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पेटेंट सं. / Patent No. : 346000
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फाइल करने की तारीख / Date of Filing : 03/06/2010
पेटेंटी / Patentee : INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT Madras),

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित ORGANIC-TEMPLATED-BOEHMITE - NANOARCHITECTURE: AN ADSORBENT COMPOSITION TO REMOVE ARSENIC AND FLUORIDE FROM DRINKING WATER नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 3rd day of June 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 ORGANIC-TEMPLATED-BOEHMITE - NANOARCHITECTURE: AN ADSORBENT COMPOSITION TO REMOVE ARSENIC AND FLUORIDE FROM DRINKING WATER as disclosed in the above mentioned application for the term of 20 years from the 3rd day of June 2010 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 03/09/2020
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 3rd day of June 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 3rd day of June 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:

ORGANIC-TEMPLATED-BOEHMITE-NANOARCHITECTURE: AN ADSORBENT COMPOSITION TO REMOVE ARSENIC AND FLUORIDE FROM DRINKING 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.

THE FOLLOWING SPECIFICATION PARTICULARLY DESCRIBES THE NATURE OF
THIS INVENTION AND THE MANNER IN WHICH IT IS TO BE PERFORMED

FIELD OF INVENTION

This invention relates to the development of a granular hybrid adsorbent comprising of an organic template and a nanoscale material of metal-oxyhydroxide such as boehmite (γ -AlOOH) of particle size less than 10 nm. The as-synthesized nanoadsorbent,

organic-templated-boehmite-nanoarchitecture (OTBN), is capable of removing inorganic ions such as arsenic and fluoride from water. It is capable of removing microorganisms as well. The organic template essentially consists of a biopolymer like chitosan and allows particles to be grown on it, exposing high-index planes to have higher activity. The material has sufficiently high inherent green strength in the granular form, in order to stay stable even in prolonged exposure to water.

PRIOR ART:

Decline in water quality and quantity has become a common problem in many countries across the world. Various contaminants like fluoride, nitrate, phosphate, pesticides and other heavy metals such as arsenic, lead, chromium, mercury, etc. have been found in groundwater sources across the world. In many places, concentrations of these pollutants are much above the drinking water standards and often the water is not even suitable for irrigation and industrial activities. Among the various inorganic pollutants reported in water bodies, arsenic and fluoride are of major concern owing to their widespread occurrence and highly detrimental effects on human health. They are now considered as the top priority drinking water pollutants (WHO, Chemical fact sheets: Fluoride. In: Guidelines for drinking-water quality (electronic resource): incorporation first addendum. Recommendations, Third Ed., Geneva, **2006**, 1, 375–377, available at http://www.who.int/water_sanitation_health/dwq/gdwq0506.pdf). Prior art related to these contaminants is discussed in different sections below.

Fluoride contamination problem

Fluorosis is a chronic menace affecting a large fraction of population worldwide. Fluorosis results from the excessive intake of fluoride contaminated water. Although it is believed that small amounts of fluoride (< 1 mg/L) is beneficial in preventing dental caries, long-term consumption of higher concentration of fluoride can cause serious health problems. Skeletal and dental fluorosis is the most prevailing health effect of long-term consumption of fluoride contaminated water. Other health effects such as bone cancer (osteosarcoma cancer), DNA damage and adverse effects on thyroid,

immune system, brain and kidney are also reported (Ayoob, S., Gupta, A.K., Fluoride in drinking water: A review on the status and stress effects, *Crit. Rev. Environ. Sci. Technol.* **2006**, 36, 433-487; Mahramanlioglu, M., Kizilcikli, I., Bicer, I.O. Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, *J. Fluorine Chem.*, **2002**, 115, 41-47; Wang, A.G., Xia, T., Chu, Q.L., Zhang, M., Liu, F., Chen, X.M., Yang, K.D. Effects of fluoride on lipid peroxidation, DNA damage and apoptosis in human embryo hepatocytes, *Biomed. Environ. Sci.*, **2004**, 17(2), 217-222; WHO Chemical fact sheets: Fluoride. In: Guidelines for drinking-water quality (electronic resource): Incorporation first addendum. Recommendations, Vol. 1, Third Ed., Geneva, 2006, 375-377, available at http://www.who.int/water_sanitation_health/dwq/gdwq0506.pdf).

Excess fluoride in groundwater is reported in many countries around the world, notably in those located in North America, Africa, and Asia. According to the latest information, more than 25 countries across the world have reported cases of endemic fluorosis. India is one of the most affected nations with more than 25 million people in 150 districts (17 states) affected by fluorosis and approximately 66 million people at the risk of suffering from it (Susheela, A.K. Fluorosis management programme in India, *Curr. Sci.*, **1999**, 77, 1250-1255). In India, the disease was first detected in Nellore district of Andhra Pradesh in 1937. In China, cases of endemic fluorosis were reported as early as in 1930's. According to a recent report, endemic fluorosis is prevalent in 29 provinces, municipalities or autonomous regions in China (Zhu, C., Bai, G., Liu, X., Li, Y., Screening high-fluoride and high-arsenic drinking waters and surveying endemic fluorosis and arsenism in Shaanxi province in western China, *Wat. Res.*, **2006**, 40(16), 3015-3022). In Korea, many incidents of dental fluorosis have been reported in children who drink water with elevated fluoride concentrations over a long period of time (Choi, S.H., Bae, K.H., Kim, D.H., Lee, S.M., Kim, J.Y., Kim, J.B., Prevalence of dental fluorosis at Jinyoung-up, Kimhae City, Korea, *J. Korean Acad. Dent. Health.*, **2004**, 28, 347-361 (in Korean)). Carrillo-Rivera et al. reported that significant amount of fluoride was found in the abstracted groundwater of San Luis Potosí, Mexico (Carrillo-Rivera, J.J., Cardona, A., Edmunds, W.M. Use of abstraction regime and knowledge of

hydrogeological conditions to control high-fluoride concentration in abstracted groundwater: San Luis Potosí basin, Mexico, *J. Hydrol.*, **2002**, 261(1-4), 24-47). Studies have shown that the problem of high fluoride content in groundwater is very acute in mainland Tanzania (Mjengera, H., Mkongo, G., Appropriate technology for use in fluoritic areas in Tanzania, 3rd Waternet/WARFSA Symposium on Water Demand Management for Sustainable Use of Water Resources, University of Dar Es Salaam, **2002**). Agrawal (1997) reported that in Sri Lanka, fluoride has a strong geographical control linked to climatic conditions, with high fluoride waters being restricted to the dry zone on the eastern side of the island. In some parts, wells have fluoride concentrations more than 10 mg/L (Agrawal, V. Groundwater quality: focus on the fluoride problem in India, *CoGeoenvironmental J.*, **1997**, p. 10). Analysis of many groundwater samples collected from different parts of Ethiopia have shown excess fluoride than the guideline concentration recommended by World Health Organization (Tekle-Haimanot, R., Melaku, Z., Kloos, H., Reimann, C., Fantaye, W., Zerihun, L., Bjorvatn, K. The geographic distribution of fluoride in surface and groundwater in Ethiopia with an emphasis on the Rift Valley, *Sci.Total Environ.*, **2006**, 367(1), 182-190). Mgalela (1997) reported high fluoride concentrations in groundwater in some parts of Gokwe district in Zimbabwe (Mgalela, R, Some aspects of saline ground waters in Gokwe District. Annals of the Zimbabwe Geological Survey, Harare Zimbabwe, **1997**). Many other cases of endemic fluorosis have been reported from various parts of the world and many new cases are likely to be discovered in future. Unfortunately, there is no specific treatment for endemic fluorosis apart from consuming water free from fluoride.

Arsenic contamination problem

Many cases of groundwater contamination with arsenic have been reported around the globe (Smedley, P.L., Kinniburgh, D.G. A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochem.*, **2002** 17, 517–568). The most significant occurrence was identified in West Bengal (India) and Bangladesh. The first case of arsenic contamination in groundwater from the Bengal Basin was recorded in 1978 in West Bengal. Reports have shown that groundwater in more than 8 districts of

West Bengal is contaminated with high levels of arsenic (Chatterjee, A., Das, D., Mondal, B.K., Chowdhury, T.R., Samanta, G. and Chakraborti, D. Arsenic in groundwater in six district of West Bengal, India: The biggest calamity in the world; Part 1. Arsenic species in drinking water and urine of the affected persons, *Analyst*, **1995**, 120, 643-650.). The major affected districts include Burdwan, Naira, Malda, Murshidabad, North-24 Parganas, South-24 Parganas, Nawadwip and Hoogly. Approximately 3.93 million persons are estimated to be affected by arsenic in West Bengal. The total affected area covers, approximately, 37,493 square kilometers. In most of the cases, arsenic concentration values ranged from 0.3 to 0.7 mg/L. Occasionally the values were as high as 1.86 and 5.0 mg/L, reported from two places in West Bengal (Mandal, B.K., Chowdhury, T.R., Samanta, G., Basu, G.K., Chakraborti, P.P., Chanda, C.R., Lodh, D., Karan, N.K., Dhar, R.K., Tamili, D.K., Das, D., Saha, K.C., Chakraborti, D. Arsenic in Groundwater in Seven Districts of West Bengal, India. The Biggest Arsenic Calamity in the World, *Curr. Sci.*, **1996**, 70(1), 976-986; Balakameswari, K., Bhale, A.G., Paramasivam, R., Muthaal, P.L., Pande, S.P. Arsenic removal from groundwater by coagulation process, *J. Ind. Wat. Work. Assoc.*, **1999**, XXXI(4), 231-235). Arsenic contamination has also been reported from various other states of India, including Chhattisgarh, Bihar, Jharkhand, Uttar Pradesh, Assam, Punjab, Karnataka and Haryana. Arsenic contamination of groundwater is much more severe in the neighboring country, Bangladesh, where the groundwater of 59 out of 64 districts is contaminated with high levels of arsenic (Department of Public Health Engineering (DPHE), British geological Survey (BGS), and Mott MacDonald International Ltd. (MMIL), **1999**. Groundwater studies for arsenic contamination in Bangladesh: Phase1 Rapid Investigation Phase, final report. Report prepared for DPHE, Government of Bangladesh, by MMIL and BGS). It is estimated that out of the 125 million inhabitants of Bangladesh, 35 to 77 million are at the risk of drinking contaminated water (Lepkowski, W. Arsenic crisis spurs scientists, *CEN*, **1999**, 17, 45-49). Besides, West Bengal (India) and Bangladesh, other countries, where occurrence of arsenic poisoning is reported, are Chile, Mexico, Japan, Taiwan, Argentina, Vietnam, Northern China, Hungary, Romania and South-Western part of U.S.A. The reported health effects of chronic arsenic exposure include lung, kidney and skin cancers;

hyperpigmentation; keratosis; and peripheral disorders (EPA, Special report on ingested inorganic arsenic-skin cancer; nutritional essentiality, **1998**, EPA/625/3-87/013F, 124).

Remedial measures

Owing to the widespread occurrence and harmful effects of arsenic and fluoride, various treatment methods are gaining importance. Various arsenic and fluoride treatment techniques have been identified over the years, and many of them have proven successful in laboratory and pilot-scale studies. Processes adapted in these technologies mainly include precipitation, ion-exchange, adsorption and membrane processes. Among these, membrane technologies (nanofiltration, reverse osmosis) and ion-exchange processes are not popular in developing countries because those are highly expensive and non-selective. In India, coagulation/precipitation methods are traditionally used to treat fluoride bearing water. The Nalgonda technique is one such method widely used in India for fluoride treatment. Recent finding shows that it removes only a small portion of the fluoride (18–33%) in the form of precipitates and converts a greater portion of fluoride (67–82%) into soluble aluminium fluoride complex and therefore this technology is erroneous (Meenakshi and Maheshwari, R.C. Fluoride in drinking water and its removal, *J. Hazard. Mater.* **2006**, 137 (1), 456-463). The production of large volumes of low-contaminated sludge is a major problem in all the coagulation/precipitation techniques. Besides, this method needs post treatment settling tank and de-watering devices, which is generally not suitable for many end users (e.g., household treatment units). It is also hard to treat the contaminated water to low levels desired as per regulations by this method, in many cases.

Adsorption onto a solid surface has been proven to be most suitable and easy method for treating various contaminants in small scale treatment systems. Though we have numerous adsorbents to remove arsenic and fluoride from drinking water, adsorption onto activated alumina (AA) is reported to be the most suitable and cost-effective technology (EPA, Technologies and Cost for removal of arsenic from drinking water, EPA Report 815-R-00-012, EPA office of water, Washington, D.C., **1999**; Das, N., Pattanaik, P., Das, R., Defluoridation of drinking water using activated titanium rich

bauxite. *J. Col. Inter. Sci.*, **2005**, 292(1), 1–10; Mondal, P., Majumder, C.B., Mohanty, B., Laboratory based approaches for arsenic remediation from contaminated water: Recent developments, *J. Hazard. Mater.*, **2006**, 137, 464–479). Extensive reports on the use of alumina based adsorbents and their effectiveness in removing fluoride and arsenic are available in open literature and few prior arts are given below.

Prior art related to fluoride removal by alumina and aluminium based compounds

- (a) Savinelli, E.A., Black A.P. Defluoridation of Water with Activated Alumina, *J. Am. Wat. Work. Assoc.*, **1958**, 50 (1), 33.
- (b) Rubel, F., Woosley, R.D. The removal of excess fluoride from drinking water by activated alumina. *J. Am. Wat. Work. 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. *Chem. Eng. J.*, **2004**, 98(1-2), 165.
- (e) Ghorai, S., Pant, K.K. Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. *Sep. Purif. Technol.*, **2005**, 42, 265–271.
- (f) Chauhan V.S., Dwivedi, P.K., Iyengar, L. Investigations on activated alumina based domestic defluoridation units. *J. Hazard. Mater.*, **2007**, B139(1), 103.
- (g) Tang, Y., Guan, X., Su, T., Gao, N., Wang, J., Fluoride adsorption onto activated alumina: Modeling the effects of pH and some competing ions, *Colloid. Surface. A: Physicochem. Eng. Aspect.*, **2009**, 337(1-3), 33-38.
- (h) Viswanathan, N., Meenakshi, S., Enriched fluoride sorption using alumina/chitosan composite. *J. Hazard. Mater.*, **2010**, 178(1-3), 226-232.
- (i) United States Patent 4159246, Removal of fluorine from water.
- (j) United States Patent US 20090305883, Defluoridation of water.

Prior art related to arsenic removal by alumina and aluminium based compounds

- (a) Lin, T.F., Wu, J.K., Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics, *Wat. Res.*, **2001**, 35(8), 2049-2057.
- (b) Singh, T.S., Pant, K.K. Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina, *Sep. Purif. Technol.*, **2004**, 36(2), 139-147.
- (c) Mondal, P. Majumder, C.B. Mohanty, B. Laboratory based approaches for arsenic remediation from contaminated water: Recent developments, *J. Hazard. Mater.*, **2006**, 137(1), 464-479.
- (d) Singh, P., Singh, T.S., Pant, K.K., Removal of arsenic from drinking water using activated alumina, *Res. J. Chem. Environ.*, **2001**, 5(3), 25.
- (e) Tripathy, S.S., Raichur, A.M., Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water, *Chem. Eng. J.*, **2008**, 138, 179–186.

Recently, nanomaterials are gaining attention as adsorbents for removing various pollutants, including organics and inorganics, from drinking water. 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, 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). In our earlier work, we removed various contaminants from drinking water: organic contaminants such as pesticides (T. Pradeep, Sreekumar Nair, A. Indian Patent 200767), 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 (T. Pradeep, S.M. Maliyekkal, Anshup, Indian Patent Application 2089/CHE/2009). In continuation of research activities on nanomaterials for

environmental remediation, we demonstrate a facile, bio-friendly and economical method to synthesize hybrid nanostructures. The hybrid nanostructure essentially consists of a biopolymer template and a nanoscale oxyhydroxide like boehmite. The invention is directed to the use of the as-synthesized material for removing contaminants from water. The novelty of method used for material synthesis can be understood after a review of prior art for nanoscale boehmite synthesis. A summary of the protocols reported earlier for the synthesis of nanoscale-boehmite is described below.

Synthesis of nanoscale-aluminum based oxides/hydroxide and oxyhydroxide.

Alumina and aluminum based oxides and oxyhydroxides are key materials in many industrial applications, including catalysis and molecular adsorption (S. Tanada, M. Kabayama, N. Kawasaki, T. Sakiyama, T. Nakamura, M. Araki, T. Tamura, *J. Colloid Interface Sci.*, **2003**, 257, 135; H.Y. Zhang, G.B. Shan, H.Z. Liu, J.M. Xing, *Chem. Eng. Commun.*, **2007**, 194, 938). Various compounds of aluminum have been prepared for various applications. After realizing the influence of size and shape of the particles on their physical and chemical properties, recent efforts have been mainly directed towards the preparation of various nanostructured alumina and alumina based compounds. As of now, several nanostructured aluminum based compounds with different morphologies, and structures have been prepared. Among the various structures of alumina and aluminum based compounds available, AlOOH and $\gamma\text{-Al}_2\text{O}_3$ are of special interest in environmental remediation due to their high ion exchange capability and high surface area. So far, material scientists have succeeded in preparing various morphologies of boehmite (AlOOH) and Al_2O_3 , such as nanowires, nanotubes, nanosheets, nanobelts, nanofibers, nanoflowers, nanoflakes, and nanorods by different methods. The details of such materials are given in the following articles.

- (a) Valc'arcel, V., P'erez, A., Cyrklaff, M., Guiti'an, F. Novel ribbon-shaped $\alpha\text{-Al}_2\text{O}_3$ fibers, *Adv. Mater.*, **1998**, 10(16), 1370-1373.
- (b) Yu, Z., and Du, Y. Preparation of nanometer-sized alumina whiskers *J. Mater. Res.*, **1998**, 13(11), 3017-3018.

- (c) Zhang, Z., Hicks, R.W., Pauly, T.R., Pinnavaia, T.J. Mesostructured forms of γ - Al_2O_3 , *J. Am. Chem. Soc.*, **2002**, 124(8), 1592-1593.
- (d) Peng, X.S., Zhang L.D., Meng G.W., Wang X.F., Wang Y.W., Wang C.Z., Wu G.S. Photoluminescence and infrared properties of α - Al_2O_3 nanowires and nanobelts, *J. Phys. Chem. B*, **2002**, 106 (43), 11163-11167.
- (e) Zhu, H.Y., Riches, J.D., Barry, J.C. γ -Alumina nanofibers prepared from aluminum hydrate with poly(ethylene oxide) surfactant, *Chem. Mater.* **2002**, 14, 2086-2093.
- (f) Qu, L., He, C., Yang, Y., He, Y., and Liu, Z, Hydrothermal synthesis of alumina nanotubes templated by anionic surfactant, *Mater. Lett.*, **2005**, 59(29-30), 4034-4037.
- (g) Chen, X.Y., Huh, H.S., and Lee, S.W, Hydrothermal synthesis of boehmite (γ - AlOOH) nanoplatelets and nanowires: pH-controlled morphologies, *Nanotechnol.*, **2007**, 18, 285608.
- (h) Chen, X.Y., Zhang, Z.J., Li, X.L., Lee, S.W. Controlled hydrothermal synthesis of colloidal boehmite (γ - AlOOH) nanorods and nanoflakes and their conversion into γ - Al_2O_3 nanocrystals, *Solid State Commun.*, **2008**, 145, 368–373.
- (i) He, T., Xiang, L., Zhu, W., Zhu, S., H_2SO_4 -assisted hydrothermal preparation of γ - AlOOH nanorods, *Mat. Lett.*, **2008**, 62, 2939–2942.
- (j) Feng, Y., Lu, W., Zhang, L., Bao, X., Yue, B., Lv, Y., Shang, X., One-Step Synthesis of Hierarchical Cantaloupe-like AlOOH Superstructures via a Hydrothermal Route, *Cryst. Growth & Design*, **2008**, 8(4), 2008 1427.
- (k) Wu, X., Wang, D., Hua, Z., Gao, G. Synthesis of γ - AlOOH (γ - Al_2O_3) self-encapsulated and hollow architectures, *Mat. Chem. Phys.*, **2008**, 109, 560–564.
- (l) Lu, C.L., Lv, J.G., Xu, L., Guo, X.F., Hou, W.H., Hu, Y., Huang, H., Crystalline nanotubes of γ - AlOOH and γ - Al_2O_3 : hydrothermal synthesis, formation mechanism and catalytic performance, *Nanotechnol.*, **2009**, 20 215604.
- (m) Liang, H., Liu, L., Yang, Z., Yang, Y., Facile hydrothermal synthesis of uniform 3D γ - AlOOH architectures assembled by nanosheets, *Cryst. Res. Technol.* **2009**, 1-4.
- (n) Zhang, L., Lu, W., Yan, L., Feng, Y., Bao, X., Ni, J., Shang, X., Lv, Y., Hydrothermal synthesis and characterization of core/shell AlOOH microspheres, *Micr. Mes. Mat.*, **2009**, 119, 208–216.

- (o) Parida, K.M. Pradhan, A.C., Das, J., Sahu, N., Synthesis and characterization of nano-sized porous gamma-alumina by control precipitation method, *Mat. Chem. Phys.*, **2009**, 113, 244–248.
- (p) Yu, X., Yu, J., Cheng, B., Jaroniec, M., Synthesis of hierarchical flower-like AlOOH and TiO₂/AlOOH superstructures and their enhanced photocatalytic properties, *J. Phys. Chem. C*, **2009**, 113, 17527–17535.

According to the literature, the boehmite (AlOOH) phase forms from aluminum hydroxide, Al(OH)₃, at about 373 K (Misra, C. Industrial Alumina Chemicals; ACS Monograph 184; American Chemical Society: Washington, DC, 1986; Chapter 2; Zhu, H.Y., Riches, J.D., Barry, J.C. γ -Alumina nanofibres prepared from aluminum hydrate with poly(ethylene oxide) surfactant, *Chem. Mater.* **2002**, 14, 2086-2093). Most of the reported AlOOH nanostructures are synthesized through hydrothermal treatment (temperature: 160-240 °C). However, a simple, quick, energy efficient, eco-friendly, and inexpensive preparation of nanoscale-AlOOH is very important for commercial applications. No reports are available so far describing room temperature sol-gel synthesis of organic templated-boehmite nanoarchitecture, with improved fluoride and arsenic removal capabilities.

The proposed synthetic method is superior to existing methods in various aspects, which has large implications to the chemical industry: (1) synthesis is done at room temperature and at atmospheric pressure (2) enhanced settleability, thereby easy and quick separation of the product (organic templates such as chitosan can act as a flocculating agent), (3) bio-friendly, facile and green synthesis, (4) easy scale-up and, (5) ability to granulate without the aid of any external agents and good physical strength in water, and finally (6) large enhancement in arsenic and fluoride removal performance.

Prior art on the preparation of aluminum based oxides in bead and granular form

Alumina is typically used in the bead form for the removal of fluoride from drinking water. Typically, reported procedure for the bead making is to add binders (organic or

inorganic) along with fine particles of alumina/aluminum hydroxide and shape the composite in form of a bead. Thereafter, the bead is heated at elevated temperatures (300-600 °C). In the ceramics industry, particles are agglomerated by spray drying using organic polymers as binders.

Binder-based method: In a typical procedure, appropriate quantity of binder is added to the alumina particles through wet blending. Therefore, the particles are transformed to the shape of a bead through spray drying or granulator or pan coating. The formed beads are firstly dehydrated and thereafter calcined at temperatures above 400 °C.

The related prior art is presented here:

(a) Agglomeration of alumina and binder therefor, US Patent 7449030

(b) Effect of Organic Binder Segregation on Sintered Strength of Dry-Pressed Alumina, Satoshi Tanaka, Chiu Chia Pin, Keizo Uematsu, *J. Am. Cer.*, **2006**, V 89 (6), 1903 – 1907.

(c) A new polyurethane binder providing high green strength of dry-pressed alumina, Marek Potoczek, Maciej Heneczkowski, Mariusz Oleksy, *Ceram. Int.*, **2003**, 29, (3), 259-264.

Oil-drop method: In a typical procedure, the gel obtained by precipitation of aluminum precursor using a base is allowed to drop into a hot oil bath, forming spherical particles as partial decomposition of the gelling agent takes place. To complete the coagulation, ageing is then performed at higher pressure and temperature. The final crystalline spherical alumina particles are obtained after washing, drying and calcining at high temperature.

The related prior art is presented here:

(a) Preparation of spherical alumina and copper oxide coated alumina sorbents by improved sol–gel granulation process, Genoveva Buelna, Y. S. Lin, *Micr. Mes. Mat.*, 42 (1), **2001**, 67-76.

(b) Method of manufacture of spherical alumina particles, US Patent 4108971.

(c) Method of preparing spheroidal alumina particles, US Patent 4250058.

From the prior art presented, it is clear that aluminum based compounds in general and alumina in particular are the most widely used and they are the basis of demonstrated technology for removing arsenic and fluoride from drinking water. However, the fluoride adsorption capacity of alumina is reported to be in the range of 1-10 mg/g, (Ghorai, S and Pant, K.K., Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina, *Sep. Purif. Technol.*, **2005**, 42(3), 265-271). The maximum arsenic adsorption capacity reported for conventional AA is around 16 mg/g (Kim, Y., Kim, C., Choi, I., Rengaraj, S., Yi, J., Arsenic removal using mesoporous alumina prepared via a templating Method, *Environ. Sci. Technol.* **2004**, 38, 924-931). The low arsenic and fluoride uptake capacity of conventional AA demands frequent regeneration and produces large amount of solid and liquid waste. The other reported problem of commercially available activated alumina is its poor kinetics, which demands large reactor volume to attain the required performance. It is now realized that size, structure and shape play important roles in chemical and physical properties of the material and smaller the crystallite size, better is the performance. However, using nanoparticles as filter medium is impractical due to difficulty in particle separation, danger of particle leaching, and poor hydraulic conductivity. Hence, it has to be granulated like any other powdered material to use as a medium for filtration. The reported methods of alumina granulation are mostly based on addition of binding agents and subsequent calcinations. Such approaches are less environmental friendly and uneconomical. In this application, we have demonstrated an easy, economical, and environment friendly method to make a granular, bio-friendly hybrid material. The material consists of a biopolymer such as chitosan and a nanoscale metal oxyhydroxide (γ -AlOOH), with large adsorption capacity to remove various anions and pathogens from water.

Prior art on the applications and stability of metal oxide-chitosan composite materials

Chitosan and chitosan-derivatives have been known for their adsorption capacity to remove various aquatic pollutants. However, still there is a need to improve the practical utility of such developed adsorbents on commercial scale (Bhatnagar, A., Sillanpää, M., Applications of chitin and chitosan-derivatives for the detoxification of water and wastewater - a short review, *Adv. Coll. Interf. Sci.* **2009**, 152, 26–38). Recently efforts have been made to improve the fluoride adsorption capacity of chitosan by incorporating metal oxides into it. Though some improvement in fluoride adsorption capacities were observed, the numbers are not significant to handle field conditions (Sundaram, C.S., Viswanathan, N., Meenakshi, S., Uptake of fluoride by nano-hydroxyapatite/chitosan, a bioinorganic composite, *Biores. Technol.*, **2008**, 99, 8226–8230; Sundaram, C.S., Viswanathan, N., Meenakshi, S., Defluoridation of water using magnesia/ chitosan composite, *J. Hazard. Mater.*, **2009**, 163, 618–624; Yao, R., Meng, F., Zhang, L., Ma, D., Wang, M., Defluoridation of water using neodymium-modified chitosan, *J. Hazard. Mater.*, **2009**, 165, 454–460). Recently, Thakre et al. (2010) studied Ti-Al supported chitosan beads for the removal of fluoride and they found that chitosan beads dried at 80 °C swells in water and clog the filter unit (Dilip Thakre, D., Jagtap, S., Sakhare, N., Nitin, L., Meshram, S., Rayalu, S., Chitosan based mesoporous Ti-Al binary metal oxide supported beads for defluoridation of water, *Chem. Eng. J.*, **2010**, 158, 2, 315–324). Hence, such media cannot be used as filter medium in water. Thakre et al. (2010) also reported that such material has to be calcined at elevated temperature (450 °C) to improve the stability and thereby utility in water purification. However, the calcination process reduces the fluoride uptake capacity. It may also decompose the organic materials such as chitosan. Hence, different methods have been adopted to increase their stability either by calcination or by cross linking with chemicals. Hence, increasing the stability of the hybrid materials consisting organic compounds like chitosan is very important to use as an adsorbent medium for water related application, to avoid any practical difficulties such as material leaching and hydraulic conductivity.

DESCRIPTION OF THE INVENTION:

In the following, we present the synthesis, characterization and water purification applications of a granulated hybrid material constructed through organic template assisted low temperature ($< 60\text{ }^{\circ}\text{C}$) sol-gel process. The process of synthesis was conducted in water medium. The uptake test results of a few contaminants like arsenic, fluoride and virus are presented. However, the result presented here should not be construed as limiting the scope of the invention.

Experimental methods

Material characterization

The identification of the phase(s) of the as-prepared samples and the samples interacted with target 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, sample was re-suspended in water by 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 JEM 3010 (JEOL, Japan). The samples prepared as above were spotted on amorphous carbon films supported on copper grids and dried at room temperature. X-ray Photoelectron Spectroscopic (XPS) analysis was done using ESCA Probe TPD of Omicron Nanotechnology. Polychromatic Mg K α was used as the X-ray source ($h\nu = 1253.6\text{ eV}$). Spectra in the required binding energy range were collected and an average was taken. Beam induced damage of the sample was reduced by adjusting the X-ray flux. Binding energy was calibrated with respect to C 1s at 284.5 eV. Fourier Transform Infrared (FT IR) spectra were collected ($450 - 4000\text{ cm}^{-1}$) using Spectrum One FTIR spectrometer (Perkin-Elmer, USA).

Adsorption studies

The as-synthesized nanomaterial was tested for arsenic (in the form of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) and fluoride (in the form of NaF) removal from water. All the uptake

capacity studies were done in a batch reactor (250 mL polypropylene conical flask). The working volume of the solution was taken as 100 mL and required quantity of adsorbent was added. The flasks were kept for shaking at 160 ± 5 rpm in an orbital shaker (Riviera, India) at room temperature. Samples were withdrawn at predetermined time intervals and analyzed for residual solute concentration.

Effect of contact time and initial solute concentration on solute uptake was studied at various solute concentrations. Equilibrium studies were performed at nearly neutral pH (7 ± 0.2) and at room temperature (30 ± 2 °C) by varying the concentrations of the solute over a wide range. Effect of adsorbent dose was investigated at a pH of 7 ± 0.2 . The pH of the samples was adjusted using dilute NaOH or HCl solution. The solute concentration of fluoride and arsenic were maintained as 10 mg/L and 1 mg/L respectively for all the studies, unless otherwise mentioned. Fluoride analysis was carried out using a calibrated specific fluoride combination electrode (Cole-Parmer Instruments Co, USA) connected to a multimeter/data acquisition system (Keithley, 2700, USA). To each sample, ionic strength and pH adjusting buffer (TISAB III) was added in equal volumes. Arsenic was analyzed using Inductive Coupled Plasma analyzer (ICP-OES, PerkinElmer, 5300 DV).

Virus removal

Virus decontamination studies were also carried out in batch reactor (Volume = 250 mL, working volume = 100 mL). All materials used for the study were sterilized initially. The virus culture at the required concentration was maintained in physiological saline water. The initial concentration of the virus inoculums was maintained as 3×10^5 plaque forming units per milliliter (PFU/mL). MS2 coliphage bacterial viruses were chosen as model organism (ATCC (American Type Culture Collection) # 15597 - BI). Different amounts of materials of OTBN were added to the inoculums and stirred separately. The material was separated from the solution at predetermined time intervals by means of a filter paper. Three successive dilutions of the adsorbent free solutions were prepared in different test tubes using sterile water. One ml of each dilution was used to inoculate sterile Petri dish to which 9 ml of sterile and cooled agar medium was poured. The agar medium was originally maintained in molten state at 42- 45 °C. The agar-inoculums

mixture was thoroughly mixed and allowed to solidify and incubated at 37 °C for 36 h. After 36 h, the plates were tested for number of viable virus cells present in a culture.

The present application describes the low temperature (< 60 °C) synthesis of a hybrid material, namely OTBN, and its application in removing contaminants from water with fast kinetics. Few examples are provided to illustrate the present invention. The examples should not be construed as limiting the scope of the invention.

Example 1

This example describes the low temperature synthesis of nanoscale-AlOOH through a simple soft chemistry route. The synthesis procedure consists of mixing the aluminum precursor solution with chitosan (dissolved in 1 - 5 % glacial acetic acid or HCl or combination thereof) with vigorous stirring. In a general procedure, a solution of aluminum precursor such as aluminum nitrate was added slowly into the chitosan solution with vigorous stirring for 60 minutes and was kept overnight without agitation. Aqueous ammonia or NaOH solution was slowly added into the metal-chitosan solution with vigorous stirring to facilitate the precipitation of the metal-chitosan composites (pH 7 – 8.0). All these steps were carried out at temperature below 30 °C. Stirring was continued for two hours. The precipitate was filtered, washed to remove any unwanted impurities, converted in the shape of beads and dried at various conditions.

Example 2

Similar method has been used to precipitate the metal chitosan composites above 30 °C and below 60 °C. The reaction products were filtered, washed to remove any unwanted impurities, converted in the shape of beads and dried at various conditions.

Example 3

The materials described in example 1 and 2 were dried using different drying protocols, including surface drying at room temperature (< 35 °C), sun drying (40 to 60 °C) and oven drying (60 to 130 °C) were adopted separately to get stable and hard granular materials. It was found that the hardness of the material largely depends upon the

drying methodology and it varies with initial metal precursors. The dried product was stored for further use. Various precursors such as aluminium nitrate, aluminium sulphate, aluminium chloride, aluminium isopropoxide , etc. were tried to study their influence on the composite formation.

Example 4

This example is to show that the as-synthesized material is capable of removing viruses from water. Around 5 gm/L of adsorbent was sufficient enough to bring down virus concentration of 5×10^5 PFU/mL to a value < 1 PFU/mL. This concentration is 500 times higher than as suggested by national science foundation (NSF) for testing virus containing challenge water. The challenge water has been kept at a higher concentration so as to reduce the volume of water to be used for studies. Therefore, every liter of water purified represents 500 liters of purified water as per the NSF standard.

35 gm of material was packed in a column with a bed height of 4 cm. Virus containing water at a concentration of 5×10^5 PFU/ml was passed through the column at 30 ml/min. After the passage of 2.5 liters, the virus content in the output water is below 500 PFU/ml; after the passage of 5 liters, the virus content in output water is below 740 PFU/ml.

Example 5

This example describes the regeneration protocol for eluting the adsorbed solute from the adsorbent. The protocol involves the treatment of the adsorbed material with 0.1 M NaOH and subsequent neutralization of this material with water adjusted to pH 2.5 (pH of the water was adjusted with H_2SO_4). The results reveal that more than 90% of the adsorbate could be eluted with 0.1 M NaOH and the material can be effectively utilized for the next cycle of adsorption process without considerable loss in its capacity.

DESCRIPTION WITH REFERENCE TO DRAWINGS AND TABULATED DATA:

Figure 1a. XRD patterns of (A) as-synthesized material reacted with 1000 mg/L fluoride; (B) as-synthesized material reacted with 100 mg/L fluoride (C) as-synthesized AlOOH; (D) Chitosan. Dotted lines correspond to the standard reflections of AlOOH (JCPDS 21-1307). The traces are shifted vertically for clarity. (Label: '+' – chitosan; '*' – AlOOH).

Figure 1b. XRD patterns of as-synthesized materials through various starting materials; A1- OTBN prepared using aluminum nitrate and ammonia as the starting materials; A2- OTBN prepared using aluminum sulfate and ammonia as the starting materials; A3- OTBN prepared using aluminum nitrate and sodium hydroxide as the starting materials; A4 to A6 - OTBN prepared using aluminum chloride and NaOH as the starting materials. All the materials except A5 and A6 were dried at 60 °C in oven. A5 was dried at room temperature and A6 was dried at 120 °C in oven.

Figure 2. FT-IR spectra of (A) the as-synthesized OTBN and (B) fluoride adsorbed OTBN. The traces are shifted vertically for clarity.

Figure 3. XPS spectra of (A) As-prepared OTBN, (B) fluoride adsorbed OTBN. (a). Survey spectra and (b, c, d) spectra of various regions.

Figure 4. TEM images of OTBN at various magnifications. The particles are seen in the image on the right (marked).

Figure 5. (a) Adsorption capacity of OTBN as function of adsorbent dose (Initial fluoride concentration = 10 mg/L), (b) adsorption capacity of OTBN as function of initial arsenate concentration. pH of the feed water = 7 ± 0.2 .

Figure 6. (a) Fluoride uptake capacity of OTBN as a function time, (b) Pseudo-second-order kinetic plots for the adsorption of fluoride onto OTBN. (E Experimental data, P-model predicted data).

Figure 7. (a) Adsorption capacity of OTBN as function of adsorbent dose (Initial arsenate concentration = 1.1 mg/L). (b) Adsorption capacity of OTBN as function of arsenate concentration. pH of the feed water = 7 ± 0.2 .

Figure 8. EDAX spectrum of arsenate adsorbed OTBN. Inset: elemental X-ray images of Al K α , As L α , O K α and As K α of the sample. The corresponding SEM image and elemental quantification is also shown in the figure inset.

DETAILED DESCRIPTION WITH REFERENCE TO DRAWINGS AND TABULATED DATA:

The as-synthesized samples showed peaks corresponding to (020), (120), (013), (200) and (231) and (251) planes (Figure 1a). All these peaks can be indexed as orthorhombic-AlOOH (JCPDS 21-1307). The broadened XRD peaks imply that crystallite size of the OTBN particles is very small. The mean crystallite size calculated from the Scherrer formula shows that nanocrystals are of an average size of 3.5 nm. The presence of organic template (chitosan) is also clear from the XRD data. Fluoride reacted OTBN samples showed no change in diffraction patterns indicating that the crystal structure is intact even after fluoride adsorption (Figure 1a). The standard reflections of orthorhombic-AlOOH are also given to validate the structure of the sample (JCPDS 21-1307). Comparing the XRD positions of the standard sample and the as-synthesized sample, a change in intensity pattern could be seen, which can be ascribed to the effect of the organic template. The intensity of the higher index planes is higher in the nanoscale material. Recent studies on the catalytic activity of metals such as Pt have shown that high-index planes exhibit much higher catalytic activity than that of common and stable, low-index planes (Gates, B.C., Huber, G.W., Marshall, C.L., Ross, P.N., Sirola, J., Wang, Y. Catalysts for Emerging Energy Applications, *MRS Bull.*, **2008**, 33, 429 - 435; Tian, N., Zou, Z.Y., Sun, S.G., Ding, Y., Wang, Z.L., Synthesis of tetrahedral platinum nanocrystals with high-index facets and high electro-oxidation activity, *Science*, **2007**, 316, 732).

Apart from the point of view of enhanced catalytic activity, the current synthesis method is interesting because it yields crystalline nanoscale-AlOOH with good green strength at much lower temperature in comparison to earlier methods. This is very valuable in the chemical industry. According to the current literature, AlOOH formation is possible only above 373 K (Zhu, H.Y., Riches, J.D., Barry, J.C. γ -Alumina nanofibres prepared from aluminum hydrate with poly(ethylene oxide) surfactant, *Chem. Mater.* **2002**, 14, 2086-2093). And most of the current syntheses of nanoscale-AlOOH have been done in hydrothermal conditions at temperature above 373 K (Please refer to the section 'synthesis of nanoscale-aluminum based oxides/hydroxide and oxyhydroxide' in the prior art).

XRD patterns of the OTBNs prepared at various physical and chemical conditions were recorded in order to understand their effects on crystal structure of OTBN. Some of the XRD patterns recorded are shown in Figure 1b. The data clearly shows the formation of AlOOH with all the aluminum precursors and temperature range (25 to 130 °C) studied. Though the crystallographic structures obtained were seemingly identical, interestingly, the OTBNs showed different physical strength when exposed to water and the details are discussed below.

Figure 2 shows the FT-IR spectra of nano-AlOOH and fluoride adsorbed nano-AlOOH in the range 450 - 4000 cm^{-1} . All the absorption bands are consistent with literature values and give additional evidence for the formation of γ -AlOOH (Lu, C.L., Lv, J.G., Xu, L., Guo, X.F., Hou, W.H., Hu, Y., Huang, H., Crystalline nanotubes of γ -AlOOH and γ - Al_2O_3 : hydrothermal synthesis, formation mechanism and catalytic performance, *Nanotechnol.*, **2009**, 20 215604; Chen, X.Y., Huh, H.S., and Lee, S.W, Hydrothermal synthesis of boehmite (γ -AlOOH) nanoplatelets and nanowires: pH-controlled morphologies, *Nanotechnol.*, **2007**, 18, 285608). The bands at 1072 and 1154 cm^{-1} are assigned to the symmetric and asymmetric stretching frequencies of Al-O-H of boehmite, respectively. The bands at 3096 and 3312 cm^{-1} are assigned to Al-OOH stretching vibrations. The band at 1636 cm^{-1} is assigned to the bending modes of adsorbed water and the broad band at 3429 cm^{-1} is due to the O-H stretching mode of adsorbed water.

The XPS survey spectra of the material before and after fluoride adsorption are shown in Figure 3. These spectra clearly confirm the existence of adsorbed fluoride along with the key elements Al and O. For understating the chemical form of the pristine and fluoride adsorbed materials, detailed scans of specific regions of key elements (Al 2p, O 1s) and adsorbed ion (F 1s) were carried out and are shown in Figure 2. The XPS spectrum of Al 2p shows peak at 74.4 eV, which is in agreement with Al in AlOOH (Moulder, J.F., Stickle, W.F., Sobol, P.E., Bomben, K.D., 1995. Handbook of X-ray Photoelectron Spectroscopy, eds. Chastain, J., King, Jr, R.C., Physical Electronics USA, Inc. 18725 Lake Drive East, Chanhassen, Minnesota 55317, USA.). Fluoride adsorption does not affect the position of Al, but a reduction in the surface positive charge is seen in O 1s, as result of which it appears at a lower binding energy.

In order to investigate the morphology of the as-synthesized samples, HRTEM images were taken and are shown in Figure 4. The as-synthesised sample looks nano-whiskers in shape. On close observation, we can see that small particles are attached to the fibrils and resembles like green peppercorns (marked in the figure). The fibrils are due to organic templates and the particles are due to AlOOH nanoparticles. It is also clear from the images that the particles are in nanosize of diameter of less than 5 nm.

The extent of fluoride adsorption by OTBN as a function of adsorbent dose was studied and the result is shown in Figure 5a. The OTBN prepared through various starting materials were also tested to assess their capability to remove fluoride. All the samples showed equally good performance. As expected, the amount of fluoride adsorbed increased with increase in material dose from 2.5 mg to 50.0 mg and became more or less constant for further increase in dose. As evident from the data, the fluoride concentration reduced to a value as low as 0.5 mg/L from an initial concentration of 10 mg/L at optimum adsorbent dose. When the OTBN dose was further increased, there was less proportionate increase in adsorption because of the limitation of fluoride ions as compared to the adsorption sites available for the reaction. From these results we can see that at 10 mg/L fluoride concentration and neutral pH, the as-synthesized

sample can remove 53 mg/g of fluoride (maximum uptake capacity, q_{\max} at a relevant fluoride concentration of 10 mg/L). This is considerably higher than most of the commercially available alumina or AlOOH based nanomaterials tested so far. A recent attempt to remove fluoride from water using nanoscale-AlOOH showed a removal capacity of 3.26 mg/g, which is around 16 times less in capacity compared to the as-synthesized hybrid material (Wang, S.G., Ma, Y., Shi, Y.J., and Gong, W.X., Defluoridation performance and mechanism of nano-scale aluminum oxide hydroxide in aqueous solution, *J. Chem. Technol. Biotechnol.* **2009**; 84: 1043–1050).

The fluoride uptake capacity as a function initial fluoride concentration (the fluoride concentrations was varied over range of 10 to 60 mg/L) is shown in Figure 5b. An increase in fluoride uptake capacity was observed with increase in initial fluoride concentrations and an uptake capacity in excess of 50 mg/g was observed at initial fluoride concentration of 60 mg/L.

Rate of adsorption has important role in the design of any adsorption process. It usually varies with physical and chemical properties of the adsorbent. In this study, batch fluoride adsorption kinetic studies were conducted using OTBN and the results are presented in Figure 6a. Results show that fluoride uptake with as-synthesized sample is very fast and most of the removal took place in the first 10 min of contact. And the equilibrium was reached in 60 min. The fluoride uptake kinetics observed in the case of OTBN is much superior to the commercially available alumina and many other adsorbents used for scavenging fluoride, which has large implications in practical applications.

To understand the process kinetics better, kinetic data of fluoride adsorption by OTBN was analyzed with various reaction kinetic models, including Lagergren pseudo-first-order, and Ho's pseudo-second-order reaction rate models. Mathematical representations of these models are given in Eqs. 1 and 2.

Pseudo-first-order equation:
$$q_t = q_e (1 - e^{-K_1 t}) \quad (1)$$

$$\text{Pseudo- second-order equation: } q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (2)$$

Where q_t is the amount of fluoride removed from aqueous solution at time t (mg/g); q_e is the amount of fluoride removed from aqueous solution at equilibrium (mg/g); K_1 is the pseudo-first-order rate constant of adsorption (1/min); K_2 is the pseudo-second-order rate constant of adsorption (g/mg.min); and t is the time (min).

The best-fit model plots (pseudo-second-order reaction model) along with the experimental plots are shown in Figure 6b. The kinetic rate constant, K_2 for 10 mg/L and 5 mg/L of fluoride were calculated to be 0.049 and 0.098 g/mg.min, respectively.

The arsenic adsorption by OTBN as a function of adsorbent dose was studied and the result is shown in Figure 7a. As-prepared OTBN dose was varied over a range of 5 to 100 mg. Studies were conducted with an initial arsenic concentration of 1.1 mg/L and at pH of 7 ± 0.2 . As evident from the data, the as-synthesized material (25 mg) could bring down the arsenic concentration to a value below detectable limit of ICP-OES (< 0.1 mg/L).

The equilibrium adsorption study of arsenic by as-synthesized material was carried out at $30 \pm 2^\circ\text{C}$ and neutral pH. The initial arsenic concentrations were varied over a wide range (5 – 100 mg/L). The results obtained from this study are shown in Figure 7b. As evident from the data, the uptake capacity increased with increase in arsenic concentrations. Since adsorption is an equilibrium mass transfer process, the initial concentration of the solute provides the major driving force to enhance the adsorption process. An adsorption capacity of 183 mg/g is observed at initial arsenic concentration of 100 mg/L. This shows that the as-synthesized material has high affinity to arsenic and is better than any other aluminum based material reported for arsenic removal at similar equilibrium concentrations studied.

Activated alumina (AA) is a commonly utilized adsorbent for removing arsenic from water. Various activated alumina showed different arsenic removal capacities depending upon the preparation methods. Granular AA (Macherey-Nagel, Germany) with a surface area of 118 m²/g is reported to have an arsenate adsorption capacity of 16 mg/g (Lin, T.-F.; Wu, J.-K. Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics *Water Res.* 2001, 35 (8), 2049–2057). A high surface (370 m²/g) area AA (Grade CATAL-AD 101, Indian Petrochemical Co., India) also shows around 16 mg/g arsenate uptake capacity. Degussa alumina with surface area of 103 m²/g shows an uptake capacity of 7 mg/g (Kim, Y., Kim, C., Choi, I., Rengaraj, S., Yi, J., Arsenic removal using mesoporous alumina prepared via a templating Method, *Environ. Sci. Technol.* **2004**, 38, 924-931). Yoldas' alumina with 300 m²/g prepared via a hydrothermal method shows an uptake capacity of 34 mg/g (Yoldas, Bulent E. Alumina sol preparation from alkoxides. *Am. Ceram. Soc. Bull.* **1975**, 54(3), 289-90). Mesoporous alumina (MA) with a large surface area (307 m²/g) and uniform pore size (3.5 nm) and a sponge like interlinked pore system developed through a post-hydrolysis method show an arsenate uptake capacity of 121 mg/g (Kim, Y., Kim, C., Choi, I., Rengaraj, S., Yi, J., Arsenic removal using mesoporous alumina prepared via a templating Method, *Environ. Sci. Technol.* **2004**, 38, 924-931). The Langmuir isotherm predicted arsenic uptake capacity of MA is reported to be 7 times higher than conventional AA (concentration range at which equilibrium study was conducted = 7.5-1500 mg/L).

In the case of as-synthesized OTBN, the maximum adsorption capacity was calculated to be the 671.4 mg/g (concentration range at which equilibrium study was conducted = 5-100 mg/L). This value was estimated based on the best fit isotherm model, which was happened to be Bradley isotherm (Rudzinski, W., Everett, D., Adsorption of gases on heterogeneous surfaces, academic press, New York, 1992.). On close comparison with experimental data, it was found the as-synthesized OTBN is at least 3 times superior to MA in removing arsenic from water.

The EDAX spectrum and X-ray elemental maps of arsenic adsorbed OTBN is shown in Figure 8. All the principal elements along with adsorbed arsenate are present in the spectrum. The X-ray elemental maps show that the sample is homogeneous and the adsorbed arsenic is uniformly distributed over the OTBN surface.

The data presented here demonstrated the synthesis of organic-templated-boehmite-nanoarchitecture below 5 nm particle size at a lower temperature ($> 25\text{ }^{\circ}\text{C}$) and its superior arsenic and fluoride adsorption from water with improved kinetics.

The methods shown here may be used for other anions or species bearing negative charges, as the significant interaction is electrostatic. Various biocompatible fibrous materials such as banana silks, cellulose, lignin, chitin etc. can be used as the template instead of chitosan. The methodology of removal can be used for gravity fed filters or otherwise with a variety of fluids, bearing contaminants. The synthesis itself can be conducted with diverse precursor species. Experiments were conducted to confirm all of these.

Our experimental evidences show that although all the OTBN prepared through various aluminum precursors resulted in same crystallographic structure (Figures 1a and 1b), the stability in water varied significantly with initial precursor and drying temperature. Table 1 shows the qualitative data obtained for the stability of OTBNs prepared through various conditions. The data show that the OTBN prepared through aluminum chloride showed maximum stability when it was surface dried at room temperature. On increasing the temperature from 30 to 120°C , the stability reduced significantly and a material lost its integrity and started disintegrating and finally become gelly. On the contrary, OTBN synthesized through aluminum sulfate route did not show much variation in stability with change in drying temperature from 30 to 100°C . The material always showed moderate stability.

Amended Claims

WE CLAIM:


1. An eco-friendly method of preparing an adsorbent composition having granules of organic-templated- boehmite-nanoarchitecture in water, with particle size less than 10 nm, wherein the adsorbent composition is used for the removal of arsenic and fluoride from water comprises of:
 - (a) preparing a composite of metal precursor and the bio-template, wherein the metal ion is complexed with the bio-template;
 - (b) hydrolyzing the mixture prepared as in step (a), wherein the metal precursor is precipitated on the bio-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 bio-template also works as a coagulant to enhance the settling ability of the floc;
 - (d) converting the semi-solid filtered material from step (c) to a specific shape;
 - (e) drying the material of a specific shape from step (d) to remove the moisture content at temperatures from about 25 °C to about 60 °C by methods including air drying or sun drying or hot air oven;
 - (f) grinding the material from step (e) in order to obtain the particles in granular form with size ranging from 0.1 to 3 mm having sufficient strength for use in various applications including water purification thereby avoiding the use of an additional binder and heating at elevated temperature.
2. A method of preparing an adsorbent composition as claimed in claim 1, involving hydrolysis of a metal precursor at a temperature using an alkaline medium in presence of a bio-template, wherein
 - (a) the bio-template is a natural biopolymer;
 - (b) the metal precursor is aluminium nitrate, aluminium chloride, aluminium sulfate, aluminium isopropoxide or a combination thereof;
 - (c) the alkaline medium is sodium hydroxide, ammonia, potassium hydroxide or a combination thereof;
 - (d) the temperature is below 60 °C.

3. A method of preparing an adsorbent composition as claimed in claim 1, wherein the adsorbent composition utilized for the removal of fluoride and arsenic from water having a fluoride adsorption capacity in excess of 50 mg/g at an initial fluoride concentration of 10 mg/l, and an arsenic adsorption capacity in excess of 19 mg/g at an initial arsenic concentration of 1.0 mg/l, wherein
- 5 (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;
- 10 (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. A method of preparing an adsorbent composition as claimed in claim 1, wherein the bio-templates includes but not limited to chitosan, banana silk and cellulose are used individually or in combination, with varying ratios.
- 15 5. A method of preparing an adsorbent composition as claimed in claim 1, wherein the bio-template is a derivative of cellulose, chitosan or banana silk or surface functionalized forms of the same.
6. A method of preparing an adsorbent composition as claimed in claim 1, wherein the bio-template is used in the solid form or in the dissolved form.
- 20 7. A method of preparing an adsorbent composition as claimed in claim 1, 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 and silicon or a combination thereof.
- 25 8. A method of preparing an adsorbent composition as claimed in claim 1, 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.
9. A method of preparing an adsorbent composition as claimed in claim 1, wherein the concentration of reagents used in the reaction is varied leading to a variation in the size of the nanoscale material from 1-100 nm, preferably in the range of 3-10 nm.
- 30

10. A method of preparing an adsorbent composition as claimed in claim 1, wherein the nanoadsorbent contains high index planes in its crystalline structure.
11. A method of preparing an adsorbent composition as claimed in claim 1, wherein the stability of the granular medium achieved by cross-linking the bio-template by reagents including but not limited to sulphates, tripolyphosphate, glutaraldehyde.
12. A method of preparing an adsorbent composition as claimed in claim 1, wherein the nanoadsorbent is calcined at temperature above 300 °C to produce nanoscale γ -alumina.
13. A method of preparing an adsorbent composition as claimed in claim 1, wherein the adsorbent is used as a filter in a filtering device in a variety of formats including but not limited to candle, molded porous block, filter bed, column, packets and bags.
14. A method of preparing an adsorbent composition as claimed in claim 1, wherein the adsorbent is used as a water treatment medium for water sources including but not limited to ground water sources, industrial sources and municipal sources.
15. A method of preparing an adsorbent composition as claimed in claim 1, wherein the adsorbent removes fluoride, arsenic and pathogens individually or in combination thereof from water.
16. A method of preparing an adsorbent composition as claimed in claim 1, wherein the adsorbent reduces fluoride, arsenic and pathogens individually or in combination thereof from media other than water.
17. A method of preparing an adsorbent composition as claimed in claim 1, wherein the adsorbent is regenerated by desorption of adsorbed species using an alkaline solution followed by surface activation using an acidic solution.

Dated at Chennai this Jan 21, 2016

Signature:



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

ABSTRACT

An eco-friendly method of preparing an adsorbent composition having granules of organic-templated- boehmite-nanoarchitecture in water, with particle size less than 10 nm, involves the hydrolysis of a metal precursor at a temperature below 60o C using an alkaline medium in presence of a bio-template. The as-synthesized nanoadsorbent material is used as a filter medium for removing arsenic and fluoride from drinking water.

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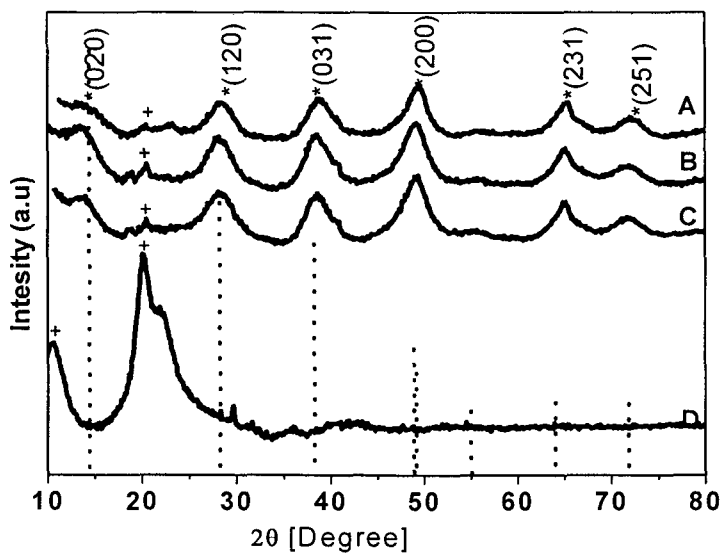


Figure 1a

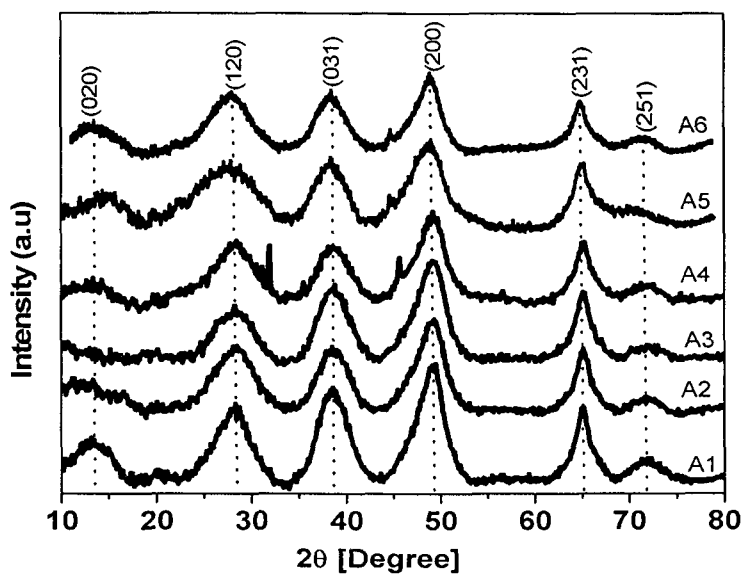



Figure 1b

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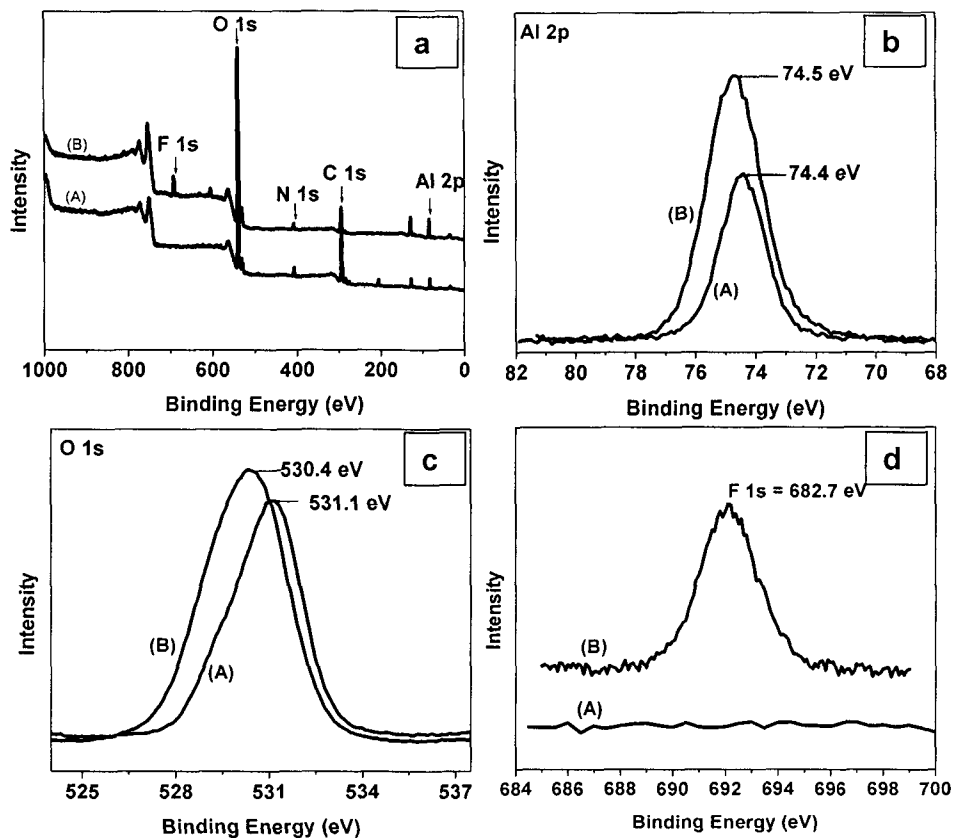



Figure 3

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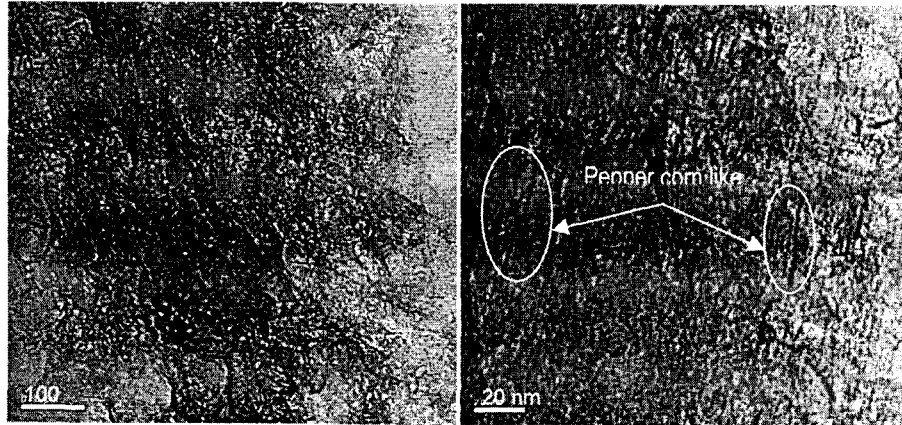



Figure 4

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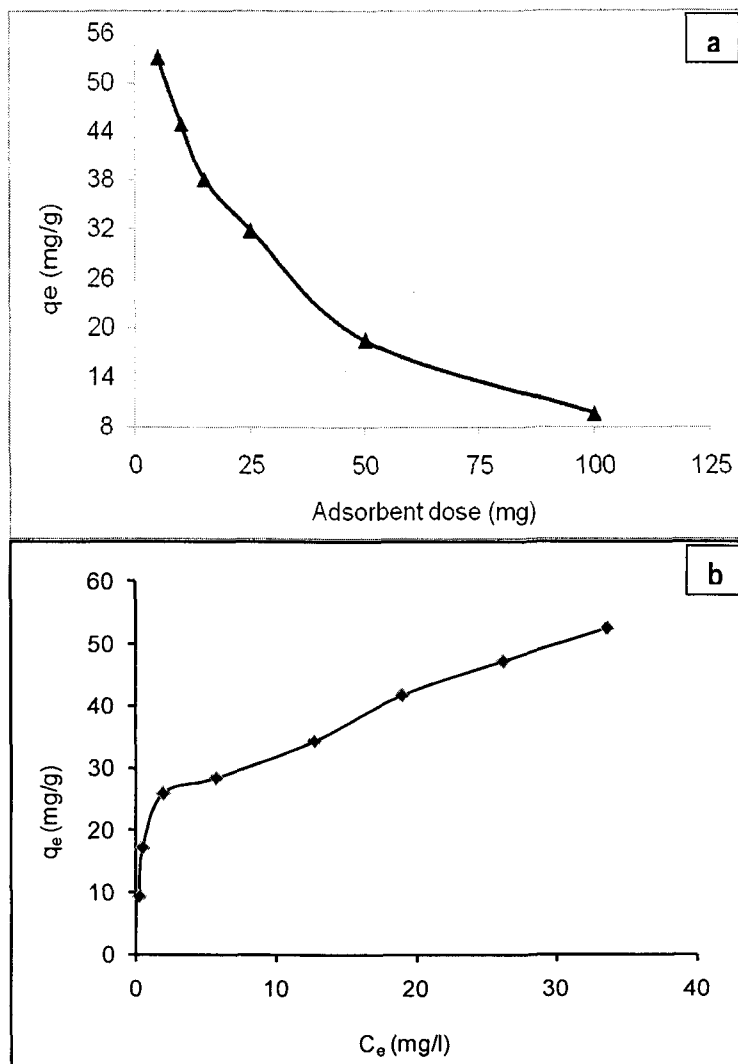


Figure 5

03rd June 2010
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No. of sheets:
Sheet No.

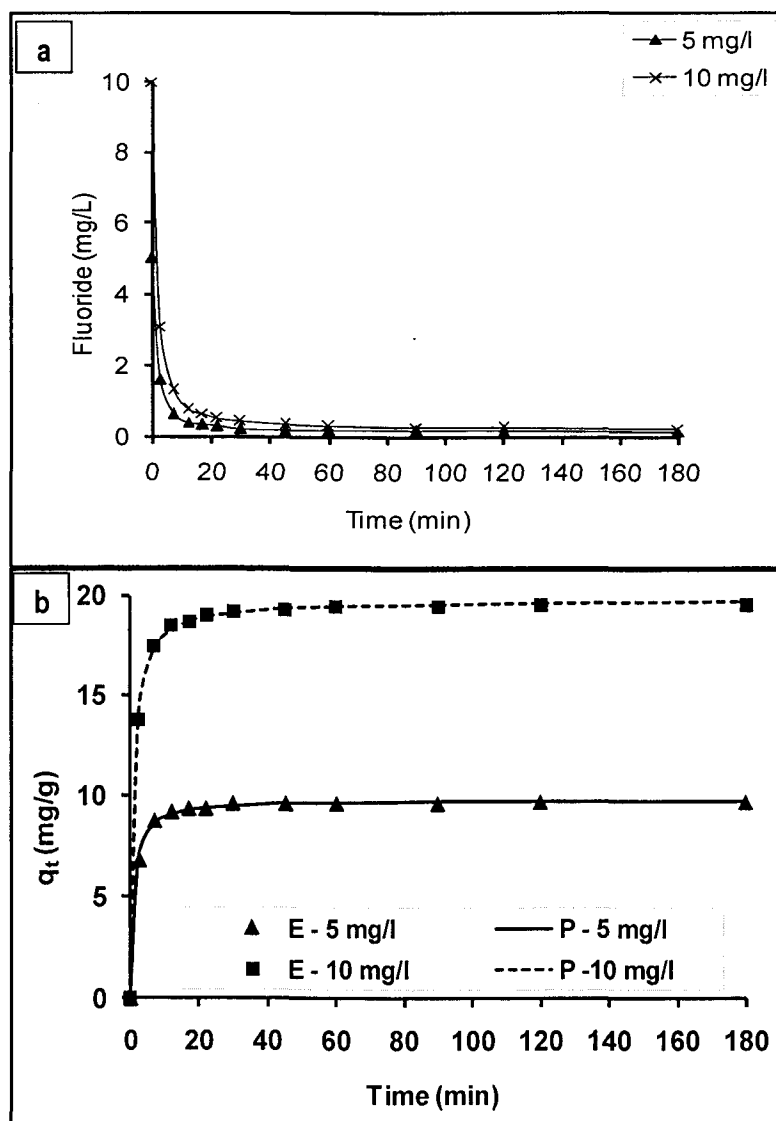
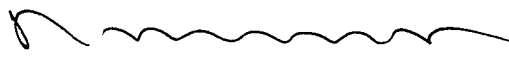


Figure 6

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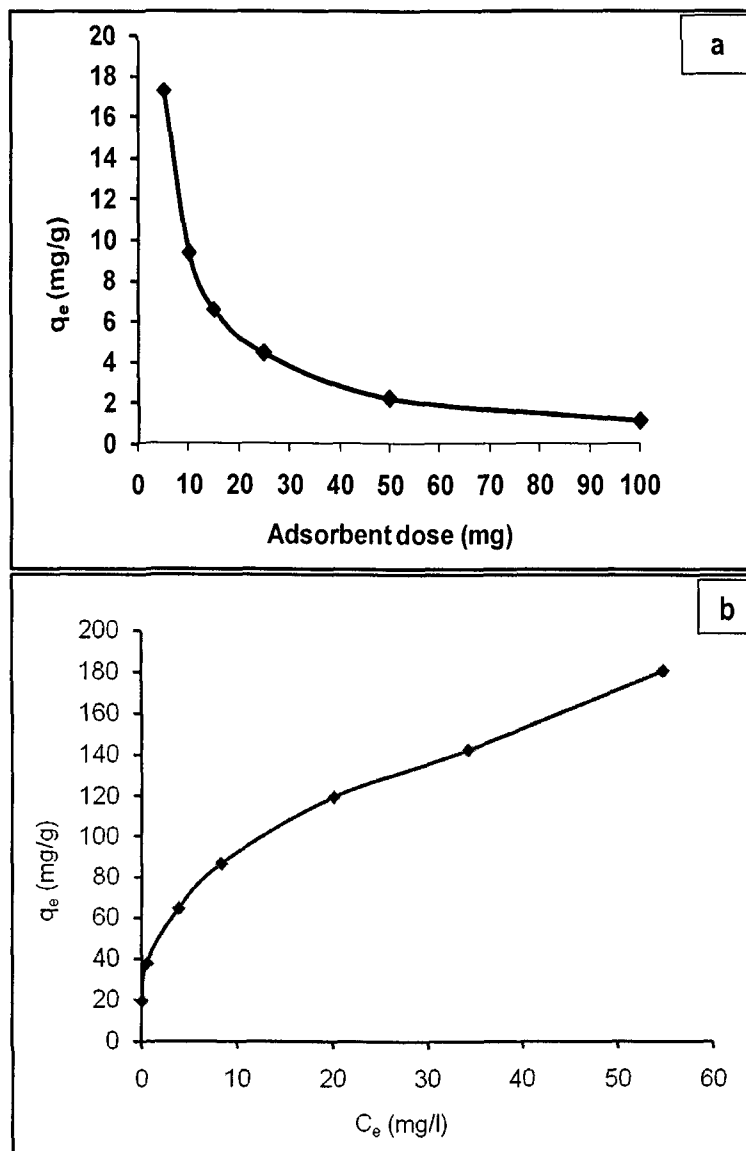


Figure 7

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Sheet No.

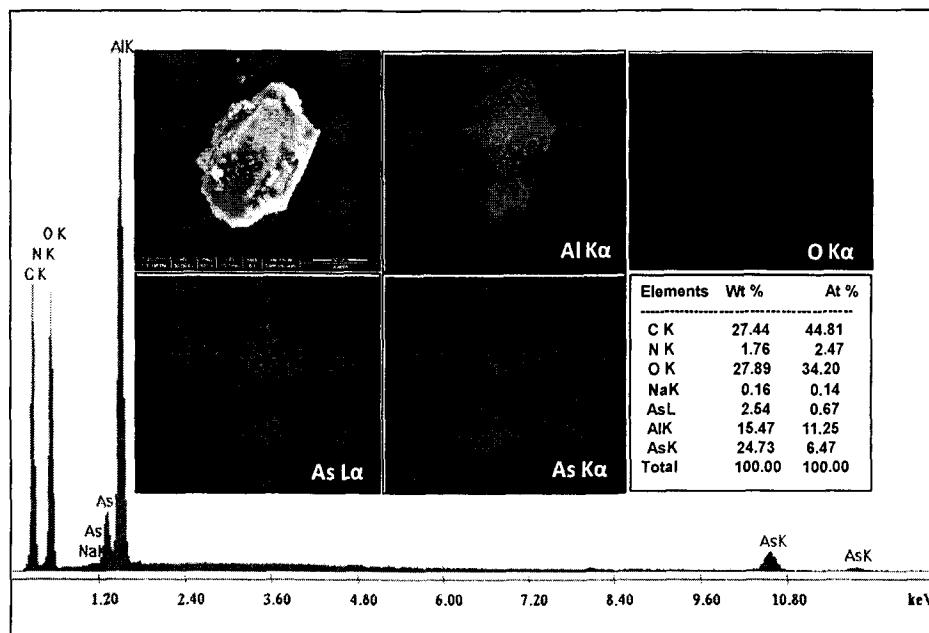
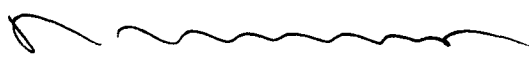


Figure 8

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Table 1

Sl. No.	Aluminum precursor used	Drying temperature	Stability in water at room temperature and pH nearly neutral pH (exposure time = 7 days)
1	Aluminum sulphate	30 °C 60 °C 100 °C	moderately stable moderately stable moderately stable
2	Aluminum chloride	30 °C 60 °C 100 °C 130 °C	Stable moderately stable unstable highly unstable

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