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PATENT CERTIFICATE
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पेटेंटी / Patentee : INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT Madras)

आविष्कारक (जहां लागू हो) / Inventor(s) : 1.THALAPPIL PRADEEP 2.MOHAN UDHAYA SANKAR 3.ANSHUP 4.AVULA ANIL KUMAR 5.CHAUDHARY AMRITA

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित WATER FILLED ORGANIC TEMPLATED METAL OXIDE/HYDROXIDE/OXYHYDROXIDE PARTICLE NETWORK FOR WATER PURIFICATION AND A DEVICE THEREOF नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 7th day of February 2013 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 WATER FILLED ORGANIC TEMPLATED METAL OXIDE/HYDROXIDE/OXYHYDROXIDE PARTICLE NETWORK FOR WATER PURIFICATION AND A DEVICE THEREOF as disclosed in the above mentioned application for the term of 20 years from the 7th day of February 2013 in accordance with the provisions of the Patents Act,1970.

अनुदान की तारीख : 14/12/2018
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, **7th day of February 2015**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 **7th day of February 2015** 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:

WATER FILLED ORGANIC TEMPLATED METAL OXIDE/HYDROXIDE/OXYHYDROXIDE PARTICLE NETWORK FOR WATER PURIFICATION AND A DEVICE THEREOF

2. APPLICANT:
(A) NAME: **INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT Madras)**
(B) NATIONALITY: Indian
(C) ADDRESS:**INDIAN INSTITUTE OF TECHNOLOGY MADRAS**
IIT P.O. Chennai - 600 036

3. Preamble to the Description

COMPLETE SPECIFICATION

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

COMPLETE SPECIFICATION

TITLE OF THE INVENTION

WATER FILLED ORGANIC TEMPLATED METAL OXIDE/HYDROXIDE/OXYHYDROXIDE PARTICLE NETWORK FOR WATER PURIFICATION AND A DEVICE THEREOF

FIELD OF THE INVENTION

The present invention relates to water purification and specifically to use of water filled organic polymer templated metal oxide/hydroxide/oxyhydroxide network for water purification. The present invention further relates to a device based on the same.

BACKGROUND OF THE INVENTION

Increasing chemical contamination of water is one of the major health problems today. Discharge of industrial wastewater and dissolution of toxic ores/minerals into water have resulted in severe chemical contamination. Purification of drinking water has become inevitable prior to consumption. Without being limited by the types of contaminants in drinking water, two kinds of contaminants are illustrated for highlighting the relevance of invention reported here: small size contaminants (e.g., fluoride/arsenic) and large size contaminants (e.g., colloidal iron).

Arsenic is a major health-related contaminant which affects drinking water quality through contamination of ground water sources. Arsenic contamination in ground water has been linked to a number of health-related disorders, such as cancer, cardiovascular system problems and mental development of children. Arsenic in ground water has been reported in over 20 countries. Several states in India are also severely affected, including West Bengal, Bihar, Assam and Uttar Pradesh. Nodal agencies involved in supplying clean drinking water have acknowledged that role of technology in providing arsenic free water, e.g., owing to availability of novel technologies, Bureau of Indian Standards (BIS) has lowered the limit for allowed arsenic concentration to 10 ppb (desirable limit, second revision of IS 10500 (Indian standard)).

Presence of iron in drinking water is not a major health hazard; however, the reddish-brown color in water is a significant aesthetic problem. Iron is usually found in several forms, most notably in dissolved and colloidal form. Concentration as low as 0.3 ppm deposits on the available surfaces and causes stain.

A number of purification technologies are in use for the removal of contaminants from drinking water. Adsorption, photo-irradiation, oxidation, filtration, coagulation/flocculation and distillation are a few examples of technologies in use for water purification. In a number of cases, two or more purification techniques are combined to effectively treat contaminated water.

Among various purification techniques, filtration is a popular fluid treatment process. Physical filtration involves the passage of contaminated fluid through a barrier which filters out selective contaminants based on size. Based on the size of the contaminant that the membrane can filter, the filtration technique can be divided into microfiltration (> 500 nm), ultrafiltration (> 5-10 nm), nanofiltration (> 1 nm) and reverse osmosis (> 0.1 nm). On the other hand, chemical filtration involves the passage of contaminated fluid through an adsorbent medium or ion exchange medium to removes selected contaminant.

Various types of membranes have been used in physical filtration. Their physical and chemical characteristics depend on a number of factors such as permeability, hydrophilicity, porosity, surface area, solvent resistance, chemical stability, flexibility and mechanical strength. Rate of transport through a membrane depends on thickness of the membrane. A number of membranes are made by chemical methods. For example, Loeb, S and Sourirajan, S (Sea Water Demineralization by Means of an Osmotic Membrane, Advances in Chemistry Series, 38, 117-132, 1963) report a thin dense layer membrane method involving fabrication of membrane containing both thin dense layer and less dense layer wherein the thin dense layer controls the transport of ions and the less dense layer gives mechanical strength to the membrane. US Patent Number 4,661,257 demonstrates a liquid membrane system wherein complexating quaternary ammonium salts are filled inside the pores of supporting membrane to remove selective ions. U.S. Patent Number 6,258,276 demonstrates a pore-filled microporous membrane wherein a microporous membrane is pore-filled by a cross-linked polyelectrolyte or hydrogel to control the transport of ions. U.S. Patent Number 7,857,978 demonstrates a biomimetic membrane wherein the transport protein such as aquaporin embedded lipid bilayer membrane is supported on a semi-permeable membrane.

Apart from solid membranes, permeable three-dimensional cross-linked network such as gel has been used as membrane in many detection and purification techniques. For example, gels have been used in gel-permeation chromatography techniques where pores of the gel separate different molecules based on their size. A practical use of gel filtration using cross-linked dextran for size exclusion chromatography is reported by in Journal of Protein Chemistry, 16(5), 463-468, 1997. Gels are also used in gel electrophoresis techniques as mentioned in U.S. Patent Number 3,766,047, where the permeable aqueous gel acts as a sieve to retard the passage of different molecules based on their charge and size under electrical field.

Chemical filtration through adsorption of contaminant on a solid surface is widely practiced for the removal of small sized contaminants, e.g., fluoride and arsenic. Activated alumina, activated carbon and zeolites are popular adsorbents. The use of adsorbents for fluoride and arsenic removal is mentioned in our previous Indian Patent Application No. 1529/CHE/2010 by the same inventors hereof, entire contents of which are herein incorporated by reference.

Attempts have been made to combine physical filtration and chemical filtration in a single system for detection and purification applications. Porath et al. (From gel filtration to adsorptive size exclusion, Journal of Protein Chemistry, 16(5), 463-468, 1997) proposes a combined size exclusion chromatography (SEC) with adsorption (Ad) into a single operation called AdSEC. It further shows that an AdSEC gel column having a volume of 5 mL could bind a high percentage of compounds having a molecular weight of between 5 kDa and 50 kDa and concentrate them about 1000 fold in a single operation. U.S. Patent Number 6,746,607 demonstrates a device for eliminating and purifying biomolecules by combining an ultrafiltration module with adsorbent IMAdSEC (Immobilized Metal ion Adsorptive Size Exclusion Chromatography) gel column. In some practices, colloidal adsorbent particles are dispersed in the contaminated fluid to adsorb the contaminants and later filtered using suitable membrane to selectively remove the contaminants adsorbed colloidal particles. The advantage of such techniques is that the adsorption capacity of an adsorbent increases with its available surface area. For example, U.S. Patent Number 6,669,851 B2 demonstrates a method of water purification using polymer colloids wherein the adsorbent polymer colloids are dispersed in the fluid contaminated with organic matter and subsequently filtered to remove the polymer colloids. U.S. Patent Number 7,014,771 and 7,309,425 demonstrate a method and an apparatus to purify arsenic contaminated water wherein a colloidal adsorbent media is dispersed in the contaminated water and subsequently filtered through a ceramic membrane precoated with adsorbent media of 10 pm thickness.

Various technologies are in use for treating arsenic contaminated water at community scale. In most cases, the water treatment plants require considerable operation cost, frequent maintenance, participation of the community and effective sludge disposal method. Many technologies fail in the field after installation due to the above mentioned requirements. In certain places, arsenic contamination is seen along with iron contamination. As arsenic has high affinity towards iron hydroxides/oxides/oxyhydroxides, a proportion of the input arsenic is seen adsorbed on the colloidal iron in the input water. Hence, removal of dissolved arsenic ion without removal of dispersed iron colloids is an incomplete treatment process. Further, removal of dissolved iron and dispersed iron colloid results in clogging of the filtration membrane due to the formation of sludge at the surface.

It is understandable that physical filtration is a simple solution for removing a wide range of contaminants: sediments, suspended solids, salinity, organic pollutants, biomolecules, inorganic pollutants, biological contaminants, etc. However, physical filtration has a number of limitations:

(1) removal of hazardous ions such as arsenic, fluoride, lead, mercury, etc using a reverse osmosis membrane results in high concentration of the said hazardous ions in the rejected fluid

(2) rate of filtration through a membrane is very slow

(3) physical filtration for removal of colloidal iron requires frequent backwash and generates sludge during backwash.

Moreover, selective removal of certain ions/molecules from a fluid without affecting other parameters is impossible by physical filtration technique. Therefore, removal of selective contaminants using high capacity adsorbent medium at high flow rate is advantageous. Filtration technique must address the removal of both small size contaminants (such as fluoride/arsenic) and large size contaminants (such as colloidal iron), without requiring backwash or sludge generation. In view of this, there remains a need for a tailor-made filter element through adsorption technique which (1) has a high adsorption capacity for selective ions, (2) does not reject the hazardous ion in concentrated form, (3) has the high filtration rate, (4) does not form sludge at the surface and (5) can be a portable fluid filter.

SUMMARY OF THE INVENTION

The present invention provides a method for preparation of adsorbent composition comprising of water insoluble aggregated nanoparticle network of organic polymer templated metal oxide/hydroxide/oxyhydroxide containing more than about 90% water, wherein the adsorbent composition is used for the rapid removal of contaminants from drinking water.

The present invention further provides a filtration device which removes specific contaminants from a fluid at high flow rate. The filtration device comprises an adsorbent nanocomposite aggregated network specifically tailor-made for the targeted contaminant which also acts as a permeable filtration element.

The high capacity adsorbent nanocomposite aggregated network filtration element does not reject any concentrated solution of contaminants into drainage and does not produce sludge at the surface of hybrid filtration element. Hence, the filtration device does not require frequent maintenance. The simplest form of filtration device is shown for the removal of iron and iron-cum-arsenic from drinking water at domestic scale.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts Arsenic (V) adsorption capacity of nanocomposite in aggregated network vis-a-vis dry powder form as a function of adsorbent dose.

Figure 2 depicts Arsenic (III) adsorption capacity of nanocomposite in aggregated network vis-a-vis dry powder form as a function of adsorbent dose.

Figure 3 depicts Iron adsorption capacity of nanocomposite in aggregated network vis- a-vis dry powder form as a function of adsorbent dose.

Figure 4 depicts Rate of adsorption of Fe^{2+} on nanocomposite aggregated network as function of time.

Figure 5 depicts Dynamic light scattering (DLS) size distribution profile as a function of standing time, (a) 10 ppm Fe^{2+} in synthetic challege water, (b) nanocomposite aggregated network in synthetic challenge water and (c) 10 ppm Fe^{2+} in presence nanocomposite aggregated network in synthetic challenge water.

Figure 6 depicts Visual view of as-prepared precipitated chitosan (in aggregated network form) and with increasing colloidal Fe^{2+} adsorption.

Figure 7 depicts Scanning electron microscopic image of (A, B) as-prepared precipitated chitosan and (C, D) colloidal Fe^{2+} adsorbed precipitated chitosan.

Figure 8 depicts Schematic view of adsorbent aggregated network based filtration device.

Figure 9 Schematic view of multiple cartridge module filtration unit.

Figure 10 depicts Iron adsorption capacity of nanocomposite aggregated network based filter element as a function of volume of contaminated water passed.

DETAILED DESCRIPTION OF THE INVENTION

The term “nanocomposite aggregated network” used hereinafter means that it is a precipitate of aggregated network present in wet form. The term “wet form” means that the precipitated aggregated network holds minimum about 90% of water by wt/wt %.

The term “nanocomposite aggregated network” includes an organic polymer templated metal oxide/hydroxide/oxyhydroxide network.

One aspect of the present invention provides a method for preparation of adsorbent composition comprising of water insoluble aggregated nanoparticle network of organic polymer templated metal oxide/hydroxide/oxyhydroxide containing more than about 90% water, wherein the adsorbent composition is used for the rapid removal of contaminants from drinking water.

Another aspect of the present invention further provides a filtration device which removes specific contaminants from a fluid at high flow rate. The filtration device comprises an adsorbent nanocomposite aggregated network specifically tailor-made for the targeted contaminant which also acts as a permeable filtration element.

Colloids and polymer cross-linked network such as gel are generally superior adsorbent due to their high surface area. However, a polymer cross-linked network such as gel show more advantage over dispersed colloids since gels are permeable and can be loaded on a porous surface. The present invention uses above advantage to develop a filter element comprising of a polymer cross-linked network comprising of the high capacity adsorbent composition which removes contaminants on contact with contaminated fluid and allows the said fluid to pass through it.

The present invention provides a high capacity adsorbent composition comprising of a polymer cross-linked nanocomposite aggregated network which removes both small size as well as large size contaminants on contact with contaminated fluid.

The present invention provides an adsorbent composition comprising a polymer cross-linked nanocomposite aggregated network which offers extremely high adsorption kinetics, thereby, requiring minimal contact time for contaminant removal.

The present invention provides an adsorbent composition comprising of a polymer cross-linked nanocomposite aggregated network which effectively removes iron, colloidal iron loaded with arsenic and arsenic ion, without forming sludge.

The present invention provides a water purification device based on adsorbent composition comprising of a polymer cross-linked nanocomposite aggregated network which removes selective ions and also acts as a permeable filter element.

The present invention provides a water purification device wherein very low contact time and very high flow rate is practicable.

The present invention deploys an adsorbent nanocomposite aggregated network filtration device for the removal of iron, iron-cum-arsenic without forming sludge at the surface of hybrid filtration element.

The polymer cross-linked nanocomposite aggregated network was taken as an adsorbent medium since the surface area of the medium is higher. The high adsorption capacity of nanocomposite aggregated network is due to the presence of nanocrystalline FeOOH in the chitosan matrix. The biopolymer-FeOOH nanocomposite ensures that no FeOOH particle is released into water during its use for water purification.

Figure 1 and 2 shows the difference in the equilibrium arsenic adsorption capacity of nanocomposite in aggregated network vis-a-vis dry form. 325X400 U.S. mesh nanocomposite in dry powder form was used in this study. The graph shows the quantity of adsorbent needed for the complete removal of arsenic. Arsenic is used in both inorganic forms (As^{5+} - Figure 1; As^{3+} - Figure 2). In figure 1 and 2, curve (a) indicates input arsenic concentration, curve (b) indicates output arsenic concentration after treating with nanocomposite in dry form and curve (c) indicates output arsenic concentration after treating with nanocomposite in wet form. With increasing quantity of adsorbent, arsenic removal efficiency increases gradually and residual arsenic concentration goes to below detection limit (0.005 mg/L). 1±0.1 ppm As^{3+} in synthetic challenge water treated with 50 mg/L adsorbent composition in dry form shows 577 ppb (Figure 2, curve (b)) whereas adsorbent composition in wet form shows 172 ppb (Figure 2, curve (c)). This trend of superior performance for adsorbent composition in the wet form continues as the quantity of adsorbent increases further. Similarly, 1±0.1 ppm As^{5+} in synthetic challenge water treated with 50 mg/L adsorbent composition in dry form shows 787 ppb (Figure 1, curve (b)) whereas adsorbent composition in wet form shows 56 ppb (Figure 1, curve (c)). This superior performance of the composition in the wet form is further reflected in the fact that an input concentration of 1±0.1 ppm is reduced to below 50 ppb through use of 100 mg/L of adsorbent in wet form, whereas over 500 mg/L of adsorbent in dry form is required for a similar performance. This means that adsorbent in the wet form exhibits at least 5 times improved performance over the same adsorbent in the dry form.

Iron contamination in ground water is widely seen in many countries. Although there is no severe health hazards due to iron contamination, its presence reduces the aesthetic of water. Foods cooked, clothes washed, containers used, places used in iron contaminated water look unpleasant due to yellow coloration. Since iron is not stable under oxygen environment, once contacted to atmospheric air it is oxidized to Fe^{3+} and subsequently precipitated due to hydrolysis. Hence, the removal of sludge from the storage container and the subsequent disposal to drainage area becomes tedious due to frequent user intervention. In the view of this, nanocomposite in wet form is tested for dissolved iron removal.

Figure 3 shows the difference in Fe^{2+} adsorption capacity of composition in the wet as well as dry form. In Figure 3, curve (a) indicates input iron concentration, curve (b) indicates output iron concentration after treating with nanocomposite in dry form and curve (c) indicates output iron concentration after treating with nanocomposite in wet form. An input concentration of 5±0.5 ppm Fe^{2+} is finally reduced to 2.2 ppm by the use of 1.0 g/L of adsorbent in dry form (curve (b)). On the contrary, only 40 mg/L dose of adsorbent in wet form is required to bring it to same output concentration (curve (c)). Bringing the output concentration to below 0.1 ppm (below detection limit) requires just 200 mg/L of adsorbent in wet form. Importantly, the adsorption capacity of the composition in wet form is several times higher than composition in dry form as the composition in wet form can repeatedly perform the function of removing Fe^{2+} from water. As it is evident from the column run, the adsorption capacity of the adsorbent composition in wet form is over 10 g/g at the relevant input concentration of 5±0.5 ppm. This is extraordinarily high adsorption capacity for any composition known in the prior art. This high adsorption capacity for dissolved iron eliminates the need of sludge management.

Figure 4 shows the kinetics of uptake of Fe^{2+} from synthetic challenge water using adsorbent composition in wet form. In Figure 4, curve (a) indicates input iron concentration and curve (b) indicates output iron concentration after treating with nanocomposite in wet form. An experiment is conducted with Fe^{2+} input concentration of 3±0.3 ppm and adsorbent quantity of 200 mg/L. It is found that output Fe^{2+} reduces to below 0.1 ppm (below detection limit) in contact time of less than 30 seconds. This is very fast rate of adsorption for any contaminant on an adsorbent surface. Very fast adsorption rate offers several advantages such as empty bed contact time (EBCT) can be significantly low, high flow rate water purification unit, easy maintenance. Very fast adsorption rate is evidently due to wet form of the composition wherein the accessibility of adsorption surface is very high. It is observed that contact time is not significantly altered, even if the input concentration is increased to 50 ppm. This is advantageous from the perspective that adsorbent composition in wet form can handle a wide concentration range, without significantly altering the EBCT of the unit.

Removal of dissolved iron by adsorbent aggregated network composition is further understood by dynamic light scattering measurement. Fe^{2+} in water is oxidized to Fe^{3+} by dissolved oxygen and subsequently hydrolyzed to form colloids. Removal of dissolved iron by adsorbent aggregated network composition is due to both adsorption of Fe^{2+} and adsorption of colloids formed during treatment process.

Figure 5 shows in situ light scattering measurement of (a) Fe^{2+} in synthetic challenge water; (b) nanocomposite aggregated network in synthetic challenge water and (c) Fe^{2+} adsorption on the nanocomposite aggregated network. As it can be seen from figure 5a, 10 ppm Fe^{2+} in synthetic challenge water forms colloidal species in water. This is related to the oxidation of Fe^{2+} to Fe^{3+} induced by dissolved oxygen in water. Therefore, in situ oxidized Fe^{2+} forms colloids in water, which increases in size with progression of time. In the first 2 minutes of addition of Fe^{2+} to water, colloids of size 1-2 pm are formed. With passage of time, colloids grow to size bigger than 5 pm. Dynamic light scattering is done in the size range of up to 7 pm only. Particles of bigger size are not observed - specifically in the case of figure 5b where the light scattering measurement of adsorbent composition in wet form reveal the presence of particles/colloids in size range of 1 pm. However, nanocomposite aggregated network largely comprises of particle with size greater than 10 pm. Figure 5a shows the light scattering measurement of Fe^{2+} in presence of adsorbent composition in wet form. It is clearly observed that there is no Fe^{2+} colloid formation in the presence of adsorbent composition in wet form. Peaks in the range of 1.5-7 pm observed in figure 5a are not observed in figure 5c. Based on the experimental evidence, majority of Fe^{2+} removal happens through the binding of oxidized Fe^{2+} colloids to the surface of adsorbent composition in wet form. While the adsorbent composition has capacity to adsorb Fe^{2+} in the ionic form, however, Fe^{2+} undergoes oxidation to oxidized Fe^{3+} colloid. Since the kinetics of adsorption is so fast (as observed in figure 4), there are no colloids seen in the water.

Figure 6 depicts the effect of oxidized Fe^{2+} colloid adsorption on precipitated chitosan surface. Adsorbent composition is prepared by dissolving chitosan in acidic medium (such as 1% HCI) followed by precipitation through use of alkaline medium (such as NaOH). The obtained precipitate is washed with copious amount of water and is referred as precipitated chitosan. Fe^{2+} removal studies using precipitated chitosan are conducted in the manner as described in Example 6. Figure 6 is the visual reference to precipitated chitosan adsorbent on a filter paper with Figure 6(0-9) refers to increasing weight ratio of; oxidized Fe^{2+} colloid to precipitated chitosan, Figure 6(0) being precipitated chitosan. It is clearly observed that with increasing weight ratio of oxidized Fe^{2+} colloid, precipitated chitosan undergoes color transformation and changes from off- white (at 0% oxidized Fe^{2+} colloid content) to dark orange (at 25% oxidized Fe^{2+} colloid content). The efficiency of removal of Fe^{2+} ion from water is equally effective (both in terms of kinetic efficiency as well as adsorption capacity) vis-a-vis nanocomposite aggregated network. Mechanism of Fe^{2+} adsorption on precipitated chitosan is also similar. Through studies with other aggregated networks (such as OTBN aggregated network (Indian Patent Application No. 1529/CHE/2010)), we have found that similar performance is obtained. Hence, it is demonstrated that the ability to remove Fe^{2+} from water is a common property observed across the range of aggregated networks.

Figure 7 provides a further visual evidence of colloidal Fe^{2+} deposition on the nanocomposite aggregated network surface. Precipitated chitosan (as described in figure 6(0) and figure 6(9)) is examined using scanning electron microscope. Figure 7(A-B) is the image of as-prepared precipitated chitosan surface. Surface of as-prepared precipitated chitosan is as expected for a large aggregated network structure, it is long-range network and the surface is fairly clean and smooth. On the contrary, upon exposure to Fe^{2+} in water, precipitated chitosan surface adsorbs colloidal particles on the surface (Figure 7(C-D)). While the chitosan network is not altered, surface is “fouled” to a significant degree. Colloidal particles of size <1 pm are observed throughout the chitosan network surface. A number of colloidal particles are small in size, which means that they have been removed from the water quite early due to which they have been unable to undergo aggregation. This is another evidence of fast kinetics of colloidal Fe^{2+} removal from water.

The concept of using aggregated network for the removal of contaminants from water is equally relevant for other species. One such example is the use of OTBN aggregated network for the removal of fluoride from water. It is observed that 50 mg adsorbent can remove 7 ppm of fluoride from synthetic challenge water (details of studies are described in Indian Application No. 1529/CHE/2010 and 4062/CHE/2011 by same inventors hereof) whereas similar performance is obtained by use of 25 mg adsorbent in wet form. Adsorption efficiency of adsorbent in wet form is therefore observable and demonstrated for smallest size water contaminant (F') as well as largest size water contaminant (colloidal Fe^{2+}). While relative performance difference between adsorbent in dry form vs. wet form varies with respect to the nature of contaminant, kinetics efficiency of contaminant removal is very high for adsorbent in wet form. This is linked to very high accessibility of water in the aggregated network which promotes the contaminant transport with minimum energy input. In the case of large size water contaminant, their transport is strongly hindered in the adsorbent network due to low pore size and poor porosities. This leads to significantly low contaminant adsorption capacity observed for a given composition. However, the same composition in wet form has almost unhindered access for the contaminant, irrespective of the contaminant size. This is unique advantage associated with the use of adsorbent in wet form. In case of highly solvated contaminants (such as fluoride), active composition (such as OTBN) in the wet form works; inactive composition (such as precipitated chitosan) does not remove fluoride irrespective of whether it is used in dry or wet form. However, in case of colloidal aggregates (especially which are prone for phase separation from water with minimum energy input), both active as well inactive composition in wet form perform with equal efficiency. Energy input required for phase separation of colloidal aggregates is provided by the availability of considerably large surface.

Using the scope of adsorbent composition in the wet form and demonstrating its utility for water purification unit, a water purification device is constructed (figure 8). Water purification device comprises a porous membrane cloth (of absolute pore size less than 2 micron) which is sleeved over a rigid porous support (of absolute pore size less than 100 micron) and edges/comers are appropriately sealed. Subsequently, the cloth-support assembly (called as element) is put on water filter housing available commercially (e.g., length: 10", inlet/outlet diameter: 1", material of construction: polypropylene). Subsequently, through the use of 1/25 HP pump, adsorbent composition in the wet form is passed through the water filtration device and it is continued till a bed of given thickness forms on the membrane cloth. The filtration device is ready for use in water purification. Through this device, a flow rate of over 5 L/min can be obtained using 1/25 HP water pump.

A variant of the design of water purification device is shown in the figure 9. The water filter housing comprises of stainless steel multi-cartridge water filter housing. Number of elements present in housing can be further increased, to accommodate higher flow rates. In another variant of the design of the water purification device, the element can comprise of pleated cartridge or string wound cartridge, which are commonly used as micron rated water purification cartridges.

Performance efficacy of the water purification device as shown in the previous figures (figures 8 and 9) is further demonstrated in figure 10. Synthetic challenge water containing 5±0.5 ppm Fe^{2+} is fed through the cartridge using 1/25 HP water pump at a flow rate of 5 L/min. Output water is collected for measurement at every 250 L and analyzed for the presence of Fe (Fe^{2+} and Fe^{3+}). It is observed that up to 3000 L, the output concentration stayed below detection limit. This clearly demonstrates the utility of the adsorption efficiency of the water purification device. It may be noted that using the design features provided in the examples of the present invention, one can fabricate the water purification device with an output flow rate capacity of over 100,000 L/h.

This application may disclose several feature limitations that support any range within the disclosed features even though a precise feature limitation is not stated verbatim in the specification because the embodiments of the invention could be practiced throughout the disclosed features. Finally, the entire disclosure of the patents and publications referred in this application, if any, are hereby incorporated herein in entirety by reference.

Experimental methods

Material characterization

Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention.

Dynamic light scattering (DLS) measurements were carried out using Zetasizer Nano ZS (Malvern). Arsenic ion concentration in the water was detected using inductively coupled plasma mass spectrometry (NexION 300, PerkinElmer). Spectrophotometric determination of Fe^{2+} and Fe^{3+} was carried out using UV-vis absorption spectrophotometer (LAMBDA 45, PerkinElmer). Surface morphology studies were carried out using a Scanning Electron Microscope (SEM) (FEI Quanta 200).

The following few examples are meant to illustrate the present invention. The examples should not be construed as limiting the scope of the invention.

EXAMPLE 1

SYNTHESIS OF ORGANIC TEMPLATED FERRIC OXYHYDROXIDENANOCOMPOSITE (REFERRED AS NANOCOMPOSITE AGGREGATEDNETWORK):

The said composite is prepared as reported in the previous patent application (486/CHE/2013). Chitosan was dissolved in 1 % HCl. Commercial chitosan was purchased from local sources. To this solution, 1 M iron salt (chosen from nitrate, sulphate, chloride, acetate, etc) was added and incubated for 1 hour. Iron-chitosan mixture was then hydrolyzed using 2 M NaOH solution. The precipitate was washed using copious amount of water to removed dissolved salts. The washed precipitated aggregated network was used for iron and arsenic adsorption study. Further, a portion of the aggregated network was dried at room temperature, crushed to granules and used for arsenic adsorption study.

EXAMPLE 2

SYNTHESIS OF ORGANIC TEMPLATED ALUMINUM OXYHYDROXIDE:

The said composition is prepared as reported in the previous patent application (1529/CHE/2010). Chitosan was dissolved in 1 % HCl. To this solution, 1 M aluminum salt (chosen from nitrate, sulphate, chloride, acetate, etc) was added and incubated for 1 hour. Aluminum-chitosan mixture was then hydrolyzed using 2 M NaOH solution. The precipitate was washed using copious amount of water to removed dissolved salts. The washed precipitated aggregated network was used for fluoride adsorption study. Further, a portion of the precipitated aggregated network was dried at room temperature, crushed to granules and used for fluoride adsorption study.

EXAMPLE 3

The method described in example 1 was modified to prepare nanocomposite material. Iron salt to chitosan ratio was varied from 95:5, 90:10, 80:20, 70:30, 60:40, 50:50, 5:95 and 0:100.

EXAMPLE 4

TESTING PROOCOL FOR ARSENIC ADSORPTION BY NANOCOMPOSITE INAGGREGATED' NETWORKAND DRY FORM:

Synthetic challenge water having total dissolved solids ~500 µS/cm was taken and pH was adjusted to 7.0 ± 0.2. 5, 10, 15, 25, 50 and 100 mg of as-prepared nanocomposite aggregated network (dry weight basis) were taken in 100 mL of synthetic challenge water spiked with 1.0 ± 0.1 ppm of As^3+ and shaken for 90 mins. The samples were centrifuged and the supernatants were collect to analyze the remaining As^{3+} in water by ICP-MS. The same procedure was repeated for As^{5+} adsorption study. For comparison, the dry form of nanocomposite was tested for As^{3+} and As^{5+} as described above.

EXAMPLE 5

METHOD TO STUDY THE IRON ADSORPTION BY NANOCOMPOSITE IN AGGREGATED NETWORK AND DRY FORM:

1, 2, 4, 10, and 20 mg of nanocomposite aggregated network (dry weight basis) were taken in 100 mL of distilled water spiked with 4.0 ± 0.5 ppm of Fe^{2+} and shaken for 30 mins. The samples were centrifuged and the supernatants were collect to analyze the remaining Fe^{2+} and Fe^{3+} in water by UV-vis absorption spectrophotometer. For comparison, 5, 10, 20, 50, and 100 mg of dry form of nanocomposite was tested for Fe^{2+} as described above. Fe^{2+} in water was estimated using 1,10-phenanthroline method and absorbance was recorded at 515 nm and Fe^{3+} in water was estimated using potassium thiocyanate method and absorbance was recorded at 480 nm.

EXAMPLE 6

METHOD TO STUDY THE RATE OF IRON ADSORPTION BY AS-PREPARED NANOCOMPOSITE IN AGGREGATED NETWORK FORM:

20 mg of as-prepared nanocomposite aggregated network (dry weight basis) was taken in 100 mL of distilled water spiked with 3.0 ± 0.5 ppm of Fe^{2+} and shaken for 1, 5, 15 and 30 min. The samples were centrifuged immediately and the supernatants were collect to analyze the remaining Fe^{2+} and Fe^{3+} in water by UV-vis absorption spectrophotometer. Fe^{2+} in water was estimated using 1,10-phenanthroline method and absorbance was recorded at 515 nm and Fe^{3+} in water was estimated using potassium thiocyanate method absorbance was recorded at 480 nm.

EXAMPLE 7

A HIGH FLOW IRON REMOVAL CARTRIDGE FABRICATED USING THE ADSORBENT NANOCOMPOSITE NETWORK FILTER ELEMENT:

100 g of as-prepared nanocomposite aggregated network (by wet weight basis) was taken in 1 L of distilled water and was loaded on a radial flow, particulate filter such as polymer spun

cartridge. The nanocomposite aggregated network loaded filtration device was hereafter used for iron removal study. 25 L of 5 ppm Fe^{2+} ($FeSO_4$) in synthetic water was freshly prepared. The iron water was filtered through the nanocomposite aggregated network loaded filtration device at 1 to 10 mL/min flow rate. Samples were collected and both Fe^{2+} and Fe^{3+} in input and output water were measured.

We Claim:

1. A method for preparing an adsorbent composition comprising of water insoluble aggregated nanoparticle network of organic polymer templated metal oxide/hydroxide/oxyhydroxide containing more than 90% water content, wherein the adsorbent composition is used in a water purification device for the removal of contaminants from drinking water comprising the steps of;
    a. mixing a metal precursor solution with the organic polymer to obtain a metal organic polymer complex solution;
    b. hydrolyzing the metal precursor to obtain a semi-solid water insoluble aggregated nanoparticle network by adding a base solution into the metal-organic polymer complex solution with vigorous stirring;
    c. filtering the semi solid water insoluble aggregated nanoparticle network on a micron filter cloth to obtain the adsorbent composition.
2. The method as claimed in claim 1, wherein the organic polymer comprises chitosan, banana silk, cellulose, nylon, starch or a combination thereof.
3. The method as claimed in claim 1, wherein water insoluble aggregated nanoparticle network is of size in the range of 1 µm to 10 µm.
4. The method as claimed in claim 1, wherein the metal precursor comprises a salt of aluminum, zinc, manganese, iron, titanium, zirconium, lanthanum, cerium, calcium, magnesium or a combination thereof.
5. The method as claimed in claim 4, wherein the anion in the metal precursor salt comprises of nitrate, chloride, sulfate, acetate, isopropoxide, or a combination thereof.
6. The method as claimed in claim 1, wherein the base comprises sodium hydroxide, ammonia, potassium hydroxide, sodium carbonate, sodium bicarbonate or a combination thereof.
7. The method as claimed in claim 1, wherein the weight ratio of metal oxide/hydroxide/oxyhydroxide to organic polymer is varied from 0% to 500%.
8. The method as claimed in claim 1, wherein the adsorbent composition is used for the removal of colloidal and dissolved iron from water with iron adsorption capacity in excess of 10 g iron per g dry weight of the adsorbent composition.

9. The method as claimed in claim 1, wherein the adsorbent composition is used for the removal of colloidal and dissolved iron from water without generating sludge and requiring no backwash.
10. The method as claimed in claim 1, wherein the adsorbent composition is used for the removal of arsenic from water with arsenic adsorption capacity in excess of 20 mg; arsenic per g dry weight of the adsorbent composition, at an input arsenic concentration of 1 ppm.
11. The method as claimed in claim 1, wherein the adsorbent composition is used for the removal of fluoride from water with fluoride adsorption capacity in excess of 50 mg fluoride per g dry weight of the adsorbent composition, at an input fluoride concentration of 10 ppm.
12. The method as claimed in claim 1, wherein the adsorbent composition used in a water purification device for the removal of contaminants from drinking water comprising the steps of;
    a. disposing the adsorbent composition on a macroporous filter element by passage of water containing adsorbent composition through the macroporous filter element
    b. mounting the macroporous filter element inside a housing tube.
13. The method as claimed in claim 12, wherein the macroporous filter element includes polymer spun cartridge, activated carbon block, filter cloth, ceramic filter for passage of contaminated water.
14. The method as claimed in claim 12, wherein empty bed contact time for the passage of contaminated water for the adsorbent composition loaded on a macroporous filter element is less than 5 seconds.
15. The method as claimed in claim 12, wherein the adsorbent composition loaded on macroporous filter is operated at an input water pressure of 0.5 psi to 50 psi.

Dated at Chennai this 18th September, 2018

Signature:

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

WATER FILLED ORGANIC TEMPLATED METAL OXIDE/HYDROXIDE/OXYHYDROXIDE PARTICLE NETWORK FOR WATER PURIFICATION AND A DEVICE THEREOF

ABSTRACT

The present invention discloses a method for preparation of adsorbent composition comprising of water insoluble aggregated nanoparticle network of organic polymer templated metal oxide/hydroxide/oxyhydroxide containing more than 90% water content, wherein the adsorbent composition is used for the rapid removal of contaminants from drinking water. Utility of adsorbent composition to remove a wide variety of contaminants is demonstrated. The present invention discloses a filtration device which removes specific contaminants from a fluid at high flow rate.

WATER FILLED ORGANIC TEMPLATED METAL OXIDE/HYDROXIDE/OXYHYDROXIDE PARTICLE NETWORK FOR WATER PURIFICATION AND A DEVICE THEREOF

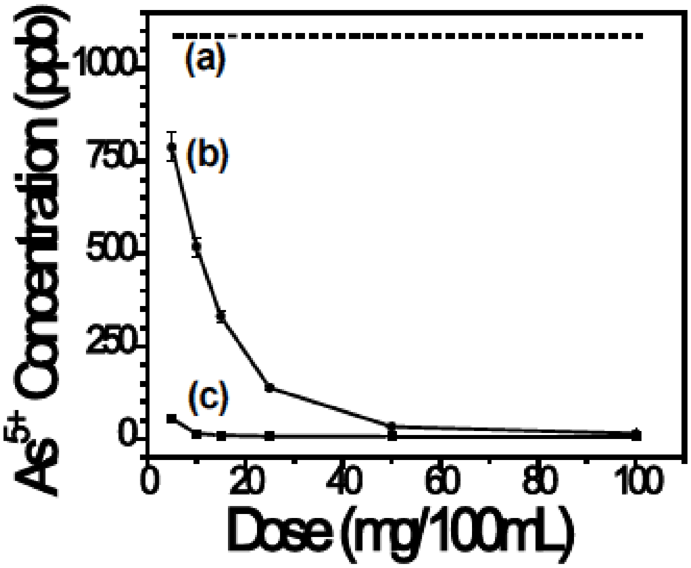

Figure 1

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D. Moses Jeyakaran
Advocate & Patent Agent
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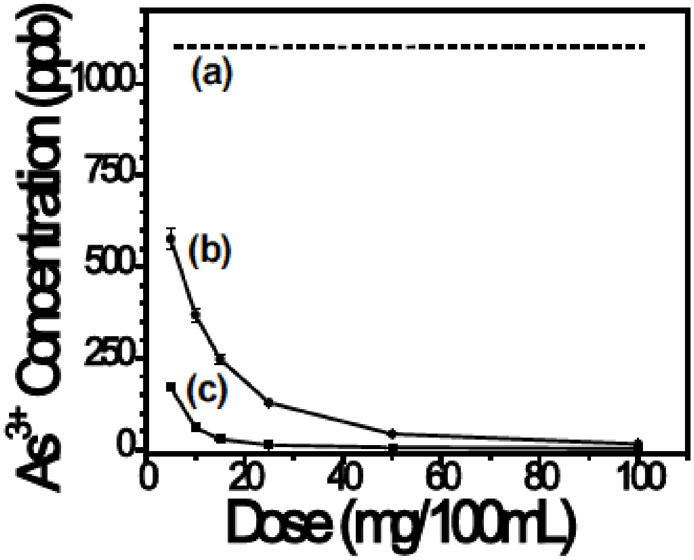

Figure 2

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Advocate & Patent Agent
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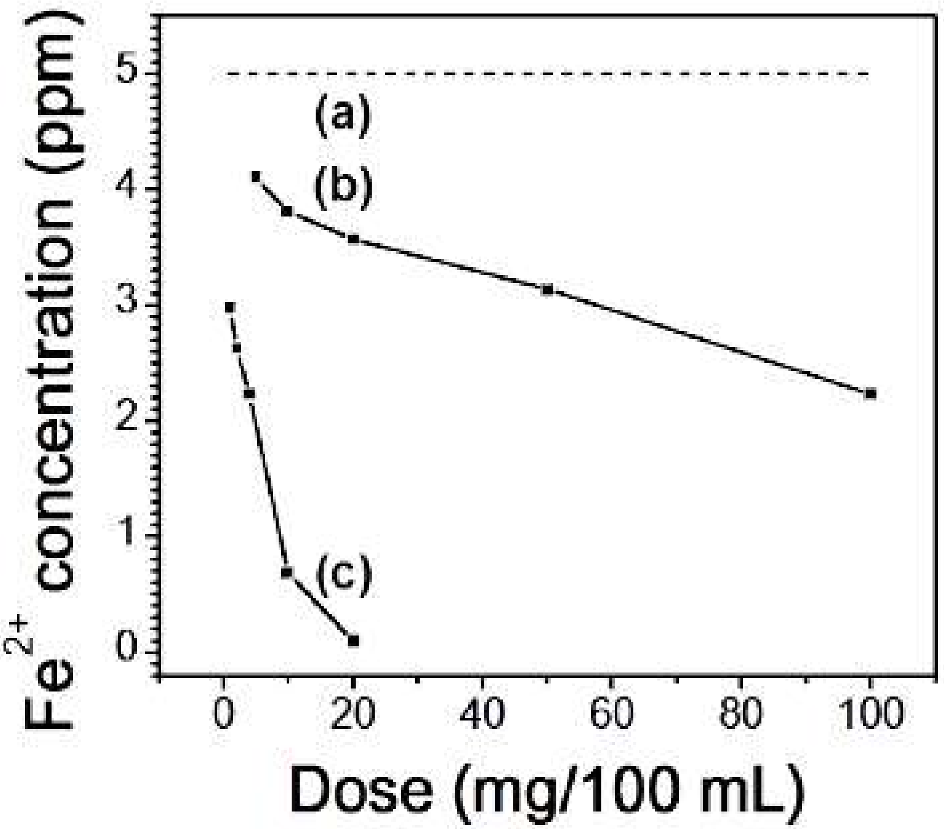

Figure 3

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Advocate & Patent Agent
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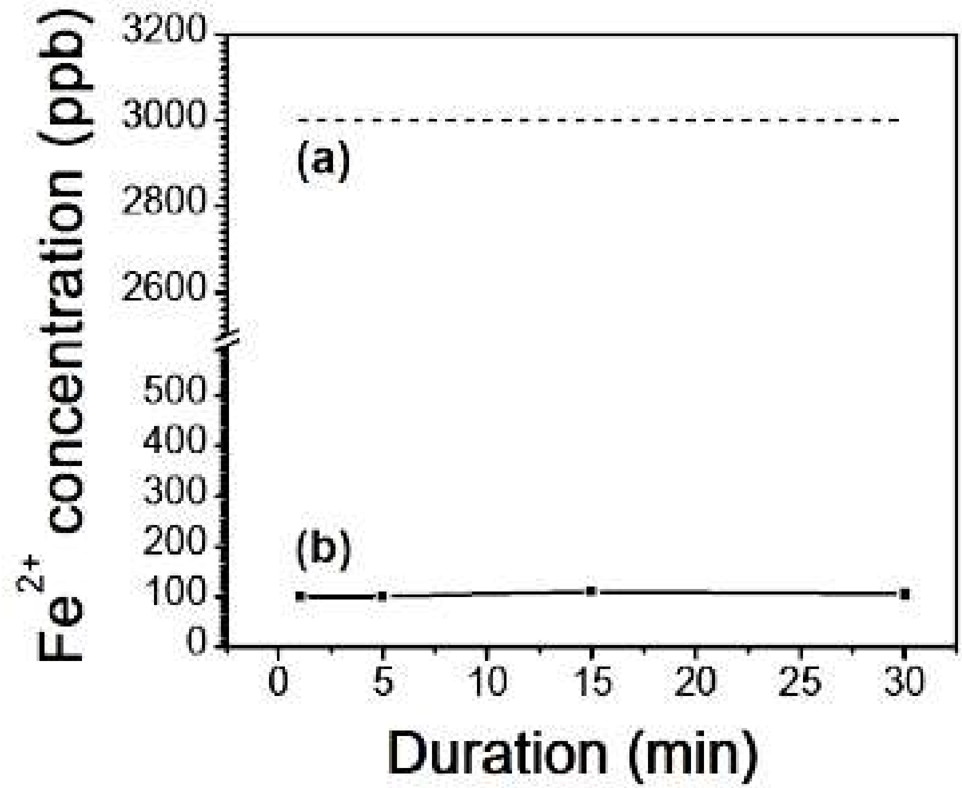

Figure 4

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Advocate & Patent Agent
IN/PA — 369

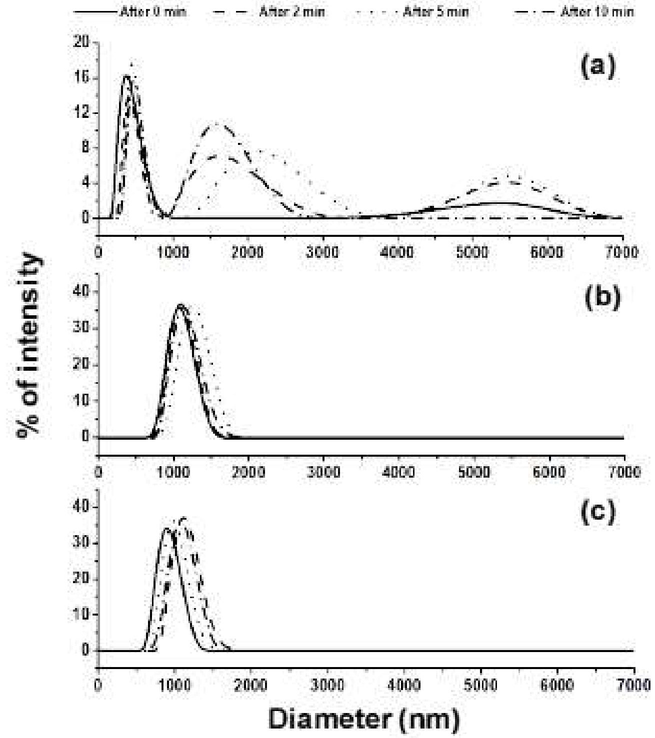

Figure 5

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Advocate & Patent Agent
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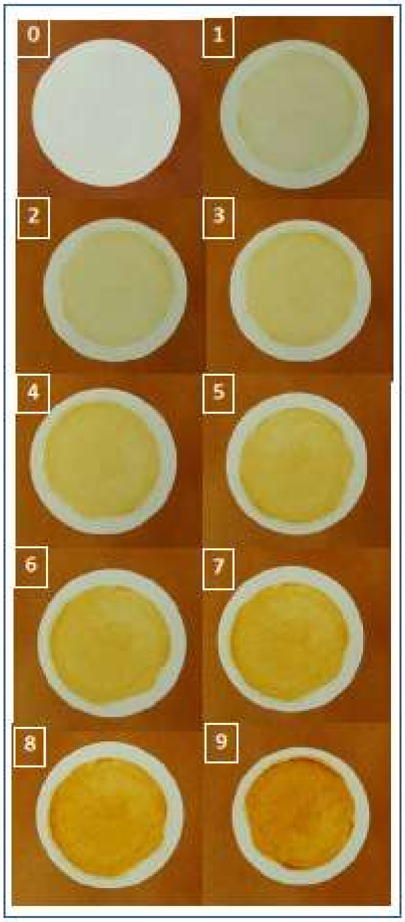

Figure 6

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Advocate & Patent Agent
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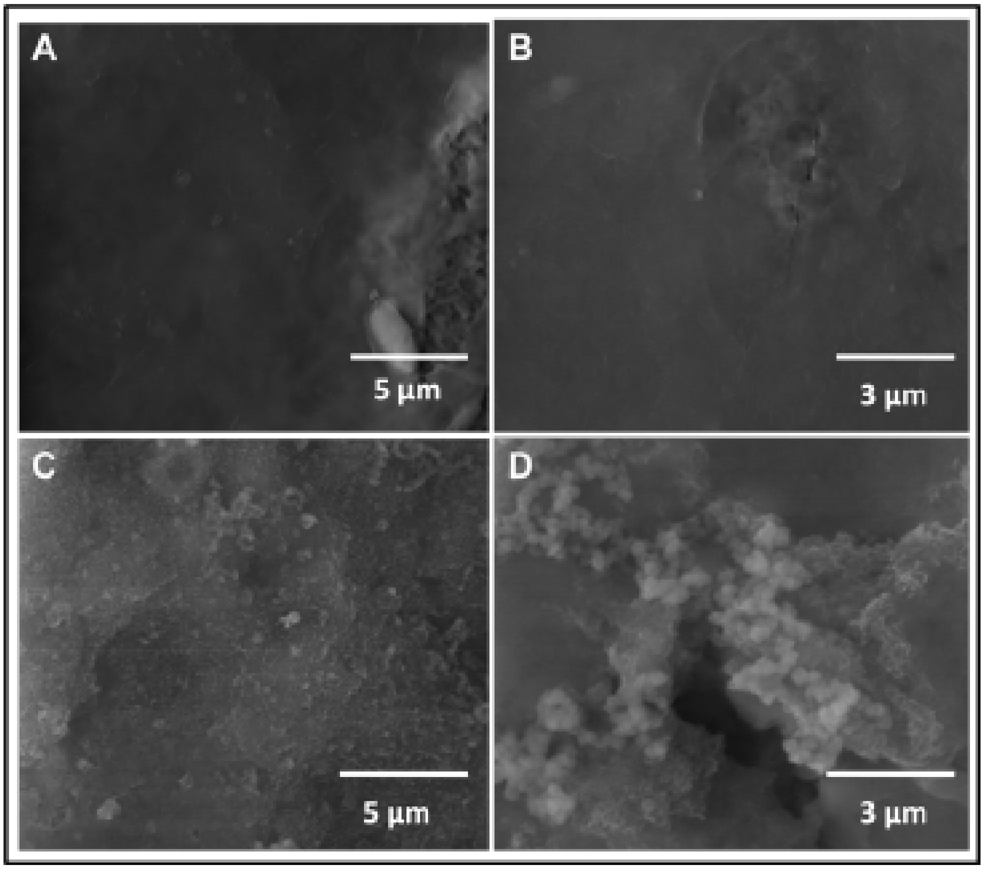

Figure 7

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D. Moses Jeyakaran
Advocate & Patent Agent
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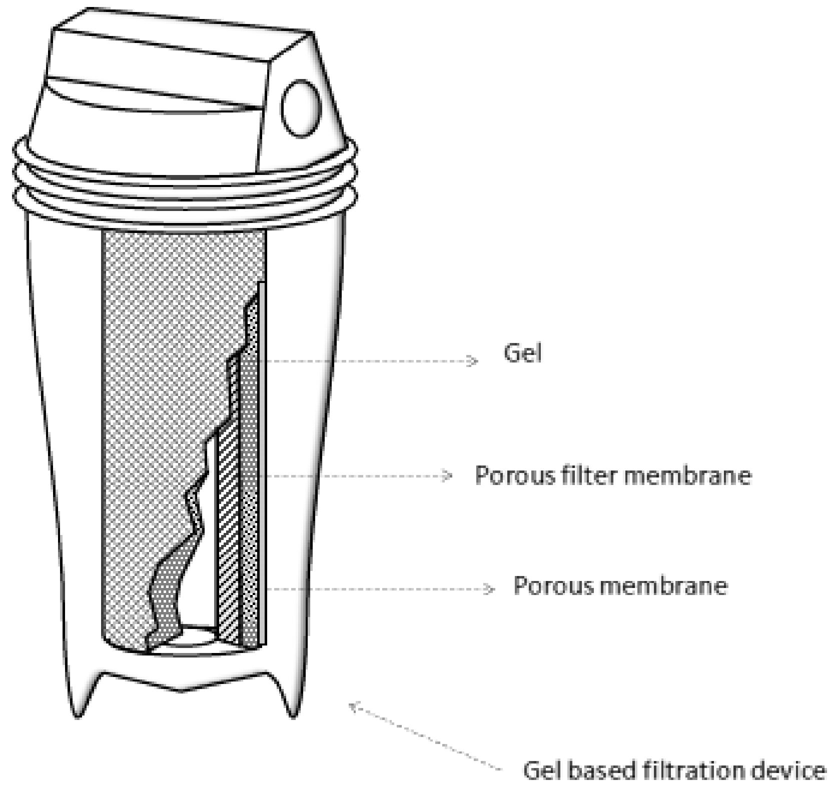

Figure 8

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Advocate & Patent Agent
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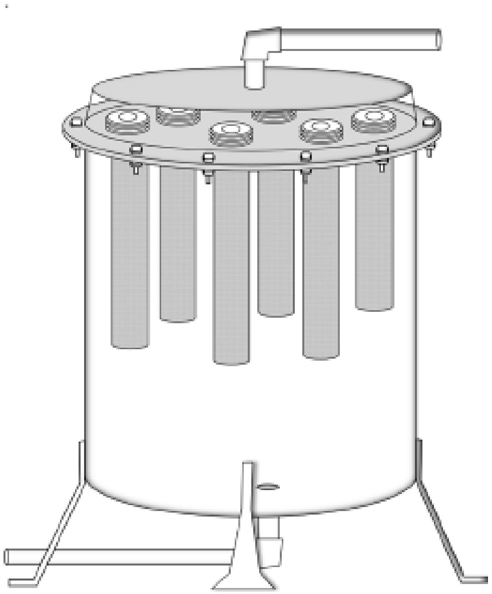

Figure 9

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Advocate & Patent Agent
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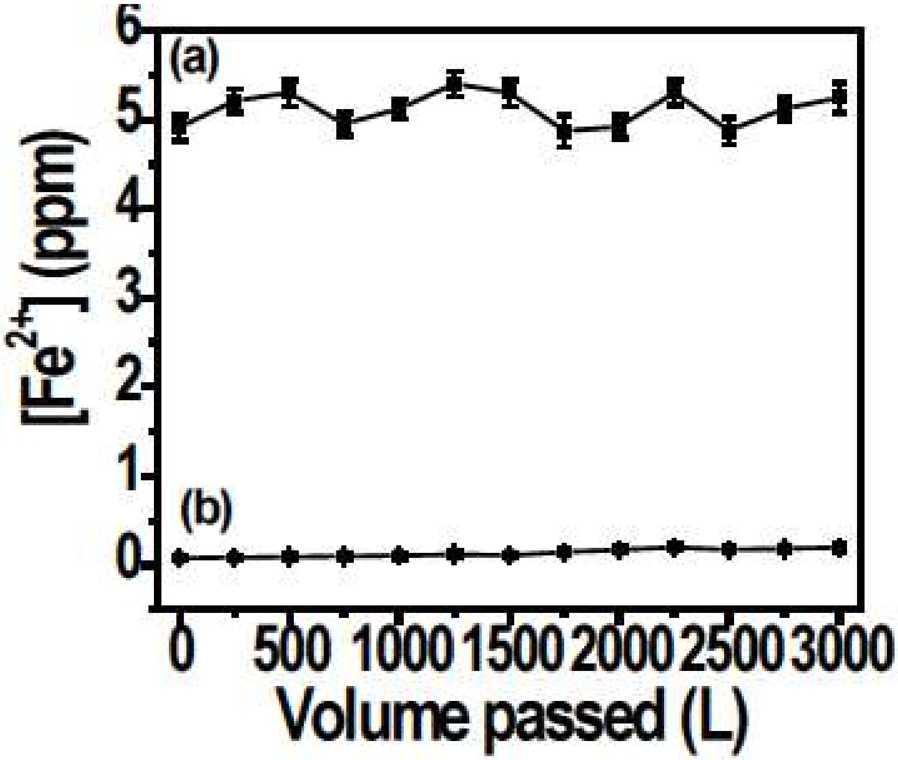

Figure 10

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D. Moses Jeyakaran
Advocate & Patent Agent
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