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प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित REMOVAL OF FLUORIDE, ALKALINITY, HEAVY METALS AND SUSPENDED SOLIDS SIMULTANEOUSLY - ADSORBENT SYNTHESIS, ADSORBENT COMPOSITION AND A DEVICE FOR AFFORDABLE DRINKING WATER नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 28th day of August 2009 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 REMOVAL OF FLUORIDE, ALKALINITY, HEAVY METALS AND SUSPENDED SOLIDS SIMULTANEOUSLY - ADSORBENT SYNTHESIS, ADSORBENT COMPOSITION AND A DEVICE FOR AFFORDABLE DRINKING WATER as disclosed in the above mentioned application for the term of 20 years from the 28th day of August 2009 in accordance with the provisions of the Patents Act,1970.

अनुदान की तारीख
Date of Grant : 10/06/2019

पेटेंट नियंत्रक
Controller of Patent

टिप्पणी – इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, **28th day of August 2011**को और उसके पश्चात प्रत्येक वर्ष मे उसी दिन देय होगी।

Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on **28th day of August 2011** and on the same day in every year thereafter.

FORM – 2

THE PATENTS ACT, 1970
(39 of 1970)
&
The Patents Rules 2003

COMPLETE SPECIFICATION
(SECTION 10 & rule 13)

TITLE

**REMOVAL OF FLUORIDE, ALKALINITY, HEAVY METALS AND SUSPENDED
SOLIDS SIMULTANEOUSLY - ADSORBENT SYNTHESIS, ADSORBENT
COMPOSITION AND A DEVICE FOR AFFORDABLE DRINKING WATER**

A P P L I C A N T

We, **INDIAN INSTITUTE OF TECHNOLOGY**, an autonomous body set up by the
government of India under an act of parliament, having its office at IIT P.O, Chennai
600 036, Tamil Nadu, India.

The following specifications particularly describes the nature of this invention and the
manner in which it is to be performed

FIELD OF INVENTION:

This invention relates to a novel natural polymer (e.g. cellulose, chitosan) mediated self-sustained combustion synthesis of extremely small particles of magnesium oxide and its application in drinking water purification (e.g. fluoride removal). The proposed method of synthesis is superior to existing combustion based synthesis in many perspectives: small size of the nanoparticle, cost-effective recovery of the material, significant improvement in the fluoride adsorption capacity. This invention also relates to the development of a simple device for removing fluoride, heavy metals and Total Dissolved Solids (TDS) from contaminated drinking water.

More specifically, the present invention relates to the removal of fluoride from drinking water using 3-7 nm particles of magnesium oxide. This invention also includes a method for removing total hardness, alkalinity and dissolved solids as well as maintaining pH as per the drinking water norms. The device includes a batch setup provided with an inlet followed by a dual media fixed bed unit, containing a sand bed followed by a manganese oxide-supported-activated alumina bed and an outlet at the end. The contaminated water is initially allowed to mix in the batch reactor for a definite period where fluoride is removed by nano-magnesia. The defluoridated water then passes through a dual media filter unit where pH, heavy metals, suspended solids and TDS are controlled and the decontaminated water flows out through the outlet provided.

PRIOR ART:

Water-related diseases constitute a major proportion of the public health problems in developing countries like India. Because of inadequate resources, availability of quality drinking water remains a dream for many people, especially in rural areas. Among diverse fresh water sources, groundwater is a major and often the preferred source of drinking water because it is expected to be free from microbial contamination and often requires little treatment. In rural part of India, a majority of water supplies (more than 80%) is obtained from groundwater (Census of India, quoted in The Times of India (Delhi edn.) Nov 7, **2003.**). Sadly, now it is clear that the groundwater resources contain a number of dissolved toxic pollutants (organic, inorganic and biological) that cause adverse health effects. 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).

Fluoride is a major inorganic contaminant present in many groundwater sources worldwide and needs immediate attention. The long-term consumption of fluoride contaminated water can cause skeletal and dental fluorosis, and can increase the risk of bone fracture, bone cancer (osteosarcoma cancer), and DNA damage (Ayoob, S., Gupta, A. K. Fluoride in drinking water: a review on the status and stress effects. *Crit. Rev. Environ. Sci. Technol.*, **2006**, 36, 433). Fluoride also has adverse effects on thyroid, immune system, brain and kidney as well. According to the recent information, fluorosis is endemic in atleast 25 countries around the world (http://www.unicef.org/wes/fluoride.pdf), including countries in Africa, Asia, and America. In India, fluorosis was first identified in Nellore district of Andhra Pradesh in 1937 (Shortt, W.E. Endemic fluorosis in Nellore District, South India. *Ind. Med. Gazette,* **1937**, 72) and it is now prevalent in more than 17 states across the country (Susheela, A.K. Fluorosis management programme in India. *Curr. Sci.*, **1999**, 77, 1250) with its concentration varying from 2 to 30 mg/l. Statistics says more than 25 million persons in India are affected by fluorosis and approximately 66 million persons are at the risk of fluorosis. Unfortunately, there is no specific treatment for endemic fluorosis apart from drinking water free from fluoride.

Apart from fluoride, the presence of heavy metals such as arsenic, mercury, lead, cadmium, etc. in drinking water continues to be a major concern because of their toxicity, accumulation in the food chain and persistent nature. Recent statistics show that various part of India and many other countries around the world are facing threat from one or more of these heavy metals (Acharyya SK, Chakraborty P, Lahiri S, Raymahashay BC, Guha S, Bhowmik A. Arsenic poisoning in the Ganges delta. *Nature*, **1999**, 7, 401(6753), 545; Nickson R, McArthur J, Burgess W, Ahmed KM, Ravenscroft P, Rahman M. Arsenic poisoning of Bangladesh groundwater. *Nature*, **1998**, 24, 395(6700), 338; http://www.indiaresource.org/documents/Plachimada Report Water Pollution.pdf). Chronic consumption of low concentration of these heavy metals can also cause various health problems, including cancerous and non cancerous diseases. Few prior arts unfolding the health issues arising from the chronic consumption of heavy metals are described in following reports:

(a) Roberts, J.R. Metal toxicity in children. In: Training manual on pediatric environmental health. CA: Children's Environmental Health Network. Emeryville, 1999 (http://www.cehn.org/cehn/trainingmanual/pdf/manual-full.pdf).

(b) Agency for Toxic Substances and Disease Registry (ATSDR), ToxFAQs Lead http://www.atsdr.cdc.gov/tfacts13.html.

(c) P.E. Marino, A. Franzblau, R. Lilis, Acute lead poisoning in construction workers: the failure of current protective standards. *Arch. Environ. Health,* **1989**, 44, 140–145.

(d) Agency for Toxic Substances and Disease Registry (ATSDR), ToxFAQs Arsenic http://www.atsdr.cdc.gov/tfacts2.pdf.

(e) http://www.lef.org/protocols/prtcl-156.shtml

Owing to the widespread occurrence and detrimental effects of these pollutants, various treatment methods have been developed over a period. A number of such methods are based on precipitation, ion-exchange, sorption and membrane processes. Among these, membrane technologies (nanofiltration, reverse osmosis) and ion exchange processes are not popular in developing countries like India because they are highly expensive. Sorption onto a solid surface is a preferred choice, especially in developing countries like India, 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 these contaminants from drinking water.

As of now, varieties of sorbents were tested for the removal of heavy metals from aqueous medium. However, the potential and widely used sorbents are activated carbon or metal oxides, such as oxides of iron, aluminium, manganese or a combination thereof or Bentonite. Compared to granular activated carbon, oxides have higher affinities and adsorption capacities and are thought to be the most important scavengers of heavy metals in aqueous solution (H.J Fan, P.R. Anderson. Copper and cadmium removal by Mn oxide-coated granular activated carbon. *Separation and Purification Technology,* **2005**, 45, 61). This is due to their relatively

high surface area, microporous structure, and presence of OH functional groups capable of reacting with metals, phosphate and other specifically sorbing ions (M.S. Al-Sewailem, E.M. Khaled, A.S. Mashhady. Retention of copper by desert sands coated with ferric hydroxides. *Geoderma*, **1999**, 89 249). Studies have also proved that metal oxides coated on suitable surfaces are more effective media because of their ease of use and ease in solid liquid separation (R. Han, W. Zou, Z. Zhang, J. Shi, J. Yang. Removal of copper(II) and lead(II) form aqueous solution by manganese oxide coated sand. I. Characterization and kinetic study. *Journal of Hazardous Materials*, **2006**, B137, 384)

Another important pollutant in drinking water, as mentioned earlier, is fluoride. A detailed report on a wide variety of sorbents utilized in the field for fluoride removal is described in the next paragraph onwards, along with the associated disadvantages leading to their limited use for field applications. Among such sorbents, nanomaterials are beginning to play a critical role for fluoride removal from drinking water. The unusual properties arise in the 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. These unique properties of nanomaterial are highly promising in the water purification process as well and have been earlier utilized by our group. They are also attractive due to ease with which they can be anchored onto solid matrices and the ability to functionalize with different functional groups to enhance their affinity towards target molecules (Savage, N., Diallo, M.S. Nanomaterials and water purification. *J. Nanopart. Res.*, **2005**, 7, 331). As a result, researches 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).

ACTIVATED ALUMINA:

Activated alumina (AA) is the most widely used sorbent for commercial scale defluoridation of drinking water, especially in developing countries like India. Extensive reports on the use of AA and its effectiveness is available in open literature and few prior arts are reported below.

(a) Savinelli, E.A. and Black A.P. Defluoridation of Water with Activated Alumina, *Journal of American Water Works Association,* **1958,** *50* (1), 33

(b) Rubel, F., Woosley, R.D. The removal of excess fluoride from drinking water by activated alumina. *Journal of American Water Works Assoc.,* **1979, 71(1),** 45

(c) Lee, D.R. Hargreaves, J.M., Badertocher, L., Rein, L., Kassir, F. Reverse osmosis and activated alumina water treatment plant for the California State prisons located near Blythe. Desalination, **1995,** *103,* 155

(d) Ghorai, S. Pant K.K. Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed. *Chemical Engineering Journal,* 2004, *98* (1-2), 165.

(e) Ghorai, S., Pant, K.K. Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. Separation *and* Purification *Technology,* **2005,** *42,* 265–271.

(f) Chauhan V.S., Dwivedi, P.K., Iyengar, L. Investigations on activated alumina based domestic defluoridation units. Journal *of Hazardous Materials,* **2007,** B139 (1), 103.

However, the main disadvantage of commercially available AA is its poor sorption kinetics due to the slow intra-particle diffusion of the fluoride ion. The reported sorption capacity of AA varies in the range of 1 - 9 mg per gm of sorbent (Ghorai, S., Pant, K.K. Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. *Separation and Purification Technology,* **2005,** *42,* 265–271). Thus, a minimum of 6.5 kg of AA is required for the design of a domestic water purification device (with a capacity to purify 6,000 liters of water [annual drinking water requirement for a family of 4 people]) catering to complete removal of 10 mg/L fluoride in drinking water. Besides, fluoride removal by AA is highly sensitive to raw water pH and alkalinity. Optimum pH for fluoride removal by AA is in the range of 5 to 6 and the sorption capacity decreases with the increase in alkalinity and pH. Unfortunately, most of the fluoride affected areas have high pH and alkalinity (Ayoob, S., Gupta, A.K. Fluoride in drinking water: a review on the status and stress effects. *Critical Reviews in Environmental Science and Technology,* **2006,** *36,* 433; Meenakshi, R.C. Maheshwari, J. Fluoride in drinking water and its removal. Hazard. Mater. 2006, *137*(1) 456.), which further reduces the efficiency of activated alumina based sorbents and demands the frequent replacement or regeneration of the materials. All these make activated alumina less attractive in house-hold use.

Recent studies suggest new methods for improving the performance of AA. Tripathy and coworkers studied the ability of the alum-impregnated activated alumina (AIAA) for F⁻ adsorption from water. AIAA removed 99% fluoride from water at an optimum pH of 6.5, contact time of 3 h, adsorbent dose of 8 g/L and with an initial F⁻ concentration of 20 mg/L (Tripathy, S.S., Bersillon, J.L., Gopal K., Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina. *Separation and Purification Technology*, **2006**; *50* (3), 310). Other recent studies show sorption of F- onto manganese dioxide-coated activated alumina is superior compared to uncoated AA. Manganese dioxide-coated activated alumina adsorbed more F⁻ than uncoated one over a wider pH range and the maximum adsorption occurred at neutral pH 7 (Maliyekkal, S.M., Sharma, A.K., Philip, L. Manganese-oxide-coated alumina: A promising sorbent for defluoridation of water. Water Research, **2006**, *40*, 3497; Tripathy, S.S., Raichur., A.M. Abatement of fluoride from water using manganese dioxide-coated activated alumina. Journal of Hazardous Materials, **2008**, 153 (3), 1043). Though some improvement in fluoride sorption performance was achieved with these modified sorbents, the sorption capacity of these materials are too less and fluoride sorption on AA remains susceptible to interference by other commonly found ions in drinking water. This information clearly demands a fluoride selective alternative sorbent that has high fluoride sorption capacity.

MAGNESIUM OXIDE:

An important environmental remediation aspect of MgO includes its potential to scavenge fluoride from drinking water and this has been known for more than 75 years (Elvove E., Removal of fluorides from drinking water, United States Patent 2207725, **1940**). Several subsequent efforts have been made to utilize the fluoride adsorption capacity of magnesium oxide and the details are contained in the following reports:

(a) Zettlemoyer, A. C., Zettlemoyer, E. A. and Walker, W. C., Active magnesia II: Adsorption of fluoride from aqueous solution. J. Am. Chem. Soc., **1947**, 69, 1312

(b) Fair G. M., Geyer J. C., Water supply and waste-water disposal, John Wiley & Sons, New York, **1954**, p. 632

(c) Venkateswarlu P., Rao N. D., Investigations on the removal of fluoride from water: rapid removal of fluoride with magnesium oxide, Indian J Med Res. **1953**, 41(4), 473.

(d) Venkateswarlu, P. and Narayana Rao, D., Investigations on the fluoride removal from water: Factors governing the adsorption of fluoride by magnesium oxide. Indian J. Med. Res., **1954**, 42, 135.

(e) Bartlet J. C., Chapman R. A., The removal of fluoride ion from aqueous solution by magnesium oxide, Canadian Journal of Chemistry, **1955**, 33, 1629.

(f) Lislie, A. L., Means and methods of defluoridation of water, United States Patent No. 3,337,453, **1967**.

(g) Viswanadham C. R., Purushottam D., Rao G. R., Vaidyanadhan D., Francis P. G., Defluoridation of water with magnesium oxide, Symposium on Fluorosis, Hyderabad, **1974**

(h) Opinya G. N., Pameijer C. N., Grön P., Simple defluoridation procedures for Kenyan borehole water, Community Dentistry and Oral Epidemiology, **1986**, 15, 2, 60.

(i) Rao S. M., Mamatha P., Reddy B. V. V., Process for the treatment of fluoride contaminated water and a domestic defluoridation unit, Indian Patent Application 614/CHE/2004, **2004.**

(j) Rao S. M., Mamatha P., Water quality in sustainable water management, Curr. Sci., **2004**, 87, 942.

(k) Nagappa B., Chandrappa G. T., Livage J. Synthesis, characterization and applications of nanostructural/nanodimensional metal oxides. Pramana - Indian Academy of Sciences, **2005**, 65, 917.

(l) Nagappa B., Chandrappa G. T., Mesoporous nanocrystalline magnesium oxide for environmental remediation, Micro. Meso. Mater., **2007**, 106(3), 212.

(m) Chandrappa G. T., Nagappa B., Method of preparing nanocrystalline MgO and ZnO products and using same for removing fluoride and arsenic from contaminated water, Indian Patent Application, 007261/DEL/2007.

(n) Sundaram C. S., Viswanathan N., Meenakshi S., Defluoridation of water using magnesia/chitosan composite, J. Haz. Mater., **2009**, 163, 2-3, 618.

A few important highlights from the work reported in the prior art is as follows:

- A fluoride adsorption capacity of 4-170 mg/g is reported for different grades of magnesium oxide when input fluoride concentration is 150 ppm. The method of preparation can lead to significant differences in the fluoride adsorption capacity. While higher surface area (reported in the range of 0.8-154 m^2/g) for magnesium oxide doesn't guarantee higher adsorption capacity, the rate of fluoride adsorption increases with increase in the surface area. Magnesium oxide exhibited higher fluoride capacity exists as an aggregated particle network of size 2-5 µm (Zettlemoyer, A. C. Active magnesia II: Adsorption of fluoride from aqueous solution. J. Am. Chem. Soc., **1947**, 69, 1312).

- Use of 0.3 g/l calcium oxide along with 0.8 g/l magnesium oxide can purify fluoride-contaminated water (fluoride concentrations 2–5 ppm). This process suffers from the disadvantages of increasing the TDS content of water (due to addition of various chemicals) along with the production of large quantity of sludge (Rao S. M., Mamatha P., Reddy B. V. V., De-fluoridation of water by IISc method. Indian Patent Application 614/CHE/2004, **2004**).

- Combustion based synthesis of magnesium oxide leads to the formation of an aggregated particle network of size in microns. The reported surface area is 107 m^2/g. X-Ray diffractogram suggests the size of individual particle to be around 12-23 nm. A dosage of 1.0-1.50 g/l of this magnesium oxide is required for bringing down the fluoride concentration from an input value of 10 ppm to 1 ppm. While this method demonstrates the increased defluoridation capacity of nano magnesium oxide over its bulk form, it suffers from a number of disadvantages: low production yield of nanomaterials, alkaline pH of treated water, loss of defluoridation capacity on exposure to water due to hydroxylation and aggregation (Nagappa B., Chandrappa G. T. Mesoporous nanocrystalline magnesium oxide for environmental remediation. Micro. Meso. Mater., **2007**, 106(3), 212).

- Modifying magnesium with chitosan to form magnesium oxide/chitosan composite (by heating magnesium oxide with chitosan at 400 °C) leads to an increase in the defluoridation capacity of magnesium oxide from 2.175 mg/g to 4.44 mg/g, when the input fluoride concentration is 10 ppm. A dose of 2 g/l for magnesium oxide/chitosan composite is required to bring down the fluoride concentration from 10 ppm to 1 ppm. However, the method suffers from the disadvantage of producing large quantity of sludge along with alkaline pH of the treated water, which is strictly not acceptable

in field conditions. (Sundaram C. S., Viswanathan N., Meenakshi S. Defluoridation of water using magnesia/chitosan composite. J. Haz. Mater., **2009**, 163, 2-3, 618).

Additional reports on the utilization of magnesium oxide suggest following highlights:

- Depending on preparation methods, MgO exhibits different sorption capacity towards contaminants (K.J. Klabunde, in: C. Mohs, L.V. Interrante, M.J. Hampden-Smith (Eds.), Chemistry of Advance Materials: An Overview, Willey-VCH Inc., **1998**, p. 314, ISBN 0-471-18590-6).

- It is important to note that the efficiency of the sorption increases with a decrease in the size of the MgO crystallites. MgO works most efficiently in the destructive sorption reaction when its particle size is on a nanometer scale. The high efficiency of the nanoparticle oxides is caused not only by their high surface area but also by the high concentration of low-coordinated sites and structural defects on their surface (V. Mishakov, A.F. Betilo, R.M. Richards, V.V. Chesnokov, V. Vladimir, I. Zaikovskii, R.A. Buyanov and K.J. Klabunde. Nanocrystalline MgO as a dehydrohalogenation catalyst. J. Catal, **2002**, 206, 40). As the particle size is scaled down to a few nanometers, the constituting atoms exhibit highly defective coordination environments. Most of the atoms have unsatisfied valencies and reside at the surface. In short, microstructural features such as small grain size, large number of interfaces and grain boundary junctions, pores, and various lattice defects that result from the chosen routes for their synthesis contribute significantly to the unique physical and chemical properties of nanomaterials.

Recently, attempts were also made to enhance the defluoridation capacity of bulk MgO by using its nano form (Nagappa, B., Chandrappa, G.T., Livage, J., *Journal of Physics*, **2005**, *65* (5) 917; Nagappa, B., Chandrappa, G.T. Mesoporous nanocrystalline magnesium oxide for environmental remediation. Micropor. Mesopor. Mater. **2007**, *106* (1-3) 212 ; Nagappa, B., Chandrappa, G.T., Defluoridation of bore well water usingcombustion derived nanocrystalline magnesium oxide. *Trans. Indian Ceramic Soc.*, **2005**, *64* (2) 87). In a typical procedure, an aqueous magnesium nitrate solution and glycine as fuel is heated at 400 °C for producing nano magnesium oxide. The material is used for defluoridation studies and it is found that a minimum dose of 1 gm is required for cleaning up 10 ppm, 1 liter fluoride solution (as per the WHO standards). It is reported that the use of nano magnesium oxide could reduce the sludge volume by a factor of 9 compared to bulk magnesium oxide.

However, there are certain issues related to the use of nano magnesium oxide for commercial drinking water purification, which have been highlighted in other prior arts:

1. Loss of reactivity on prolonged exposure to water: Due to their enhanced hydrophilicity, alkaline earth metal oxide nanoparticles rapidly deactivate in the presence of moisture and CO_2 during storage with access to the atmosphere. Upon adsorption of moisture, magnesium oxide undergoes partial deactivation leading to significant decrease in contaminant removal efficiency (Bedilo, A.F., Sigel, M.J., Koper,O.B., Melgunov, M.S., Klabunde, K.J. Synthesis of carbon-coated MgO nanoparticles. J. Mater. Chem., **2002**, *12*, 3599; M. S. Melgunov, M.S., Melgunova, E.A., Zaikovskii, V. I., Fenelonov, V.B. Carbon Dispersion and Morphology in Carbon-Coated Nanocrystalline MgO. *Langmuir*, **2003**, 19 (24) 10426). The use of magnesium oxide nanoparticles in drinking water also leads to significant increase in the pH of the treated water and makes it non-drinkable (due to alkaline nature of the material). This is attributed to the high point of zero charge value of magnesium oxide. (Parks, G.A. The isoelectric points of solid oxides, solid hydroxide, and aqueous hydroxo complex systems. *Chem. Rev.*, **1965**, *65*, 177).

2. Aggregation of nano-magnesium oxide particles in solution phase: Nano magnesium oxide as prepared by the combustion synthesis exists as porous aggregates of 1-2 microns in size, with individual particles having a size of 12-23 nm. Due to large surface energy, nanoparticles have a natural tendency to aggregate in the solution phase, leading to significant loss in the reactivity. Therefore, it is important to protect the surface from aggregation through the anchoring of protecting agents on nanoparticle surface or anchoring the nanoparticle on support, so as to restrict the mobility and contact of nanoparticles (Jeevanandam, P. Klabunde, K.J. Studies on surfactant-coated magnesium oxide nanoparticles. *Langmuir*, **2003**, 19 (13), 5491; United States Patent Application 20050045031, Air-stable metal oxide nanoparticles).

3. Low recovery of nano magnesium oxide: The combustion reaction between magnesium nitrate and glycine is reported to produce MgO nano particles (Nagappa B., Chandrappa G. T. Mesoporous nanocrystalline magnesium oxide for environmental remediation. Micro. Meso. Mater., **2007**, 106(3), 212). However, this reaction is very spontaneous with the evolution of large amount of gaseous

byproducts, the formed MgO nanoparticles being extremely fine, escape along with the gases, thereby reducing the recovery of particles significantly. Thus, a large-scale production requires complicated controlling mechanism for the recovery of nanoparticle (Mukasyan AS, Dinka P. Apparatus for synthesizing nanopowder, has carrier substrate, solution applicator, dryer and combustion chamber having ignition source for igniting impregnated carrier substrate to initiate combustion synthesis. 2007. PCT application WO2007019332-A1).

Various other protocols have been developed for the synthesis of nano magnesium oxide and are based on organometallic precursors of magnesium (Sol-gel process), hydrothermal process and solvothermal method. Representative examples of such protocols are reported in the following prior art:

(a) United States Patent Application 20040065619, Carbon-coated metal oxide nanoparticles.

(b) K. J. Klabunde, J. Stark, O. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiang, I. Lagadic, D. Zhang, J. Nanocrystals as stoichiometric reagents with unique surface chemistry. *Phys. Chem.*, **1996**, 100, 30, 12142. V. M. Boddu, D. S. Viswanath, S. W. Maloney. Synthesis and Characterization of Coralline Magnesium Oxide Nanoparticles. *Journal of the American Ceramic Society*, **2008**, 91, 5, 1718.

(c) A Subramania, G Vijaya Kumar, A R Sathiya Priya, T Vasudevan. Polyol-mediated thermolysis process for the synthesis of MgO nanoparticles and nanowires. *Nanotechnology*, **2007**, 18, 225601.

LAYERED DOUBLE HYDROXIDES: Layered Double Hydroxide (LDH) has positively charged layered structure with charge balancing anions located in the interlayer region.

A number of studies have been conducted on synthesis and use of LDH for fluoride removal and is reported in the following prior art:

Synthesis of LDH

Process for Preparing Organically Modified Layered Double Hydroxide, United States Patent Application 20080300352, E. Schomaker, R. Winters.

Mandal and Mayadevi (2007) studied the fluoride adsorption by Zn–Al layered double hydroxides (LDHs) and found that fluoride adsorption was influenced by the chemical composition of the LDHs. A Zn/Al ratio of 0.97 showed the highest fluoride

sorption capacity (4.16 mg/g). The adsorption increased after calcination of LDH up to 500 °C.

Liang (2007) used calcined MgAl-CO3 layered double hydroxides (CLDH) to remove fluoride with the reconstruction of their original layered structure in the presence of appropriate anions. They found that equilibrium defluoridation capacity decreased with increase in temperature, the optimum pH was 6 and the maximum capacity was 231.2 mg/g at 30 ^{0}C. Wu et al. (2007) developed a tri metal oxide for fluoride removal by co-precipitation of Fe(II), Al(III) and Ce(IV) salt solutions with a molar ratio of 1:4:1 under alkaline conditions. This sorbent showed amorphous structure and relatively stable fluoride adsorption performance at calcination temperatures lower than 600 °C. The optimum pH range was 6.0–6.5 and a high fluoride adsorption capacity of 178 mg g−1 was acquired under an equilibrium fluoride concentration of 84.5 mg /L, adsorbent dose of 150 mg /L and at a pH of 7.0. Wang et al., (2007) studied the fluoride adsorption by synthetic Mg/Al–CO3 hydrotalcite-like compounds (HT) and their calcined products (HTC). They reported that fluoride uptake by HTC was much stronger than their precursors, HT. The adsorption isotherm for HTC at pH 7 was linear and did not follow Langmuir equation.

Representative examples of such protocols are reported in the following prior art:

(a) Mandal, S. and S. Mayadevi, Adsorption of fluoride ions by Zn–Al layered double hydroxides. Applied Clay Science, doi:10.1016/j.clay.2007.07.004.

(b) Wu, X., Y. Zhang, X. Dou and M. Yang Fluoride removal performance of a novel Fe–Al–Ce trimetal oxide adsorbent. *Chemosphere*, **2007**, 69 (11), 1758-1764.

(c) Liang, L.V. Defluoridation of drinking water by calcined MgAl-CO3 layered double hydroxides. *Desalination*, **2007**, 208(1-3), 125.

PRIOR ART ON APPLICATION OF MAGNESIUM OXIDE AND MAGNESIUM OXIDE BASED COMPOSITION FOR DRINKING WATER PURIFICATION: HEAVY METAL REMOVAL:

Transition metal oxides are one of the most commercialized sorbents for heavy metals. Typically used metal oxides are: MnO_2, Fe_2O_3, TiO_2 and FeOOH. Magnesium oxide as well as manganese oxide based compositions have also been studied for removal of heavy metals from water and waste water sources. The mechanism of sorption is largely explained by precipitation, ion exchange and

complexation of contaminant heavy metals ions with the negatively charge OH⁻ group present in the hydrolyzed metal oxides. The efficiency of adsorption is further enhanced at the nanoscale due to the presence of numerous high-energy active sites, responsible for the adsorption of metal ions. A number of reports in this direction has been published and is captured through the following prior art:

(a) Zhang, S. Cheng, F. Tao, Z. Gao, F. Chen, J. Removal of nickel ions from wastewater by $Mg(OH)_2/MgO$ nanostructures embedded in Al_2O_3 membranes. *Journal of Alloys and Compounds*, **2006**, 426, 281.

(b) Erena, E., Afsinb B., Onalc, Y. Removal of lead ions by acid activated and manganese oxide-coated bentonite. *J. Haz Mater*, 2009 161 677.

(c) Runping, H. Weihua, Z. Zongpei, Z. Jie, S. Jiujun, Y., Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand: I. Characterization and kinetic study. *J. Haz Mater.*, **2006**, 137, 384.

(d) Chen, H., Wong, M., Xiao, D., Clifford, D., Water treatment composition comprising nanostructured materials. PCT Application WO 2007/047624.

Anti-bacterial properties:

A recently studied property of nanoscale metal oxide is their application in the emoval of microorganisms from drinking water. The anti-bacterial effect is quite significant on both gram-positive and gram-negative bacteria and is manifested in bacteriocidal manner. The mechanism behind anti-bacterial properties of metal oxide is not fully elucidated, however, it is suggested that the inherent alkaline nature of magnesium oxide and possible formation and stabilization of superoxide anions in the alkaline environment leads to its anti-microbial properties. It has also been suggested that anti-bacterial performance increases dramatically with the decrease in the size of the nano-magnesia. A number of reports in this direction has been published and is captured through the following prior art:

(a) Stoimenov, P.K., Klinger, R.L., Marchin, G.L., Klabunde, K.J., Metal Oxide Nanoparticles as Bactericidal Agents. *Langmuir*, **2002**, *18* (17), 6679.

(b) Huang, L., Li, D.-Q.,. Lin, Y.-J., Wei, M., Evans, D., Duan G.X., Controllable preparation of Nano-MgO and investigation of its bactericidal properties. *Journal of Inorganic Biochemistry*, 2005, 99, 986.

(c) Sawai, J., Kojima, H., Igarashi, H., Hashimoto, A., Shoji, S., Sawaki, T., Hakoda, A., Kawada, E., Kokugan, T., Shimizu, M., Antibacterial

characteristics of magnesium oxide powder. *World Journal of Microbiology and Biotechnology*, **2000**, *16*, 187.

(d)   Lin, Y.J., Li, D.Q., Wang, G., Huang, L., Duan, X., Preparation and bactericidal property of MgO nanoparticles on γ-Al_2O_3. *J Mater Sci Mater Med.*, **2005** ,*16*, 53.

To further enhance the anti-bacterial properties of the nano-magnesia, halogenated adducts have also been utilized and reported in the following prior art:

(a)   P.K. Stoimenov, V. Zaikovski, K.J. Klabunde, Novel Halogen and Interhalogen Adducts of Nanoscale Magnesium Oxide. *J. Am. Chem. Soc.*, **2003**, *125*, 12907.

(b)   P.K. Stoimenov, R.L. Klinger, G.L. Marchin, K.J. Klabunde, Metal Oxide Nanoparticles as Bactericidal Agents. *Langmuir*, **2002**, 18, 6679.

However, it can be interpreted from the currently underway toxicity studies that nanoparticles can also interfere with biological activities of human body (Michael P. Holsapple, William H. Farlandt, Timothy D. Landry, Nancy A. Monteiro-Riviere, Janet M. Carter, Nigel J. Walker and Karluss V. Thomas, Research Strategies for Safety Evaluation of Nanomaterials, Part II: Toxicological and Safety Evaluation of Nanomaterials, Current Challenges and Data Needs, *Toxicological Sciences*, **2005** 88(1),12) Thus, it is very important that for commercial applications, nanoparticles should be anchored on a suitable support prior to use. An anchored nanoparticle is prevented from any release in the drinking water, while keeping its nano properties intact. The choice of support to be used for such purpose becomes critical (W. Jiang, H. Mashayekhi, B. Xing, Bacterial toxicity comparison between nano- and micro-scaled oxide particles. *Environmental Pollution,* **2009**, 157(5) 1619; S.J. Klaine, P.J. Alvarez, G.E. Batley, T.F. Fernandes, R.D. Handy, D.Y. Lyon, S. Mahendra, M.J. McLaughlin, J.R. Lead, Critical review of Nanomaterials in the Environment. *Environmental Toxicology and Chemistry,* **2008**, *27* (9) 1825.)

From the prior art presented, it is clear that while there are a range of materials known to remove fluoride, no viable solutions, which can be implemented in the field, exist. The problems include the after effects of media in water (such as alkalinity), prohibitive cost for the lower income group families, strong competition from co-

existing ions, inability to use several media in conjunction so as to tackle all the prevalent problems of drinking water, issues of disposal of spent media, etc. It is in this context that we decided to undertake an effort to develop a filter incorporating the well-known properties of materials as well as add new properties of specific materials in an integrated and cost effective fashion so as to tackle fluoride and heavy metal contamination in an affordable way. In developing such a filter, cost effective synthetic methods for the materials had to be developed and several materials had to be integrated. New design strategies have to be applied so that the device can be implemented in the field.

Realizing the cost of synthesis, simplicity and morphological characteristics of magnesium oxide nanoparticles as important parameters for the use in commercial applications, it is imperative that combustion route offers the best choice (Singanahally, T.A., Alexander S. M. Combustion synthesis and nanomaterials. *Current Opinion in Solid State and Materials Science*, doi:10.1016/j.cossms.2008.12.002). However, in order to commercially utilize nano magnesium oxide for drinking water applications e.g. fluoride removal, following improvements is necessary:

- Increasing the yield of nano magnesium oxide synthesis, without a significant decrease in the fluoride removal performance of the material. This invention application describes an inventive step to mix urea and glycine in a particular ratio, so as keep the performance intact while decreasing the production of voluminous gases and the subsequent material losses.

- Finding efficient fuel or a combination of fuels for the use in synthesis, which reduces the cost and yield without compromising the fluoride removal performance. This patent application describes an inventive step to mix urea and glycine in a particular ratio, so as keep the performance intact while decreasing the cost of production dramatically. The cost of urea in the Indian market is INR 24/kg whereas the cost of glycine is INR 400/kg.

- Develop a mechanism for pH control of the water purified with nano magnesium oxide. This patent application describes a novel method to control the pH through the use of manganese oxide coated alumina. This property of controlling the pH arises due to the inherent near neutral ZPC value of manganese oxide, though defluoridation and antibacterial properties of magnesium oxide are known for quite

long time. The main difficulties in using magnesium oxide in drinking water treatment was the alkaline pH (>10) of the treated water generated due to high pH_{zpc} (12.7) of magnesium oxide. As far drinking water norms are concerned, anything outside the range of pH 6.5 to 8.5 are not acceptable. So far no simple solution exists to tackle this problem in a user friendly manner. Here we have proposed a new simple and user friendly solution to this problem through the sorption of excess hydroxyl ion by manganese oxide coated alumina. In this supported manganese oxide was either prepared in nano or bulk form. In addition to pH control, the manganese oxide supported activated alumina could remove various heavy metals/cations such as arsenic, mercury, lead, manganese, etc. The adsorption of cations may give an additional advantage in controlling the pH by release of H^+ ions or by charge neutralization.

- Develop a suitable support for anchoring nano magnesium oxide so that aggregation of particles can be prevented. Since the conclusive results from nano-toxicity have still not emerged, it is extremely critical that only known bio-friendly materials are used as support media. This patent application describes a novel method to load magnesium oxide and magnesium oxide based compositions on bio-friendly supports such as cellulose.

A note on prior art for pH control:

A number of methods have been used for the control of alkaline pH. Traditionally, the methods have been based on commercially available ion-exchange resins such as Amberlite IRA series (Rohm & Haas Company), Tulsion CXO-9H (Thermax Ltd.). This approach is based on the concept of ion-exchange i.e. either substitution of specific anion in the resin with the free OH^- ion present in the water or substitution of H^+ ion in the resin with the cation in the water. Addition of various chemical reagents such as sodium bisulfate has been also utilized for the reduction of alkaline pH to permissible limits (pH value of 6.5 to 8.5). This approach is based on hydrolytic decomposition of the chemical reagent leading to consumption of free OH (pH control depends on the pKa of the chemical reagent). In an alternative approach, a combination of zirconium dioxide, ferric oxide, sulfur modified iron, titanium dioxide and alumina can be used for controlling the alkaline pH. This approach works on the principle of point of zero charge (PZC) for the oxide surface. At pH>PZC, oxide

surface is negatively charged due to release of H+ ions in the water whereas at pH<PZC, the surface is positively charge due to release of OH- ions in the water.

Prior art:

Bortun A. I., Bortun M. N., Fischer F. J., pH adjuster-based system for treating liquids, US Patent Number 7,169,297.

Here, we demonstrate a device for the removal of fluoride, alkalinity, hardness, suspended solids, heavy metals and TDS from contaminated drinking water. The sorbent/filter media used in this device consist of nano-magnesia, fine sand and manganese oxide-supported-activated alumina. Nano-magnesia is an efficient and cost-effective sorbent for the removal of fluoride. This sorbent can be effectively used in a stirred vessel batch reactor design, which is the first part of the device. Apart from removing fluoride, this sorbent was found to be effective in removing various cations such as Mn^{2+}, Fe^{3+}, Ca^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+} etc. The second part of the device consists of a dual media filter packed with sand and manganese oxide-supported-activated alumina. This part is mainly used to remove suspended solids and maintain pH as per the permissible limits. It has been observed that this fixed bed unit is also effective in removing various cations such as Ca^{2+}, Mg^{2+}, Mn^{2+} and Hg^{2+}, Pb^{2+} etc. The use of manganese oxide in removing heavy metals such as Pb, Cd, Cu, Ni, has been reported already (Han, R., Zou, W., Li, H., Li, Y., Shi, J. Copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite. *J. Hazard. Mater.,* **2006**, *137*, 934; Tripathy, S.S., Bersillon, J.L., Gopal, K. Adsorption of Cd2+ on hydrous manganese dioxide from aqueous solutions. *Desalination,* **2006** *194* (1-3), 11; Boonfueng. T., Axe, L., Xu, Y., Tyson, T.A. Nickel and lead sequestration in manganese oxide-coated montmorillonite. *J. Colloid. Interface. Sci.* **2006,** *303* (1), 87). It is also worth to note that the higher pH of the fluoride removed water, input of the second stage, helps in better sorption of heavy metals due to a negative surface charge (pH of zero point of charge of manganese oxide coated alumina is found to be 7.5±0.2.)

Hence, the first part of the device is to be used for removal of fluoride, and heavy metals. The second part of the device is to be used for the removal of heavy metals, suspended solids and pH control.

DESCRIPTION OF THE INVENTION:

The present invention describes a cost effective and high yield synthesis of extremely small particles of magnesium oxide and its application in drinking water purification. The invention also describes a treatment device consisting of,

(i) a batch reactor containing nano-magnesia based sorbents for defluoridation and removal of heavy metals from drinking water.

(ii) a dual filter media consisting of fine sand and magnesium oxide-supported-activated alumina for controlling pH, heavy metals, suspended solids and total dissolved solids.

Initially, various sorbents were tested for their fluoride removal potential in batch reactor at identical experimental condition. The aim of this study was to select the right sorbents that has high capacity and fast removal kinetics. In practical point of view, these two factors are very important because low capacity sorbents demands frequent replacement or regeneration, which ultimately generate huge amount of contaminated sludge of environmental concern. Similarly, low reaction rate demands large reactor volume which may not be feasible for all the end users. So an elaborate screening studies were carried out with various commercially viable sorbets to asses their fluoride uptake capacity. The sorbent materials and their fluoride removal potential are summarized in Table 1. Based on this study and literature data we have came to a conclusion that magnesium oxide, especially in its nano form, has huge potential and its fluoride uptake capacity is higher than any other sorbent reported so far in similar condition. However, the main stumbling block in using magnesia for field applications is the alkaline pH imparted by it to the treated water. Thus, our method involves an additional filter setup for maintaining the pH well within the drinking water norms. The filter device is also capable of removing heavy metals, suspended solids and TDS present in the water. We develop a device to remove all these parameters so as to produce palatable drinking water. In order to make the solid liquid separation process easy and to overcome engineering problem like poor hydraulic conductivity, nano-magnesia was also supported on suitable environmental friendly supports such as cellulose fibers and activated carbon.

The following examples are provided to illustrate the present invention of synthesizing nano-magnesia and supporting it on suitable supports for use in the

setup of drinking water purification device. The examples should not be construed as limiting the scope of the invention.

Sl.No	Adsorbent	Abbreviation	Fluoride removal capacity (mg/g)	Remarks
1	Activated Alumina -I	AA-I	3.87	SRL chemicals, India Grade: 1, neutral, Particle size =7-290 mesh ASTM
2	Activated Alumina -II	AA-II	3.1	Bee Chems, Kanpur, India; Particle size =0.5-1.5 mm
3	Nano Activated Alumina	NAA	11.69	Indigenously Prepared
4	Iron Oxide	IO	2.98	Bulk, Merk Private Limited, Mumbai, India
5	Nano Iron (III) Oxide	NIO	12.8	Indigenously Prepared
6	Magnesium Oxide	MOL	81.2	Light, Thomas Backer, India
7	Magnesium Oxide	MOC	9.95	Commercial, Supplier Unknown
8	Nano Magnesium Oxide	NMO	203	Indigenously Prepared
9	Nano Titanium Oxide	NTO	17.22	Indigenously Prepared
10	Nano Titanium Oxide	NTOD	4.84	Degussa, P25
11	Nano Zinc Oxide	NZO	7.3	Indigenously Prepared
12	Titanium Oxide	TOB	1.6	Bulk, Rankem Fine Chemicals, India
13	Nano Silica	NS	6.5	Bee Chems, Kanpur, India; Grade 30C
14	Manganese Dioxide	MDO	0.85	Bulk, Sdfine Chemicals, India
15	Montmorillonite	MMN	2.3	Aldrich Chemicals, India K10
16	Fe/Al/Ce mixed oxide	IACMO	21.55	Indigenously Prepared
17	Mg/Al/Ce mixed oxide	IACMO	49.6	Indigenously Prepared
18	Mg/Al mixed oxide	MAMO	74.97	Indigenously Prepared
19	Zero valent iron	ZVI	17.6	Indigenously Prepared

Example 1

This example describes a new combustion route to prepare nano-magnesium oxide that gives 100% yield with the formation of extremely small nanoparticles (3 -7 nm). This approach also offers extremely small nano magnesium oxide (3-7 nm) in relation to the existing combustion based synthesis methods. The synthesis is based on self propagated combustion of the magnesium nitrate trapped in the natural cellulose fibers or chitosan. Cellulose and chitosan are natural composites with complex hierarchical cellular structure. It is known that natural cellulose fibers have a porous structure and are composed of microfibrils of 10-30-nm width that are three-dimensionally connected with each other (Mark, H. F., Kroschwitz, J. I., Eds. Encyclopedia of Polymer Science and Technology; John Wiley & Sons: New York, 1985; Vol. 3, p 60). Recent investigation shows that the pores of cellulose fibers can act as nano reactors for the synthesis of various nanparticles (He, J., Kunitake, T. and Nakao, A. Facile in situ synthesis of noble metal nanoparticles in porous cellulose fibers. Chem. Mater. **2003**, 15, 4401). In this study, we have used cellulose or chitosan as a template for creating nano particles by infiltrating nitrate metal salt and subsequent calcinations in presence of fuels like urea and glycine. The infiltrated metal ions possibly bind to cellulose macromolecules via electrostatic interactions, because the electron-rich oxygen atoms of polar hydroxyl and ether groups of cellulose provides a negative charge to the cellulose fiber. Chitosan is a partially acetylated glucosamine polymer mainly results from deaceylation of chitin. This process produces a chain of amino groups along the chitosan structure and it is know to have good binding ability with various metals and makes chitosan acts a good metal holding template. Such template assisted synthesis helps in reducing the agglomeration of the particles during calcinations process and results in the formation well dispersed nanoparticles. The following section describes the details of the synthesis process.

In a typical synthesis process, magnesium nitrate, urea, glycine and cellulose fiber or chitosan (procured from local sources) support were initially mixed and kept overnight. The mixture was then heated in a hot plate under stirring for 20 min to evaporate the excess water and subsequently fired in a muffle furnace at 450 °C for 45 min. White aerogel kind of powder was formed in the reactor and no escape of the particles was found during the combustion process, and thus the recovery was almost 100%.

Considering the higher cost of the glycine and vigorous reaction between glycine and nitrate, glycine to magnesium nitrate ratio of 0.6 was used (compared to stoichiometric ratio of 1.1). This concentration was chosen because below this value, more precipitation of magnesium nitrate was observed during solvent evaporation process. And concentration higher than this resulted in flying of the nanomaterial from the reaction vessel. A cheaper fuel, such as urea was also added to the mixture to compensate for the fuel requirement so as to obtain enough heat during combustion. The ratio of urea was varied according to the following expression.

$$F / O = \left[\frac{G_{MF}}{N_{MF}} \times 0.9 \right] + \left[\frac{U_{MF}}{N_{MF}} \times 0.6 \right]$$

Where, G_{MF} is the molar fraction of glycine; U_{MF} is the molar fraction of urea, N_{MF} is the molar fraction of nitrate. The F/O ratio was taken as 0.75. The mixing of fibrous materials also helped in preventing the escape of the particle along with the evolved gases and controlling the particle size to a lower value (3-7 nm) compared to the earlier reported combustion method (12-23 nm) (Nagappa and Chandrappa, 2007). The cost estimate analysis also suggests that 20% reduction in the material cost is achieved when compared with the earlier reported combustion method. The nano magnesia prepared through cellulose fiber mediated reaction was named as NMF and sample prepared through chitosan mediated reaction was labeled as NMC.

Example 2

The raw materials cost are very important in any commercial materials synthesis process. Choosing a by product or waste material as a starting material for the synthesis is more sustainable because it considerably reduces the burden of waste disposal and adds value to the waste material. In India, large amount of rice husk, a byproduct of rice processing, comprises of 23% of the rice is generated each year. This rice husk possesses a significant waste disposal problem and has to be utilized effectively. It is known that rice husk contains about 75% volatile organic matter and remaining 25 % is ash out of which 85 – 90 % is amorphous silica.

In this example, a low cost combustion synthesis protocol was adopted for making nano-magnesia. We used rice husk as a fuel source to replace the conventional

fuels such as urea, glycine, alanine, hydrazide, etc. to initiate decomposition reaction of precursor magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$). The use of rice husk has dual implication: (i) the presence of compounds such as cellulose, hemi-cellulose, and lignin present in rice husk act as fuel and generate enough heat for combustion reaction (ii) The amorphous silica present in the rice husk act as a support for nano magnesia, which in turn reduces the agglomeration of the particle.

The typical synthesis involves soaking of rice husk (thoroughly pre-washed with water) in magnesium nitrate solution overnight. The excess magnesium nitrate solution was then separated from the solids. The magnesium nitrate impregnated rice husk was then fired at 600 ^{0}C for 2 h in a muffle furnace. A white fine powder was obtained at the end of the burning. The sample prepared through this route was named as SNM.

Example 3

Using pure metal oxides, especially in nano forms, as a filter media is not favorable for both economic reasons and unfavorable physical and chemical characteristics. However, nanoparticles immobilized on a suitable surface may provide an effective surface and may be a promising media for pollutants removal from aqueous medium. In this example, nano magnesia was supported on cellulose fiber. The synthesis involves soaking of 2 gm of cellulose fiber (pre-washed with water or ethanol to remove any impurities) in 1 - 2 %, 10 ml PVP/PVA in water or ethanol solution. After 3 h of soaking, solution was decanted and cut into small pieces. The as-prepared cellulose fiber was then mixed with nano magnesia in a mixer. Thorough mixing enabled a coating of nano-magneisa on cellulose fiber, which was subsequently dried at 100 ^{0}C. This nano-magneisa supported cellulose fiber material was named as CFNM.

Fluoride uptake capacities of sorbents were investigated in a batch reactor (250 mL polypropylene conical flask). The working volume of synthetic fluoride solution was taken as 100 mL and required quantity of nanoabsorbent was added. Immediately after the addition of sorbents, the flasks were kept for shaking at 120 ± 5 rpm in an orbital shaker (Riviera, India) at room temperature. Samples were withdrawn at predetermined time intervals and analyzed for residual fluoride concentrations using a calibrated specific fluoride combination electrode (Cole-Parmer Instruments Co,

U.S.A) connected to a multimeter/data acquisition system (Keithley, 2700, U.S.A). To each sample, ionic strength and pH adjusting buffer (TISAB III) was added in equal volumes (Chidambaram, S., Ramanathan, A.L., Vasudevan, S., Fluoride removal studies in water using natural materials: technical note. *Water SA.*, **2003**, *29(3)*, 339; Agarwal, M., Rai, K., Shrivastav, R., Dass, S., Deflouridation of water using amended clay. *J. Cleaner Prod.* **2003**, *11(4)*, 439). Effect of contact time and initial fluoride concentration on uptake was studied at two different fluoride concentrations of 5 and 10 mg/L. Equilibrium studies were performed at neutral pH (7 ± 0.1) and at room temperature by varying the concentrations of the fluoride solution over a wide range (5 - 200 mg/L). Effect of adsorbent dose was investigated at a pH of 7 ± 0.1 and fluoride concentration of 10 mg/L. Effect of pH on fluoride sorption was also carried out by varying the pH from 3 to 11. The pH of the samples was adjusted using dilute NaOH or HCl.

A treatment device consisting of a completely mixed batch reactor followed by a dual media filter; together meant to remove fluoride, heavy metals, suspended solids, and TDS as well as maintain pH well below the norms was made. The schematic of the device is shown in Fig.1. The treatment device consists of a 10 liter bucket reactor fitted with a tap at the outlet. The reactor is followed by a vertical fixed-bed filter unit consisting of a 20 cm fine sand layer cartridge at the top (0.25-0.44 mm) and a 20 cm manganese oxide-supported alumina cartridge at the bottom (0.3-1.3 mm). Manganese oxide supported activated alumina was prepared by calcining manganese acetate impregnated activated alumina (Grade: AD-101F, BET surface area = 242 m^2/g) at 400 ^{0}C using a procedure similar to that of Kapteijn and co-workers et al. [Kapteijn, F., van Langeveld, A. D., Moulijn, J. A., Andreini, A., Vuurman, M. A., Turek, A. M., Jehng, J-M., and Wachs, I. E., Alumina-Supported Manganese Oxide Catalysts:I. Characterization: Effect of Precursor and Loading. *J. Catal.*, **1994**, *150(1)*, 94]. A sieve on which a cotton cloth was placed to remove any suspended materials was also attached at the top of the fixed-bed filter unit. The reactor was operated in the batch mode. Required quantity of sorbent was added to the fluoride contaminated water under stirring conditions, which was carried out by means of an electric mixing paddle and the stirring was continued for 60 min followed by 30 min settling. The supernatant water was then passed through the cotton cloth into the fixed-bed filter unit, where it percolates through sand and

manganese oxide supported activated alumina bed at a flow rate of 3.78 m^3/m^2.h (empty bed contact time = 3.2 min). The sand filter bed acts as an extra safety device collecting any suspended matter, which might escape through the cloth filter. The sand bed also provides additional safety for bacterial removal. The prime purpose of manganese oxide-coated alumina bed was to bring down the alkaline pH imparted by magnesia treated water to permissible levels. It may also provide additional safety against bacteria due to the oxidizing capacity of manganese oxide. The mixing may be carried out manually in areas where electricity or cost or availability is a concern.

The identification of the phase(s) of the as-prepared sample and fluoride reacted sample was carried out by X-ray powder diffraction (Bruker AXS, D8 Discover, U.S.A) using Cu-Kα radiation at λ = 1.5418 Å. For this, 50 mg/L of sorbents were reacted with 1000 mg/L of fluoride. The reacted sample was casted on glass plate and dried in oven at 100 ^{0}C for 1 h. The un-reacted sorbents were also casted on glass plate to record the X-ray pattern. 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 (EDX) (FEI Quanta 200). For this, the sample prepared as mentioned above was re-suspended in acetonitrile by means of ultra-sonication for 10 min 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.

DESCRIPTION WITH REFERENCE TO DRAWINGS AND TABULATED DATA:

The treatment device used in this system consists of a 10 L batch reactor made of plastic followed by a glass column (inner diameter = 18 mm, Length = 50 mm). The sand and manganese oxide-supported-activated alumina was filled in the column. The depth of each layer was 20 cm. The flow rate through the column (3.78 m^3/m^2.h) was controlled by a tap provided at the outlet of the batch reactor and another one at the outlet of the column.

Figure 1. Schematic representation of the setup used to study the fluoride uptake and control the alkaline pH of the fluoride treated water.

In this experiments, a 10 liter capacity batch reactor followed by a post-treatment unit, as described in the experimental section (see Figure 1 for a schematic) was used to treat the fluoride contaminated water. The study was carried out with a field water sample collected from Kotlapalli Panchayath of Puttaparthi, Anantapur district, Andhra Pradesh, India – a fluoride affected area. The required quantity of magnesia nano-particle was added to the raw water and stirred by means of a paddle mixer. The mixing may also be carried out manually.

Table 2. The water quality parameters of the raw water (collected from Kotlapalli Panchayath of Puttaparthi, Anantapur district, Andhra Pradesh, India) are listed. The water quality characteristics of treated water samples tapped from sampling port 1 and 2 are also given.

Table 2

Parameters	Influent water (Kotlapalli Panchayath Puttaparthi, Andhra Pradesh, India)	Effluent water	
		Sampling port 1	Sampling port 2
pH @ 25 ^{0}C	8.01	10.1	7.79
Fluoride	2.34	0.38	<0.1
Total Alkalinity (as $CaCO_3$)	217	326	61
Total Hardness (as $CaCO_3$)	178	303	28
Conductivity @ 25 ^{0}C	565 μmhos cm^{-1}	658 μmhos cm^{-1}	216 μmhos cm^{-1}
Organic carbon	< 0.5	<0.5	<0.5
Total Dissolved Solids	384	412	142
Calcium (as Ca^{2+})	36	8	1.6
Magnesium (as Mg^{2+})	22	69	5.9
Sulphate (as SO_4^{2-})	25	14	4.7
Chloride (as Cl^{-1})	13	13	11.6
Phosphate (as PO_4^{-3})	<0.02	<0.02	<0.02
Iron (as Fe^{3+})	<0.001	<0.001	<0.001
Nitrate (as NO_3^-)	38.9	44.5	37.4
Turbidity (as NTU)	0.2 NTU	-	0.1 NTU
Silica (as SiO_2)	47.4	0.69	0.03
Manganese	<0.001	<0.001	<0.03

From the table it is clear that both fluoride and alkaline pH of the fluoride treated water meet the safe drinking water standards. It is also clear that the TDS (Total Dissolved Solids) level of the effluent water was considerably reduced and the treatment process did not add any unwanted chemicals into the effluent.

Example 1

CHARACTERIZATION OF THE SYSTEM

The system was characterized with various techniques such as powder X-ray diffraction (XRD), Scanning Electron Microscope and X-ray photoelectron spectroscopy.

Figure 2. The XRD patterns of magnesia nano-particles (NMF) and fluoride reacted magnesia nanoparticles.

The magnesia nano-particles showed peaks corresponding to (111), (200), (220) and (222) planes, indicating the presence of cubic MgO and the peaks can be assigned to a pure phase of periclase MgO (JCPDS: 71-1176). The mean crystallite size calculated from the Scherrer formula shows that nanocrystals are of an average size of 6.9 nm. Fluoride reacted MgO samples showed diffraction patterns corresponding to brucite.

Figure 3. SEM image NMF and fluoride treated NMF.

SEM images show that (Figure 3a) as-synthesized magnesia nanoparticles are porous. The porous nature of the material may be attributed to sudden escape of the combustion gases. SEM micrographs of magnesia nanoparticles and fluoride reacted magnesia nanoparticles (Figure 3b) have shown clear difference in the surface morphologies. After reaction with fluoride, porous nature of nano MgO had been destroyed and a flower like structure was formed, this may be attributed to the hydration and subsequent formation of $Mg(OH)_2$.

Figure 4. The HRTEM micrographs and EDX spectrum of NMF.

From Figure 4a we can see that the size of the most particles is ≤ 5 nm, which is in agreement with the mean crystallite size calculated from the Scherrer formula. The particle shape was not specific. Figure 4b shows the expanded image of an as-synthesized magnesia nanoparticle. A lattice image was clearly observed and the

lattice spacing is matching with the (200) plane of periclase MgO. The EDX spectrum of MgO nanoparticles showed in Fig. 4c further confirms the formation of MgO and its phase purity.

Figure 5. Effect of pH and other co-existing ions on fluoride removal by nano magnesia.

Influence of pH on fluoride sorption by magnesia nano particles was investigated and the data are shown in Figure 5a. The results reveal that fluoride sorption by magnesia nano-particles is less sensitive to pH variations. Hence, this material can be employed in the filed irrespective of the initial pH of input water without losing its sorption capacity.

Figures 5b and 5c show the effect of various co-existing anions and cations on fluoride removal by magnesia nano-particles, respectively. The results show that most of the ions have little effect on fluoride removal by magnesia nano-particles, indicating the selective nature of nano-magnesia towards fluoride.

Figure 6. Comparison of various isotherm models for fluoride sorption onto NMF

Fig. 6 shows the isotherm plots obtained for the sorption of fluoride by NMF. The estimated isotherm parameters from these model fits are given in Table 3. The experimental data fitted relatively well with Freundlich model, which is evident from the low RMSE and χ^2 values. The predicted fluoride sorption adsorption capacity of NM is 20.66 (mg/g) (mg/L)$^{-1/n}$.

Example 2

Figure 7. XRD pattern of SMN and fluoride reacted SMN.

The SMN showed peaks corresponding to (111), (200), (220) and (222) planes, indicating the presence of cubic MgO and the peaks can be assigned to a pure phase of periclase MgO (JCPDS: 71-1176).

Figure 8. SEM image, elemental map and EDAX spectrum SNM and fluoride treated SNM.

Figure 8a and 8b show the SEM images of as synthesized SNM and fluoride reacted SNM, respectively. EDX analysis of SNM shows the presence of principal elements Mg, O and Si, which indirectly show the presence of MgO and SiO_2 in SNM sample

(Figure 8c). The EDX spectrum of fluoride reacted SNM clearly shows the presence of fluoride along with the principal elements Mg, O and Si (Figure 8d). Elemental maps of SNM and fluoride reacted SNM-particles are shown in Figure 8e and 8f, respectively. From these analyses, the existence of sorbed fluoride on the sample is very evident.

Figure 9. HRTEM micrographs of SNM

Figure 9a shows the presence of small nanoparticles on silica surface. The average size of the particles is less than 8nm. Figure 9b shows the lattice image of such magnified particle and the lattice spacing is matching with the (200) plane of periclase MgO. Figure 9c shows the HRTEM image of fluoride reacted SNM. A lattice-resolved HRTEM image of fluoride reacted SNM is shown in Figure 9d.

Figure 10. Effect of pH and adsorption capacity.

pH of the feed water is one of the important factors which affect the fluoride sorption capacity of any sorbents. Influence of pH on fluoride sorption by SNM particles shows no significant effect on its sorption capacity (Fig.10a), indicating the effective use of this material in filed situations irrespective of the initial pH of feed water. . Figure 10b show the isotherm plots for the removal of fluoride by SNM. The maximum fluoride uptake capacity of was found to be 49.09 mg/g.

Example 3

Figure 11. SEM micrographs of cellulose fiber and magnesia supported cellulose fiber CFNM.

Figure 11a and b show the SEM images of uncoated and magnesia coated cellulose fiber, respectively.

A clear difference in surface morphologies was observed between magnesia coated and uncoated cellulose fiber. The magnesia coated cellulose fiber shows the existence of small particles on the surface of the fiber whereas the uncoated fiber shows a smooth surface (figures 11a and 11b). Elemental map and EDX analysis of CFNM shows the presence of principal elements Mg, O and C, which indirectly show the presence of MgO on the cellulose fiber (Figure 11c). The EDX spectrum of fluoride reacted CFNM clearly shows the presence of fluoride along with the other principal elements (figure 11d). The existence of sorbed fluoride on the sample is very evident from these data.

pH control of output water

In field conditions, the major limitation of using MgO as sorbent is the high alkaline pH (>10) of the treated water. Hence, the treated water pH must maintained between 6.5 – 8.5. In this study, a user friendly method was proposed by making use of the OH⁻ ion scavenging capacity of metal oxide sorbents. A double metal oxide media, namely, manganese oxide coated alumina was used as the sorbent in this study. Manganese oxide coating on activated alumina surface was done by pore volume impregnation of alumina with potassium permanganate and its subsequent reduction with ethanol. The pH control of fluoride treated water was carried out in a glass column packed with manganese oxide coated alumina at a flow rate of 3.7 ± 0.2 $m^3/m^2.h$. The characteristics of influent and effluent water are listed in Table 2. The effluent solution was collected at various intervals. The reuse potentials of this sorbents were also tested by regenerating the already exhausted sorbents with H_2SO_4 (0.25 N).

The results of this study are showed in Fig. 12. The results revealed that manganese oxide coated alumina could reduce the pH of the fluoride treated water to an acceptable limit. The regeneration capacity of the sorbents was also found to be excellent and no significant reduction in performance was observed up to 2 cycles of adsorption process, which makes the sorbent more economical and viable option for field conditions.

WE CLAIM:

1. A self-sustained combustion synthesis method for preparing metal oxide nanoparticles, the said method comprises;

   a. mixing a metal precursor salt in a metal holding template having pore-containing microfibrils with a fuel mixture of urea and glycine in the ratio of 3:4;

   b. the obtained mixture from step a) is kept overnight and heated in a hot plate under stirring for 20 min to evaporate excess water and fired in a muffle furnace at 450°C for 45 min resulting in the formation of fine white powder;

   wherein the metal precursor salt trapped in metal holding template in the presence of fuels urea and glycine reduces the agglomeration of the particles during calcinations process resulting in the formation of well dispersed metal oxide nanoparticles.

2. The method as claimed in claim 1, wherein the size of the prepared metal oxide nanoparticles is preferably in the range of 3-7 nm.

3. The method as claimed in claim 1, wherein the fuel is a mixture of urea and glycine with the molar ratio of glycine to metal precursor salt is more than 0.25 and less than 1.

4. The method as claimed in claim 1, wherein the fuel is rice husk.

5. The method as claimed in claim 1, wherein the metal holding template is natural source selected from the group includes cellulose fiber, chitosan, silk, linen, jute, cotton, lignin, ramie, hemp, wood, bamboo, saw wood powder or a combination thereof.

6. The method as claimed in claim 5, wherein cellulose includes derivatives of cellulose, comprising cellulose acetate, carboxymethyl cellulose or surface functionalized cellulose.

7. The method as claimed in claim 1, wherein the metal is magnesium, calcium, aluminum, zinc, manganese, iron, titanium, zirconium, lanthanum, silicon or a combination thereof.

8. The method as claimed in claim 1, wherein the salt is a nitrate salt, chloride salt, acetate salt or a combination thereof.

9. The method as claimed in claim 1, wherein the metal precursor salt is magnesium nitrate.

10. The method as claimed in claim 1, wherein the metal holding matrix holds the metal precursor and the metal particles are formed inside the pores of the metal holding matrix.

11. The method as claimed in claim 1, wherein the metal holding matrix prevents aggregation of the nanoparticles.

12. The method as claimed in claim 1, wherein the metal oxide nanoparticles removes fluoride from water.

13. A water filtering device for removing plurality of contaminants comprises

   a. a batch reactor unit comprising magnesium oxide nanoparticles, and

b. a dual media fixed bed unit comprising a sand bed and a manganese oxide supported activated alumina

wherein the fluoride particles are adsorbed by the magnesium oxide nanoparticles in the batch reactor unit and pH, heavy metals, suspended solids and TDS are controlled by the manganese oxide supported activated alumina unit.

14. The device as claimed in claim 13, wherein the manganese oxide supported activated alumina is loaded on a metal holding template.

15. The device as claimed in claim 14, wherein the metal holding template is a natural cellulose fiber, chitosan or a combination thereof.

Dated at Chennai this June 04, 2019

Signature:

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

REMOVAL OF FLUORIDE, ALKALINITY, HEAVY METALS AND SUSPENDED SOLIDS SIMULTANEOUSLY - ADSORBENT SYNTHESIS, ADSORBENT COMPOSITION AND A DEVICE FOR AFFORDABLE DRINKING WATER

ABSTRACT

The present invention reveals a novel natural polymer mediated self-sustained combustion synthesis method for preparing extremely fine nano-magnesia and its application in drinking water purification. This invention also related to the development of a purification device for drinking water application. The device consists of a two stage filtration system to remove fluoride, alkalinity, heavy metals from drinking water and control the alkaline pH of the fluoride removed water. The filter system comprises of a batch mixing unit followed by a fixed bed unit. The treatment method involves mixing fluoride contaminated water with nano-magnesia in a batch reactor followed by settling of fluoride sorbed nano-magnesia. The second part of the system consists of a sand bed followed by manganese oxide-coated activated alumina (supported manganese oxide was prepared either in bulk or nano form) fixed bed through which the water from the first stage flows and controls the suspended solids and pH of the water within the limit. This device is also capable of removing heavy metals and bacteria as well.

Mixing unit

Bucket reactor

Sampling port 1

Cloth filter

Sand

Manganese oxide
supported
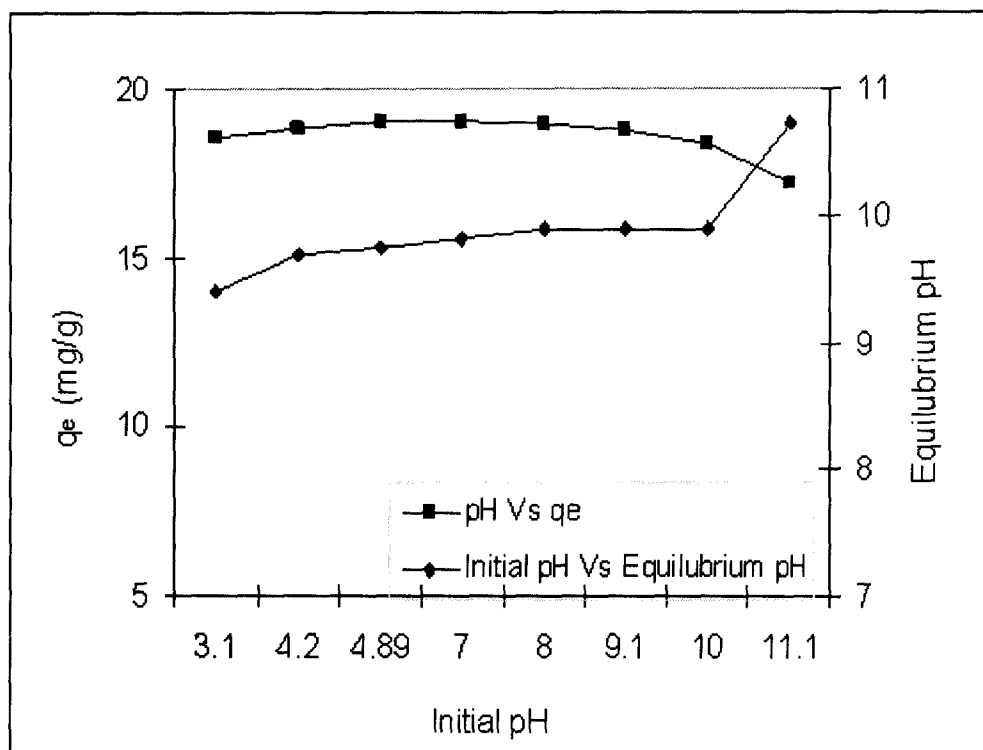activated alumina

Sampling port 2
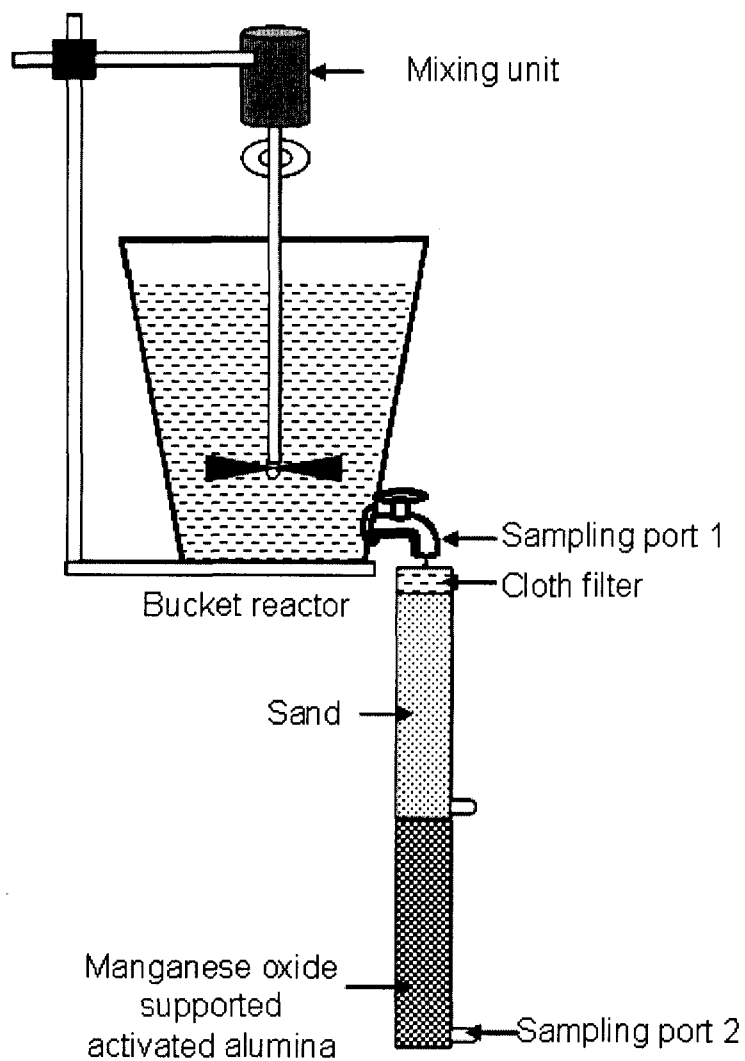
FIG 1

For **INDIAN INSTITUTE OF TECHNOLOGY,**
By its attorney,
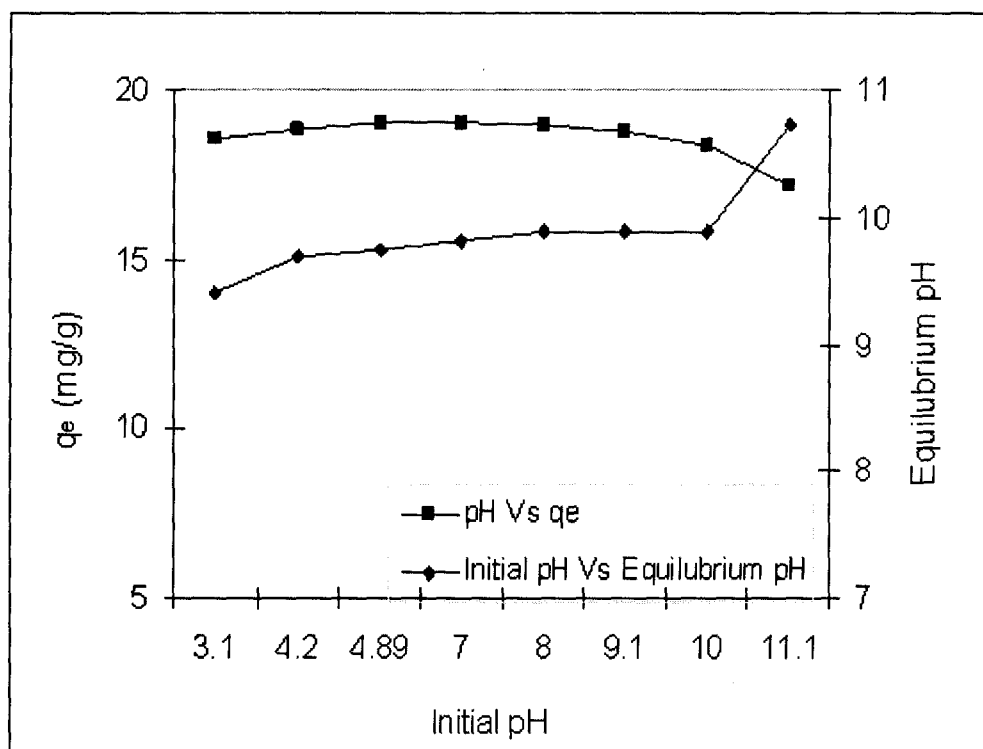
(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)
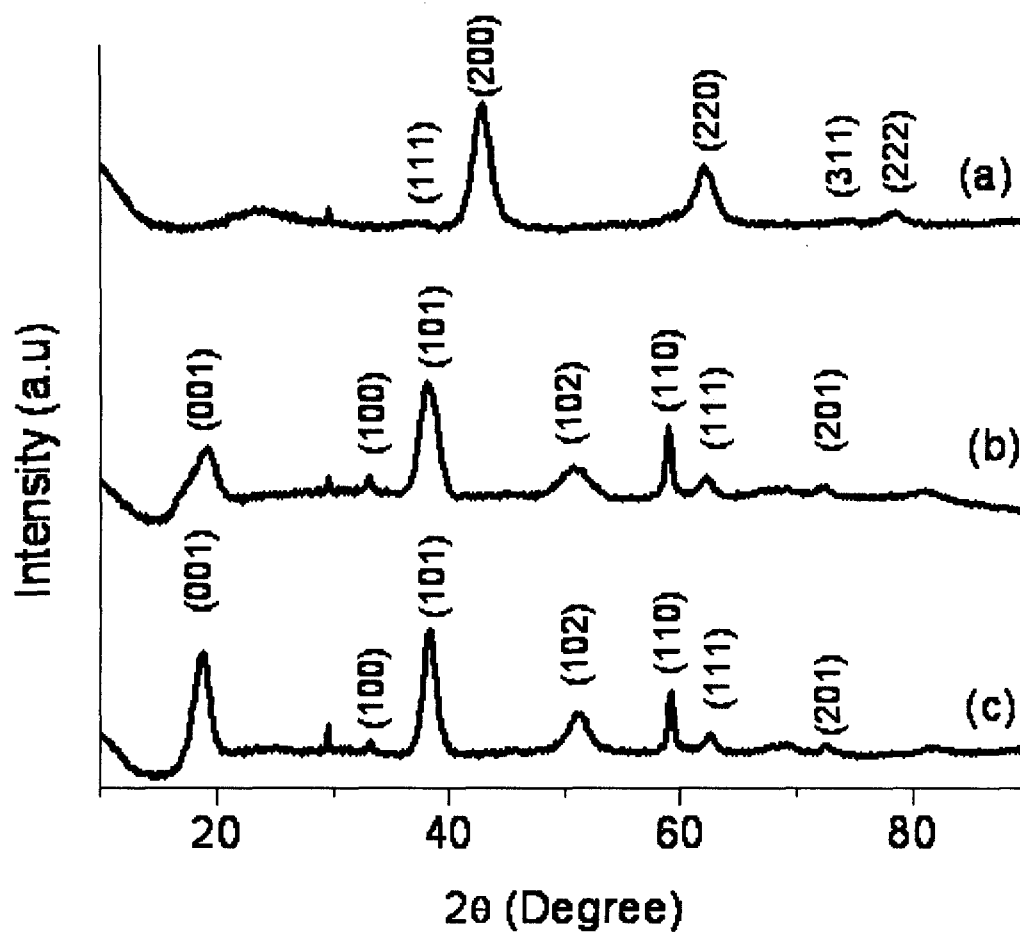
FIG 2

For **INDIAN INSTITUTE OF TECHNOLOGY**,
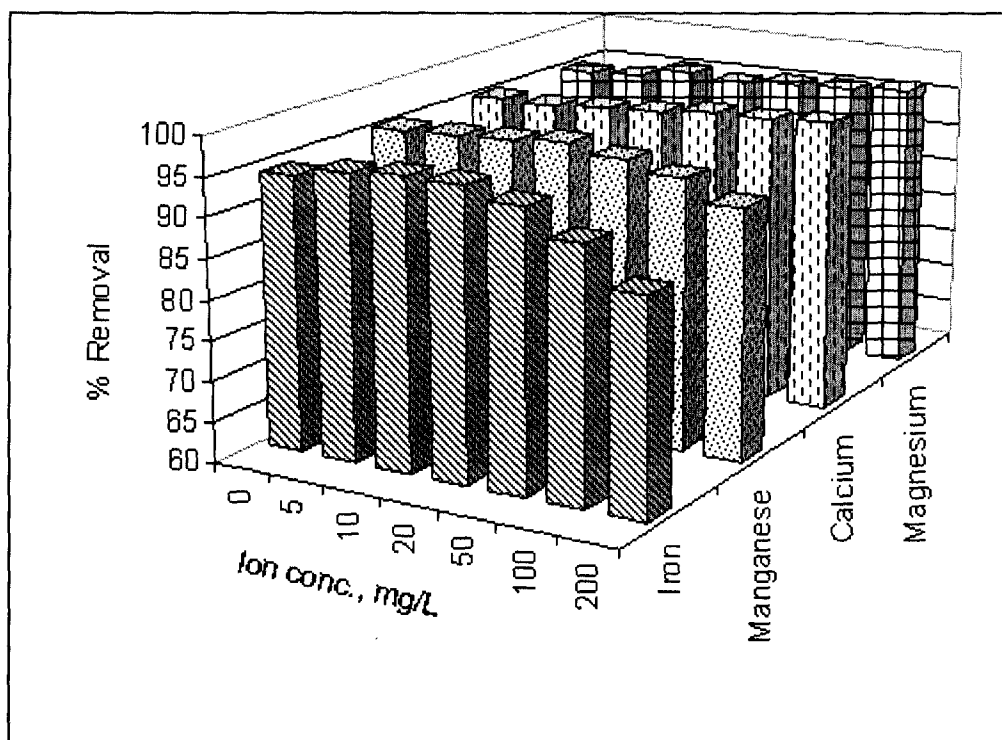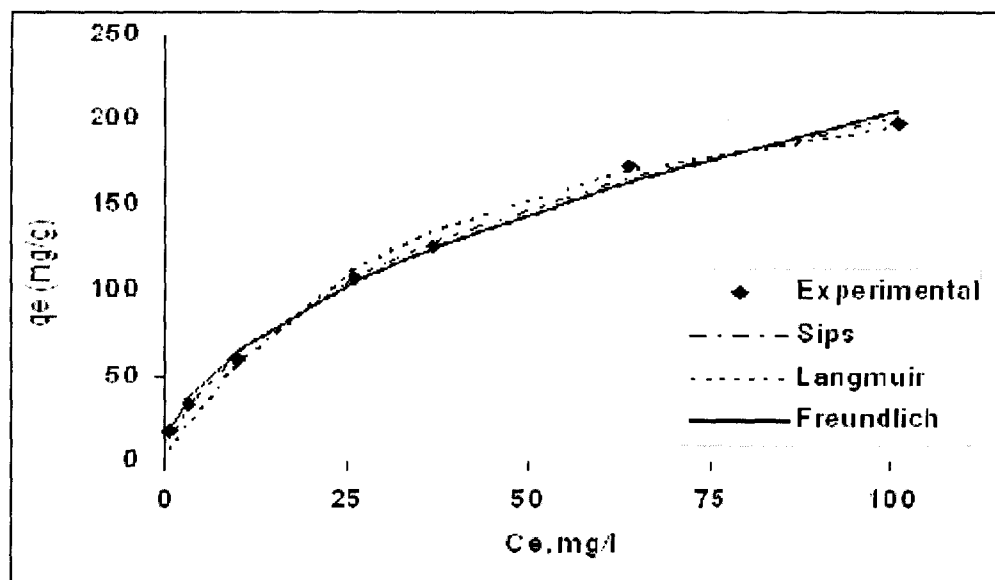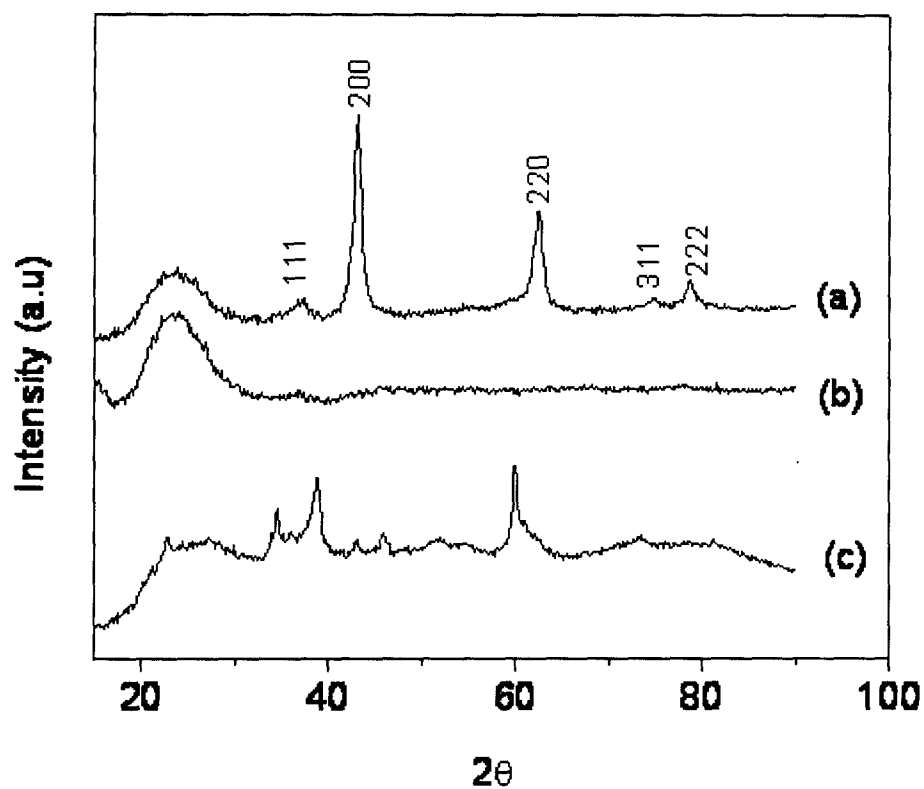By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)
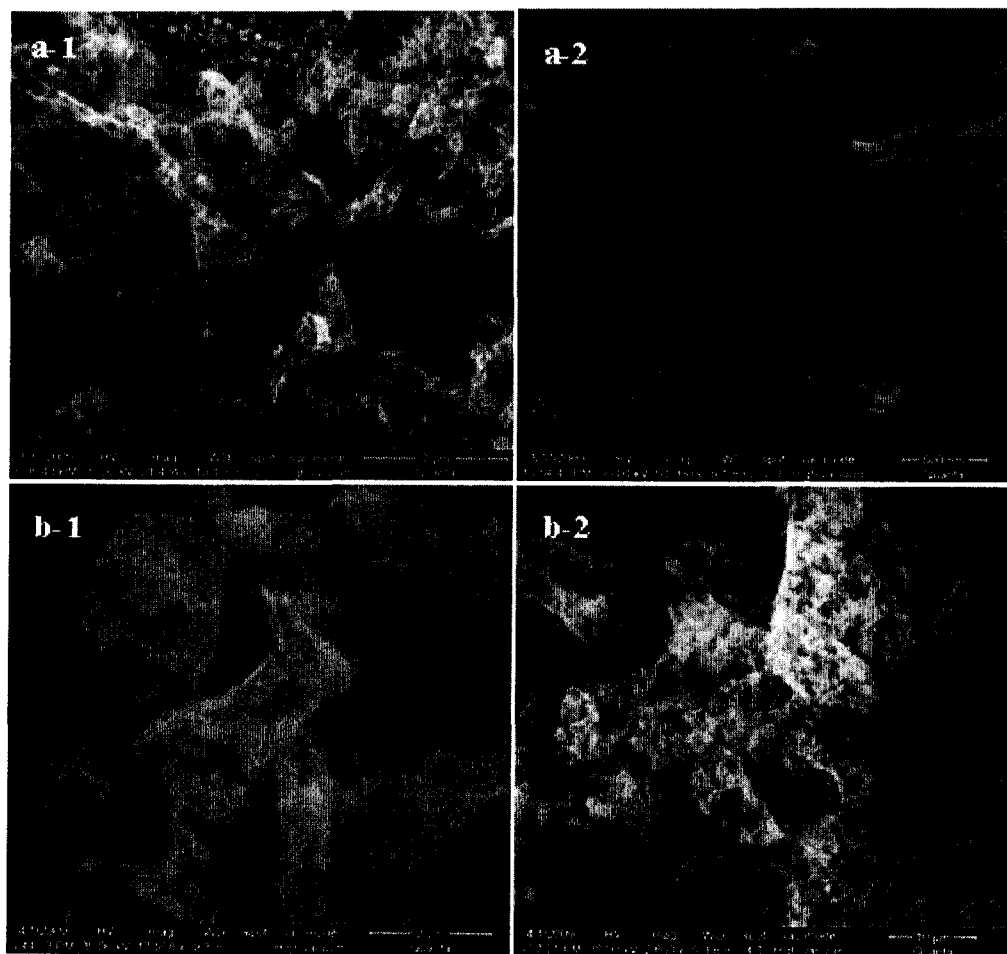
FIG 3

For **INDIAN INSTITUTE OF TECHNOLOGY**,
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

Element	Weight%	Atomic%
C K	3.4	5.5
O K	39.5	48.5
Mg K	57.0	45.9
Totals	100.0	100.0
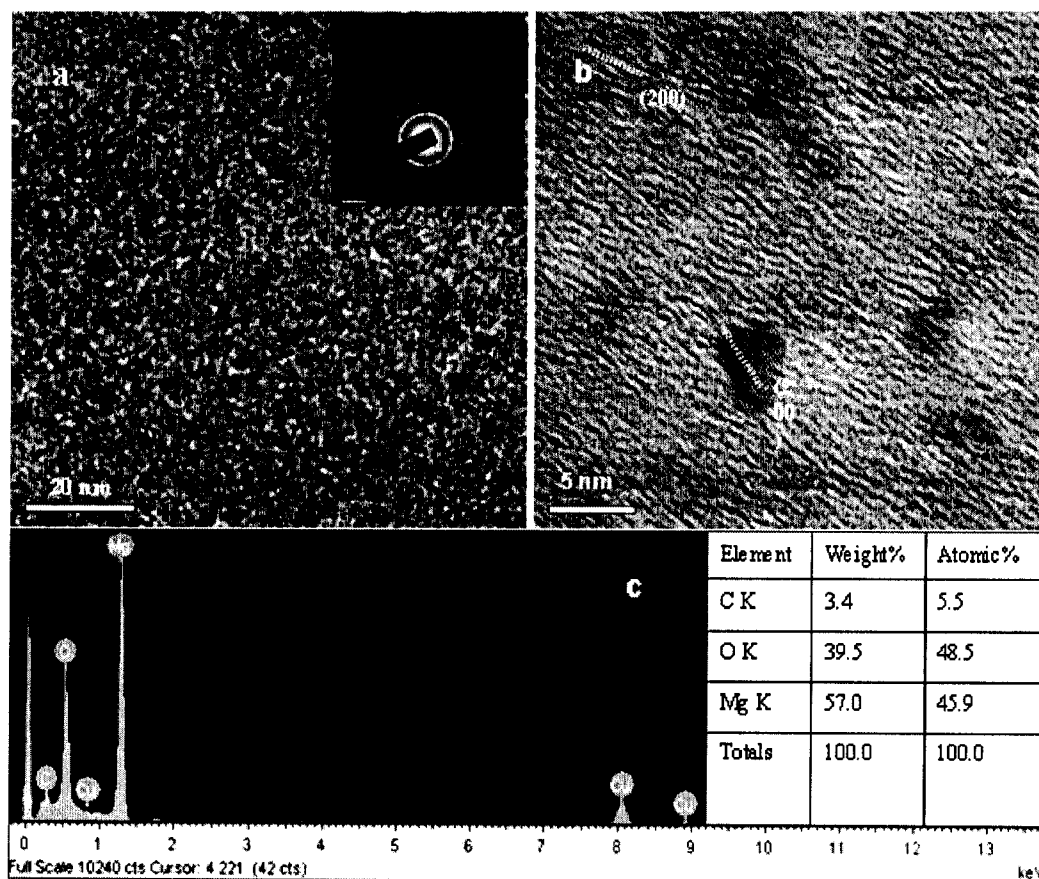
FIG 4

For **INDIAN INSTITUTE OF TECHNOLOGY**,
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

FIG 5a

For **INDIAN INSTITUTE OF TECHNOLOGY**,
By its attorney,

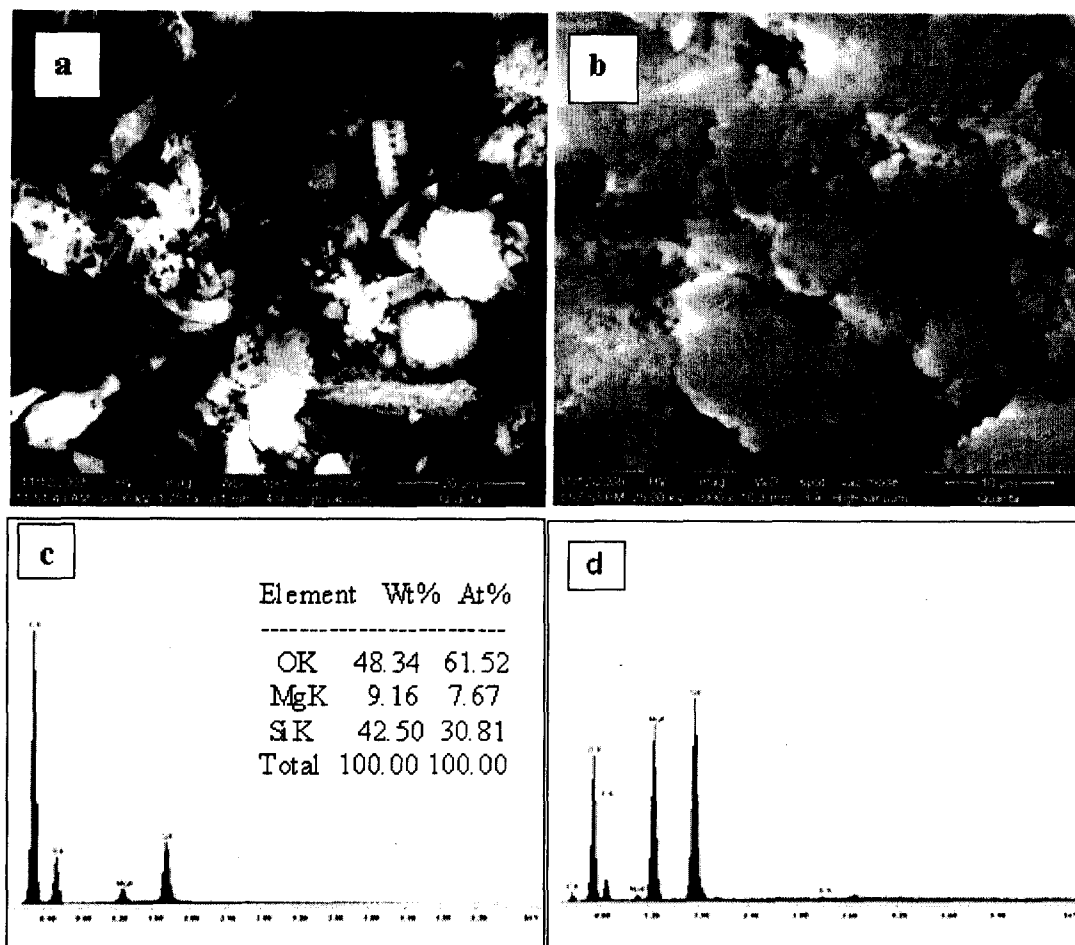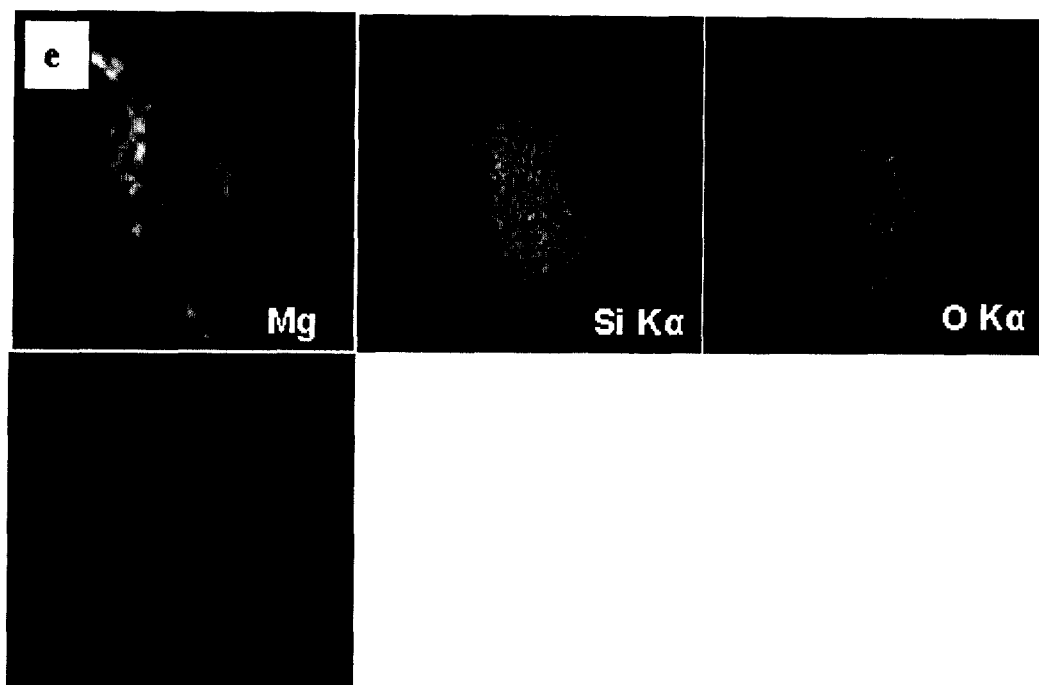(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

FIG 5b

For **INDIAN INSTITUTE OF TECHNOLOGY**,
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

FIG 5c

For **INDIAN INSTITUTE OF TECHNOLOGY**,
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

| Isotherm models	Freundlich	Langmuir	Sips
Isotherm parameters	$K_F = 20.66$	$q_L = 267.82$	$K_s = 0.005$
	$n = 2.01$	$b = 0.027$	$q_s = 515.21$
	-	-	$m_s = 0.65$
RMSE	5.16	7.37	3.68
X^2	1.67	34.6	2.22

FIG 6

For **INDIAN INSTITUTE OF TECHNOLOGY**,
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

FIG 7

For **INDIAN INSTITUTE OF TECHNOLOGY,**
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

Element	Wt%	At%
OK	48.34	61.52
MgK	9.16	7.67
SiK	42.50	30.81
Total	100.00	100.00

FIG 8(a-d)

For **INDIAN INSTITUTE OF TECHNOLOGY**,

By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

FIG 8 e

For **INDIAN INSTITUTE OF TECHNOLOGY**,
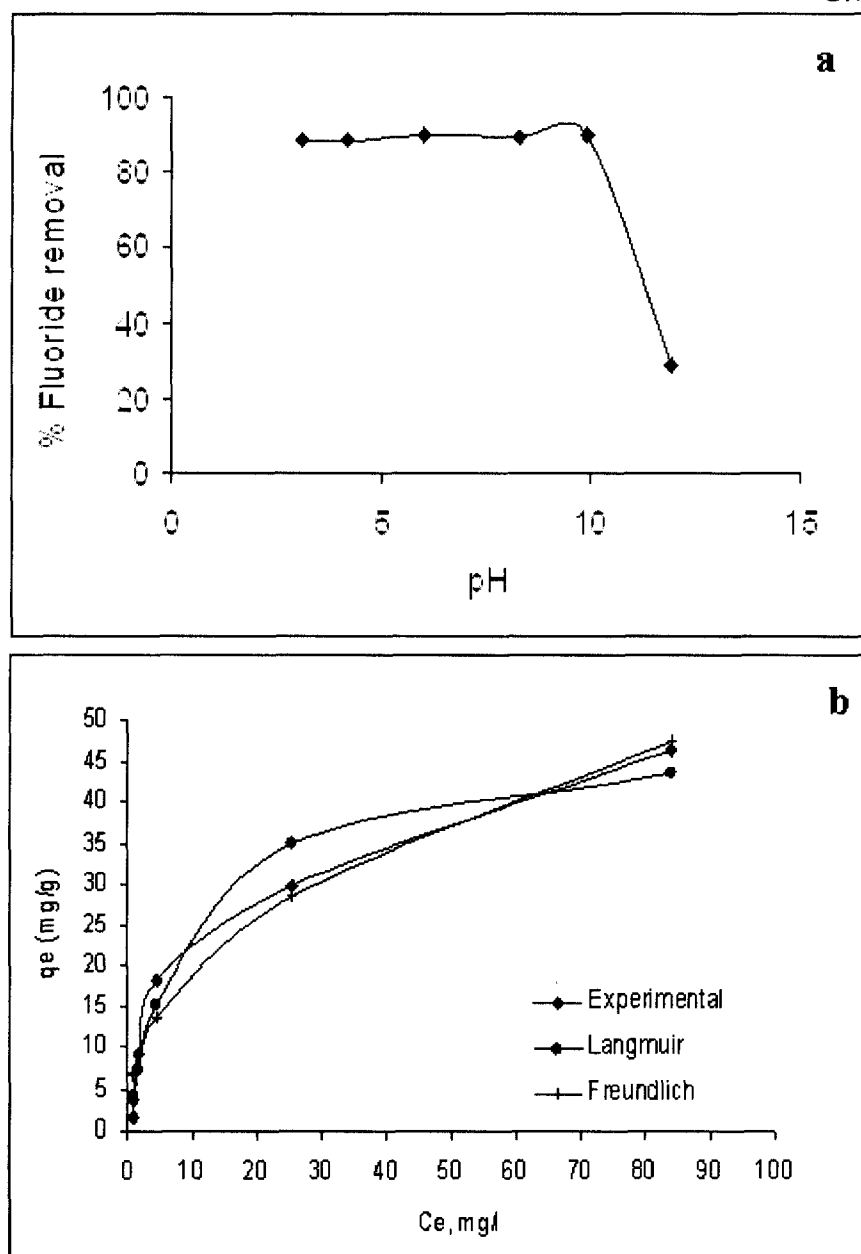By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)
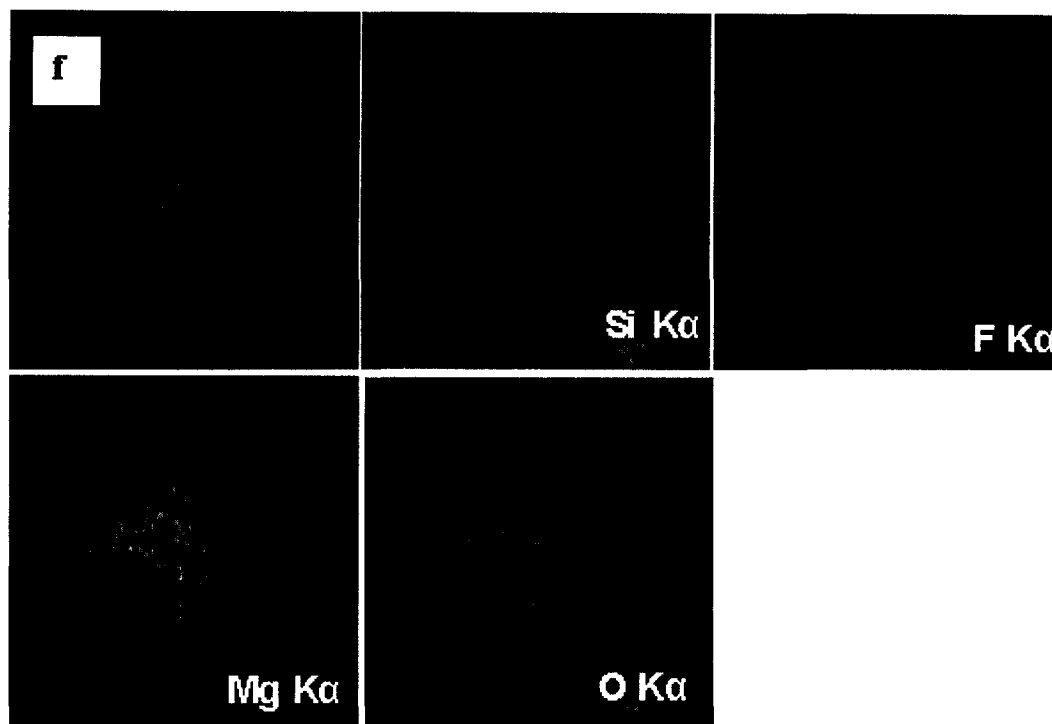
FIG 8 f

For **INDIAN INSTITUTE OF TECHNOLOGY**,
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(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)
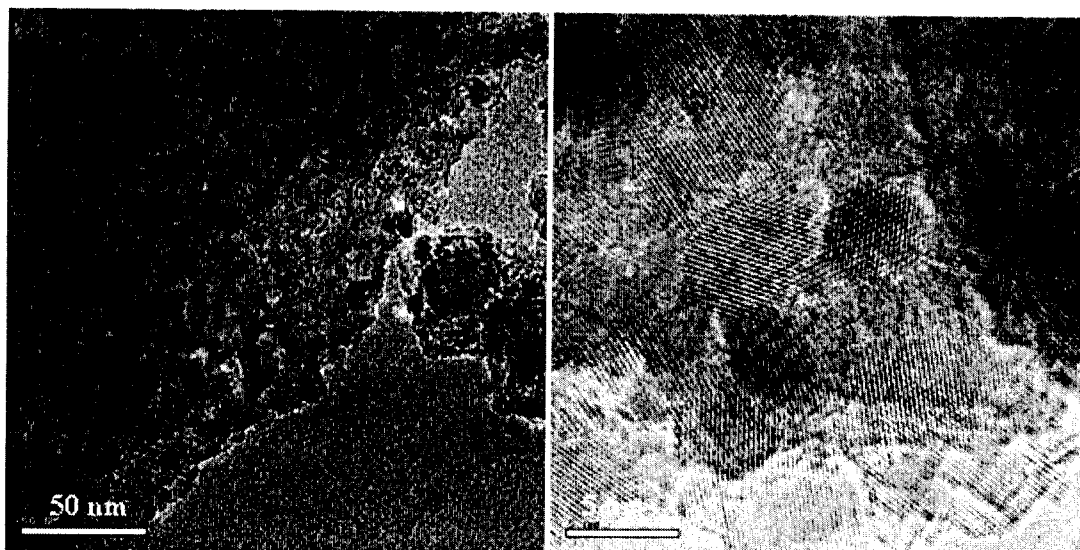
FIG 9(a, b)

For **INDIAN INSTITUTE OF TECHNOLOGY**,
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

FIG 10 (a,b)

For **INDIAN INSTITUTE OF TECHNOLOGY**,
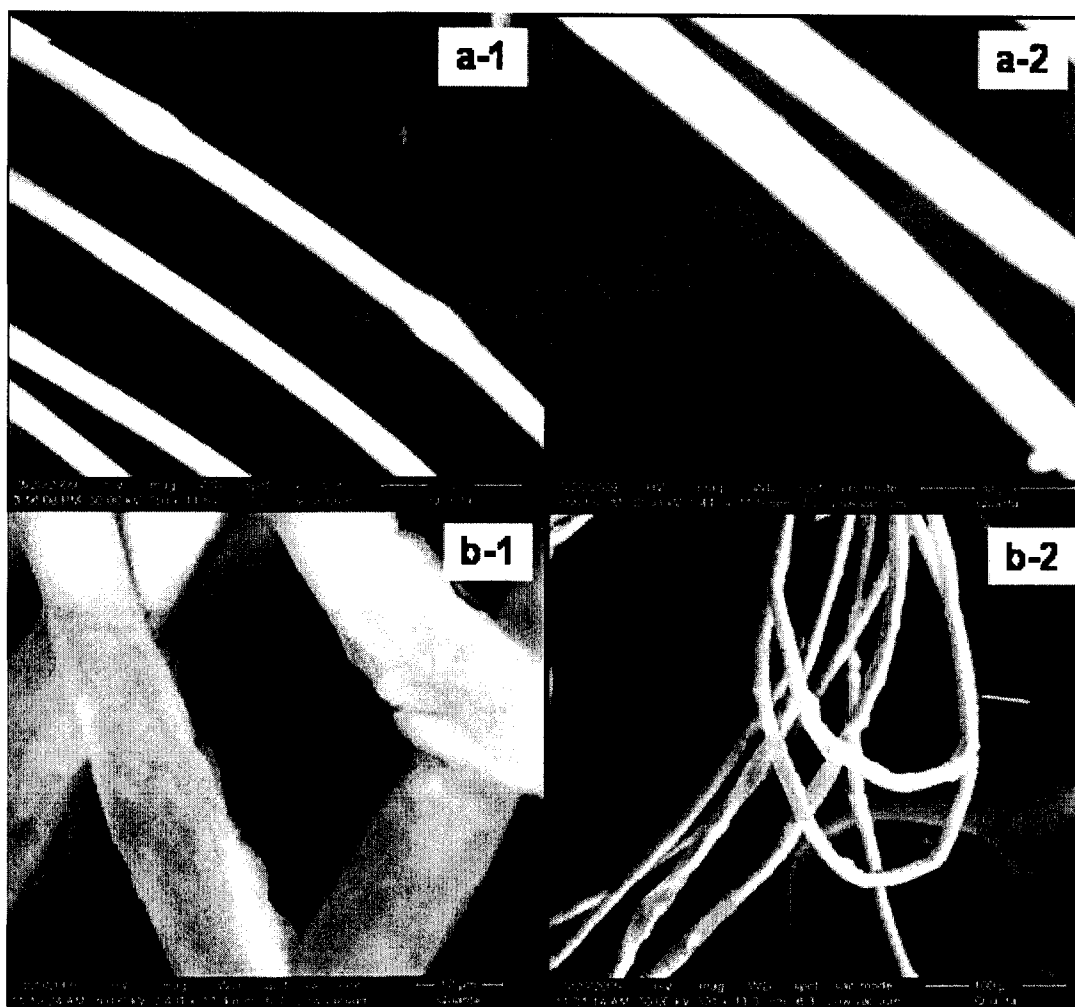By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

FIG 11(a-1, a-2, b-1, b-2)

For **INDIAN INSTITUTE OF TECHNOLOGY**,
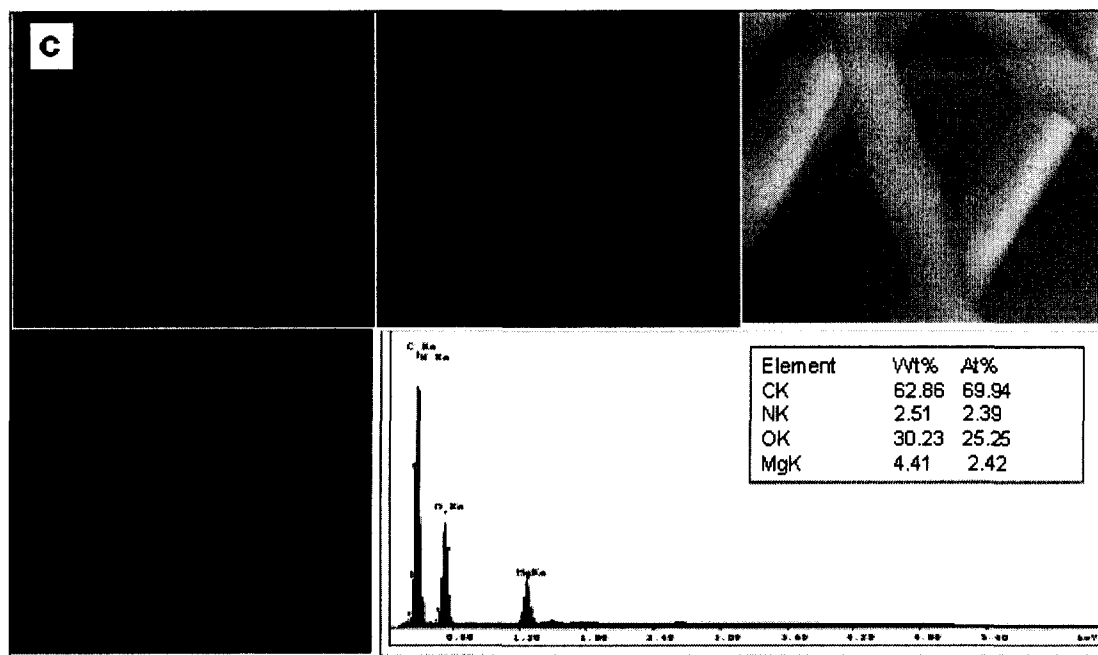By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

Element	Wt%	At%
CK	62.86	69.94
NK	2.51	2.39
OK	30.23	25.25
MgK	4.41	2.42

FIG 11(c)

For **INDIAN INSTITUTE OF TECHNOLOGY,**
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
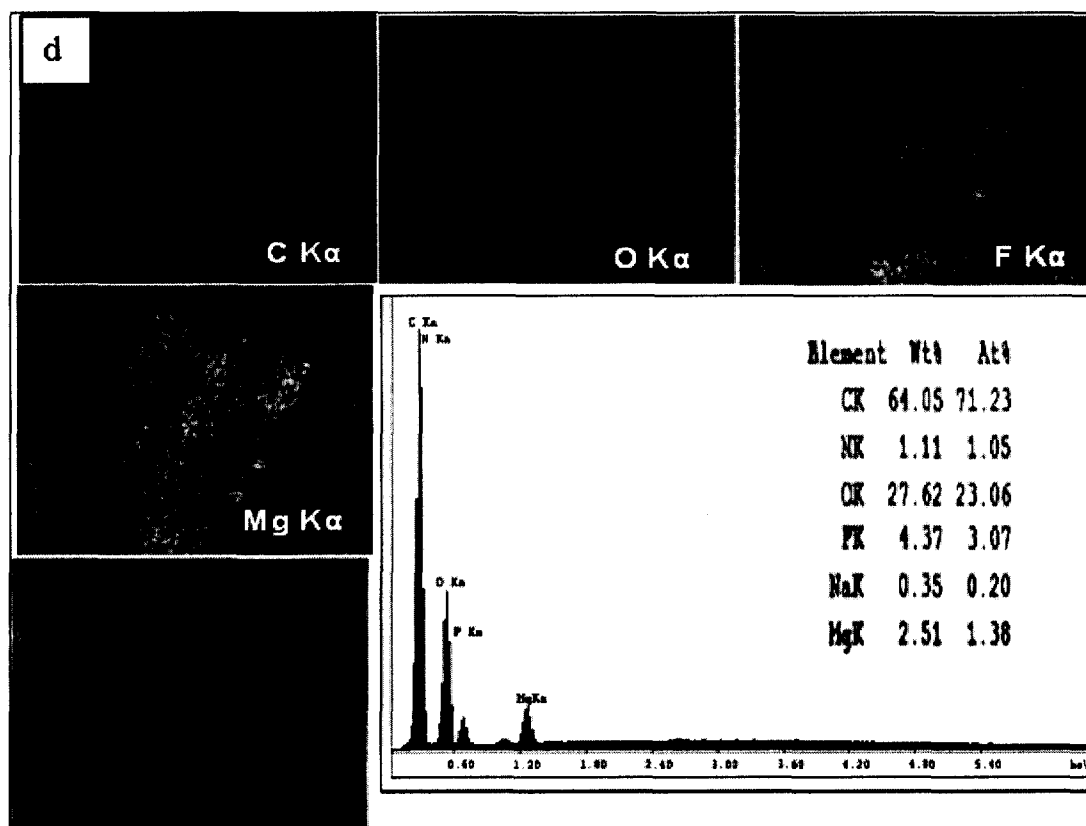**(BRINDA MOHAN)**

FIG 11(d)

For **INDIAN INSTITUTE OF TECHNOLOGY,**
By its attorney,

(ARUNACHALAM APPAJI MOHAN)
(BRINDA MOHAN)

FIG 12

For **INDIAN INSTITUTE OF TECHNOLOGY**,
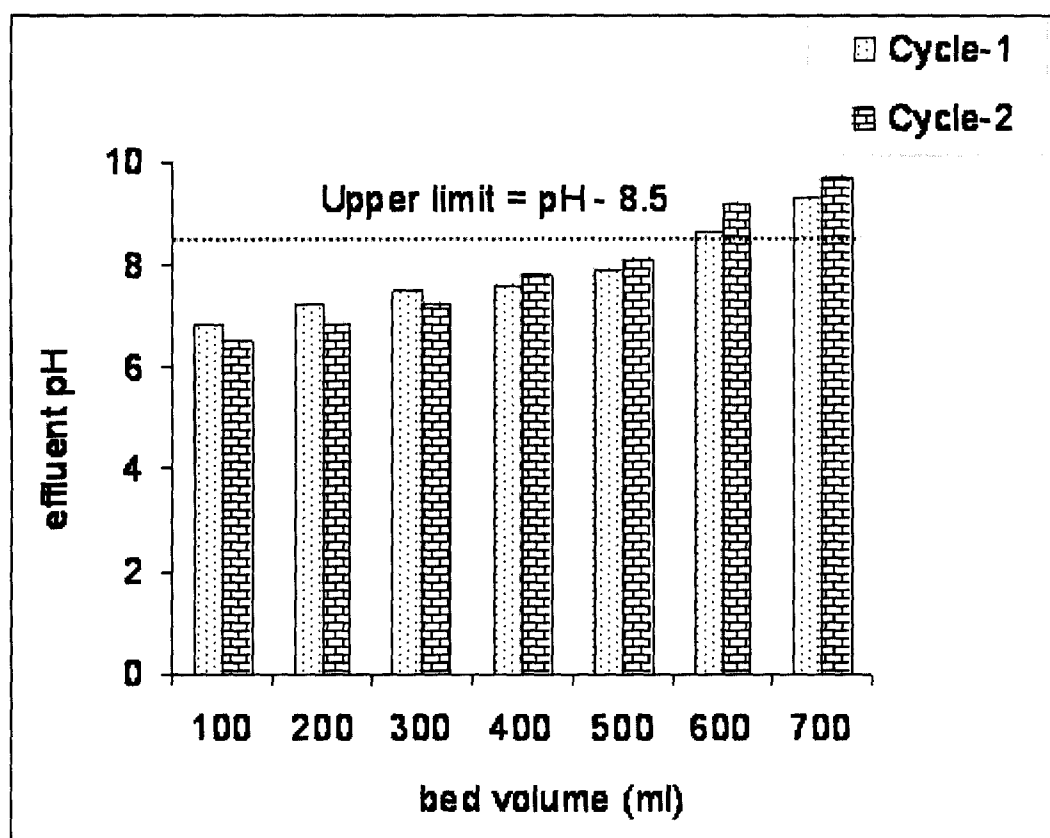By its attorney,

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(BRINDA MOHAN)