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पेटेंट प्रमाणपत्र
PATENT CERTIFICATE

(Rule 74 Of The Patents Rules)

पेटेंट सं. / Patent No.	:	286929
आवेदन सं. / Application No.	:	4062/CHE/2011
फाइल करने की तारीख / Date of Filing	:	24/11/2011
पेटेंटी / Patentee	:	INDIAN INSTITUTE OF TECHNOLOGY

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित MULTILAYER ORGANIC-TEMPLATED-BOEHMITE-NANOARCHITECTURE FOR FLUORIDE REMOVAL नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 24th day of November 2011 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 MULTILAYER ORGANIC-TEMPLATED-BOEHMITE-NANOARCHITECTURE FOR FLUORIDE REMOVAL as disclosed in the above mentioned application for the term of 20 years from the 24th day of November 2011 in accordance with the provisions of the Patents Act,1970.

एकस्य कार्यालय THE PATENT OFFICE GOVT.OF INDIA भारत सरकार

अनुदान की तारीख :
Date of Grant : 31/08/2017

पेटेंट नियंत्रक
Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, **24th day of November 2013**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 **24th day of November 2013** and on the same day in every year thereafter.

24 NOV 2011

FORM – 2

THE PATENTS ACT, 1970

(39 of 1970)

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The Patents Rules 2003

COMPLETE SPECIFICATION

(SECTION 10 & rule 13)

ORIGINAL

TITLE

MULTILAYER ORGANIC-TEMPLATED-BOEHMITE-NANOARCHITECTURE FOR FLUORIDE REMOVAL

APPLICANT

4062 /CHE/ 2011

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

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

FIELD OF INVENTION

The present disclosure relates to nanoscale shell of metal oxide/hydroxide on an organic-templated-boehmite-nanoarchitecture, along with methods of preparation and its use for water purification.

PRIOR ART:

Aluminum based compositions have been exhaustively studied for the removal of inorganic anions from drinking water (e.g., fluoride/arsenate). Use of aluminum based compositions is more pertinent for fluoride adsorption from water due to its relatively higher fluoride adsorption capacity vis-à-vis other adsorbents as well as no additional requirement of pre/post-filtration. Improvement in the capacity of aluminum based compositions has been looked at from various approaches. It is also important to understand that practically all aluminum based compositions in the field use require frequent regeneration, largely to reduce the cost of water purification. However, traditionally followed practice of regeneration (alkali treatment followed by acidification) leads to secondary contamination of water sources such as high fluoride concentration in the sludge, leaching of aluminum in water and high dissolved salt content of the sludge. Prior art related to fluoride removal using aluminum based compositions and associated challenges are covered in detail in our previous patent application (1529/CHE/2010).

Some of the most recent prior art on fluoride removal using aluminum and/or chitosan based compositions are highlighted here.

(a) Miretzky P., Cirelli A. F., Fluoride removal from water by chitosan derivatives and composites: A review, Journal of Fluorine Chemistry 132 (2011) 231–240

(b) Jagtap S., Yenkie M. K., Das S., Rayalu S., Synthesis and characterization of lanthanum impregnated chitosan flakes for fluoride removal in water, Desalination 273 (2011) 267–275

(c) Fluoride removal from water by adsorption—A review, Bhatnagar A., Kumar E., Mika Sillanpää M., Chemical Engineering Journal, 171 (2011) 811-840

(d) Liu R., Gong W., Lan H., Gao Y., Liu H., Qu J., Defluoridation by freshly prepared aluminum hydroxides, 175 (2011) 144-149

BACKGROUND OF THE INVENTION

The motivation of our research group is to solve the problem of fluoride removal from drinking water, considering the following boundary conditions:

(i) Adsorbent composition should be implementable at the household level (i.e., high adsorption kinetics and low empty bed contact time)

(ii) Adsorbent composition requires no regeneration, thereby generating no secondary contamination

(iii) Adsorbent composition should be easy-to-use and maintain (i.e., requiring no pre/post-filtration)

(iv) Adsorbent dose should be able to reduce any input concentration <10 ppm to below 1 ppm (National Sanitation Foundation norm for challenge water to be used for fluoride removal claim: 8 ppm as input concentration for the challenge water and <1 ppm for output water).

(iv) Most importantly, cost of water purification should not exceed <Re. 1 per 10 L of purified water (affordability) and quantity of adsorbent should not exceed 2-3 g per 10 L of purified water (ease of use).

We believe that once such a solution is ready, considering the widespread contamination of fluoride across the globe, it will have a major positive effect on the health of the society as it can be used to provide point-of-use water filters.

Our previous patent application (Organic-templated-boehmite-nanoarchitecture: an adsorbent composition to remove arsenic and fluoride from drinking water, 1529/CHE/2010) describes a method to produce aluminum oxyhydroxide-chitosan composite at room temperature. There are a number of advantages in the adsorbent composition: green chemistry based preparation at room temperature, binder free granulation, ease of filter-ability/washability and easy-to-adapt method for preparation of mixed metal hydroxides/oxides.

It was reported that an adsorbent dose of 500 mg/L is sufficient to remove fluoride concentration below 0.5 ppm, when input fluoride is varied from 1-10 mg/L. The composite exhibits a fluoride adsorption capacity of over 53 mg/g at an initial fluoride concentration of 10 mg/L in deionized water. Owing to the presence of competing anions in ground water, the fluoride adsorption capacity of the composition diminishes and an adsorbent dose of 1.5 g/L is required to remove fluoride concentration below 0.5 ppm, when input fluoride concentration in ground water is varied from 1-10 mg/L. Cost of the material is approximately Rs. 350 per kg. This translates to a material cost of Rs. 5 per 10 L (assuming a household requires 10 L of fluoride free drinking water per day).

The invention reported in this application is an effort in the direction to develop a solution within the boundary condition defined earlier. Here, an adsorbent dose of 0.75 g/L is required to remove fluoride concentration below 0.5 ppm, when input fluoride concentration in ground water is varied from 1-10 mg/L. This translates to a material cost of Rs. 2.5 per 10 L of water. This leads to 50% reduction in the material cost vis-à-vis earlier reported composition, thereby enabling us to reach closer to material cost target of Re. 1 per 10 L of water.

We, therefore, report an adsorbent composition for the removal of fluoride from water, comprising nanoscale shell of metal oxyhydroxide/hydroxide/oxide on organic-templated-boehmite-nanoarchitecture (OTBN, addressed as core). The novelty of the invention is the preparation of nanoscale metal hydroxide particle shell on OTBN as core, with size of the shell being less than 3 nm which exhibits high anion adsorption capacity from water. Preparation of nanoscale metal hydroxide of size less than 3 nm is achieved by precipitation of metal ion on the surface of OTBN. Highest fluoride adsorption capacity is achieved when weight ratio of aluminum in shell to aluminum in core (Al_{shell}:Al_{core}) reaches 90%. Consequently, a 100% improvement in the fluoride adsorption capacity is reported vis-à-vis OTBN.

DESCRIPTION OF THE INVENTION:

The present invention can be understood more readily by reference to the following detailed description of the invention and the Examples included therein.

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. 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. Although any methods and materials similar to or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

The present disclosure relates to a composition based on nanoscale shell of metal oxide/hydroxide on OTBN. In one aspect, the invention comprises of a granular composite of nanoscale multi-layer metal oxyhydroxide (further called "shell") on OTBN (further called "core"). In another aspect, such a granular composite is prepared by formation of multi-layer on OTBN in the gel form. In another aspect, such a granular composite is prepared by the formation of a multi-layer on OTBN in the solid form.

In another aspect, the present disclosure provides methods for the preparation of nanoscale metal oxide/hydroxide/oxyhydroxide shell on OTBN. In general aspect, the methods of the present invention comprise of contacting a metal precursor with the OTBN in gel state in aqueous medium and then contacting the resulting mixture with a base. In another aspect, the metal precursor in the aqueous medium is contacted with OTBN in the solid state and then contacting the resulting mixture with a base.

In various aspects, metal precursor can comprise of a salt of a metal or a solution thereof. In one aspect, the metal component can comprise of aluminum, iron, titanium, manganese, cobalt, nickel, copper, silver, zinc, lanthanum, cerium, zirconium, calcium, magnesium, barium or a combination thereof. In one aspect, a metal precursor comprises of a solution of an aluminum salt comprising aluminum sulfate. In another aspect, a metal precursor comprises of a solution of an aluminum salt comprising aluminum nitrate, aluminum acetate, aluminum chloride, aluminum isopropoxide or a combination thereof. In other aspect, the metal precursor can comprise of a mixture of two or more individual metal precursors in any desired ratio, such as, for example, from about 20:1 to about 1:20, for example, about 20:1, 10:1, 5:1, 2:1, 1:1, 1:2, 1:5, 1:10, 1:20.

The base used in the hydrolysis of metal precursor can comprise of any suitable base. In one aspect, a base can comprise of sodium hydroxide, ammonia, potassium hydroxide, or a combination thereof. In other aspects, other bases or combination of bases and/or solutions thereof can be used, and the present invention is not intended to be limited to any particular base. In one aspect, upon addition of base to a mixture of metal precursor and OTBN, metal ions can hydrolyze and precipitate in the form of a nanoscale layer on OTBN surface.

Upon precipitation of metal precursor with the base, a semi-solid precipitate comprising nanoscale metal hydroxide/oxide/oxyhydroxide shell on OTBN is obtained. In one aspect, the thickness of the resulting shell layer can be in the range of about 1 nm to about 10 nm. In another aspect, the thickness of the resulting shell layer can be in the range of from about 1 nm to about 5 nm.

The semi-solid precipitate is typically subjected to filtration and washing with copious amounts of water followed by drying to obtain the desired granular composite.

In various aspects, the present invention provides methods for preparing nanoscale shell of metal oxide/hydroxide on OTBN. In another aspect, the composition can be used for the removal of inorganic anions from drinking water such as arsenic and fluoride.

Experimental methods

Material characterization

The identification of the phase(s) of the as-prepared samples were carried out by X-ray powder diffraction (Bruker AXS, D8 Discover, USA) using Cu-Kα radiation at λ = 1.5418 Å. 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 Kα was used as the X-ray source (hv = 1253.6 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. 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.

Adsorption studies

The adsorbent composition was tested for 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 a duration of 1.5 h and analyzed for residual solute concentration.

The water used for studies was either deionized water or tap water (composition is mentioned herewith), and it is mentioned in the respective figures.

EXAMPLES

The present application describes the methods for preparing nanoscale shell of metal oxide/hydroxide on OTBN. The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention.

Example 1

This example describes the formation of aluminum hydroxide as a nanoscale layer on OTBN. OTBN was prepared as reported in the previous patent application (1529/CHE/2010). The OTBN gel obtained after washing the salt content was used for the formation of a nanoscale layer over it. The OTBN gel was again re-dispersed in water, to which aluminum precursor such as aluminum sulfate was added drop-wise. The ratio of Al in the shell to Al in the core can be varied anywhere between 0.5-300%. After stirring the solution for 2 hours, aqueous sodium hydroxide (2 M NaOH) was added to the solution drop-wise so that the metal precursor was hydrolyzed. Then the solution was allowed to stir for half an hour, filtered and washed with copious amounts of water. The obtained gel was then dried at room temperature for further studies.

Example 2

This example describes the formation of nanoscale multilayer metal oxide/hydroxide on OTBN, wherein the method of preparation of OTBN is modified. 0.2 M aluminum precursor solution was slowly added to a diluted chitosan solution (0.75 g/L) with vigorous stirring for 60 minutes and was kept overnight without agitation. Thereafter, aqueous 2 M NaOH was slowly added into the metal-chitosan solution with vigorous stirring to facilitate the precipitation of the metal-chitosan

composites. All these steps were carried out at temperature below 30 °C. The precipitate was filtered and washed with copious amount of water. The gel was then re-dispersed in water.

In a second step, aluminum precursor solution was added to the above solution. The ratio of Al in the shell layer to Al in the core can be varied anywhere between 0.5-300%. After stirring the solution for 2 hours, aqueous sodium hydroxide (NaOH) was added to the solution drop wise so that metal precursor underwent hydrolysis. Then the solution was allowed to stir for half an hour, filtered and washed with copious amounts of water. The obtained gel was then dried at room temperature for further studies.

Example 3

This example describes the formation of nanoscale metal oxide/hydroxide/oxyhydroxide shell on OTBN, wherein the method of preparation of OTBN was varied. Precipitated chitosan solution was prepared by adding aqueous NaOH to chitosan solution. Aluminum precursor solution was slowly added to a precipitated chitosan solution with vigorous stirring for 60 minutes and was kept overnight without agitation. Thereafter, aqueous 2 M NaOH was slowly added so as to facilitate the hydrolysis of metal precursor in precipitated chitosan matrix. All these steps were carried out at temperature below 30 °C. The precipitate was filtered and washed with copious amounts of water. The gel was then re-dispersed in water.

In a second step, aluminum precursor solution was added to the above solution. The ratio of Al in the shell layer to Al in core can be varied anywhere between 0.5-100%. After stirring the solution for 2 hours, aqueous 2 M NaOH was added to the solution drop wise so that metal precursor underwent hydrolysis reaction. Then the solution was allowed to stir for half an hour, filtered and washed with copious amounts of water. The obtained gel was then dried at room temperature for further studies.

Example 4

The dried OTBN powder was crushed to a particle size of 100-150 micron. The powder was stirred in the water, using a shaker. Aluminum precursor solution was then slowly added. The ratio of Al in the shell layer to Al in core can be varied anywhere between 0.5-100%. After stirring the mixture for 2 hours, aqueous 2 M NaOH was added drop-wise so as to hydrolyze the

metal precursor. Then the mixture was allowed to stir for half an hour, filtered and washed with copious amounts of water. The obtained powder was then dried at room temperature for further studies.

Example 5

This example describes the formation of a multi-layer of metal oxide/hydroxide on the core composition. The composition as described in example 1, 2 and 3 can be used, either as a gel or a powder. 1 M aluminum precursor was added drop-wise to the composition. After continuing to stir the solution for an hour, 2 M NaOH was slowly added to hydrolyze the metal precursor. Subsequently, iron precursor was added drop-wise to the composition followed by hydrolysis using aqueous 2 M NaOH. The obtained composition was then filtered and washed with copious amounts of water. The composition was dried at room temperature for further studies.

If the core composition is designated as A, shell 1 composition is designated as B, shell 2 composition is designated as C, then it will be apparent to those skilled in the art that compositions designated as AB, ABC, ACB, ABAB, ABCABC or a combination thereof can be prepared by the steps described in this invention.

Example 6

This example describes the formation of multi-element multi-layer OTBN. The composition as described in example 1, 2 and 3 can be used, either as a gel or a powder. A homogeneous solution containing 0.5 M aluminum sulfate and 0.5 M ferric sulfate was added drop-wise to the composition. After continuing to stir the solution for an hour, 2 M NaOH was slowly added to hydrolyze the metal precursors. The obtained composition was then filtered and washed with copious amounts of water. The composition was dried at room temperature for further studies.

Example 7

This example describes the formation of ferric hydroxide as a nanoscale layer on the OTBN. Methods of preparation as detailed in example 1, 2 and 3 were used, wherein iron(III) precursor such as ferric sulfate was used. Subsequently the metal precursor was hydrolyzed. Semi-solid precipitate was filtered, washed with copious amounts of water and dried for further use.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the claims.

DESCRIPTION WITH REFERENCE TO DRAWINGS AND TABULATED DATA:

Figure 1. A schematic representation of chemical reactions involved in the method for preparation of composition, in accordance with an embodiment of the present invention.

Figure 2. XRD patterns of (a) as-synthesized parent material OTBN (indexed to the standard reflections of AlOOH (JCPDS 21-1307)), (b) nanoscale aluminum hydroxide coated OTBN (ratio of Al content in shell to Al content in OTBN = 0.45) and (c) nanoscale aluminum hydroxide coated on OTBN (ratio of Al content in shell to Al content in OTBN = 0.9). Upon formation of nanoscale shell on the core, changes in the crystalline behavior can be observed through disappearance of crystalline planes.

Figure 3. TEM image of nanoscale aluminum hydroxide coated on OTBN. Presence of shell around core is marked by arrows.

Figure 4. XPS survey spectra of (a) nanoscale aluminum hydroxide coated OTBN and (b) nanoscale aluminum hydroxide coated OTBN exposed to 100 mg/L fluoride. The spectra clearly confirm the existence of adsorbed fluoride along with disappearance of sulfate ion in the F^- treated composition.

Figure 5. XPS spectra of (A) Al 2p, (B) O 1s, (C) F 1s and (D) S 2p, for adsorbent composition (a) before and (b) after exposure to 100 mg/L fluoride.

Figure 6. EDAX spectrum of nanoscale aluminum hydroxide coated OTBN. Inset: elemental X-ray images of Al Kα, O Kα, C Kα and S Kα of the sample. The corresponding SEM image and elemental quantification are shown in the inset.

Figure 7. EDAX spectrum of nanoscale aluminum hydroxide coated OTBN after exposure to 100 mg/L fluoride with 5 mg adsorbent dose (in deionized water). Inset: elemental X-ray images

of Al Kα, O Kα, C Kα, F Kα and S Kα of the sample. The corresponding SEM image and elemental quantification are shown in the inset.

Figure 8. (a) Adsorption capacity of OTBN, (b) adsorption capacity of nanoscale aluminum hydroxide coated OTBN as function of adsorbent dose in deionized water (initial fluoride concentration = 10 mg/L).

Figure 9. Adsorption capacity of nanoscale aluminum hydroxide coated OTBN as a function of varying aluminum content in nanoscale shell vis-à-vis aluminum content in the core (initial fluoride concentration = 10 mg/L, ground water).

DETAILED DESCRIPTION WITH REFERENCE TO DRAWINGS AND TABULATED DATA:

Figure 1 illustrates a reaction 100 through which the granular composite of OTBN is obtained (preferred embodiments described in previous invention, 1529/CHE/2010). Reaction 100 is initiated with preparing a biopolymer solution 102 of a biopolymer flake 101, subsequently a metal precursor solution 103 is added to biopolymer solution 102 to obtain a metal-biopolymer complex solution 105, as a next step a base 104 is added to metal-biopolymer complex solution 105 to obtain the composite of biopolymer and nanoscale metal-oxyhydroxide particles. Eventually, a semi solid precipitate 106 constituting of nanoscale metal-oxyhydroxide particles aligned on chitosan is obtained, which is subsequently washed with copious amounts of water.

This filtered composite gel 106 is again homogeneously dispersed in distilled water. Metal precursor solution 103 is then added to metal oxyhydroxide particles-biopolymer composite 106. Metal oxyhydroxide particles-biopolymer composite 106 and metal ions of metal precursor solution 103 interact with each other through a number of functional groups to obtain metal ion complexed metal oxyhydroxide particles-biopolymer composite 107. Further, base 104 is added to 107. Upon addition of base 104, metal ions 103 hydrolyze and precipitate on Metal oxyhydroxide particles-biopolymer composite 106 as core-shell particle. Eventually, a semi solid precipitate 108 constituting of core-shell particles aligned on chitosan matrix is obtained, which is washed with copious amounts of water and is dried at a temperature between 30-60 °C.

Figure 2 illustrates the crystallographic features of OTBN and nanoscale aluminum hydroxide coated OTBN. The as-synthesized core composition showed peaks corresponding to (020), (120), (013), (200) and (231) and (251) planes (Figure 2, curve a). All these peaks can be

indexed as orthorhombic-AlOOH (JCPDS 21-1307). This is further detailed in our previous patent application (1529/CHE/2010). XRD pattern of nanoscale aluminum hydroxide coated OTBN is shown in Figure 2b. There are two major changes observed in the patterns of OTBN and nanoscale aluminum hydroxide coated OTBN. Peaks indexed to (031) and (200) have broadened and therefore merged; so is the case with the peaks indexed to (231) and (251). Peak broadening may be interpreted as decreasing crystallite size as well as reduction in crystalline behavior of the material. The first possibility indicates the formation of a thin nanoscale shell on the surface of OTBN, wherein the particle size is extremely small. It is also possible that nanoscale shell may be amorphous in nature and due to its surface coverage, the crystalline features of OTBN are not pronounced. With the increasing percentage of nanoscale shell, the crystalline features are even further masked which indicates that nanoscale shell is amorphous in nature.

Figure 3 depicts the HRTEM image of the nanoscale coated OTBN. The formation of nanoscale shell on OTBN is evident from the images. It appears that nanoscale shell has encapsulated more than one particle. Individual OTBN particles can be observed in the images. The contrast between OTBN and nanoscale shell may be due to the differences in the focal plane.

Figure 4 illustrates the X-ray photoelectron spectroscopy (XPS) survey spectra of coated OTBN before and after the adsorption of fluoride. In order to understand the chemical changes in the composition upon adsorption of fluoride, detailed scans of specific regions of key elements (Al, 2p, O 1s, F 1s, S 2p) were carried out. Figure 5 shows the corresponding spectra of various regions of interest. These spectra confirm the existence of adsorbed fluoride along with the key elements, aluminum and oxygen. The XPS spectrum of aluminum 2p level shows a peak at 75.5 eV. Fluoride adsorption leads to a mild shift in the position of aluminum and it appears at lower binding energy; simultaneously a reduction in the surface positive charge is seen in oxygen, as a result of which 1s appears at a lower binding energy, with reduced intensity. Reduction in the intensity may be attributed to the loss of sulfate ion upon fluoride adsorption.

An interesting observation is the complete elimination of sulfur from the composition upon fluoride adsorption. This means that fluoride ion replaces sulfate from the binding sites. It is to be noted that presence of sulfate is due to the use of aluminum sulfate as metal precursor and it is widely reported that sulfate ions adsorb on the surface of aluminum hydroxide. We also propose that sulfate plays an important role in protecting the sites of adsorbent composition; due to the presence of sulfate ion, other interfering ions with lower preference (such as chloride,

nitrate, etc.) don't absorb on the surface. While the number of surface sites available on the adsorbent surface is fixed and limited, there is always a competition between various ions usually found in water. Typically, the occupation of sites by various ions depends on preference for adsorption and ion concentration. Ions such as fluoride and arsenic typically have high preference but are found in low preference. Therefore, it is important to protect the surface sites so that maximum adsorption capacity can be obtained. In the particular case of our adsorbent composition, this is accomplished by adsorption of sulfate ions on the surface sites. Sulfate ions are easily replaced by fluoride ion due to higher preference and therefore the adsorbent composition exhibits high fluoride adsorption capacity.

Figure 6 details the SEM-EDAX spectrum of nanoscale aluminum hydroxide coated OTBN along with the elemental images and composition. It is interesting to note that SO_4^{2-} content in the composition is more than 15% (5% sulfur content). The adsorbed sulfate gets replaced with fluoride. This is reflected in Figure 7 which is the corresponding data for nanoscale aluminum hydroxide coated OTBN upon fluoride adsorption (F^- concentration = 10 ppm). Fluoride concentration in the adsorbed composition is more than 5% whereas sulfur concentration has reduced to less than 1%. It is therefore observed that adsorbed fluoride concentration is excessively high and considering that it is observed at low input fluoride concentration, the composition is highly promising for fluoride removal.

Figure 8 illustrates the extent of fluoride adsorption by nanoscale aluminum hydroxide coated OTBN and OTBN as a function of adsorbent dose. The working volume of the contaminated water was taken to be 100 ml and the quantity of adsorbent dose was varied between 5 mg to 25 mg. It is very clear that nanoscale aluminum hydroxide coated OTBN has a significant improvement in the performance vis-à-vis OTBN. This was highlighted more significantly in the case when low adsorbent dose was used. It is expected that as the adsorbent dose increases, the concentration of fluoride in water decreases. The variation in capacity with adsorbent dose is minimal at higher dose because residual fluoride concentration is very less.

At the adsorbent dose of 5 mg, the disclosed composition has fluoride adsorption capacity of 105 mg/g whereas OTBN has a fluoride adsorption capacity of 67 mg/g. This is not only a significant improvement in the fluoride adsorption capacity of aluminum based compounds, but it is also considerably higher than the adsorption capacity of OTBN.

Figure 9 illustrates the fluoride adsorption capacity of nanoscale aluminum hydroxide coated OTBN as function of % Al content in the nanoscale shell (calculated as Al content in shell/Al

content in core). The studies were conducted in ground water spiked with initial fluoride concentration of 10 mg/L. pH of the ground water was measured to be 7.8 and conductivity to be 640 µS/cm. Ion analysis for ground water (after spiking with fluoride) is as follows:

Ion	Concentration (ppm)	Ion	Concentration (ppm)
Fluoride	10.6 ppm	Sodium	53.7 ppm
Chloride	86.4 ppm	Potassium	2.33 ppm
Nitrate	1.84 ppm	Magnesium	14.34 ppm
Sulfate	32.4 ppm	Calcium	28.7 ppm
Silicate	15.9 ppm		

The core composition (OTBN, shell percentage = 0%) showed fluoride adsorption capacity of 7.5 mg/g in ground water. The decrease in fluoride adsorption capacity in ground water is due to higher pH which is known to reduce the capacity of aluminum based compounds and the presence of interfering anions such as silicate. Increasing the thickness of nanoscale shell (expressed as ratio of weight of Al in shell to weight of Al in core) increases the fluoride adsorption capacity and a maximum is reached at weight ratio of Al_{shell}:Al_{core} of 90%. Observed fluoride adsorption capacity is 15 mg/g. Upon further increase in the shell thickness, fluoride adsorption capacity eventually decreases. Hence, the optimum shell thickness is noted for a weight ratio of Al_{shell}:Al_{core} at 90%.

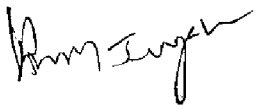
This application may disclose several feature limitations that support any range within the disclosed features even though a precise feature limitation is not stated verbatim in the specification because the embodiments of the invention could be practiced throughout the disclosed features.

We Claim: CLEAN COPY

1. A method of preparing an adsorbent composition comprising a nanoscale layer of metal oxyhydroxide/hydroxide/oxide on organic-templated-boehmite-nanoarchitecture (OTBN), with particle size of nanoscale layer less than 3 nm, wherein the adsorbent composition is used for the removal of fluoride from drinking water comprising the steps of;
    a. contacting a metal precursor with OTBN to obtain a metal ion-OTBN complex; and then
    b. contacting the metal ion-OTBN complex with a base to obtain nanoscale coating of metal hydroxide/oxyhydroxide/oxide on OTBN.
    c. recovering the precipitated material from step(b) by filtration and washing the precipitated material with copious amount of water.
    d. drying the material of obtained from step(c) to remove the moisture content at temperatures below 60 °C by methods such as air drying or sun drying to obtain rock-like material
    e. Grinding the rock-like material from step(d) in order to obtain the particles in granular form.
2. The method as claimed in claim 1, wherein the metal precursor is hydrolyzed using an alkaline medium in presence of OTBN.
3. The method as claimed in claim 1, wherein the adsorbent composition is utilized for the removal of fluoride and arsenic from water having a fluoride adsorption capacity in excess of 100 mg/g at an initial fluoride concentration of 10 mg/l.
4. The method as claimed in claim 1, wherein OTBN is used as a homogeneous aqueous dispersion, water-insoluble granules suspended in aqueous medium or a combination thereof.
5. The method as claimed in claim 1, wherein the metal precursor comprises a salt of aluminum, iron, titanium, manganese, cobalt, nickel, copper, silver, zinc, lanthanum, cerium, zirconium, calcium, magnesium, barium or a combination thereof.
6. The method as claimed in claim 1, wherein the metal precursor comprises aluminum sulfate.
7. The method as claimed in claim 1, wherein the metal precursor comprise aluminum nitrate, aluminum chloride, aluminum isopropoxide, aluminum acetate or a combination thereof.
8. The method as claimed in claim 1, wherein the base comprises sodium hydroxide, potassium hydroxide, ammonia, or a combination thereof.

9. The method as claimed in claim 1, wherein the size of the nanoscale metal hydroxide/oxide/oxyhydroxide coating is in the range of from about 1 nm to about 10 nm.
10. The method as claimed in claim 1, wherein the steps are repeated n times with same or different metal precursor to obtain multilayer OTBN where n is chosen between 1 to 5.
11. The method as claimed in claim 1, wherein the adsorbent composition is suitable for use in the removal of contaminants from water.
12. The method as claimed in claim 11, wherein contaminants comprise of fluoride, arsenic or a combination thereof.
13. A method as explained in claim 1 involving hydrolysis of a non-metal precursor using an alkaline medium in presence of OTBN.
14. The method of claim 13, wherein the non-metal precursor comprises a salt of silicon, germanium, tellurium, gallium, indium, or a combination thereof.
15. A method as explained in claim 1 involving hydrolysis of an acid soluble polymer using an alkaline medium in presence of OTBN.
16. The method of claim 15, wherein the acid soluble polymer comprises biopolymer chitosan, nylon or a combination thereof.
17. The method as claimed in claim 1, wherein the adsorbent composition is used in a variety of formats such as candle, molded porous block, filter bed, column, packets, sachets or bags.

Dated at Chennai this August 12, 2017

Signature: 

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

MULTILAYER ORGANIC-TEMPLATED-BOEHMITE-NANOARCHITECTURE FOR FLUORIDE REMOVAL

ABSTRACT

This invention relates to a composition comprising a nanoscale shell of metal oxide/hydroxide on an organic-templated-boehmite-nanoarchitecture (OTBN). The nanoscale shell is prepared by impregnating OTBN with the metal ion or non-metal ion, followed by in-situ hydrolysis of the deposited ion on the OTBN surface. The thickness of the shell is less than 3 nm, which is less than the size of the core (OTBN). The above-described method for nanoscale shell preparation is a versatile procedure as any metal or non-metal ion (including transition metals and/or rare earth metals) can be used. Additionally, number of layers of the shell is flexible, thereby leading to a multilayer nanoscale hybrid composition. The adsorbent composition is capable of removing inorganic anions such as fluoride from water, with an adsorption capacity at least twice reported previously for OTBN.

24 NOV 2011

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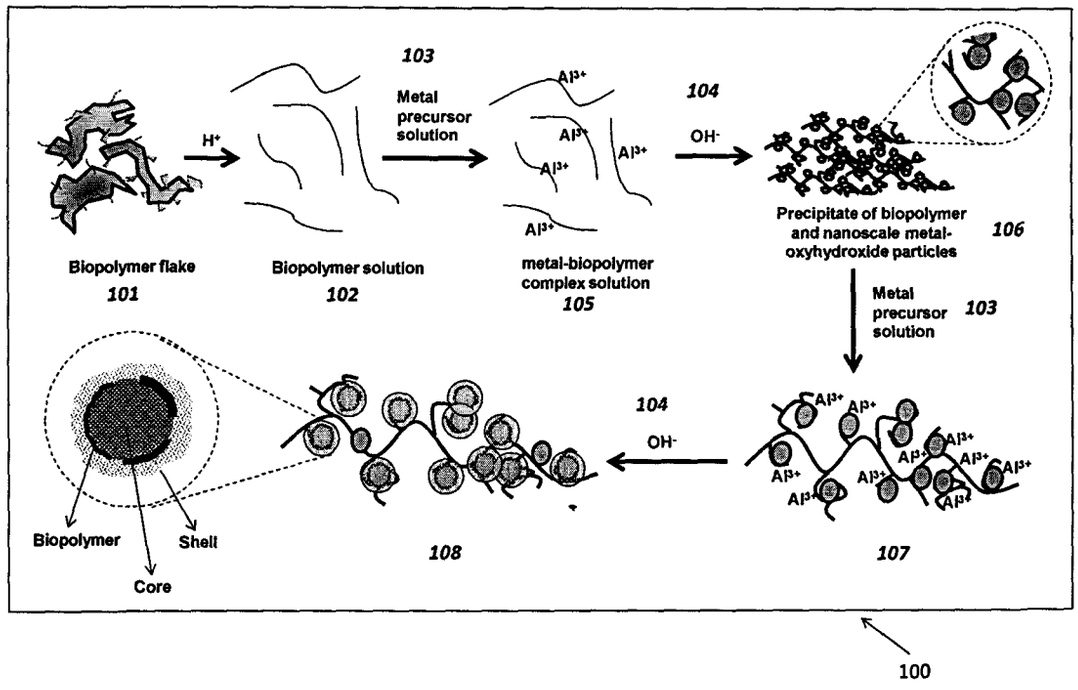

Figure 1

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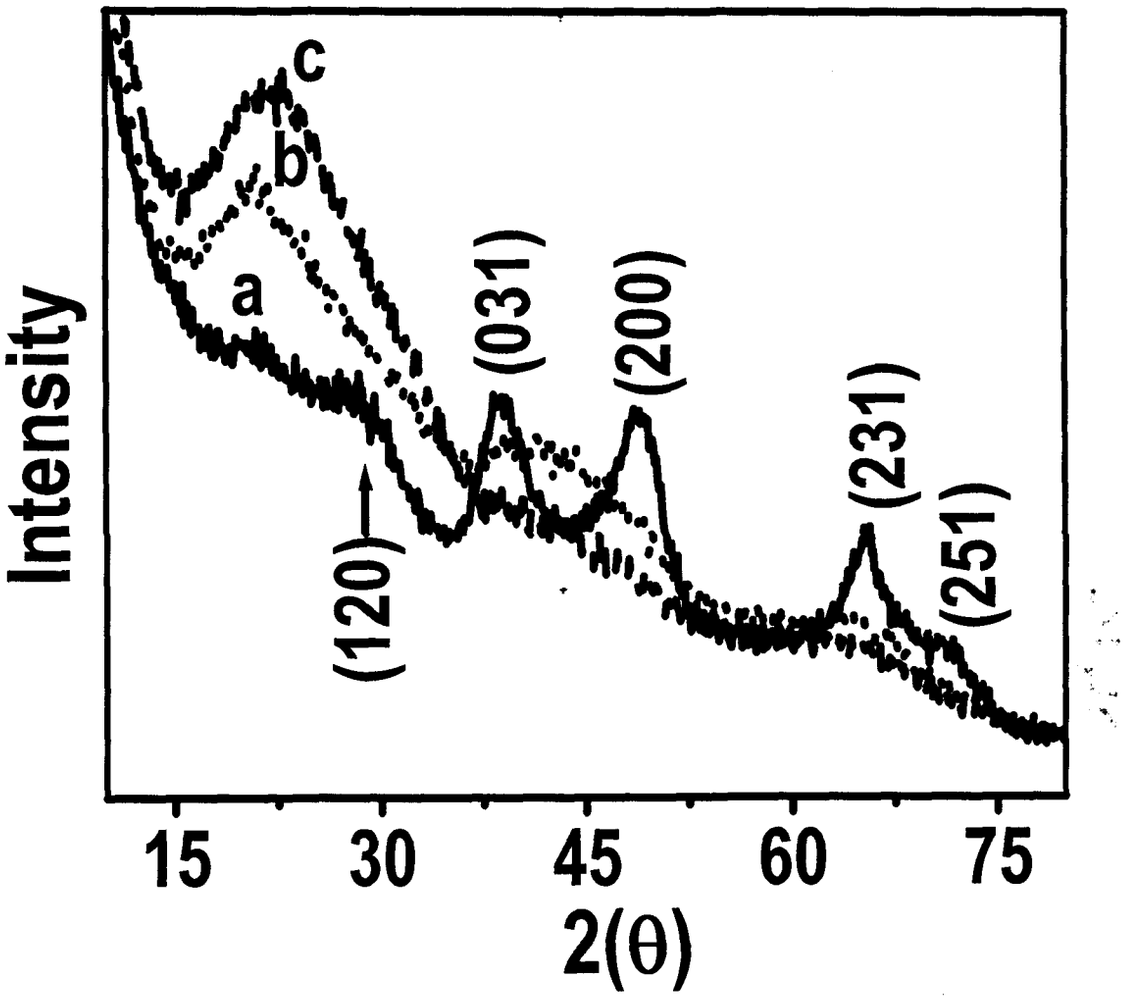

Figure 2

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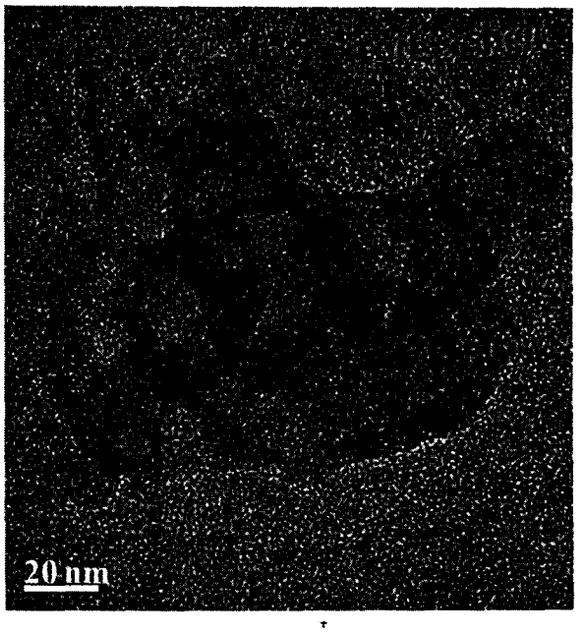

Figure 3

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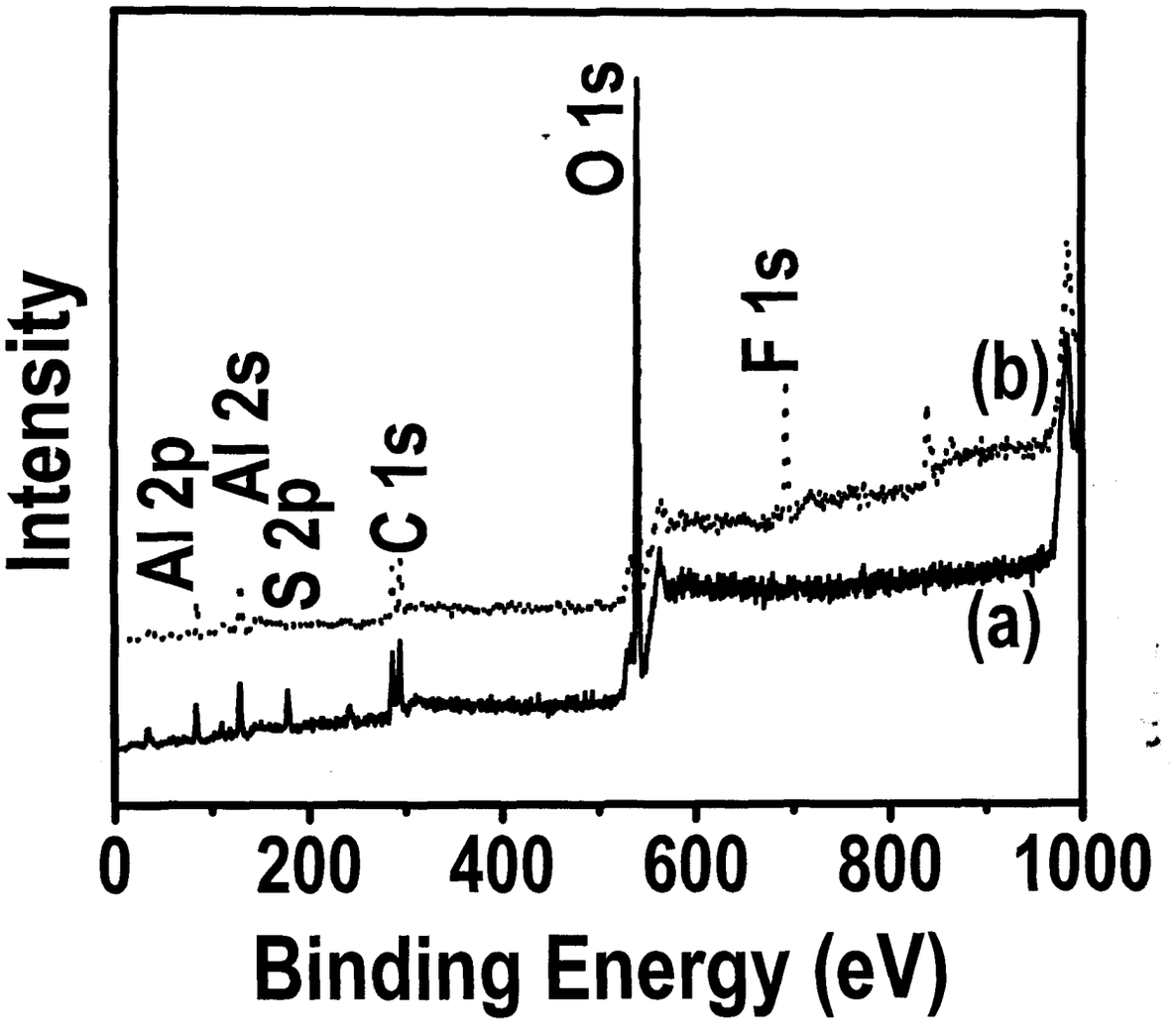

Figure 4

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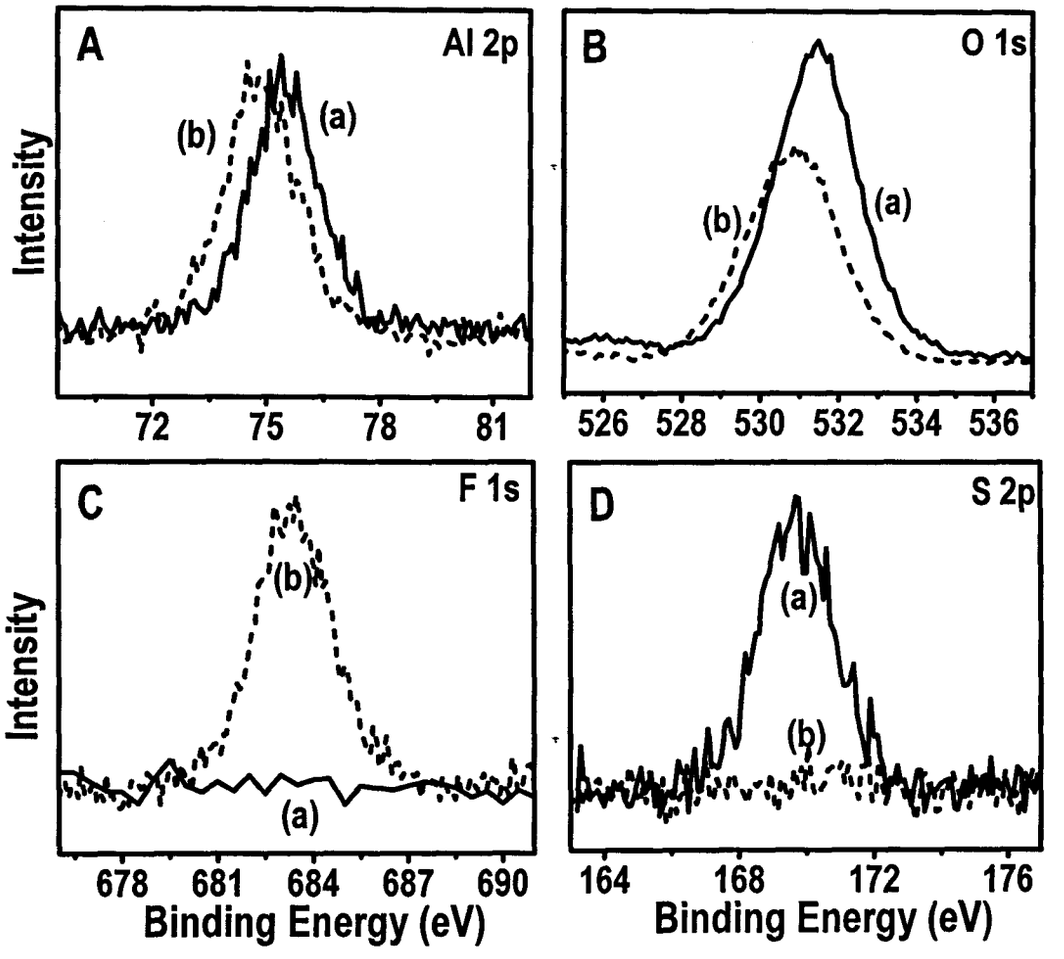

Figure 5

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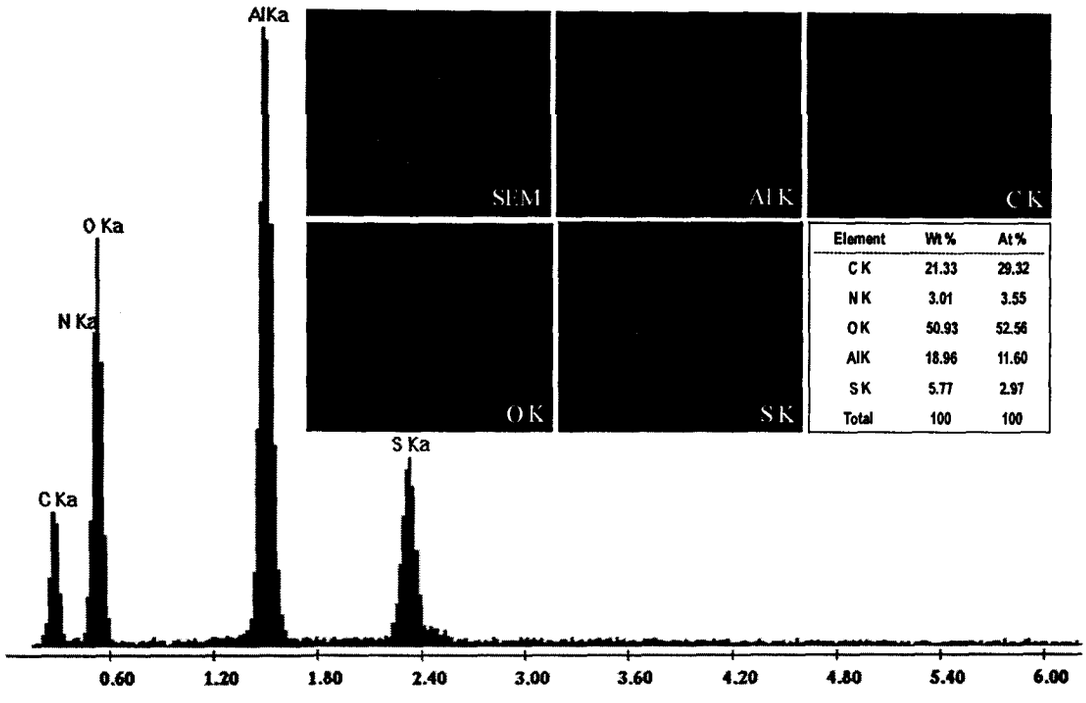

Figure 6

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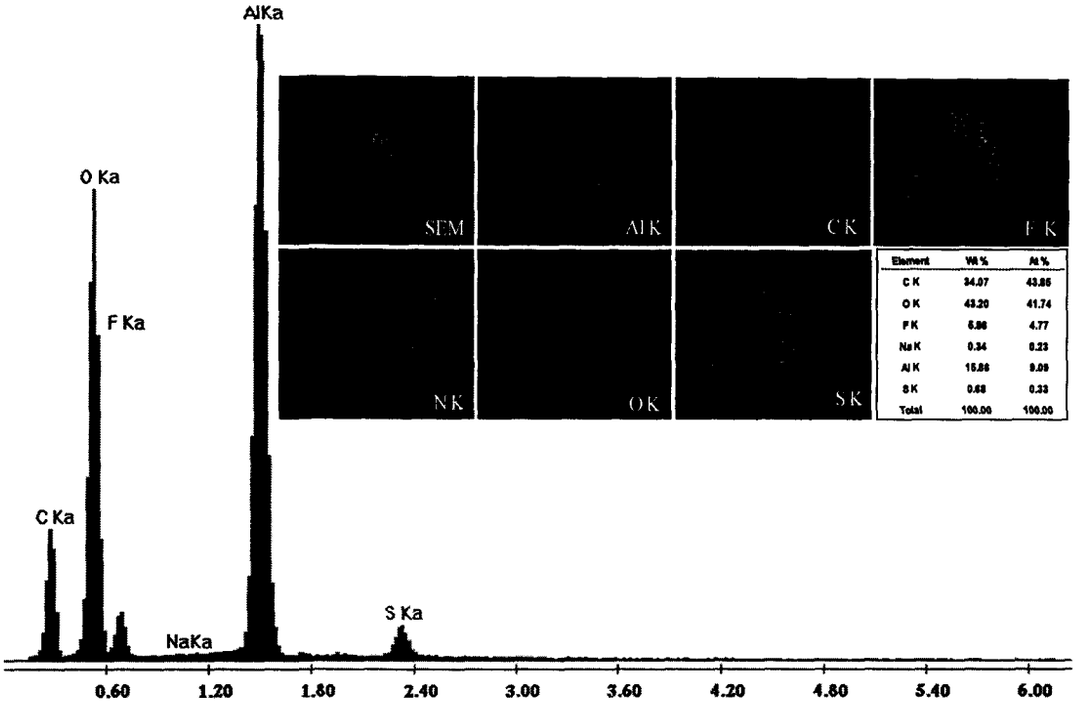

Figure 7

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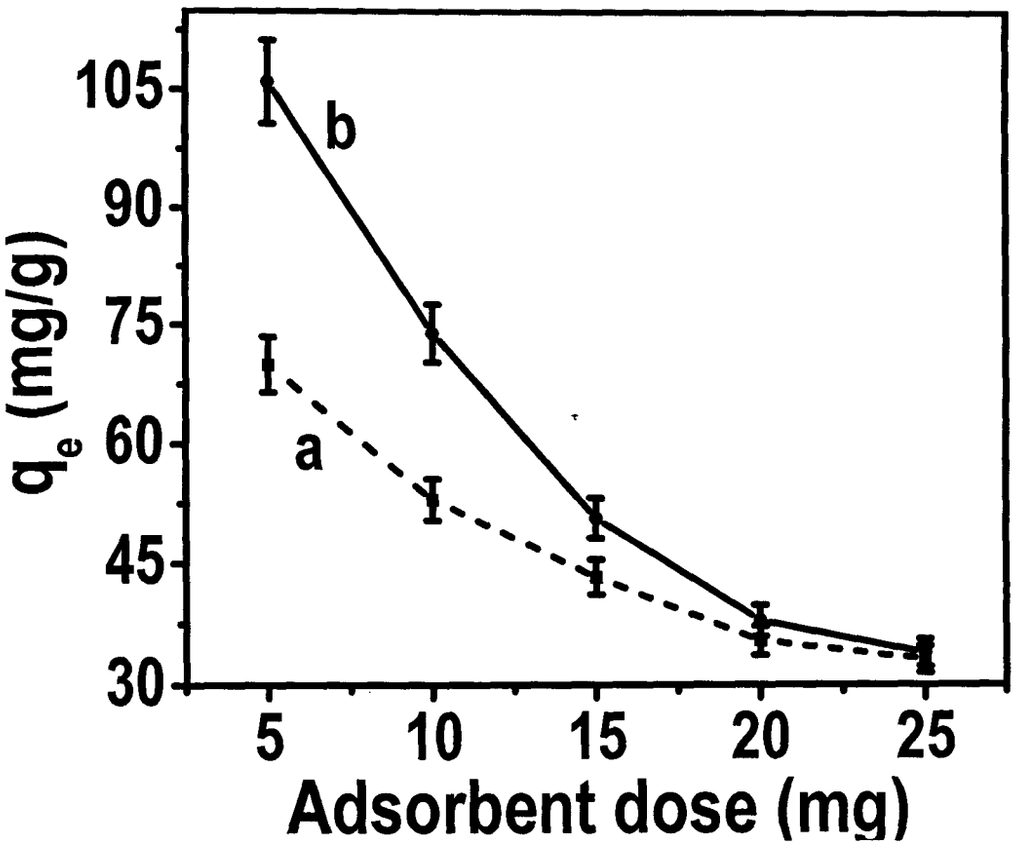

Figure 8

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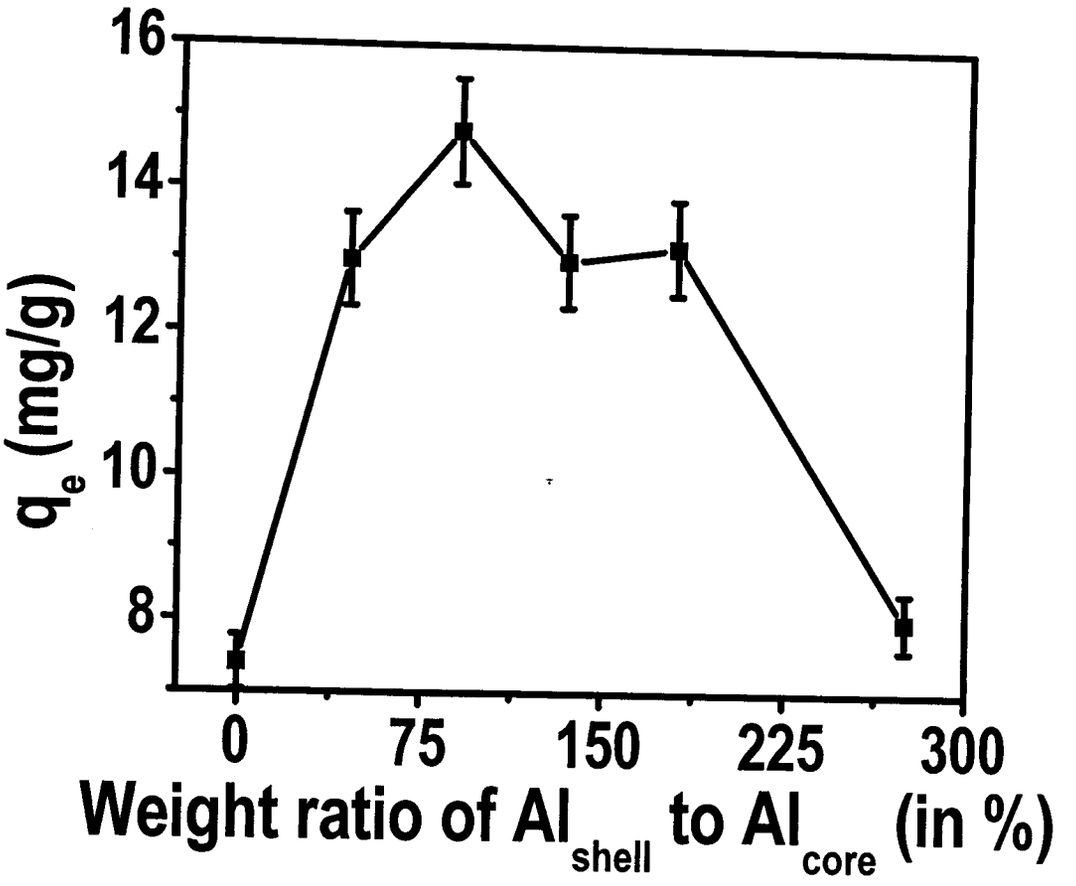

Figure 9

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