



**INTELLECTUAL
PROPERTY INDIA**

PATENTS | DESIGNS | TRADE MARKS
GEOGRAPHICAL INDICATIONS



सत्यमेव जयते

भारत सरकार
GOVERNMENT OF INDIA

पेटेंट कार्यालय
THE PATENT OFFICE

पेटेंट प्रमाणपत्र
PATENT CERTIFICATE
(Rule 74 Of The Patents Rules)

क्रमांक : 044114057
SL No :



पेटेंट सं. / Patent No. : 322218
आवेदन सं. / Application No. : 486/CHE/2013
फाइल करने की तारीख / Date of Filing : 04/02/2013
पेटेंटी / Patentee : INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT Madras)

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित A GRANULATION COMPOSITION FOR POWDER INGREDIENTS नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 4th 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 A GRANULATION COMPOSITION FOR POWDER INGREDIENTS as disclosed in the above mentioned application for the term of 20 years from the 4th day of February 2013 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 01/10/2019
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 4th day of February 2015 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 4th day of February 2015 and on the same day in every year thereafter.

4 FEB 2013

ORIGINAL

No 486 /CHE/ 2013

<div>FORM 2 THE PATENTS ACT, 1970 (39 OF 1970) & The Patents Rules, 2003 COMPLETE SPECIFICATION (Refer section 10 and rule 13)</div>
<div>TITLE OF THE INVENTION: A GRANULATION COMPOSITION FOR POWDER INGREDIENTS</div>
<div>2. APPLICANT: (A) NAME: INDIAN INSTITUTE OF TECHNOLOGY MADRAS, 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 (B) NATIONALITY: Indian (C) ADDRESS: INDIAN INSTITUTE OF TECHNOLOGY MADRAS IIT P.O Chennai - 600 036</div>
<div>3. Preamble to the Description COMPLETE SPECIFICATION The following specification describes the invention</div>

COMPLETE SPECIFICATION

TITLE OF THE INVENTION

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

FIELD OF INVENTION

The present invention relates to water based application, e.g., in the field of water purification and specifically to the preparation and use of granular compositions. More specifically, the invention relates to the preparation of granular composites of compositions useful for water-based application, especially those which are in fine dust form and are therefore as-it-is ineligible for direct use in water purification. Further more specifically, the invention relates to the preparation of active ingredient blended carrier composition which is in granular form wherein active ingredient can be a fine powder (such as nanoscale aggregates) and weight ratio in the composition up to 50%. While typically carrier composition is inactive, in this particular case, the carrier composition itself can act as an active composition when required.

BACKGROUND OF THE INVENTION

A number of materials have recently been prepared for water related application, especially for water purification. These materials exhibit improved performance vis-à-vis existing composition, thereby improving the efficiency of water purification. Amongst these materials, nanomaterials are increasingly playing critical role in various aspects of water purification (Savage, N., Diallo, M., Duncan, J., Street, A., Sustich, R., (Ed), *Nanotechnology Applications for Clean Water*. William Andrew, New York, 2008 and the chapters therein; Pradeep, T., Anshup, Noble metal nanoparticles for water purification: A critical review. *Thin Solid Films* 2009, 517, 6441).

A number of these materials are obtained in the fine powder form, presumably due to poor inherent binding ability as well as absence of long-range order associated with crystallinity. However, such materials cannot be used as-it-is for water purification

because of difficulties in particle separation, danger of particle leaching, and poor hydraulic conductivity. A number of such examples are well known in the literature and a few representative examples are cited here:

1. Reduced graphene oxide–metal/metal oxide composites: Facile synthesis and application in water purification, T.S. Sreeprasad, S. M. Maliyekkal, K. P. Lisha, T. Pradeep, *J. Haz. Mater.*, 2011, 186, 1, 921–931
2. Water-Dispersible Magnetite-Reduced Graphene Oxide Composites for Arsenic Removal, V. Chandra, J. Park, Y. Chun, J. Woo Lee, I.-C. Hwang, K. S. Kim, *ACS Nano*, 2010, 4 (7), pp 3979–3986
3. Atomically precise silver clusters for efficient chlorocarbon degradation, M. S. Bootharaju, G. K. Deepesh, T. Udayabhaskararao and T. Pradeep, *J. Mater. Chem. A*, 1 (2013) 611-620
4. Ag₇ and Ag₈ quantum clusters supported on alumina: New catalysts for organic reactions, Annamalai Leelavathi, Udayabhaskararao and T. Pradeep, *International Journal of Nanoscience*, 4 & 5 (2011) 839-843

Hence, such powder materials required granulation prior to their use as filtration medium. There are a number of techniques available for conversion of powder medium to granular form. A popular method is to use organic/inorganic binders for preparing agglomerated particles followed by sintering or spray drying. Representative prior art is as follows:

- (a) Agglomeration of alumina and binder therefor as described in US Patent No. 7,449,030
- (b) Water treatment composition comprising nanostructured materials as described in EP Patent Application No. 1954634

However, such approaches are less environment-friendly and uneconomical, as they lead to loss of adsorption capacity due to use of binders and higher temperature.

Another general method for conversion of powder medium to granular form is to support the powder medium on a carrier composition. Conventionally, activated

alumina, silica or iron oxides (in granular form) have been used. Examples are shown in Rautaray et al. in Indian patent application 1571/MUM/2008, PCT Application No. PCT/IB2011/002740 and European Patent Application No. EP1715947. In all such cases, active ingredient is bound to the carrier composition. This leads to a disadvantage that available surface of the active ingredient is wasted in binding to the carrier composition, thereby leading to reduced adsorption capacity for target contaminant on active ingredient. Simultaneously, the loading of active ingredient to carrier is fairly low, to a maximum extent of 5%; therefore, a large volume of the composition is actually occupied by carrier (inactive ingredient). It may be noted that carrier compositions are usually bulk materials and therefore suffer from low adsorption surface area. It can therefore be an advantageous situation if the carrier is also an active composition for water-related applications.

Researchers have looked at newer methods to synthesize iron oxide compositions in the laboratory and use them for water purification. Often, these compositions are prepared through water based routes below 100 °C. The references on use of iron oxide and its use for water purification is shown through a representative list:

1. Sol-gel mediated synthesis of Fe_2O_3 nanorods, K. Woo, H. J. Lee, J.-P Ahn, Y. S. Park, *Adv. Mater.*, 2003, 15, 20, 1761-1764
2. Granular ferric hydroxide—a new adsorbent for the removal of arsenic from natural water, W. Driehaus, M. Jekel, U. Hildebrandt, *Water SRT—Aqua Aqua*, 1998, 47, 1, 30-35.

It may be understood from the references that a number of active ingredients cannot be used as it is (in many cases) because they are available in powder form. A representative example of such an ingredient is graphene. Use of powder for water related application is prohibitive because they offer very high pressure drop for water flow, thereby, significantly reducing hydraulic conductivity. In order to effectively load active ingredient on carrier composition, following parameters are crucial: loading

percentage of active ingredient, homogenous dispersion of active ingredient in the matrix and ability to hold the active ingredient in trapped form rather than bound form.

According to above references, iron oxide composites are not shown to be an effective carrier of active ingredient and typical carrier compositions are not active ingredient for water based applications. Considering that carrier composition occupy a significant volume fraction, it is therefore highly desirable if the carrier composition is also an active ingredient. An important use of iron oxide composite based carrier composition is to remove contaminants from water, e.g., arsenic removal from water. With increasing need of arsenic removal from drinking water, newer adsorbents with higher arsenic adsorption capacity are crucial.

In the light of the foregoing, there exists a need in the art to provide a composition that addresses the aforementioned problems and other disadvantages reflected in the prior art.

SUMMARY OF THE INVENTION

The present invention provides granular forms of a number of active ingredients, which are commonly found in powder form. This is demonstrated through the use of organic templated ferric oxyhydroxide composition as a carrier for diverse active ingredients. The diversity of active ingredients which can be granulated using organic templated ferric oxyhydroxide is also demonstrated through granulation of a variety of compositions useful for water related applications:

- (a) water soluble materials such as sugar
- (b) partially soluble materials such as pesticides
- (c) insoluble materials such as metal oxides-reduced graphene oxide (RGO) composite.

It is further shown that the weight proportion of active ingredient to carrier composition is no less than 20% and up to 50% and active ingredient is in unbound but trapped state. Even after the addition of material to the carrier in weight proportion in excess of 40%, the strength of the composition is not affected and composition stays stable in water.

Strength of the carrier composition is not affected even if water soluble materials are removed from the carrier.

The present invention demonstrates the utility of granular form active ingredient-organic templated ferric oxyhydroxide in various water-related applications.

The present invention further demonstrates the utility of composition as an active ingredient for water-related application, such as, removal of arsenic from water with superior arsenic adsorption capacity vis-à-vis compositions reported in the prior art.

The present invention provides a method for the preparation of granular form of diverse active ingredients, by gel-phase blending of organic templated ferric oxyhydroxide with active ingredients. The loading ratio (weight proportion of active ingredient to carrier composition) can be as high as 50%. The use of same is further demonstrated through use of various active ingredients required in water-related applications:

- (i) water soluble material (e.g., sugar) loaded in organic templated ferric oxyhydroxide
- (ii) partially water soluble material (e.g., pesticide) loaded in organic templated ferric oxyhydroxide
- (iii) water insoluble material (e.g., MnO_2 -RGO) loaded in organic templated ferric oxyhydroxide

According to the present invention, utility of carrier composition as a useful active ingredient for water-related application is also demonstrated through removal of arsenic from drinking water. It is shown that the arsenic adsorption capacity of the composition is significantly better than the composition known in prior art.

The organic-templated ferric oxyhydroxide is a novel carrier composition for various types of materials. It can carry up to 50% of its own weight without significantly altering the strength of the granular composition. Carrier composition does not lose its stability in water, even if material added to the carrier is water soluble. This provides a number of new opportunities with this composition: slow release of water soluble

material (e.g., sugar), solubility limited release of toxic ingredients (e.g., pesticides), use of powder ingredient for water purification without limitation of poor hydraulic conductivity and no loss of active surface area due to un-bound form of active ingredient.

The present invention provides a method to prepare granular composition of diverse active ingredients through blending with a carrier composition and its subsequent use for water-related application, such as water purification.

The present invention related to active ingredient-carrier composition is not limited to water-related application, e.g., it can be similarly be adopted for air-related application.

It may be understood that both the foregoing and the following detailed description are exemplary and explanatory only and are not restrictive of the invention as described.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. (A) Scanning electron micrograph of granular ferric oxyhydroxide-chitosan composite upon exposure to water for over 4 months (B) High resolution transmission electron micrograph of the ferric oxyhydroxide-chitosan composite.

Figure 2. Column data for the removal of 150 ± 10 ppb of Pb^{2+} using 50 g of RGO-MnO₂ loaded ferric oxyhydroxide-chitosan composite

Figure 3. Release of chlorpyrifos in water from chlorpyrifos-ferric oxyhydroxide-chitosan composite

Figure 4. Release of sugar in water from sugar-ferric oxyhydroxide-chitosan composite

Figure 5. Residual arsenite ion concentration as a function of adsorbent dose (a) GFH (dry weight basis) (b) composition reported in this invention (initial concentration = 1 ± 0.1 ppm, volume = 100 mL synthetic challenge water, contact time = 90 min)

Figure 6. Residual arsenate ion concentration as a function of adsorbent dose (a) GFH (dry weight basis) (b) composition reported in this invention (initial concentration = 1 ± 0.1 ppm, volume = 100 mL synthetic challenge water, contact time = 90 min)

Figure 7. Elemental X-ray images of arsenite adsorbed adsorbent composition (As^{3+} = 100 ppm, synthetic challenge water, contact time = 90 min)

Figure 8. Elemental X-ray images of arsenite adsorbed adsorbent composition (As^{5+} = 100 ppm, synthetic challenge water, contact time = 90 min)

Figure 9. (A) XPS survey spectrum and (B-D) spectra of various regions of interest. (D) Curve fitted O 1s spectrum of as it is composition (E) Curve fitted O 1s spectrum of as it is composition with adsorbed As^{5+} (c) Curve fitted O 1s spectrum of as it is composition with adsorbed As^{3+}

Figure 10. Langmuir isotherm for arsenite ion adsorbed (mmol/g) as a function of arsenite ion concentration (mmol/l) (initial adsorbent dose = 30 mg, volume = 30 mL deionized water, contact time = 90 min)

Figure 11. Langmuir isotherm for arsenate ion adsorbed (mmol/g) as a function of arsenate ion concentration (mmol/l) (initial adsorbent dose = 30 mg, volume = 30 mL deionized water, contact time = 90 min)

DETAILED DESCRIPTION OF THE INVENTION

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

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one having ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are described below.

As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a metal" includes mixtures of two or more metals.

Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

As used herein, the terms "optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

Disclosed are the components to be used to prepare the compositions of the invention as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds cannot be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are

possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the invention. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the methods of the invention.

Each of the materials disclosed herein are either commercially available and/or the methods for the production thereof are known to those of skill in the art.

It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed structures, and that these structures will typically achieve the same result.

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. 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.

A method of preparation of granular composition of diverse active ingredients which are usually in powder form is described. Use of such granular composition is further demonstrated for a number of applications. In order to prepare the granular composition of powder active ingredients, we have utilized unique granulation ability of organic-templated-ferric oxyhydroxide. The strength of granular composition originates due to inherent granular property of organic-templated-ferric oxyhydroxide. This property is especially significant for ferric oxyhydroxide vis-à-vis other hydrous oxides prepared through similar route. As a carrier composition, organic-templated ferric oxyhydroxide can carry powder material up to 50% of its weight – without any significant alteration in long-term stability of the granule in water medium. Nature of active ingredient can be of wide variety: water soluble, partially water soluble or water insoluble. This is especially relevant from the perspective of water purification wherein a number of nanoparticles are in powder form and therefore not directly useful as a water treatment composition. Once immobilized in the matrix of organic-templated ferric oxyhydroxide, they can be used directly for water purification. In such a case, the act of water purification will be done by active ingredient immobilized in the matrix, wherein matrix is an inactive carrier.

The present invention demonstrates that matrix (organic-templated ferric oxyhydroxide) can be an active carrier in a few cases, such as, removal of arsenic from water. It is further demonstrated that the capability of the composition to remove both forms of arsenic from drinking water, with arsenic adsorption capacity far higher than composition known in prior art.

Nanoscale ferric oxyhydroxide is prepared within the chitosan matrix, where chitosan is a biopolymer with several advantages such as being biodegradable and inexpensive. Another important benefit of using chitosan as matrix is that it forms a network of size 1-10 μm . When ferric oxyhydroxide nanoparticles are prepared inside the matrix, they bond strongly with the matrix, due to which they can easily be purified through the use of a membrane cloth filter.

The present disclosure relates to the preparation of granular composition of diverse active ingredients in powder form using nanoscale ferric oxyhydroxide dispersed in organic template as a carrier composition. In one aspect, the invention comprises of a granular composite of powder ingredient blended in ferric oxyhydroxide on an organic template.

In various aspects, organic templated ferric oxyhydroxide is used as a carrier composition for a number of active ingredients, with weight proportion of active ingredient to carrier composition up to 50%. In one aspect, active ingredient is water soluble materials which require slow dissolution in water. In another aspect, water soluble materials exhibit very high solubility, but are required in water in trace quantities. In yet another aspect, active ingredient is partially water soluble. In another aspect, partially water soluble materials exhibit ppm scale solubility and are required to be prevented for overdosing beyond the solubility. In yet another aspect, active ingredient is water insoluble and powder in nature. In another aspect, water insoluble materials are active ingredient for water purification but disintegrate in water thereby deteriorating hydraulic conductivity.

In various aspects, nanoscale ferric oxyhydroxide on chitosan (prior to the step of drying of composition, i.e., when the moisture content is above 50%) is blended with nanoscale metal oxide on chitosan (with variable moisture content from 10-90%) wherein metal is chosen amongst aluminium, titanium, zinc, manganese, iron, zirconium, lanthanum, cerium, silicon or a combination thereof.

In various aspects, the composition is demonstrated to be a useful active ingredient itself. In another aspect, the composition is utilized for the removal of contaminants from drinking water such as arsenite and arsenate.

The invention may be further described by the accompanied drawings. Figure 1A shows SEM image of the ferric oxyhydroxide-chitosan composite in the granular form (52X72 mesh), which has been exposed to running water for 3 months. The composite

exhibits excellent mechanical strength and doesn't degrade in water. Therefore, upon use for water purification, there are no fine particles leached in the water (which is a common phenomenon for a number of other adsorbents). This is especially important from the perspective of ensuring nanoparticles free drinking water.

It is well-known that hydrous iron oxide as found in the Nature exhibit reasonable mechanical strength (as they occur in crystalline form). In the case of ferric oxyhydroxide-chitosan composite, it is highly amorphous (data not shown). Here, the role of chitosan is very crucial in improving the strength of ferric oxyhydroxide-chitosan composite through binding with ferric oxyhydroxide nanocrystals.

HRTEM images of the ferric oxyhydroxide-chitosan composite is shown in figure 1B. Ferric oxyhydroxide nanoparticles are not prominently visible in the large area image due to their small size. Inset of figure 1B shows the higher magnification TEM images of the nanoscale ferric oxyhydroxide. The particle size is less than 5 nm. It can be seen that ferric oxyhydroxide nanoparticles are well-dispersed in the chitosan matrix. The metal oxide nanoparticles are homogeneously sized. The sheet-like organic polymer chitosan is seen clearly (figure 1B). Upon closer observation, we can see that the nanoparticles are anchored onto the chitosan nanoarchitecture. Outside the chitosan structure, no nanoparticles were present. This again confirms the composite formation, wherein ferric oxyhydroxide nanoparticles are formed only inside the chitosan nanoarchitecture. This holds several advantages: (i) small and uniform sized nanoparticles are obtained (ii) nanoparticles never leaches out of the nanoarchitecture, thereby, ensuring their safe use in water purification (iii) nanoparticles do not undergo aggregation, even when high contaminant concentration is loaded on the surface of nanoparticles.

Figure 2 shows the efficacy of ferric oxyhydroxide-chitosan matrix as a carrier for powder compositions such as nano-MnO₂. Curve (a) indicates the input Pb²⁺ concentration and curve (b) indicates the output Pb²⁺ concentration after treatment. 50 g of MnO₂-graphene oxide loaded ferric oxyhydroxide-chitosan granular composite was packed in a column and fed with 1500 L of water spiked with 150±10 ppb of Pb²⁺ at 50 mL/min flow rate. The concentration of lead in the effluent water, measured by

inductively coupled plasma mass spectrometry (ICP MS) was consistently below 10 ± 1 ppb, adhering to the WHO norms (Figure 4). This demonstrates that the active ingredient loaded in the ferric oxyhydroxide-chitosan matrix is amply accessible by water, thereby, ensuring that composition can be utilized as an effective water purification composition.

Figure 3 shows the release of chlorpyrifos in water treated with chlorpyrifos loaded ferric oxyhydroxide-chitosan granular composite. The experiment is conducted by shaking 100 mL of de-ionized water with 10 mg of composite for the duration of 5 minutes. After the completion of 5 minutes, fresh water is used and shaken for second round of contact. Trials are continued in similar pattern. As it can be seen, chlorpyrifos release in the water is fairly stable, never crosses the equilibrium solubility and happens over a large volume of water. Through this mechanism, high toxicity of pesticides to non-target living beings can be prevented by avoiding overdosing of pesticides in water prior to use over crops. A column study was also conducted by packing the 5 g chlorpyrifos loaded ferric oxyhydroxide-chitosan composite in a column and de-ionized water is passed at a flow rate of 50 mL/min. Absorption spectra of output water is measured at regular interval. It is found that chlorpyrifos release in water is nearly consistent and around the similar concentration as obtained in batch trials.

Figure 4 shows the release of sugar in water treated with sugar loaded ferric oxyhydroxide-chitosan composite. The experiment is conducted by shaking 100 mL of deionized water with 100 mg of composite for the duration of 10 minutes. Water samples are collected at every minute of contact and analyzed for residual sugar content in water. Analysis of sugar in water is done by using Pavy's solution. As it can be seen, sugar release in the water is fairly systematic and follows asymptotic behavior. Sugar release begins after the passage of 1 minute and it reaches equilibrium value at near 5 minutes. On the contrary, similar quantity of sugar dissolves in water in less than 0.5 minutes of contact. Therefore, a delay of 6 times is introduced after incorporation of sugar in the matrix.

Figure 5 and 6 represents the comparative performance of arsenic adsorbent composition as reported here vis-à-vis commercially available granular ferric hydroxide (GFH sourced from Harbauer GmbH) for As^{3+} and As^{5+} , respectively. GFH is obtained in

the wet form and it is used as it is; performance data is however reported on dry weight basis. In figure 5 and 6, curve (a) indicates the adsorption performance of GFH and curve (b) indicates the adsorption performance of composition reported here. It is clearly observed that ferric oxyhydroxide-chitosan composite exhibits superior performance vis-à-vis GFH. 1 ± 0.1 ppm arsenic in synthetic challenge water treated with 250 mg/L adsorbent composition shows 16 ppb (As^{5+}) and 78 ppb (As^{3+}). Whereas, to reach similar output concentration level, dry weight of GFH required is 1.25 g/L (As^{5+}) and 1.0 g/L (As^{3+}).

There are a number of unique advantages associated with the use of composition as an active adsorbent composition: composition doesn't show significant drop in the performance even when used with synthetic challenge water containing interfering ions. 1 ± 0.1 ppm arsenic in de-ionized water treated with 250 mg/L adsorbent composition shows 4.5 ppb (As^{5+}) and 92 ppb (As^{3+}). Whereas 1 ± 0.1 ppm arsenic in synthetic challenge water treated with 250 mg/L adsorbent composition shows 16 ppb (As^{5+}) and 78 ppb (As^{3+}). Role of chitosan is further evident from the fact that 1 ± 0.1 ppm arsenic in synthetic challenge water treated with 250 mg/L adsorbent composition (prepared without chitosan) shows 312 ppb (As^{5+}) and 125 ppb (As^{3+}). This clearly establishes the importance of chitosan in the preparation of composite.

Figure 7 and 8 show the SEM-EDAX spectrum and elemental maps of arsenic adsorbed composition. For the purpose of the study, 25 mg of adsorbent was shaken with 100 ppm, 50 mL arsenic in synthetic challenge water. All the principal elements including adsorbed arsenic are present in the spectrum. Elemental maps confirm that distribution of arsenic is homogeneous and extremely high. In case of As(III) adsorbed composition, arsenic content in the composition is around 14.9% whereas in case of As(V) adsorbed composition, it is around 12%. This is in consonance with earlier result that performance of the composition is almost similar for both forms of arsenic.

Figure 9 illustrates the XPS spectra of as-synthesized composition and arsenic adsorbed composition. The survey spectra of As(III) and As(V) adsorbed composition confirms the presence of arsenic in the adsorbed state. The Fe 2p region of pristine and arsenic adsorbed composition are shown in figure 8 (C). As 3d region of As^{3+} adsorbed

composition shows peak at 44.6 eV and As⁵⁺ adsorbed composition shows at 46.8 eV. The peak observed at 529.0 eV is close to the characteristic peak position for bulk oxygen (O²⁻) (Figure 8E). The peak appearing as a shoulder at 531.7 eV is also of uncharacteristically high intensity.

Arsenic adsorption isotherm of as-synthesized composite was carried out in 0.04 M NaCl at pH 7. As-synthesized composite adsorbs approximately 1.064 mmol/g at an equilibrium As(III) concentration of 0.15 mM and 0.27 mmol/g at an equilibrium As(V) concentration of 0.15 mM. Langmuir isotherm was plotted for the arsenic adsorption (figure 10 and 11) using the expression as follows:

The linear form of the Langmuir adsorption isotherm equation is as follows:

$$C_e/q_e = C_e/Q_{max} + 1/Q_{max}(b)$$

where, C_e (mmol/L) is the equilibrium concentration of arsenic in the solution, q_e (mmol/L) is the quantity of arsenic adsorbed and Q_{max} (mmol/L) is the monolayer adsorption capacity, and b (L/mmol) is the Langmuir adsorption constant related to the free energy of adsorption and $1/Q_{max}$ and $1/Q_{max}(b)$ are the Langmuir constants.

The Langmuir isotherm equation was used to estimate the maximum adsorption capacity of the adsorbent composition under the conditions 298 K, pH 7.0, 90 min. contact time and 1.0 g/L adsorbent dose while varying initial arsenic concentration from 0.5 to 30 mg/L. The values of the isotherm constants, for As(III) adsorption are 1.60 and 0.0114, respectively and for As(V) adsorption are 3.63 and 0.008, respectively.

Method of preparing organic templated ferric oxyhydroxide is derived from preferred embodiments described in Indian Application No. 1529/CHE/2010. An aqueous organic polymer solution is taken with inorganic iron salt and hydrolyzed using a suitable base. The organic polymer acts as a template, controls the size of particle and gives the mechanical strength to the composite after drying at room temperature.

The identification of the phase(s) of the as-prepared sample was carried out by X-ray powder diffraction (Bruker AXS, D8 Discover, USA) using Cu-K_α radiation at $\lambda =$

1.5418 Å. 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 ($h\nu = 1253.6$ 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. Arsenic and lead ion concentration in the water was detected using inductively coupled plasma mass spectrometry (Nexlon 300D ICP-MS, Perkin Elmer). Chlorpyrifos concentration in water was detected by concentration dependent UV/Vis spectra (Lambda 25 spectrometer, Perkin-Elmer). Sugar concentration was determined through titration procedure.

For adsorption studies, MnO₂ loaded chitosan-ferric oxyhydroxide composite was tested for Pb²⁺ removal from water. The as-synthesized adsorbent composition was tested for arsenic (in the form of sodium arsenate or sodium arsenite) removal from water.

All the uptake capacity studies were done in a batch mode (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 \pm 5 rpm in an orbital shaker (Riviera, India) at room temperature (25 \pm 2 °C). Samples were withdrawn at predetermined time intervals and analyzed for residual solute concentration. The water used for studies is either deionized water or synthetic challenge water (composition is mentioned herewith), and it is mentioned in the respective figures.

The present application describes the methods for preparing granular composition of diverse active ingredients usually available in powder form. This is achieved through blending powder ingredients in nanoscale ferric oxyhydroxide-chitosan composite. 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

THE ROOM TEMPERATURE SYNTHESIS OF NANOSCALE FERRIC OXYHYDROXIDE EMBEDDED IN ORGANIC TEMPLATE THROUGH A SIMPLE SOFT CHEMISTRY ROUTE:

The Fe(III) precursor solution (such as ferric chloride) was mixed with chitosan (dissolved in 1 - 5 % glacial acetic acid or HCl or combination thereof) by drop-wise addition with vigorous stirring. The mixture was then left overnight without agitation. Aqueous NaOH solution 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 a temperature of about 25 ± 2 °C. Stirring was continued for half an hour. The precipitate was filtered, washed to remove any unwanted impurities, converted in the shape of beads and dried at ambient condition.

EXAMPLE 2

THE UTILITY OF FERRIC OXYHYDROXIDE-CHITOSAN COMPOSITE AS A CARRIER OF VARIOUS ACTIVE INGREDIENTS:

The objective was that ingredient may be incorporated in such a proportion such that the mechanical strength of the ferric oxyhydroxide-chitosan composite was not significantly altered, which may allow its use for water purification. The porous nature of the ferric oxyhydroxide-chitosan composite allows the accessibility of water to such ingredients.

For the purpose of illustration, a water insoluble composition was demonstrated. Reduced graphene oxide-MnO₂ composite (Indian Application No. 2563/CHE/2010) was mixed in varying proportions with ferric oxyhydroxide-chitosan composite. Ferric oxyhydroxide-chitosan composite in the precipitate form was washed and filtered. Moisture content in the precipitate form may vary from 50-90%. Subsequently, it was mixed with reduced graphene oxide-MnO₂ composite. The mixture was prepared in an appropriate ratio, for example, with a dominant weight percentage for ferric oxyhydroxide-chitosan composite (wt/wt). Thereafter, the precipitate was dried at ambient condition.

It may be noted that graphene oxide-MnO₂ composite is taken as a representative example of a number of water insoluble materials, for example but not limited to, water treatment compositions, metal nanoparticles and luminescent metal clusters.

EXAMPLE 3

UTILITY OF FERRIC OXYHYDROXIDE-CHITOSAN COMPOSITE AS A CARRIER OF VARIOUS INGREDIENTS:

For the purpose of illustration, a partially water insoluble composition is demonstrated. A pesticide named chlorpyrifos was mixed in varying proportions with ferric oxyhydroxide-chitosan composite. Ferric oxyhydroxide-chitosan composite in the precipitate form was washed and filtered. Moisture content in the precipitate form may vary from 50-90%. Subsequently, it was mixed with chlorpyrifos dissolved in acetone (60 mg chlorpyrifos/0.1 mL acetone). The mixture was prepared in an appropriate ratio, for example, with a dominant weight percentage for ferric oxyhydroxide-chitosan composite (wt/wt). Thereafter, the precipitate was dried at ambient condition.

It may be noted that chlorpyrifos is taken as a representative example of a number of partially water soluble materials, for example but not limited to, partially soluble minerals (such as MgCO₃).

EXAMPLE 4

UTILITY OF FERRIC OXYHYDROXIDE-CHITOSAN COMPOSITE AS A CARRIER OF VARIOUS INGREDIENTS:

For the purpose of illustration, a water soluble composition is demonstrated. Sugar was mixed in varying proportions with ferric oxyhydroxide-chitosan composite. Ferric oxyhydroxide-chitosan composite in the precipitate form was washed and filtered. Moisture content in the precipitate form may vary from 50-90%. Subsequently, it was mixed with sugar dissolved in water (100 mg sugar/1 mL water). The mixture was prepared in an appropriate ratio, preferably with a dominant weight percentage for ferric oxyhydroxide-chitosan composite (wt/wt). Thereafter, the precipitate is dried at ambient condition.

It is to be noted that sugar is taken as a representative example of a number of water soluble materials, for example but not limited to, vitamin supplements, trace minerals/elements (such as zinc), chemicals imparting taste/smell.

EXAMPLE 5

INCORPORATION OF VARIOUS METAL OXIDE/HYDROXIDE/ OXYHYDROXIDE-CHITOSAN COMPOSITE WITHIN FERRIC OXYHYDROXIDE-CHITOSAN TEMPLATE:

Precipitated ferric oxyhydroxide-chitosan composite was washed and filtered. Moisture content in the precipitate form may vary from 50-90%. Subsequently, it was mixed with desired metal oxide/hydroxide/oxyhydroxide-chitosan composite prepared separately (Indian Application Nos. 1529/CHE/2010, 947/CHE/2011, 4062/CHE/2011, 1521/CHE/2012). Metal was chosen from the following list: zinc, manganese, iron, aluminum, zirconium, lanthanum, cerium, silicon. The mixture was prepared in an appropriate ratio, for example, with a dominant weight percentage for ferric oxyhydroxide-chitosan composite (wt/wt). Thereafter, the precipitate was dried at ambient condition.

Example 6

INCORPORATION OF NANOPARTICLES WITHIN FERRIC OXYHYDROXIDE-CHITOSAN TEMPLATE:

Precipitated ferric oxyhydroxide-chitosan composite was washed and filtered. Moisture content in the precipitate form may vary from 50-90%. Subsequently, a nanoparticle dispersion (e.g., Al_2O_3 nanoparticles dispersed in water) was homogenized with ferric oxyhydroxide-chitosan composite. The mixture was prepared in an appropriate ratio, preferably with a dominant weight percentage for ferric oxyhydroxide-chitosan composite (wt/wt). Once the blending of nanoparticles in carrier composition was complete, the precipitate was dried at ambient condition.

It may be noted that the desired metal oxide/hydroxide/oxyhydroxide-chitosan composite can be loaded either in precipitated form or in dried powder form.

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.

1. A method of preparing a granular composition in aqueous medium consisting of active ingredient homogenized in organic templated ferric oxyhydroxide carrier composition comprises:
 - a. mixing a Fe(III) precursor solution with a biopolymer to obtain a Fe(III) biopolymer complex solution;
 - b. adding aqueous NaOH solution to the Fe(III) biopolymer solution under vigorous stirring to precipitate organic templated semi solid material;
 - c. filtering the semi solid precipitate on a micron filter cloth;
 - d. dispersing active ingredient in a solvent;
 - e. mixing the dispersion with semi-solid precipitate;
 - f. drying the material obtained from step (e) to remove the moisture content at temperatures below 60 °C by air drying or sun drying, and
 - g. grinding the material from step (f) in order to obtain the particles in granular form wherein the active ingredient is a powdered metal oxide/hydroxide/oxyhydroxide composite with a weight loading ratio of up to 50% and the carrier composition is stable in water.
2. The method as claimed in claim 1, wherein the metal is selected from a group comprising of aluminum, zinc, manganese, zirconium, lanthanum, cerium, silicon, or a combination thereof.
3. The method as claimed in claim 1, wherein the biopolymer is chitosan, banana silk, nylon, cellulose or a combination thereof.
4. The method as claimed in claim 1, wherein the biopolymer is a functionalized form of chitosan, banana silk, cellulose or a combination thereof.
5. The method as claimed in claim 1, wherein the ferric precursor is at least one selected from the group comprising ferric nitrate, ferric chloride, ferric sulfate or a combination thereof.
6. The method as claimed in claim 1, wherein the granular composition functions as an adsorbent for removing contaminants from water and acts as a novel template for slowly releasing the active ingredients in air.
7. The method as claimed in claim 6, wherein the contaminants are arsenate, arsenite, or a combination thereof.

8. The method as claimed in claim 1, wherein the granular composition removes nanoparticles of size above 1 nm from a medium.

Dated at Chennai this September 20, 2019

Signature: 

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

ABSTRACT

The present invention discloses a method of preparation of a granular composite of diverse active ingredients of relevance for water-related applications. The granular composition comprises of active ingredient homogenized in the aggregated network of organic templated ferric oxyhydroxide ("carrier composition"). The ability to prepare granular composite! is independent of the nature of active ingredient and is derived from carrier composition. The weight proportion of active ingredient to carrier composition is no less than 20% and up to 50% and active ingredient is in unbound but trapped state. Addition of active ingredient doesn't cause any significant deterioration in the strength of the carrier composition. The application of active ingredient-carrier composition is demonstrated for a number of applications. It is to be noted that carrier composition itself can be an active ingredient, such as an adsorbent for arsenic removal from water with excessively high arsenic adsorption capacity vis-a-vis compositions reported in prior art.

ORIGINAL

No 486 /CHE/ 2013

- 4 FEB 2013

INDIAN INSTITUTE OF TECHNOLOGY MADRAS

1 of 11

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

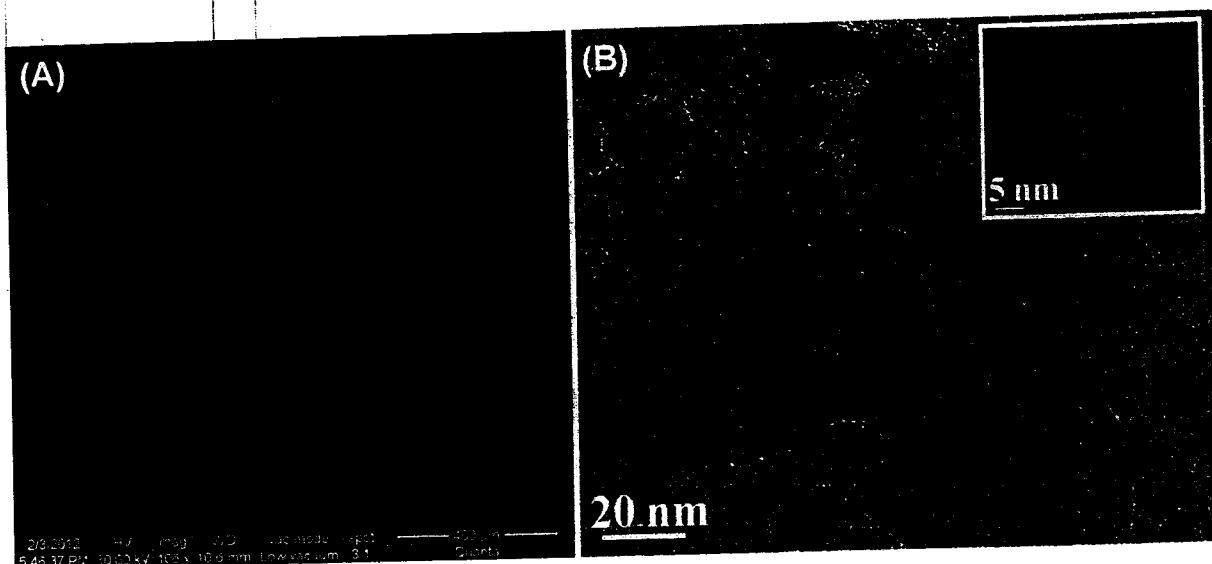


FIGURE 1

Signature:

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

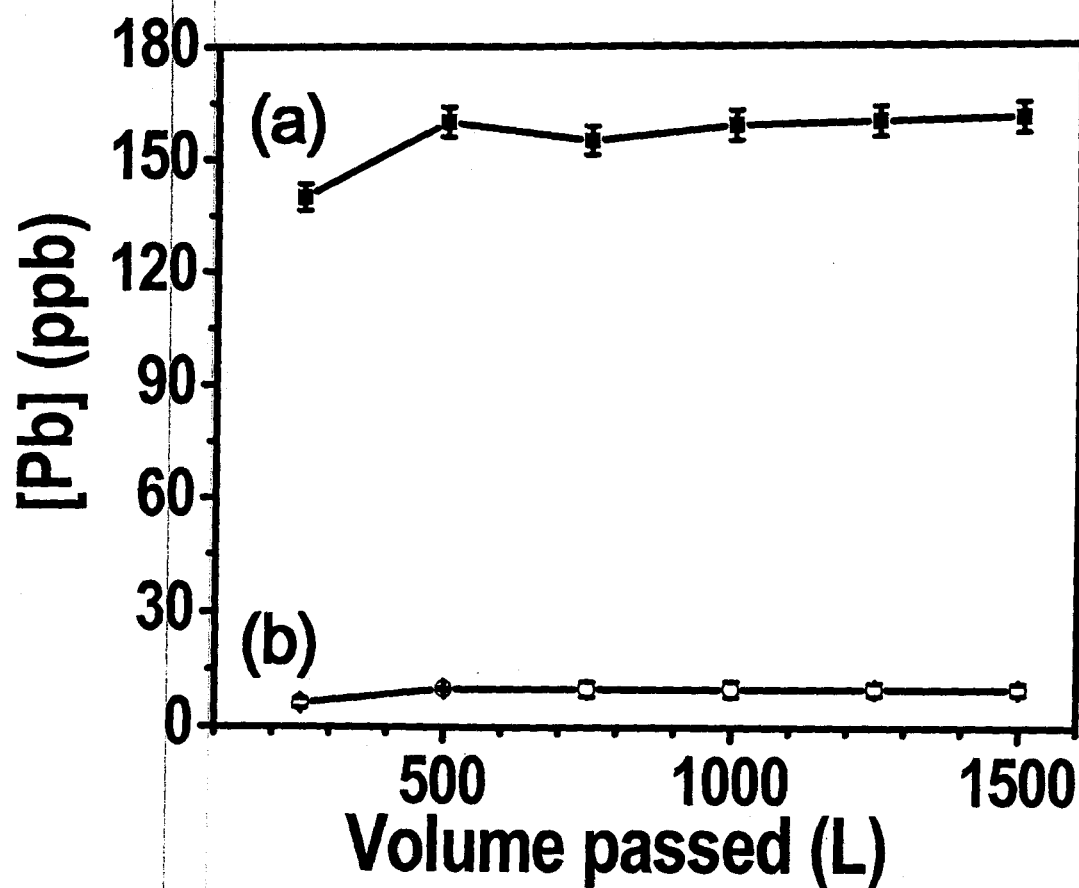


FIGURE 2

Signature:

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

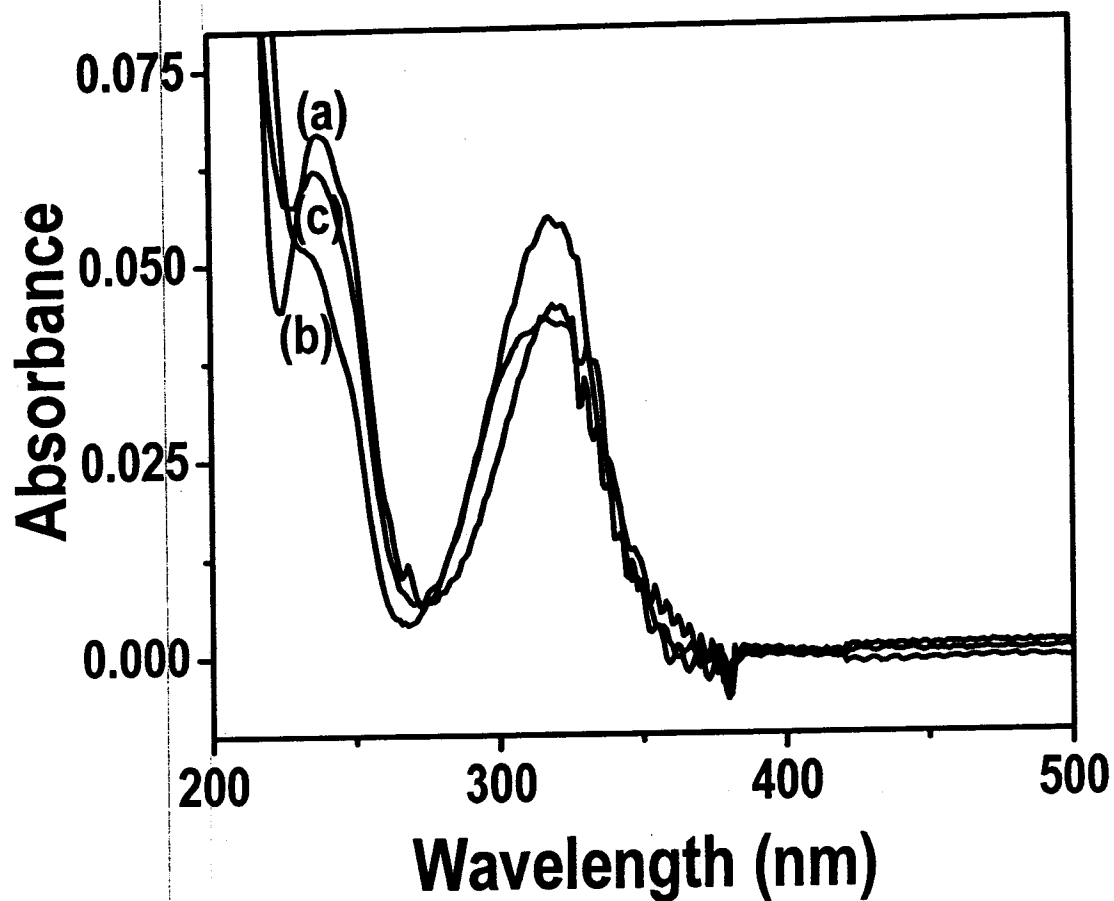


FIGURE 3

Signature:

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

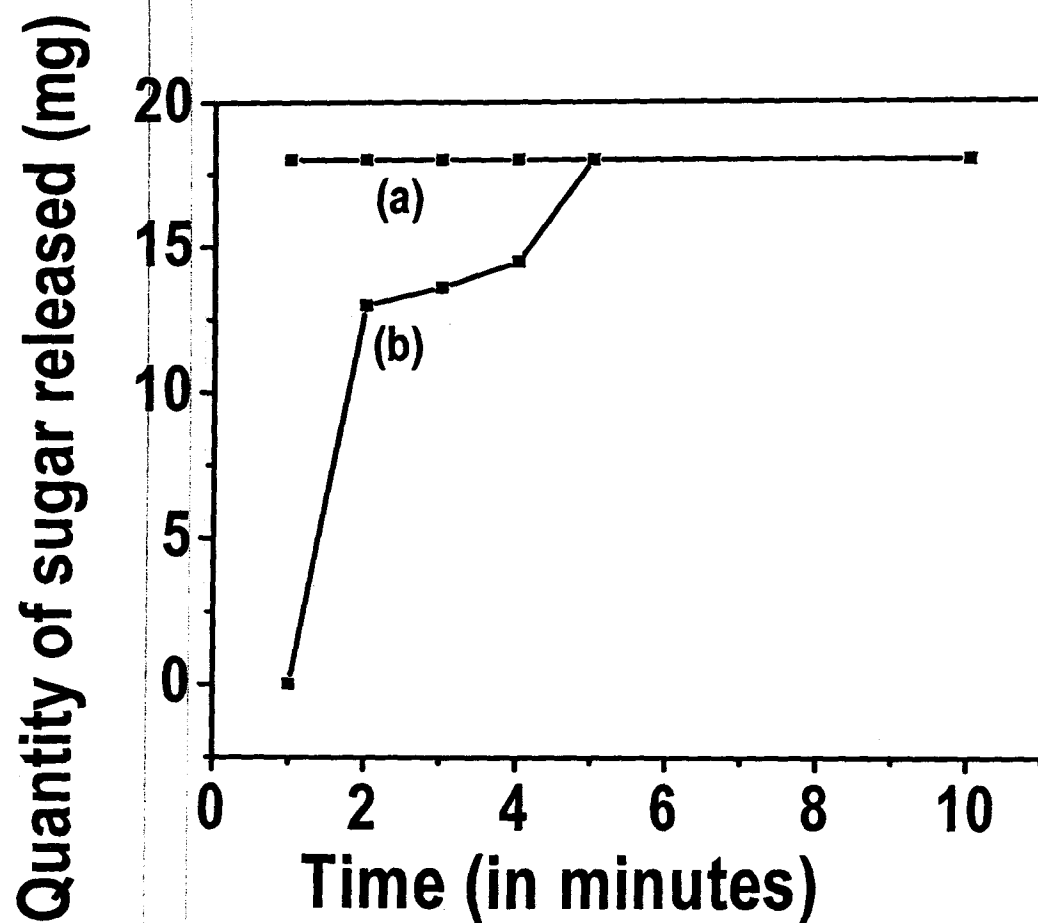


FIGURE 4

Signature:

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

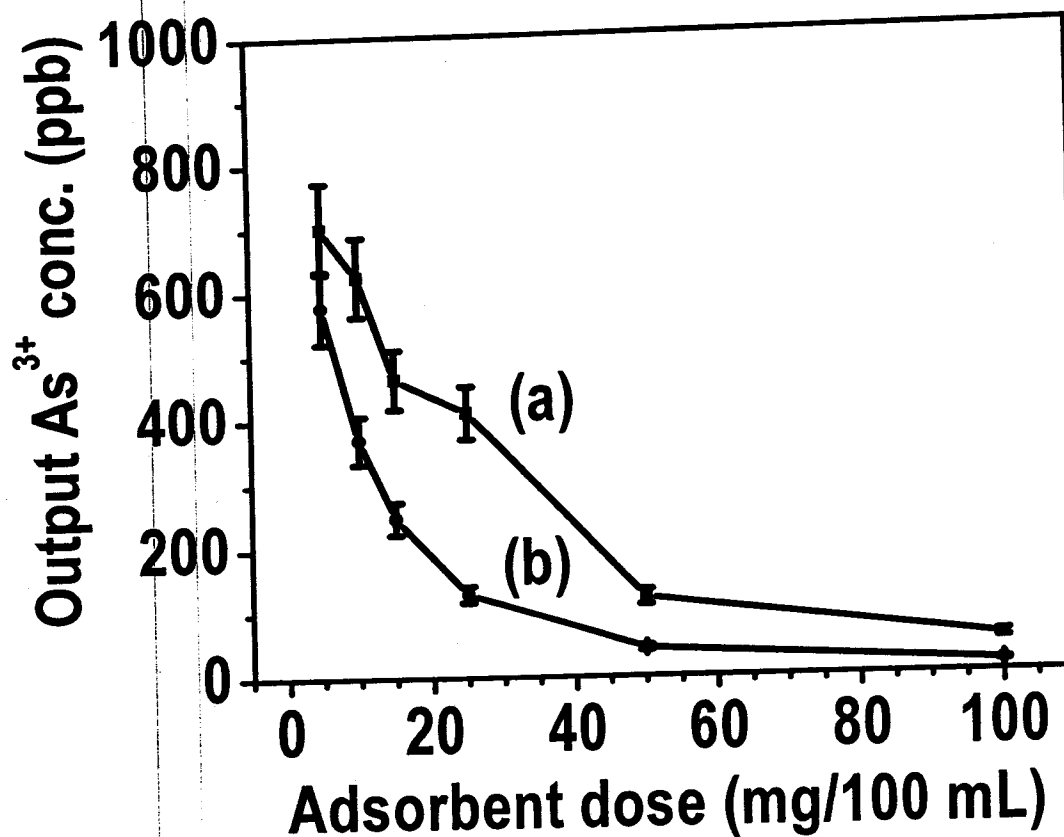


FIGURE 5

Signature:

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

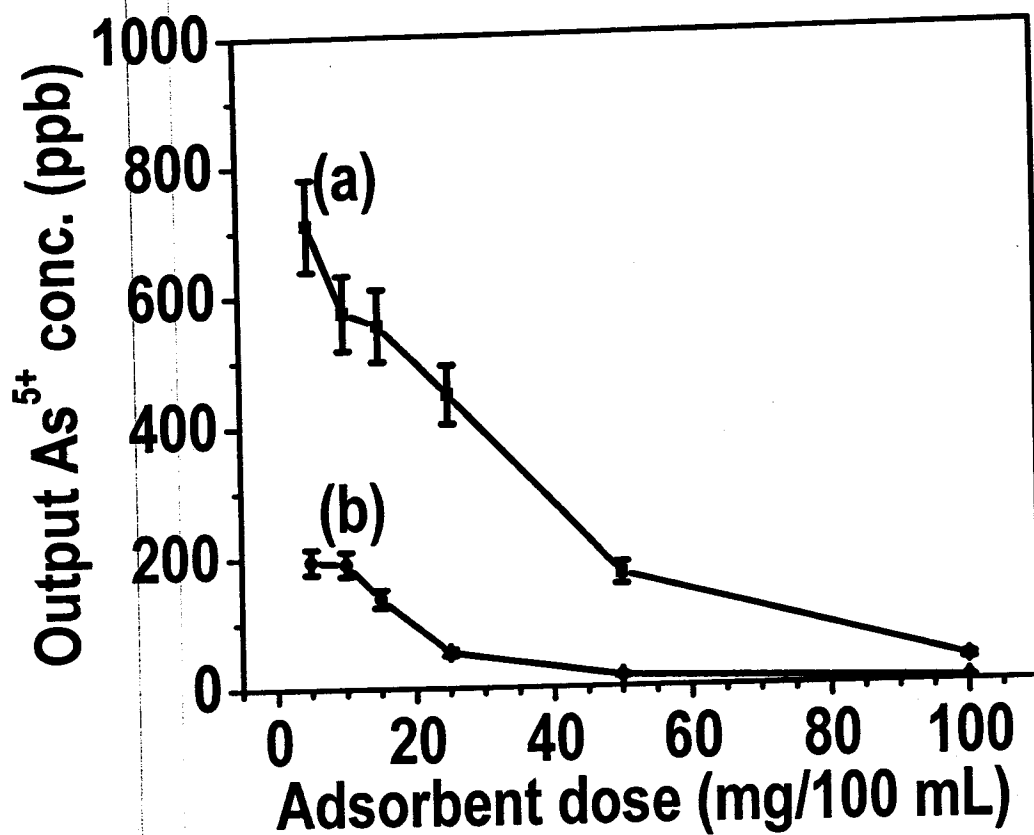


FIGURE 6

Signature:

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

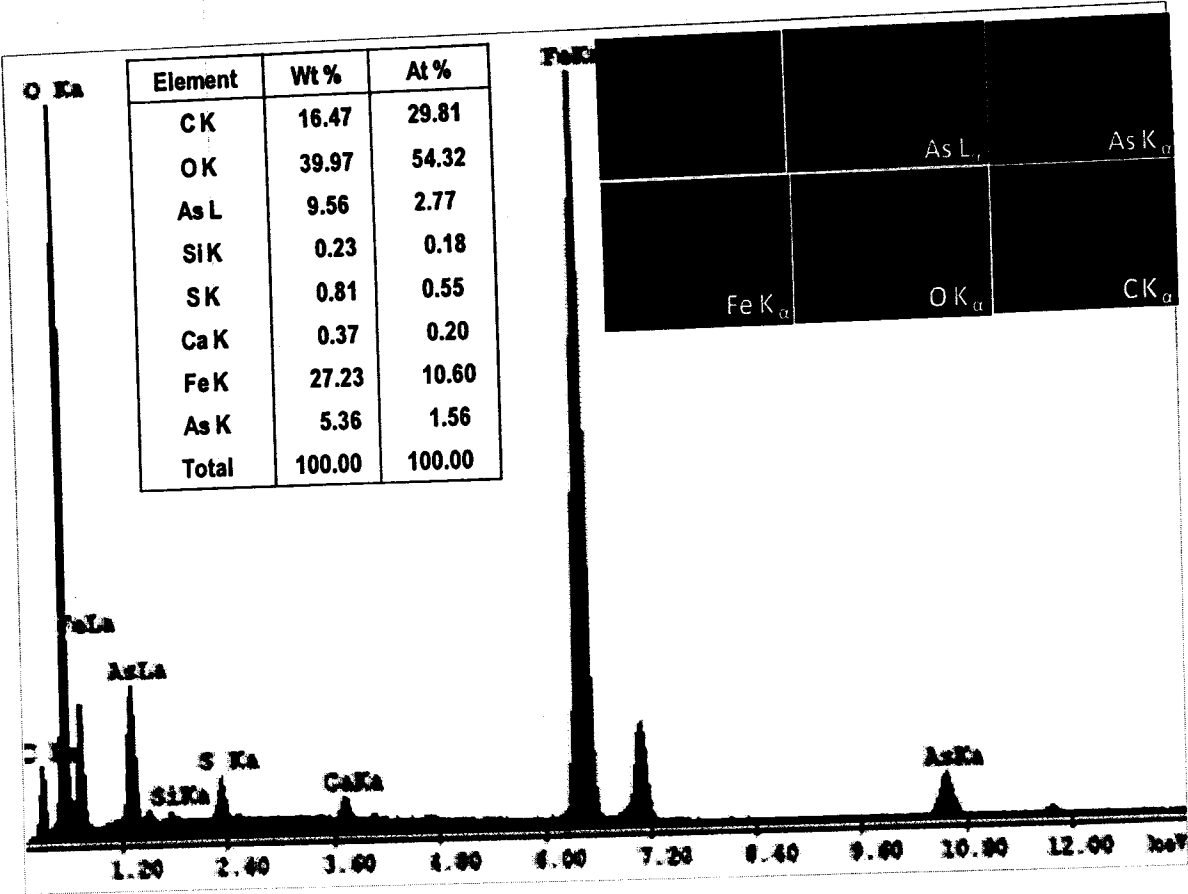



FIGURE 7

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

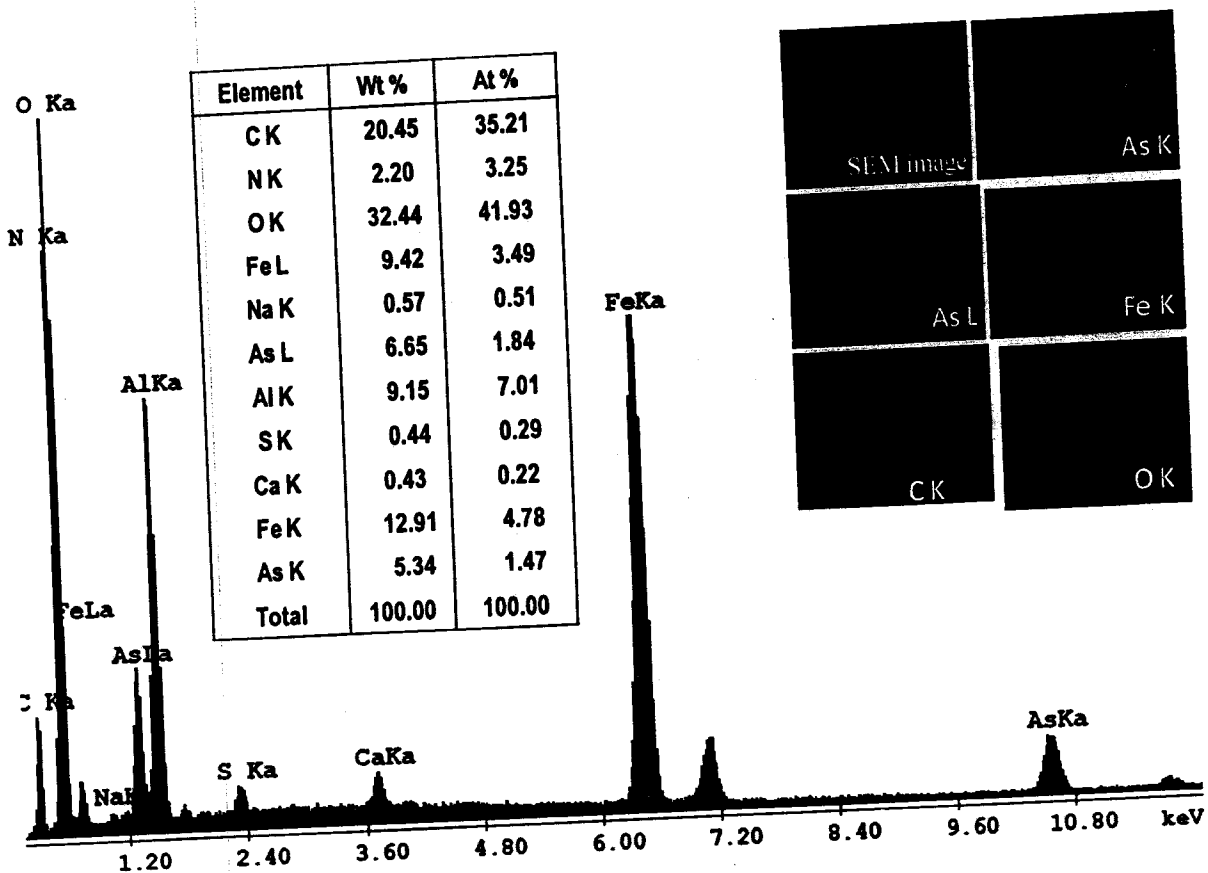



FIGURE 8

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

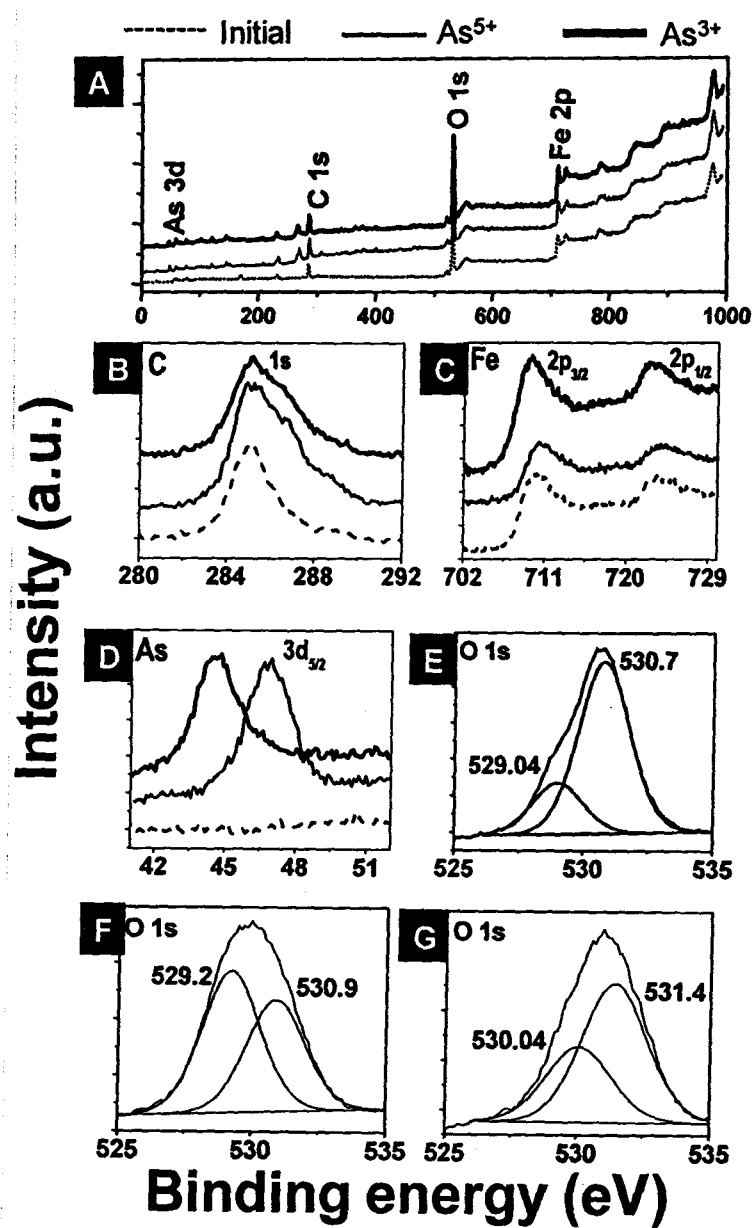


FIGURE 9

Signature:

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

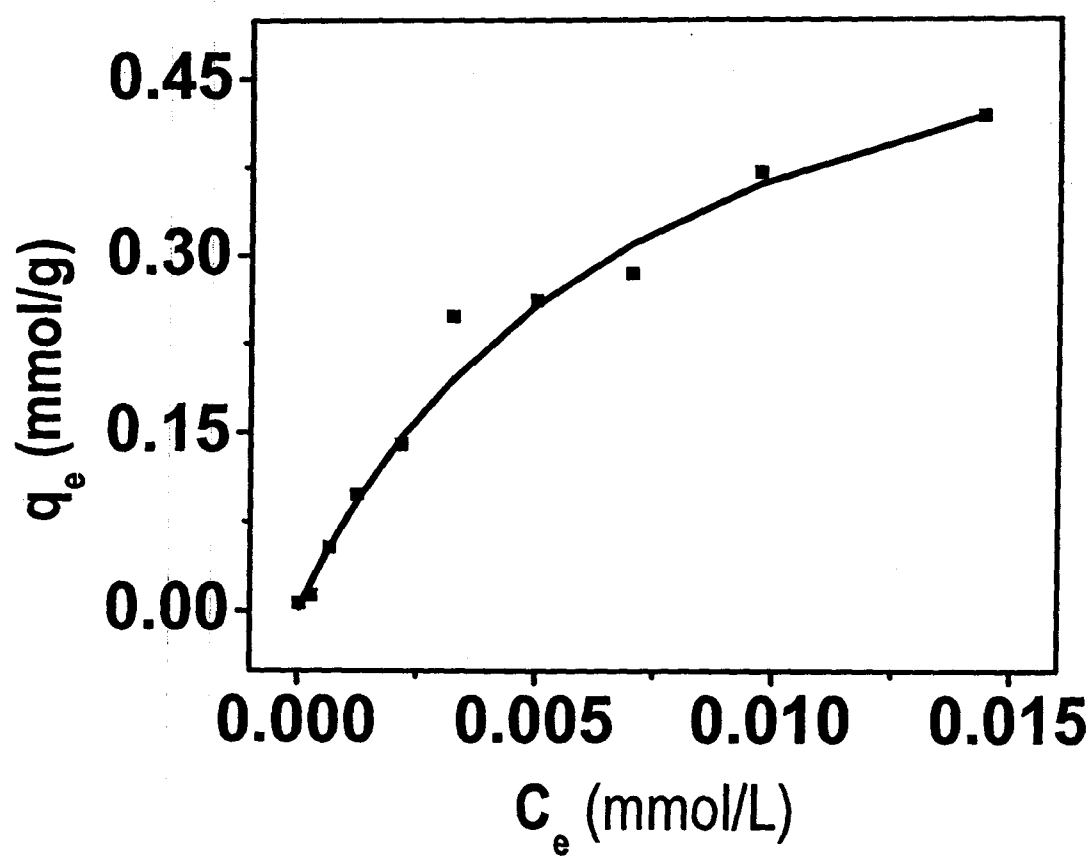


FIGURE 10

Signature:

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

A GRANULATION COMPOSITION FOR POWDER INGREDIENTS

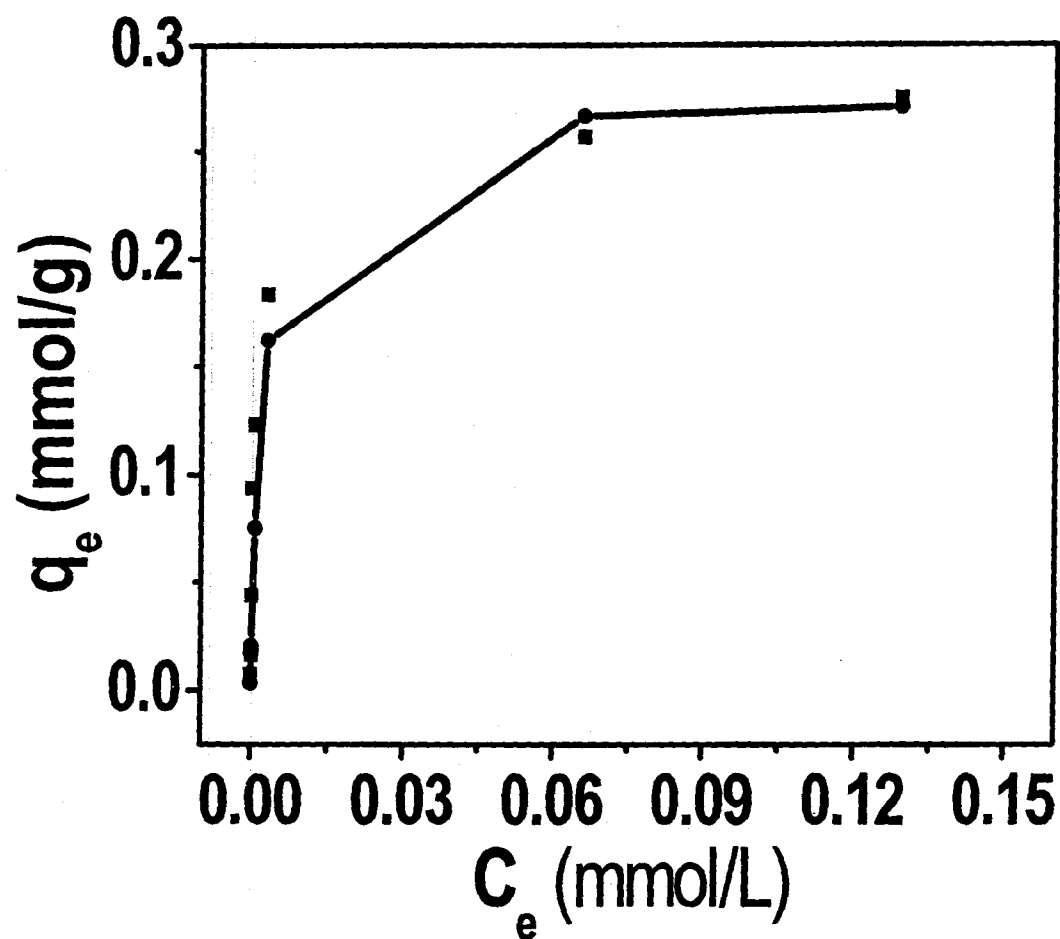


FIGURE 11

Signature:

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