group comprising of compounds including but not limited to aluminum, zinc, manganese, iron, titanium, zirconium, lanthanum, cerium, silicon or a combination thereof.
10. An adsorbent composition as claimed in claim 2, wherein the drying of the filtered material includes but not limited to freeze drying, surface drying, hot air drying, spray drying, vacuum drying or a combination thereof.
11. An adsorbent composition as claimed in claim 2, wherein the adsorbent is prepared through soft chemistry route using zinc and manganese precursors or their mixtures in solvents including water, methanol, ethanol, isopropanol or a combination thereof.
12. An adsorbent composition as claimed in claim 2, wherein the dissolution of zinc during its use in water purification is prevented by use of supporting matrix and co-precipitation with a metal ion.
13. A filtering device comprising an adsorbent composition as claimed in claim 1 or claim 2, wherein the filter is used in a variety of formats including but not limited to candle, molded porous block, filter bed, column, packets and bags.
14. A water treatment medium based on an adsorbent composition as claimed in claim 1 or claim 2, wherein the source of input water are from any sources including ground water sources, industrial sources, municipal sources.
15. A supported filtering media based on an adsorbent composition as claimed in claim 1 or claim 2, wherein the filter media is used in a variety of formats including but not limited to packing inside the ceramic candle, filter bed, column, packets and bags.
16. A filtering media based on an adsorbent composition as claimed in claim 1 or claim 2, wherein the source of input water are from any sources including ground water sources, industrial sources, municipal sources.

Dated at Chennai this February 28, 2017

Signature:



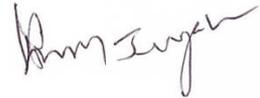
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ABSTRACT

A SINGLE COMPONENT METHOD AND A DEVICE FOR PATHOGENS AND HEAVY METALS FREE WATER

The present invention relates to the preparation of nanoscale composite metal oxide composition, its application as an antibacterial and antiviral composition and also as a filter medium for removing heavy metals. More specifically relates to an eco-friendly synthesis of a novel nanomaterial comprising Mn-Zn composite metal oxide formed by the assembly of MnZnO nanosheets of thickness <15 nm. The as-prepared material was also supported on various matrices such as chitosan, cellulose, carbon, rice husk and alumina. This novel composition is used for the removal of bacteria, viruses and heavy metals such as mercury and arsenic from contaminated water and also used as filter medium for removing the same.

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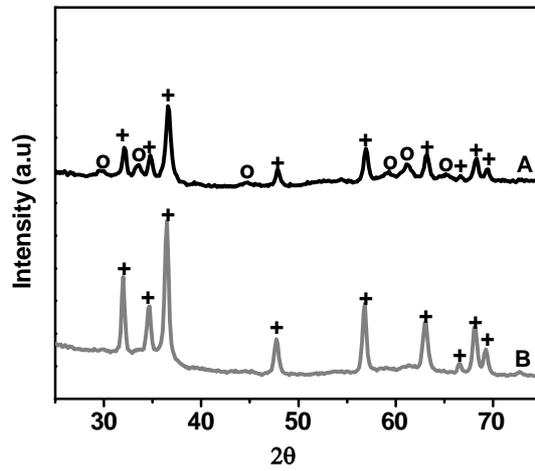


Figure 1

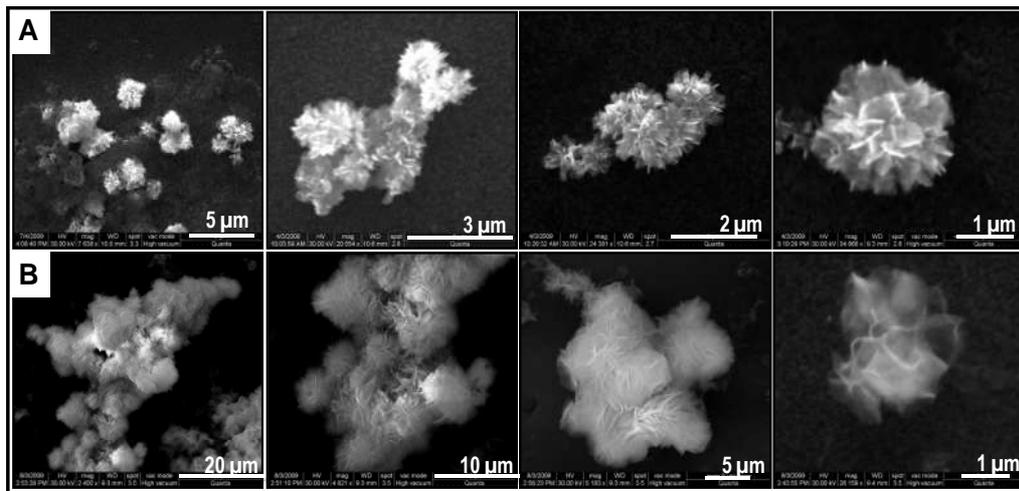
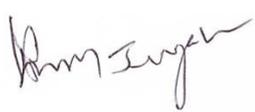


Figure 2

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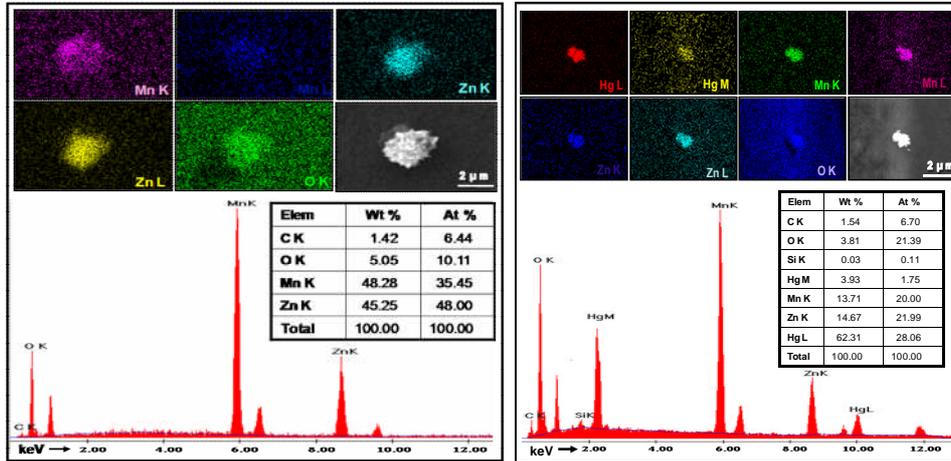


Figure 3

Figure 4

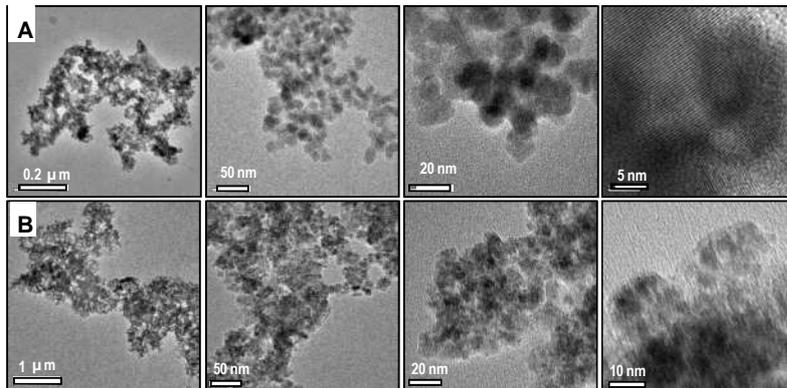
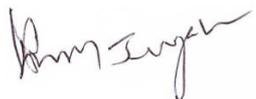


Figure 5

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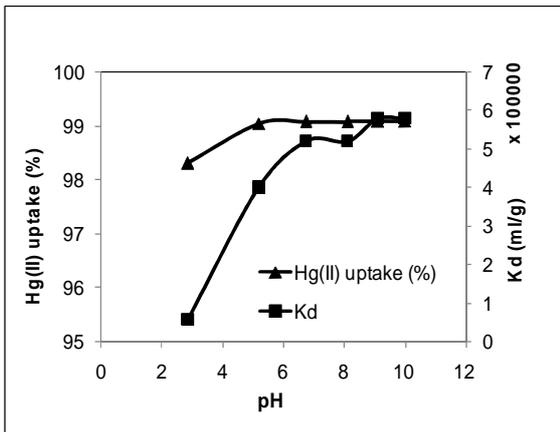


Figure 6

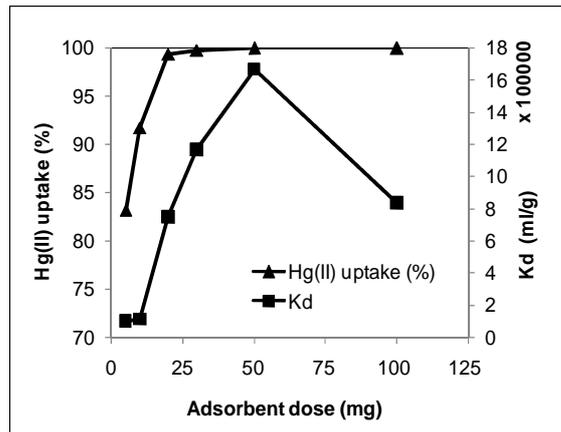


Figure 7

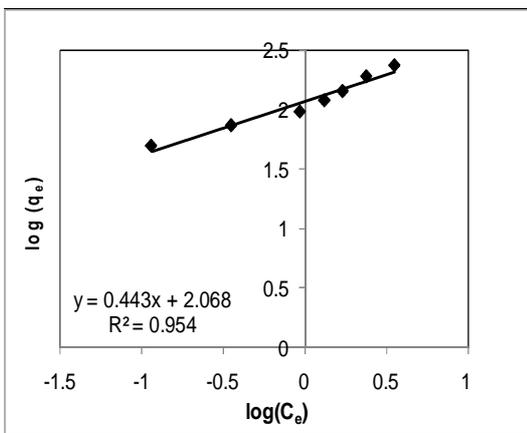


Figure 8

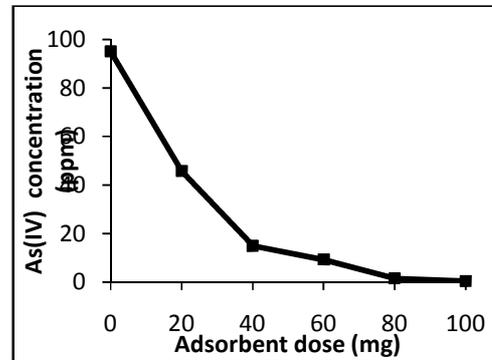


Figure 9

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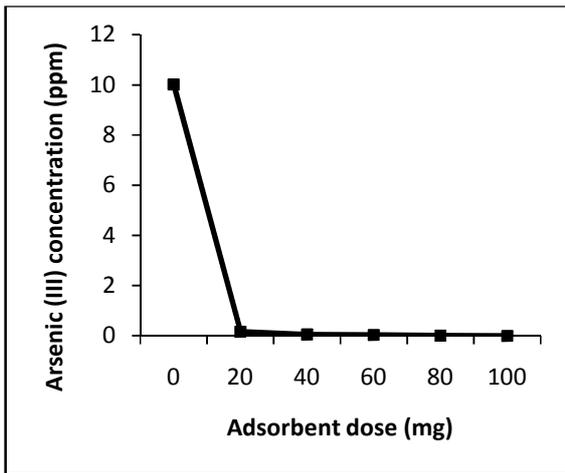


Figure 10

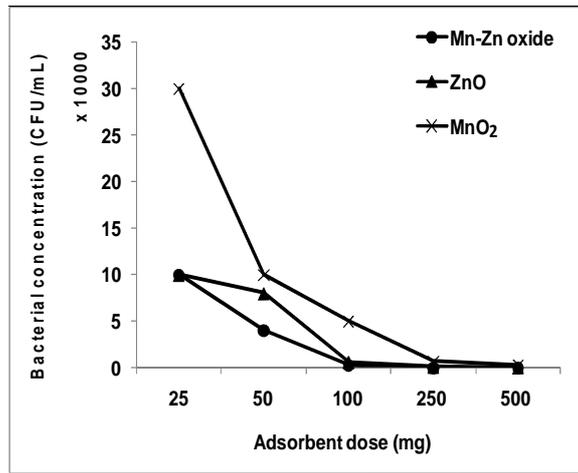


Figure 11

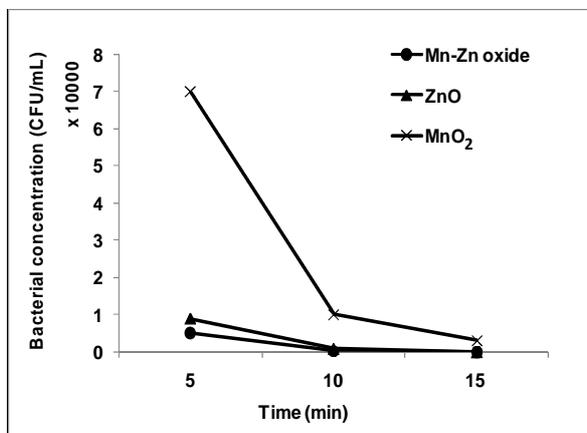


Figure 12

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APPLICATION NUMBER: 2433/CHE/2010

A SINGLE COMPONENT METHOD AND A DEVICE FOR PATHOGENS AND HEAVY METALS
FREE WATER

Table 1: Powder form supported material for Virus (MS2) removal.

S. No.	SAMPLES	PFU/1 ML	% OF REMOVAL
1	Raw water	26 000 000	-
2	After 0.5 liters	0	100
3	After 1.0 liters	0	100

Table 2: Bead form supported material for Virus (MS2) removal.

S. No.	SAMPLES	PFU/1 ML	% OF REMOVAL
1	Raw water	6 000 000	-
2	After 0.8 liters	0	100
3	After 1.6 liters	32 000	99.46

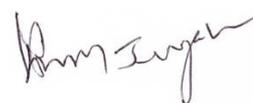
Table 3: Powder form supported nanomaterial for E-coli removal.

S. No.	SAMPLES	PFU/1 ML	% OF REMOVAL
1	Raw water	8 000 000	-
2	After 0.6 liters	200	99.999
3	After 1.2 liters	3000	99.999

Table 4: Bead form supported nanomaterial for E-coli removal.

S. No.	SAMPLES	PFU/1 ML	% OF REMOVAL
1	Raw water	500 000 000	-
2	After 1.0 liters	0	100
3	After 2.2 liters	0	100

Signature:



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