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PATENT CERTIFICATE**
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क्रमांक : 044107360
SL No :



पेटेंट सं. / Patent No. : 302262
आवेदन सं. / Application No. : 3587/CHE/2011
फाइल करने की तारीख / Date of Filing : 19/10/2011
पेटेंटी / Patentee : INDIAN INSTITUTE OF TECHNOLOGY

प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित **REMOVAL OF PESTICIDES FROM WATER USING GRAPHENIC MATERIALS** नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 19th day of October 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 **REMOVAL OF PESTICIDES FROM WATER USING GRAPHENIC MATERIALS** as disclosed in the above mentioned application for the term of 20 years from the 19th day of October 2011 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 17/10/2018
Date of Grant :

पेटेंट नियंत्रक
Controller of Patent

OKSupte

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, **19th day of October 2013** 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 **19th day of October 2013** 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:

REMOVAL OF PESTICIDES FROM WATER USING GRAPHENIC MATERIALS

2. APPLICANT:

(A) NAME: **INDIAN INSTITUTE OF TECHNOLOGY 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.

FIELD OF INVENTION

[0001] This invention discloses the unprecedented ability of graphenic materials for scavenging pesticides from water enabling them to be used as water purifying media. Specifically, the present invention relates to the use of reduced graphene oxide (RGO) and graphene oxide (GO) for the removal of pesticides which belong to the organochlorine and organophosphate categories. More specifically, the invention relates to the use of RGO and GO for the removal of endosulfan (ES), malathion (ML) and chlorpyrifos (CP) present in water to make clean water.

PRIOR ART

[0002] Water, being a universal solvent, is affected by a number of contaminants and those contaminants are regulated as per drinking water norms (<http://www.epa.gov/safewater/contaminants/index.html>). Therefore, more efforts have to be made to find suitable materials and methods to effectively address diverse contaminants. Pesticides are one such important category of contaminants that are widely detected in surface and groundwater. Due to possible entry of these contaminants into human and animal food chains, health hazards posed by pesticides have become a huge area of concern for both developing and developed countries worldwide (J. Weber, C.J. Halsall, D. Muir, C. Teixeira, J. Small, K. Solomon, M. Hermanson, H. Hung, T. Bidleman, Endosulfan, a global pesticide: A review of its fate in the environment and occurrence in the Arctic, *Sci. Tot. Environ.*, 408(15), 2010, 2966-2984.; N. Xue, D. Zhang, X. Xu, Organochlorinated pesticide multi-residues in surface sediments from Beijing Guanting reservoir, *Water Res.* 40, 2006, 183-194.; Analysis of pesticide residue in soft drinks, Center for Science and Environment, 2003, New Delhi, India).

[0003] Carbon is an interesting material and has a wide variety of applications in various fields including water purification. In-fact, water purification is the oldest and most commonly used application of carbon materials. It has been extensively used as adsorbent for removing taste and odor compounds, pesticides, heavy metals, etc. (B. Srivastava, V. Jhelum, D.D. Basu, P.K. Patanjali, Adsorbent for pesticide uptake from contaminated water: A review, *J. Sci. Ind. Res.*, 68, 2009, 839-850.; Y. Matsui, D.R.U. Knappe, K. Waki and H. Ohira, Pesticide adsorption by granular activated carbon adsorbers. 2. Effects of pesticide and natural organic matter characteristics on pesticide breakthrough curves, *Environ. Sci. Technol.* 2002, 36, 3432-3438.).

Different forms of carbon and their composites have been investigated, which aims at improving the adsorption efficiency and are described in the prior arts reported below:

- (a) Pradeep, T.; Anshup. Noble Metal Nanoparticles for water purification: A critical review. *Thin Solid Films* 2009, 517, 6441-6478.
- (b) K.Y. Foo, B.H. Hameed, Detoxification of pesticide waste via activated carbon adsorption process, *J. Hazard. Mater.*, 175(1-3), 2010, 1-11.
- (c) Chen, J.; Zou, J.; Zeng, J.; Song, X.; Ji, J.; Wang, Y.; Ha, J.; Chen, X. Preparation and evaluation of graphene-coated solid-phase microextraction fiber. *Anal. Chim. Acta* 2010, 678, 44-49.
- (d) M.V. López-Ramón, M.A. Fontecha-Cámara, M.A. Álvarez-Merino and C. Moreno-Castilla, Removal of diuron and amitrole from water under static and dynamic
- (e) S. Qu, F. Huang, S. Yu, G. Chen and J. Kong, Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with Fe₂O₃ particles, *J. Hazard. Mater.* 160 (2008), 643-647.
- (f) B. Pan, D. Lin, H. Mashayekhi and B.S. Xing, Adsorption and hysteresis of bisphenol A and 17 α -ethinyl estradiol on carbon nanomaterials, *Environ. Sci. Technol.*, 42, 2008, 5280-5485.
- (g) C. Lu, Y.L. Chung and K.F. Chang, Adsorption of trihalomethanes from water with carbon nanotubes, *Water Res.* 39, 2005, 1183-1189.
- (h) R.Q. Long and R. Yang, Carbon nanotubes as superior sorbent for dioxin removal, *J. Am. Chem. Soc.* 123, 2001, 2058-2059.

[0004] Recent efforts show that carbon nanotubes (CNTs) are efficient in scavenging organic compounds. Chen et al. studied the adsorption affinity of CNTs to organic compounds having varied physical and chemical properties (W. Chen, L. Duan and D.Q. Zhu, Adsorption of polar and nonpolar organic chemicals to carbon nanotubes, *Environ. Sci. Technol.*, 41, 2007, 8295-8300). They reported that for a given nanotube, the adsorption affinity correlated poorly with hydrophobicity but increased in the order, nonpolar aliphatic < nonpolar aromatics < nitroaromatics. Lin and Xing studied the interaction of polar aromatic compounds with CNTs, they found a direct correlation between the number of aromatic rings on the compound and the adsorption affinity of CNTs (D.H. Lin and B.S. Xing, Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups, *Environ. Sci. Technol.*, 42, 2008), 7254-7259). Very recently, Chen and co-workers studied the effect of lead

on the adsorption of diuron and dichlobenil from water on multiwalled carbon nanotubes (MWCNTs) (G.C Chen, X.Q. Shan, Z.G Pei, H. Wang, L.R. Zheng, J. Zhang and Y.N Xie, Adsorption of diuron and dichlobenil on multiwalled carbon nanotubes as affected by lead, J. Hazard. Mater., Article in Press, doi:10.1016/j.jhazmat.2011.01.095.) They found that the adsorption of the pesticides is highly correlated with specific surface areas and micropore volumes of MWCNTs. They also observed an inverse correlation between the oxygen content of MWCNTs and adsorption of pesticides.

[0005] CNTs were reported to be cyto-toxic (M.L. Schipper, N. Nakayama-Ratchford, C.R. Davis, N.W.S. Kam, P.Chu, Z. Liu, X. Sun, H. Dai, S.S. Gambhir, A pilot toxicology study of single-walled carbon nanotubes in a small sample of mice. Nat. Nanotechnol., 3, 2008, 216–221.; A. Magrez, S. Kasas, V. Salicio, N. Pasquier, J.W. Seo, M. Celio, S. Catsicas, B. Schwaller, L. Forro, Cellular toxicity of carbon-based nanomaterials. Nano Lett., 6, 2006, 1121–1125) that would limit their utility in drinking water purification. Graphene, the latest member of the carbon family, seems to be a better alternative for this purpose due to its unique two-dimensional nature, larger surface area (C.N.R. Rao, A.K. Sood, K.S. Subrahmanyam, A. Govindaraj, Graphene: The New two-dimensional nanomaterial. Angewandte Chemie International Edition, 48, 2009, 7752-7777), and less cytotoxicity (W. Hu, C. Peng, W. Luo, M. Lv, X. Li, D. Li, Q. Huang, and C. Fan, Graphene-based antibacterial paper. ACS Nano, 4, 2010, 4317-4323).

[0006] Recent investigations show that graphene and its precursor, graphite oxide (GO), and their composites are promising candidates for removing heavy metals from water (V. Chandra, J. Park, Y. Chun, J.W. Lee, I.C. Hwang, and K.S. Kim, Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal, ACS Nano 4(7), 2010, 3979-3986.; S.T. Yang, Y. Chang, H. Wang, G. Liu, S. Chen, Y. Wang, Y. Liu, A. Cao. Folding/aggregation of graphene oxide and its application in Cu²⁺ removal, J. Colloid Interf. Sci., 351(1), 2010, 122-127.; K. Zhang, V. Dwivedi, C. Chi, J. Wu, Graphene oxide/ferric hydroxide composites for efficient arsenate removal from drinking water, J. Hazard. Mater., 182(1-3), 2010, 162-168). The antibacterial properties of GO and RGO have also been studied and it has been found that both are antibacterial (W. Hu, C. Peng, W. Luo, M. Lv, X. Li, D. Li, Q. Huang, and C. Fan, Graphene-Based Antibacterial Paper. ACS Nano, 4, 2010, 4317-4323). Sreeprasad et al. have reported a new methodology to make series of RGO-metal and metal oxide composites and studied their application for Hg(II) removal from water (T.S. Sreeprasad, S.M. Maliyekkal, K.P. Lisha, T. Pradeep. Reduced graphene oxide–metal/metal oxide composites: Facile synthesis and

application in water purification. *J. Hazard. Mater.*, 186(1), 2011, 921-931). Surprisingly, no efforts has been made to prove the applicability of GO and RGO as pesticide removal media from water.

[0007] The study discloses the unprecedented pesticide adsorption ability of GO and RGO from water and thus application in water purification. Water purification by removing the said pollutants can be achieved by contacting the said material with contaminated water for a specific duration. The said materials are highly efficient in removing the said contaminants when compared with existing methods. The main advantage of the said material over other adsorbents is its high pesticide removal capacity and thereby less problem of waste sludge after treatment. Adsorption capacities as high as ~1200 mg/g, 1100 mg/g and 800 mg/g were observed at 2 mg/L of initial CP, ES and ML, respectively. The observed amount of pesticide (in the case of CP and ML) adsorbed on the graphene surface is estimated to be more than the self weight of the adsorbent, which is unprecedented. It is around 10 -10000 times higher than the adsorption capacities of various adsorbents reported in the literature. Prior arts describing the adsorption capacities of few recent adsorbents for the removal of these pesticides are:

- a. Mishra, P.C., Patel, R.K. Removal of endosulfan by sal wood charcoal. *J. Haz. Mater.* 2008, 152, 730-736l.
- b. Memon, S., Memon, N., Memon, S., Latif, Y. An efficient calix[4]arene based silica sorbent for the removal of endosulfan from water. *J. Haz. Mater.* 2011, 186, 1696-1703.
- c. Kushwaha, S., Sreelatha, G., Padmaja, P. Evaluation of acid-treated palm shell powder for its effectiveness in the adsorption of organophosphorus pesticides: Isotherm, kinetics, and thermodynamics. *J. Chem. Eng. Data* 2011, 56, 2407-2415.

Other advantages include: high specificity and hence less interference from other common ions present in water, less toxicity compared to other carbon based materials like CNTs and hence suitability in field application, and antibacterial property and unlikely accumulation of bacteria on the filter media. Besides the said merits, the said material can be easily immobilized on cheap substrates like sand and used as filtering medium that reduced many engineering limitations of the said material in down to earth applications like water purification. This aspect of the said material has been demonstrated in our previous investigation (2563/CHE/2011). Prior arts describing the synthesis and use of graphene materials and their composites are:

- (a) Mastalir, A., Kira'ly, Z., Benko, M., De'ka'ny, I. Graphite oxide as a novel host material of catalytically active Pd nanoparticles. *Catal. Lett.* 2008, 124, 34.
- (b) Stankovich, S., Dikin, D. A., Dommett, G. H. B., Kohlhaas, K. M., Zimney, E. J., Stach, E. A., Piner, R. D., Nguyen, S. T., Ruoff, R. S., Graphene-based composite materials. *Nature* 2006, 442, 282.
- (c) Wang, D.-W., Li, F., Zhao, J., Ren, W., Chen, Z.-G., Tan, J., Wu, Z.-S., Gentle, I., Lu, G. Q., Cheng, H.-M., Fabrication of graphene/polyaniline composite paper via in situ anodic electropolymerization for high-performance flexible electrode. *ACS Nano* 2009, 3, 1745.
- (d) Xu, C., Wang, X., Zhu, J., Graphene-metal particle nanocomposites. *J. Phys. Chem. C* 2008, 112, 19841.
- (e) Yoo, E., Okata, T., Akita, T., Kohyama, M., Nakamura, J., Honma, I., Enhanced electrocatalytic activity of Pt subnanoclusters on graphene nanosheet surface. *Nano Lett.* 2009, 9, 2255-2259.
- (f) Scheuermann, G. M., Rumi, L., Steurer, P., Bannwarth, W., Mul'lhaupt, R., Palladium nanoparticles on graphite oxide and its functionalized graphene derivatives as highly active catalysts for the Suzuki-Miyaura coupling reaction. *J. Am. Chem. Soc.* 2009, 131, 8262.
- (g) Williams, G., Seger, B., Kamat, P. V., TiO₂-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano* 2008, 2, 1487.
- (h) Lambert, T. N., Chavez, C. A., Hernandez-Sanchez, B.; Lu, P.; Bell, N. S.; Ambrosini, A., Friedman, T., Boyle, T. J., Wheeler, D. R., Huber, D. L., Synthesis and characterization of titania-graphene nanocomposites. *J. Phys. Chem C* 2009, 113, 19812
- (i) Wang, D., Choi, D., Li, J., Yang, Z., Nie, Z., Kou, R., Hu, D., Wang, C., Saraf, L. V., Zhang, J., Aksay, I. A., Liu, J., Self-assembled TiO₂-graphene hybrid nanostructures for enhanced Li-ion insertion. *ACS Nano* 2009, 3, 907.
- (j) Tung, V. C., Chen, L.-M., Allen, M. J., Wassei, J. K., Nelson, K., Kaner, R. B., Yang, Y., Low-temperature solution processing of graphene-carbon nanotube hybrid materials for high-performance transparent conductors. *Nano Lett.* 2009, 9, 1949.
- (k) WO 2009/143405 A3-Synthesis of graphene sheets and nanoparticle composite of the same.
- (l) United States patent 2010/0036023 A1- Graphite nanocomposites.
- (m) United States patent 2006/0191835 A1- Compositions and methods of remediations devices with nanostructures sorbents.

- (n) United States patent 2010/0081587 A1-Nanocomposites of graphene and metal oxide materials.
- (o) United states patent 2010/0096597 A1-Functional graphene-rubber nanocomposites.
- (p) United States patent 2010/0096595 A1-Functional graphene-polymer nanocomposite for gas barrier applications.
- (q) United States patent 2010/0021819 A1-Graphene composites for electrochemical cell electrodes.
- (r) United States patent 2006/0122451 A1-Binding and in situ destruction of chemical agents and other contaminants.
- (s) United States patent 2009/0020764 A1-Graphene-based transistor.

MATERIAL CHARACTERIZATION:

[0008] UV/Vis spectrum of GO and RGO was measured using a Perkin-Elmer Lambda 25 V/Vis spectrophotometer. ATR-IR measurements were done using a PerkinElmer, Spectrum 100 spectrometer. Raman spectra of GO and RGO were collected using a confocal Raman spectroscopy (WiTec GmbH CRM 200). XPS measurements were done with Omicron ESCA Probe spectrometer with unmonochromatized Mg K_α X-rays ($h\nu = 1253.6$ eV). The energy resolution of the spectrometer was set at 0.1 eV at pass energy of 20 eV. Binding energy was corrected with respect to C 1s at 284.5 eV. High-resolution transmission electron microscope (HRTEM) with a UHR polepiece was used to image the samples (JEOL 3011, 300 kV). Surface morphology, elemental analysis and elemental mapping studies were carried out using scanning electron microscopy (SEM) equipped with energy dispersive analysis of X-rays (EDAX) (FEI Quanta 200, Czechoslovakia). The samples were analyzed using desorption electrospray ionization mass spectroscopy (DESI-MS). All the mass spectra were acquired under the identical conditions of 2 mL/min solvent flow rate, 110 psi nebulizer gas (N₂) pressure, and 5 kV spray voltage on an ion trap LTQ XL mass spectrometer (Thermo Scientific, San Jose, CA) equipped with a 2D moving stage (Prosolia, Indianapolis, IN).

DESCRIPTION OF THE INVENTION:

[0009] The invention relates to the identification of a material for the removal of pesticide from water. More specifically, the invention is concerned with the use of GO and RGO, a new class of

carbon nanomaterials as absorbents for the removal of pesticides from water and thus aid in water purification. The following examples are provided to illustrate the basis and practice of the present invention. The first example shows the material synthesis procedure and the second example shows methodology adapted to determine the effectiveness of GO/RGO in removing pesticide in water. Third example describes the procedure adapted to support the graphene on substrates like cellulose. In the subsequent example, the methodology used to test the re-use potential of the RGO as adsorbent to remove pesticides is described. However, the result presented here should not be construed as limiting the scope of the invention.

Example 1

[0010] Synthesis of GO and RGO is illustrated in this example. GO synthesis from graphite powder was carried out based on the modified Hummers method reported by Kovtyukhova et al. (Hummers, W. S., Offeman, R. E., Preparation of graphitic oxide. *J. Am. Chem. Soc.* 1958, 80, 1339.; Kovtyukhova, N. I., Ollivier, P. J., Martin, B. R., Mallouk, T. E., Chizhik, S. A., Buzaneva, E. V., Gorchinskiy, A. D., Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem. Mater.* 1999, 11, 771). The volumes were scaled up to match our requirements. Complete oxidation was ensured by preceding the actual oxidation by a pre-oxidation step. The pre-oxidized graphite is reported to undergo complete oxidation during the oxidation step to form GO. Detailed procedure is reported elsewhere. (Kovtyukhova, N. I., Ollivier, P. J., Martin, B. R., Mallouk, T. E., Chizhik, S. A., Buzaneva, E. V., Gorchinskiy, A. D., Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem. Mater.* 1999, 11, 771).

[0011] The GO reduction was carried out similar to a procedure reported by Li et al. (Li, D.; Muller, M. B., Gilje, S., Kaner, R. B., Wallace, G. G., Processable aqueous dispersions of graphene nanosheets. *Nat. Nanotech.* 2008, 3, 101). Briefly, GO was exfoliated by sonication and hydrazine hydrate solution (35 wt% in water) was added and stirred. The solution was made alkaline by the addition of ammonia solution (28 wt% in water). The mixture was heated at 90 °C. The reduction of GO to RGO happens in about 2h. Detailed procedure for the reduction and the post reduction processing is reported elsewhere (Li, D., Muller, M. B., Gilje, S., Kaner, R. B., Wallace, G. G., Processable aqueous dispersions of graphene nanosheets. *Nat. Nanotech.* 2008, 3, 101). This sample will be referred as purified reduced graphene oxide sheets (RGO).

Example 2

[0012] The pesticide uptake capacities of GO and RGO dispersions were investigated in 20 mL batch reactor. Working volume was maintained as 10 mL. Homogenous dispersions of GO and RGO were taken in the reactor separately and the target pesticide was added into this solution to get the required concentration of the contaminant. All the adsorption experiments were conducted at room temperature ($30\pm 2^\circ\text{C}$). Selected properties of the pesticides used are given in Table 2. The solutions contained a small amount of ethanol ($<0.5\%$ by volume), which was added with the pesticide stock solution. The solutions were kept for stirring at ambient conditions. The solid-liquid separation was done by membrane filtration. The filtrate was analyzed to quantify the target pesticide in the aqueous phase by high pressure liquid chromatography (HPLC) (Dionex, UltiMate 3000) equipped with an UltiMate 3000 variable wave length detector and a packed column of Agilent C18, 100A. Analysis of CP was carried out at a wavelength of 267 nm. Acetonitrile:water (80:20) mixture was used as the mobile phase and a total flow rate of 1 mL/min was maintained. ES and ML were also analysed at similar settings but at a wavelength of 214 nm. The effect of pH, contact time, adsorbent dose, and co-existing ions were evaluated by varying the parameters in appropriate window. Except kinetics, all other studies were conducted by batch equilibration method. For conducting adsorption experiments in real water, the water was simulated by spiking required concentration of target pesticide into groundwater. The water quality characteristics of the groundwater are given in Table 1. Control samples were kept in all the cases to assess the removal of the pesticides by methods other than adsorption by RGO/GO. All the experiments were conducted in duplicate with proper control and the samples were analyzed immediately.

Example 3

[0013] This example describes the preparation of RGO@cellulose. To support RGO composites on cellulose, the following protocol was adopted. Initially, RGO (0.01%) and chitosan solution (0.8 % chitosan in 1.5 % acetic acid) was mixed in 5:1 ratio. The mixture was stirred thoroughly to obtain a homogenous dispersion. 100 mL of the homogeneous dispersion was added to 10 g of cellulose and mixed thoroughly in a mixer. The composite was dried at 40°C . To stabilize the coating, the dried samples were soaked in a pH 9 solution for about 30 min and subsequently washed with distilled water until the pH of the wash water became nearly neutral. The composite was again dried at 40°C overnight and stored in polythene bags for further use.

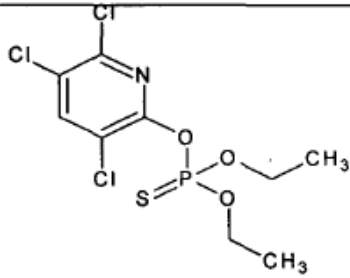
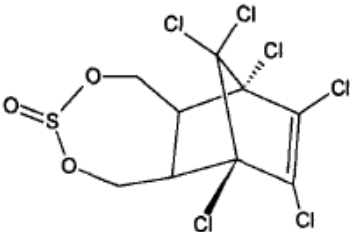
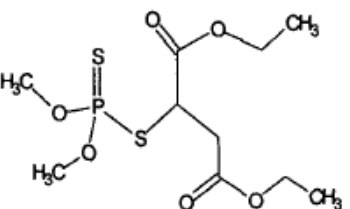
Example 4

[0014] Reusability of the pesticides was tested by desorbing the initially absorbed pesticides using n-hexane. The test was restricted to CP since all the three pesticides studied, showed similar behavior. To begin with, CP of 2 mg/L was initially adsorbed onto RGO at neutral pH and at room temperature ($30\pm 2^{\circ}\text{C}$). After achieving equilibrium, 5 mL of n-hexane was added to the reactor and stirred for 30 min. After 30 min, n-hexane was separated from the reactor carefully and the solvent was evaporated by means of a rotavapor. The desorbed pesticide was re-dissolved in equal volume of ethanol and analyzed using HPLC as described above. After the first cycle, the material was separated from the solvent and reused for the subsequent adsorption and desorption cycles.

Table 1. Water quality characteristics of the groundwater used in this study

Parameters	Concentration (mg/L)*
pH @ 25 °C	7.4
Fluoride	2.27
Total Alkalinity (as CaCO_3)	326
Total Hardness (as CaCO_3)	465
Conductivity @ 25 °C	1226 $\mu\text{mhos/cm}$
Organic carbon	< 0.5
Total Dissolved Solids	762
Calcium (as Ca)	113
Magnesium (as Mg)	44
Sulphate (as SO_4)	80
Chloride (as Cl^{-1})	96
Phosphate (as PO_4^{-3})	<0.02
Iron (as Fe)	0.003
Nitrate (as NO_3^{-})	50.31
Turbidity (as NTU)	0.1 NTU
Silica (as SiO_2)	43.72
Manganese	<0.001

Table 2. Selected properties of the pesticide studied.

Pesticide	Structure	Mol. Wt. (g/mol)	Water solubility	Log K _{ow}
Chlorpyrifos		350.62	2 (25 °C)	4.69
Endosulfan		406.9	α -Endosulfan 0.32 β -Endosulfan 0.33 (22°C)	3.55- 3.62
Malathion		330.36	130 mg/L (25 °C)	2.89

DRAWINGS ACCOMPANYING AND TABULATED DATA

[0014] Figure 1. (A) UV/Vis, (B) ATR-IR and (C) Raman and (D) XPS spectra of GO and RGO. Inset of the A shows the photograph of the as-synthesized GO and RGO dispersion. Traces are shifted vertically for clarity.

[0015] Figure 2. A) EDAX spectrum of the RGO. Inset shows the EDAX images of various elements present along with a SEM image of RGO, (B) SEM images of RGO. (C) TEM images of RGO. Inset of C shows the magnified TEM image of RGO.

[0016] Figure 3. Adsorption of (A) chlorpyrifos (B) endosulfan, and (C) malathion as a function of RGO/GO dose, (D) K_d value obtained for the adsorption of chlorpyrifos onto RGO and GO as function of their dose. Initial concentration of the solute = 2 mg/L, pH = 7 ± 0.2 , and temperature = $30 \pm 2^\circ\text{C}$.

[0017] Figure 4. Adsorption of (A) endosulfan, and (B) malathion as a function of RGO/GO dose, Initial concentration of the solute = 2 mg/L, pH = 7 ± 0.2 , and temperature = $30 \pm 2^\circ\text{C}$.

[0018] Figure 5. (A) HPLC spectra of (a) initial 2 mg/L of chlorpyrifos, (b) residual chlorpyrifos after contact with RGO dispersed in DW and (c) GO dispersed in DW, (d) residual chlorpyrifos after contact with RGO dispersed in GW and (e) GO dispersed in GW. Time dependent removal of (B) chlorpyrifos, (C) endosulfan, and (D) malathion by RGO. Inset of B shows the enlarged view (range: 11-14 min) of figure A. DW-represents pesticide spiked in deionized water; GW-represents pesticide spiked in groundwater.

[0019] Figure 6. HPLC traces of (A) malathion, and (B) endosulfan. (a) and (b) show residual pesticide concentration after contact with RGO dispersed in DW and GW, respectively. (c) and (d) show residual pesticide concentration after contact with GO dispersed in DW and GW, respectively. Initial conc. of the pesticide = 2 mg/L; pH = nearly neutral; temperature = $30 \pm 20^\circ\text{C}$; GW-represent groundwater; DW-represent deionized water.

[0020] Figure 7. A) Effect of pH on the adsorption of chlorpyrifos by RGO/GO. Line diagrams (secondary axis) show the measured initial concentrations of the pesticides at various pHs. (B) HPLC traces of initial and desorbed CP. a, b, c and d show initial CP and CP desorbed in three consecutive desorption cycles, respectively. PA indicates peak area; DW indicates deionized water spiked with pesticide; GW indicates groundwater spiked with pesticide.

[0021] Figure 8. (A) UV/Vis spectra of RGO recorded at the end of each adsorption-desorption cycle. (B) Performance comparison of RGO for three consecutive cycles of adsorption/desorption process. RGO dose = 0.01 %; Initial concentration of CP = 2 mg/L; Temperature = $30 \pm 20^\circ\text{C}$.

[0022] Figure 9. (A) Positive ion DESI mass spectrum of chlorpyrifos on glass palte. (B) MS/MS analysis of m/z 352. Inset of A shows an expanded view of the molecular ion peak and a comparison with the theoretical isotope pattern.

[0023] Figure 10. (A) Positive ion DESI mass spectrum of chlorpyrifos on RGO surface. (B) MS/MS analysis of m/z 352. Inset of B shows an expanded view of the molecular ion peak and a comparison with the theoretical isotope pattern.

[0024] Figure 11. TEM image of RGO after adsorption of chlorpyrifos. Inset of A shows the magnified TEM image. (B) SEM image of RGO after adsorption of chlorpyrifos. Inset of B shows magnified SEM images of the chlorpyrifos adsorbed RGO. (C) EDAX spectrum of RGO loaded with chlorpyrifos. Inset of C shows the X-ray images of various elements present in RGO along with a SEM image.

[0025] Figure 12. (A) Schematic showing the preparation of RGO@cellulose.

[0026] Figure 13. (A) EDAX spectrum of RGO@cellulose after contact with pesticide. (B) SEM image of parent cellulose. (C and D) SEM image of RGO@cellulose. (E) Photograph showing parent cellulose and RGO@cellulose.

DESCRIPTION WITH REFERENCE TO DRAWINGS AND TABULATED DATA:

[0027] The UV/Vis spectral features of GO and RGO are shown in Figure 1A. The absorption peak at 232 nm showed the typical characteristic of GO and the red shift in the peak (268 nm) after hydrazine reduction confirmed the transformation of GO to RGO. The ATR-IR spectra of GO and RGO are shown in Figure 1B. GO showed characteristic peaks at 1217 cm^{-1} (epoxy C-O), 1415 cm^{-1} (carboxy C-O), 1614 (aromatic C=C), and 1720 cm^{-1} (C=O in carboxylic acid), and 1035 cm^{-1} (epoxy or alkoxy C-O). The broad band between 3200-3400 cm^{-1} can be attributed to O-H stretching vibrations. In the case of RGO, most of the peaks due to oxygen functionalities disappeared. The peak at 1415 cm^{-1} almost vanished after reduction with hydrazine. The peaks at 1575 cm^{-1} and 1100 cm^{-1} are due to the aromatic C=C and C-O stretching vibrations, respectively. Raman spectra of GO and RGO were collected. As shown in Figure 1C, the Raman spectrum of GO showed D-band at 1345 cm^{-1} and G-band at 1609 cm^{-1} . After chemical reduction, the D-band position remained the same but G-band shifted to a lower frequency

region (1590 cm^{-1}), confirming the reduction of GO to RGO. GO and RGO were characterized by XPS as well. Figure 1D shows the XPS spectra of GO and RGO. GO showed four components in the C 1s spectrum. The prominent peak centered on 284.5 eV was attributed to nonoxygenated ring C 1s. Other three peaks centered around 288.8 eV, 287.6 eV and 286.3 eV were ascribed to C(O)O, C=O and C-O, respectively. After the chemical reduction of GO, C1s spectrum showed a major peak centered around 284.6 eV corresponding to non-oxygenated ring carbon. The peak centered at 288.9 eV is assigned to C(O)O. Evidently, the oxygenated peak at 286.3 eV due to C-O disappeared completely.

[0028] The RGO was analyzed by EDAX and the spectrum is shown in Figure 2A. The corresponding elemental maps are shown in the inset of Figure 2A. A SEM image of RGO is given in the inset of Figure 2B. From the data, we can see that the sample is devoid of impurities and is transparent. HRTEM images of GO and RGO are shown in Figure 2B and 2C, respectively. The graphenic nature of the materials can be seen from the characteristic ripples present on the sheets of GO and RGO. The edges and wrinkles were measured to be around $\sim 1\text{--}1.5\text{ nm}$ thick, which is close to a bilayer thickness.

[0029] Both GO and RGO were tested for pesticides removal at room temperature and neutral pH and the data for CP are shown in Figure 3A. Unit uptake capacities of CP were increased with decreasing RGO dose. This might be due to increased mass transfer at higher adsorbate/adsorbent ratio. Better separation of RGO/GO sheets at higher dilution and thereby increased available surface area could be another reason for the significant increase in uptake capacity at lower doses. The CP uptake capacity of RGO was found to be as high as $\sim 1200\text{ mg/g}$. The uptake capacity of GO to the pesticide was found to be approximately 10 - 20% less than that of RGO. The affinity of RGO and GO to pesticides was also estimated from the distribution coefficient (K_d) (Figure 3B), a widely used tool to compare the adsorbent performance. The K_d value showed that both RGO and GO are excellent adsorbents ($K_d \gg 10^4\text{ mL/g}$) for pesticide removal.

[0030] Similar adsorption trends were observed in the case of other pesticides as well, i.e. ES and ML. The uptake capacities as a function of GO/RGO dose for the pesticides ES and ML are given in Figure 4. The data showed adsorption capacities of 1100 mg/L and 800 for ES and ML, respectively.

[0031] Figure 5A shows the HPLC trace of CP before and after contact with 0.0125 g/L of RGO. The corresponding HPLC spectra of ES and ML are given in Figure 6. The data showed no interference, irrespective of the pesticides studied, and thus proved the possible utility of RGO and GO in water purification.

[0032] The rate of adsorption of CP, ES and ML onto RGO was tested and the data for CP are given in Figures 5B. The data for ES and ML are given in supplementary data of Figure 6. The kinetic data exhibited rapid removal of the pesticides. More than 90% of the pesticides removal happened in < 10 min contact time, no traces of pesticide were detected after 30 min of contact with RGO. Control samples were also run to account for any possible volatilization and hydrolysis and they showed insignificant effect.

[0033] RGO was tested for pesticides uptake from water, both deionized and groundwater, as a function of pH under batch equilibrium condition. Figure 7A shows insignificant variation in CP uptake capacity over the pH range studied (pH ~3 to 9). Similar behavior was observed with ML and ES as well. The pH independent adsorption behavior of RGO also indicates that the surface functional group ($-\text{COO}^-$) present on the RGO surface is not involved in the adsorption of the pesticides.

[0034] For checking the reuse potential of the RGO, successive adsorption-desorption cycles were conducted. The reuse capacity was studied for three consecutive cycles of adsorption/desorption. The HPLC spectra obtained during three desorption cycles are shown in Figure 7B. The percentage removal of CP for the corresponding adsorption cycle is shown in Figure 8. More than 90% desorption and insignificant reduction in CP uptake capacity was seen with repeated use. In the course of the study, we also observed that a good portion of RGO, which is initially dispersed in water, came to the water-hexane interface, indicating nonpolar nature of the RGO. However, we could re-disperse the RGO effectively by ultrasonication. The UV and Raman features of the cycled RGO were also collected (Figure 8). No significant change in spectral features was seen, indicating that RGO is intact even after repeated use.

[0035] The adsorption of pesticides onto RGO was also illustrated using desorption electrospray ionization (DESI) mass spectrometry measurements. CP on glass plate showed characteristic molecular ion at m/z 352 (Figure 9). The MS/MS of this ion confirmed the identity of the species (inset of Figure 9). RGO loaded with CP showed characteristic molecular ion peak at m/z 352 (Figure 10). The isotopic pattern exhibited by the molecular ion peak is similar

to the theoretically predicted isotopic pattern, confirming the presence of CP on RGO. The MS-MS measurement further confirmed the identity (Figure 10). The fragmented ion at m/z 324 is due to the loss of C_2H_4 formed from the molecular ion at m/z 352. The loss of C_2H_4 from the fragmented ion at 324 resulted in the ion at m/z 296. The fragmented ion at m/z 200 was assigned to $[C_5H_3Cl_3NO]^+$.

[0036] Figures 11A and 11B show the TEM and SEM images of RGO after adsorption of CP, respectively. We can see that the thickness of the sheet increased after pesticide adsorption. However, the shape of the sheet was preserved and RGO remained in suspension without any visible aggregation.

[0037] The cellulose-RGO composite was prepared by using chitosan (ch), a natural linear biopolyaminosaccharide, as the RGO binding and stabilizing agent. The composite was presumed to be formed by the electrostatic interaction between the negative functional group ($-COO^-$) on the RGO surface and the positive functional group ($-NH_3^+$) on chitosan ($pK_a = 6.5$) that is solubilized in mild acetic acid. The electrostatic interaction between the $-OH$ group on the cellulose and the free $-NH_3^+$ on chitosan is hypothesized as the reason for the attachment of the RGO-Ch composites on the cellulose surface. The as-synthesized composite was tested for the pesticide uptake capacity. A cartoon representation of the reaction scheme is shown in Figure 12. Since, all the three pesticides showed more or less similar adsorption behavior, only CP was tested for demonstrating pesticide uptake capacity of the composite.

[0038] The SEM images and EDAX spectra of parent cellulose and the composites before and after CP adsorption are also taken. Figure 13A shows the EDAX spectrum of RGO loaded with CP. The spectrum confirms the presence of CP on the composites, which is evident from the presence of P, S and Cl. The presence of chitosan is confirmed by the nitrogen signal in composites. The SEM images showed that cellulose fibers (Figure 13B) are almost cylindrical in shape, with dimensions ranging from 5–10 μm . No significant changes in morphology were observed after RGO incorporation. However, in some pockets we could see some projection as shown in Figures 13C and D. Photograph in Figure 13E shows clear change in color after the incorporation of RGO, which further strengthened the claims.

Summary

[0039] According to one aspect of the invention, the present disclosure provided a method for the removal of pesticides from water, which comprises of contacting the contaminated water with graphene oxide (GO) and/or reduced graphene oxide (RGO).

[0040] In another aspect, the invention provides a method for the removal of pesticides from water, in presence of other common ions present in water, which comprises of contacting the water with GO and/or RGO.

[0041] In yet another aspect, the present disclosure provides a method to regenerate and reuse the said material for several cycles by contacting the said material with non-toxic solvents like ethanol for specified time duration.

[0042] The amount of said material required to treat a fixed quantity of pesticide in water to a levels below the allowable limit will largely depend on the concentration and the type of pesticide present in the water. The type of adsorbents (RGO or GO) and the time of contact also decides the effectiveness of the pollutant removal. Under ideal conditions, using RGO as sole adsorbent, 0.0001% of adsorbent dose and contact time of < 30 minutes can cleanup up to 99.99 percent of 2 mg/L of dissolved or dispersed pesticide in water giving an adsorption capacity of ~1200 mg/g, in the case of CP. Under similar conditions, pesticides like ES and ML showed adsorption capacities of 1100 mg/L and 800 mg/L, respectively. No material so far tested for this purpose showed pesticide retention capacity more than it's self-weight.

The result can be achieved irrespective of the background ions normally present in water (see table 1 for the composition of the water). However, the effectiveness of the treatment of pesticide by the said method is related to solid/liquid ratios. The figures given above are merely illustrative and are not to be taken as limiting the invention.

[0043] The manner of achieving contact between the water and adsorbent does not form a part of this invention. However, many suitable techniques are available from the prior arts for the said process. The possibilities include: water mixer-settlers; dip-bags, fixed beds or columns. The material may also be used after supporting on suitable substrates.

[0044] The important advantage of using GO and/or RGO as pesticide removal media is the huge capacity of the material and thus less waste sludge, specificity of the adsorbent to the pesticide, reusability and thereby economic viability, non toxic nature of the material, and the antibacterial property of the material and thereby less clogging and less danger of microbial contamination.

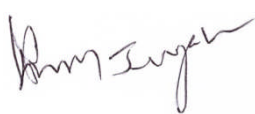
[0045] Another important aspect of the said materials is their potential re-usability and easy disposability. Both RGO and GO used as absorbents can be regenerated for use by washing with organic solvents. Other possible way of regeneration includes prolonged ultrasonication and heating. GO/RGO after use may be readily disposed of by burning.

WE CLAIM:

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1. A method of removing pesticides in water by contacting contaminated water with reduced graphene oxide (RGO) and/or graphene oxide (GO) wherein the said method comprises
 - a. dispersing the adsorbent reduced graphene oxide (RGO) and/or graphene oxide (GO) in the contaminated water
 - b. supporting RGO/GO on an inert solid surface and using the supported GO/RGO as adsorbent media
 - c. water mediated electrostatic interaction of pesticide with graphene surfacewherein the pesticide retention capacity is more than the self-weight of the adsorbent, reduced graphene oxide (RGO) and/or graphene oxide.
2. The method as claimed in claim 1, wherein the pesticides include endosulfan (ES), malathion (ML) and chlorpyrifos (CP)
3. The method as claimed in claim 1, wherein 0.0001% of reduced graphene oxide (RGO) and/or graphene oxide (GO) removes up to 99.99% of target pesticide within 30 min contacts containing up to 2 mg/L of dissolved or dispersed pesticide in water.
4. The method as claimed in claim 1, wherein the reduced graphene oxide (RGO) and/or graphene oxide (GO) are used in the solid form or in the dispersed form or in the supported form.
5. The method as claimed in claim 4, wherein the reduced graphene oxide (RGO) and/or graphene oxide (GO) is immobilized on cellulose fibers.
6. The method as claimed in claims 1 and 4, wherein removing pesticides in water by contacting contaminated water with reduced graphene oxide (RGO) and/or graphene oxide (GO) in the supported form comprises
 - a. Mixing reduced graphene oxide (RGO) and/or graphene oxide (GO) and chitosan in a ratio of 5:1
 - b. Stirring the solution thoroughly to obtain a homogenous dispersion
 - c. Mixing the cellulose fibers with the homogenous dispersion to obtain a composite
 - d. Drying the composite at 40 °C
7. The method as claimed in claim 6, wherein the composite is packed in a column setup to obtain an adsorbent bed.
8. The method as claimed in claim 6, wherein the supported adsorbent can be used as a filtering device to remove pesticides from water.
9. The method as claimed in claim 1, wherein the pesticide loaded reduced graphene oxide (RGO) and/or graphene oxide (GO) is regenerated by contacting the said adsorbent with organic solvents like ethanol.

Dated at Chennai this August 10, 2017


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

REMOVAL OF PESTICIDES FROM WATER USING GRAPHENIC MATERIALS

ABSTRACT

A novel method of removing pesticides in water by contacting the water with reduced graphene oxide (RGO) and/or graphene oxide (GO) adsorbent. The method involves a water mediated electrostatic interaction of pesticide with graphene surface. The reduced graphene oxide (RGO) and/or graphene oxide (GO) adsorbent were found to be excellent candidates for the removal of pesticides and can retain pesticides like chlorpyrifose (CP) and endosulfan (ES) more than their self-weight. Adsorption showed no significant effect with change in pH and presence of co-existing ions, indicating the utility of the material in water purification process.

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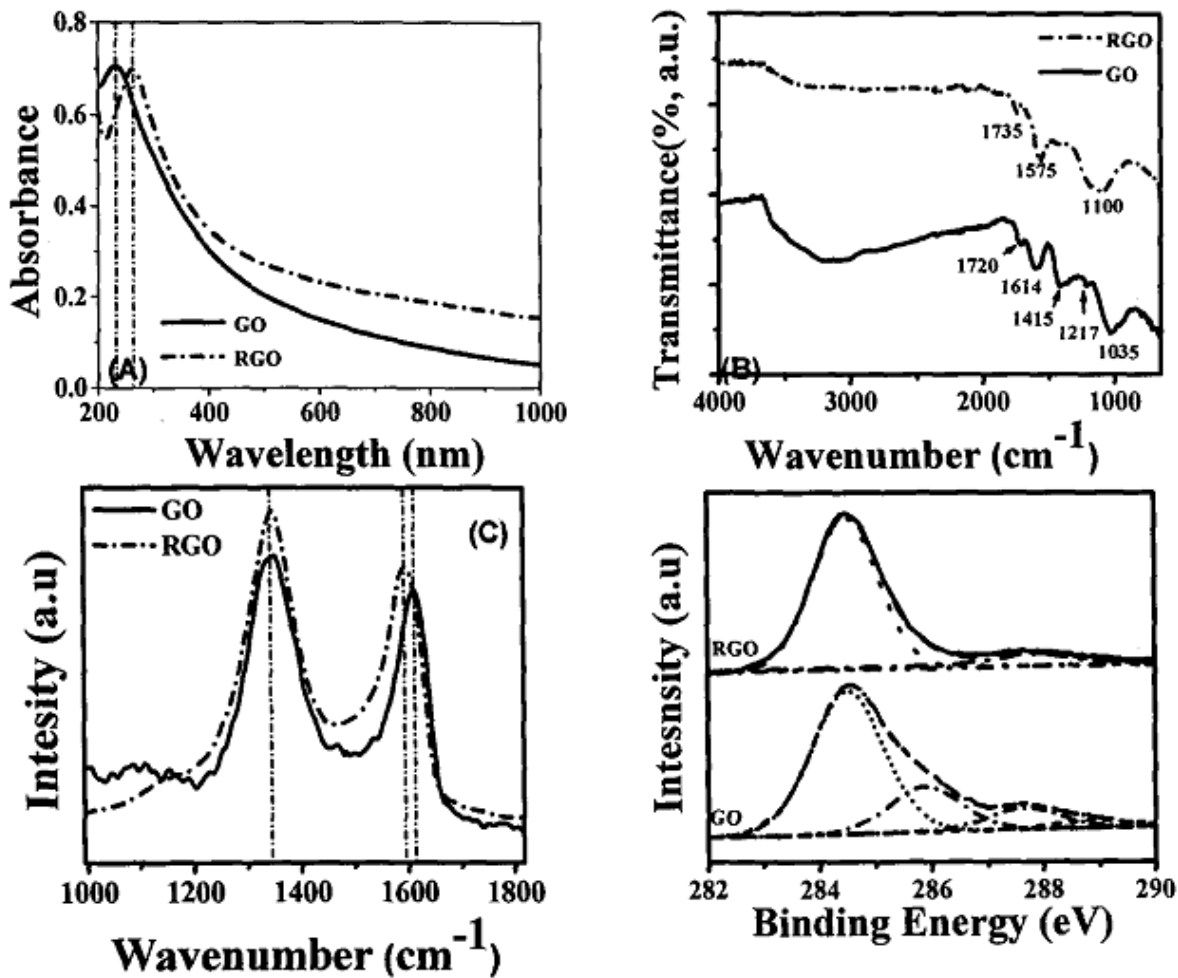


Figure 1

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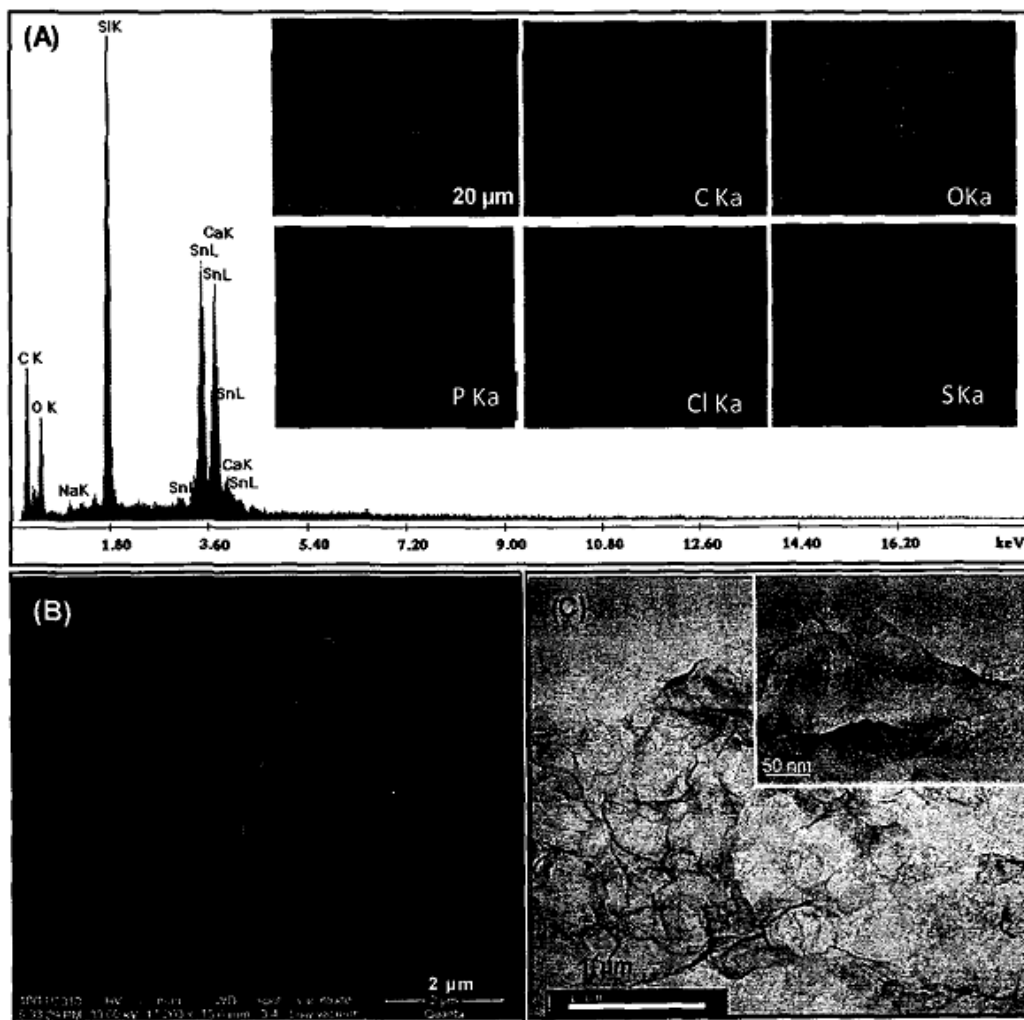


Figure 2

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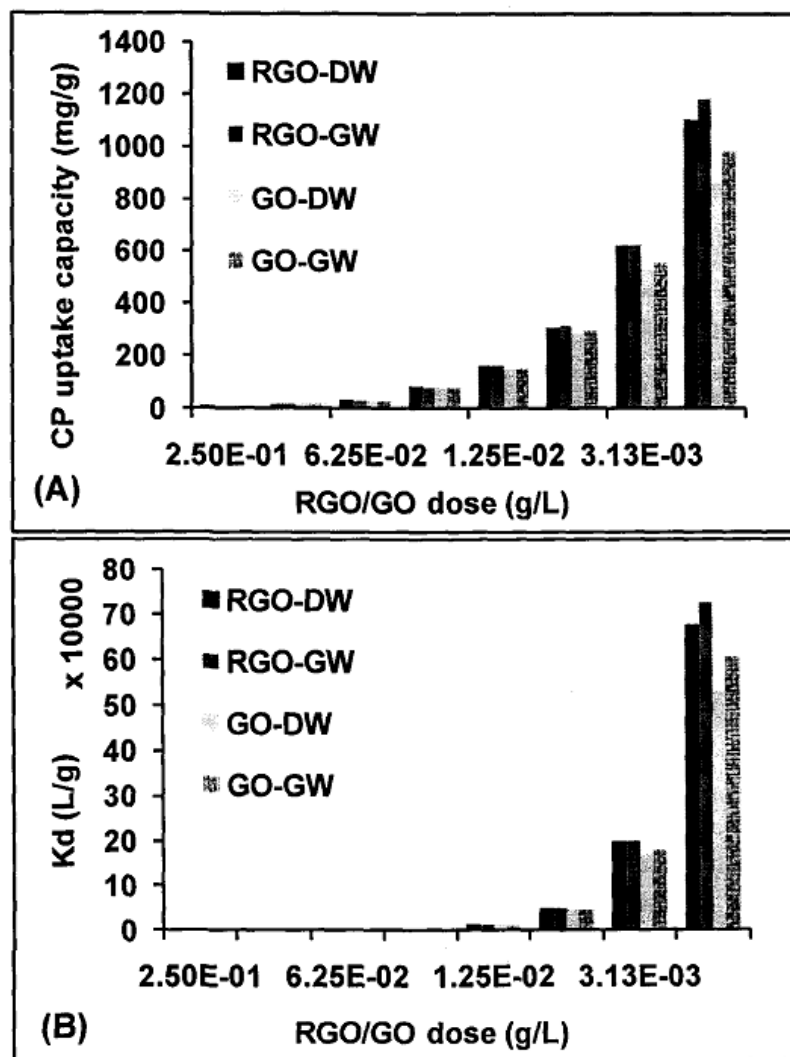


Figure 3

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Advocate & Patent Agent
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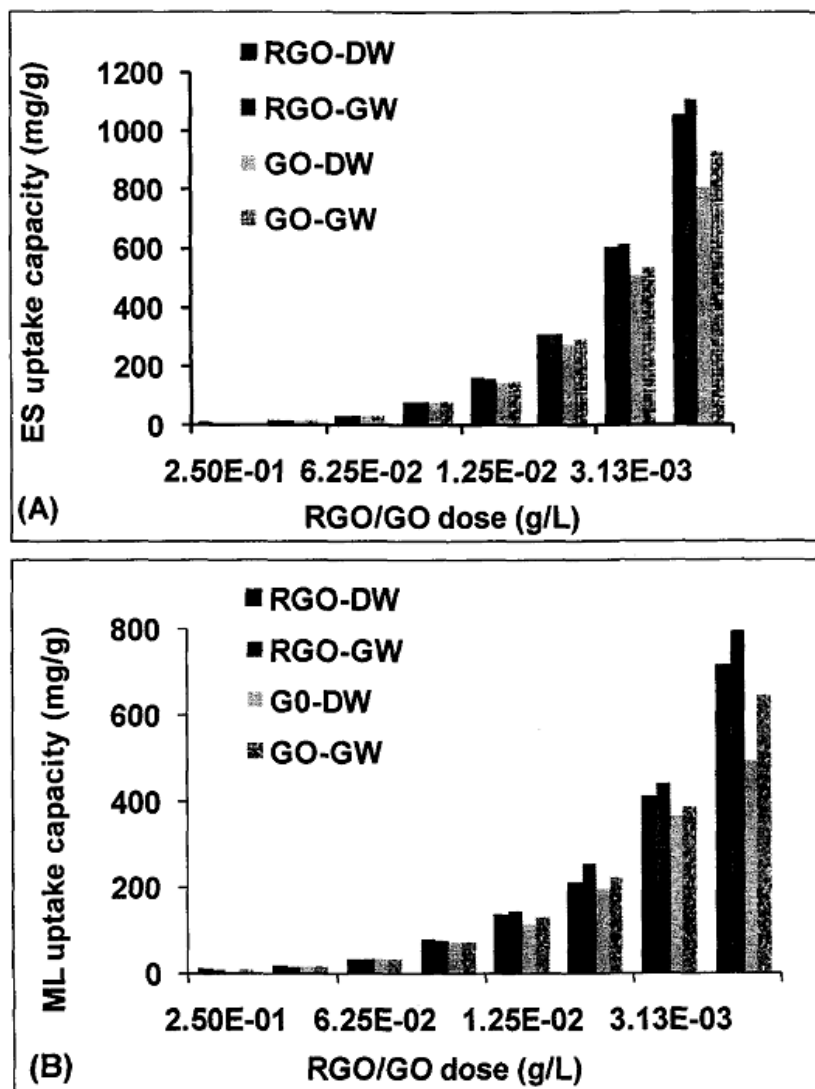


Figure 4

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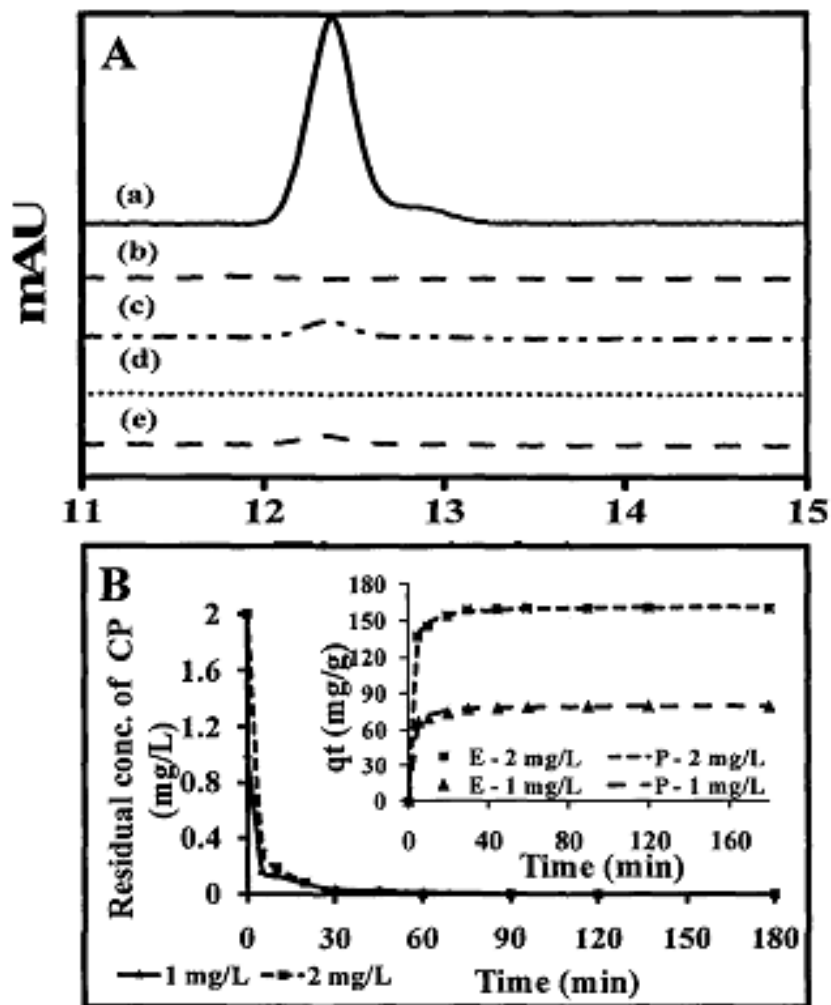


FIGURE 5

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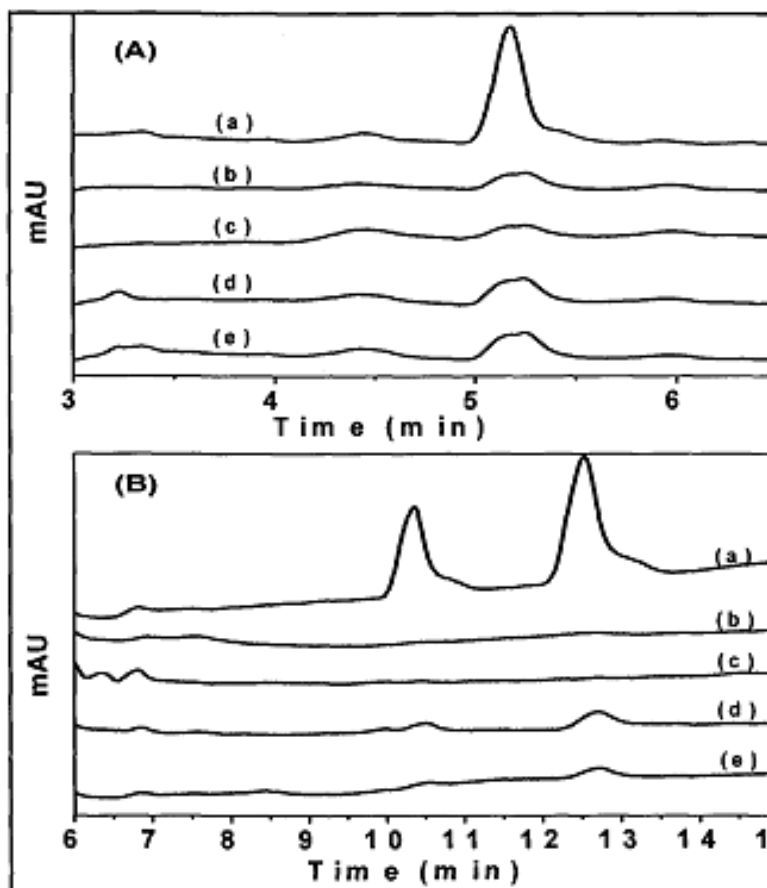


Figure 6

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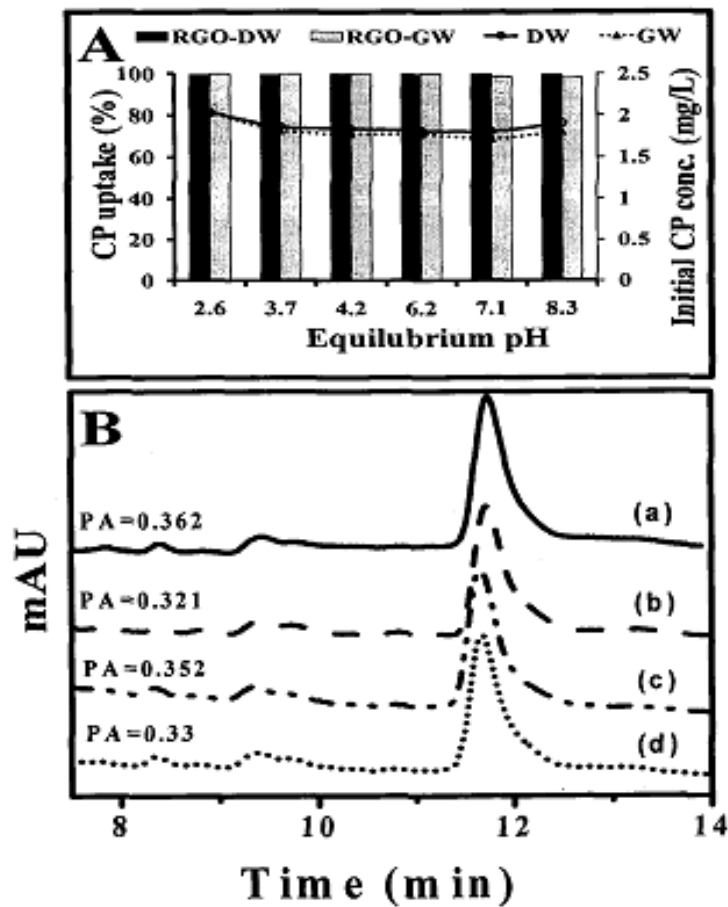


Figure 7

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D. Moses Jeyakaran
Advocate & Patent Agent
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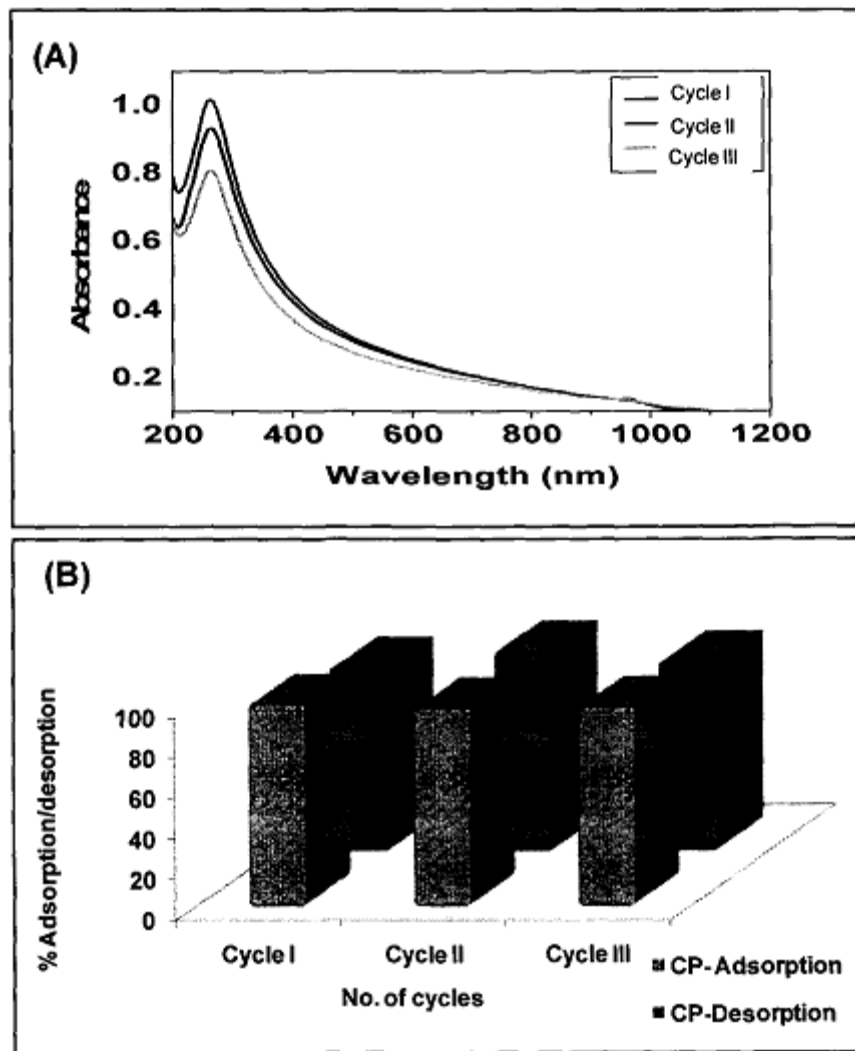


Figure 8

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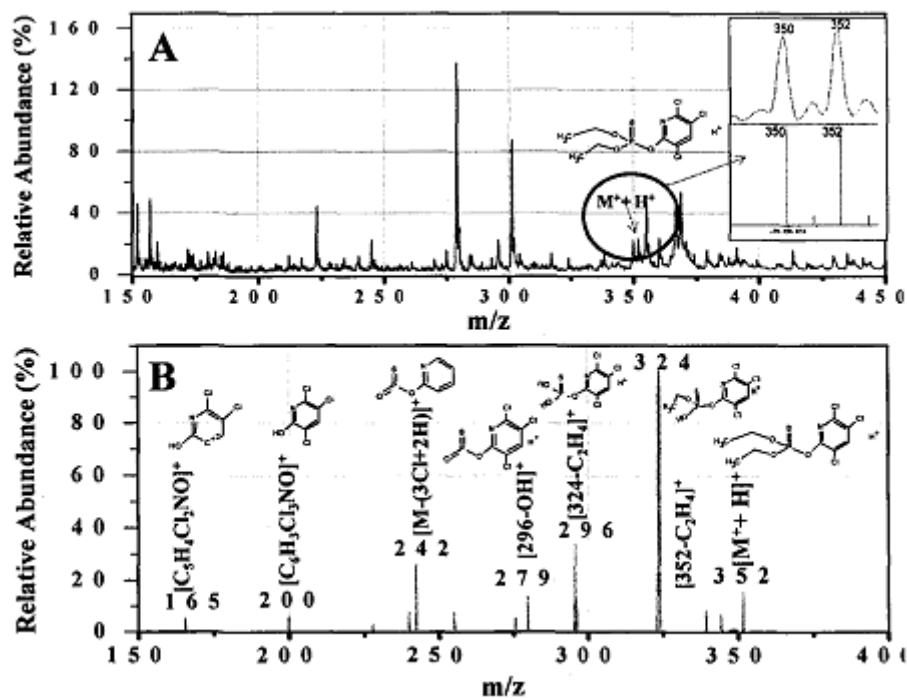


Figure 9

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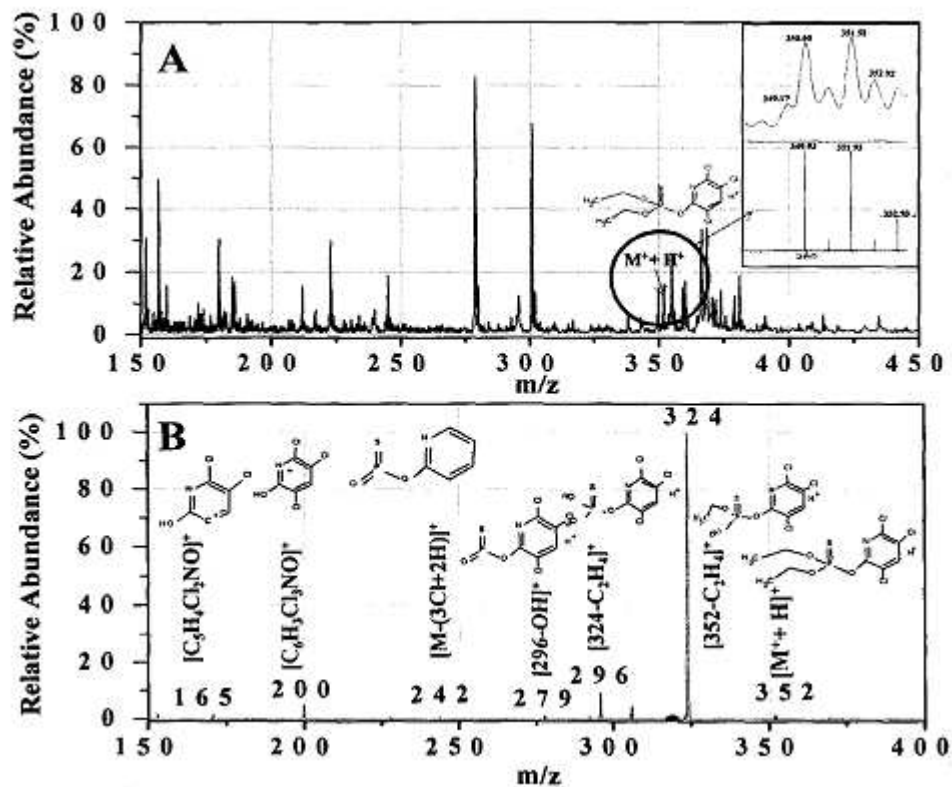


FIGURE 10

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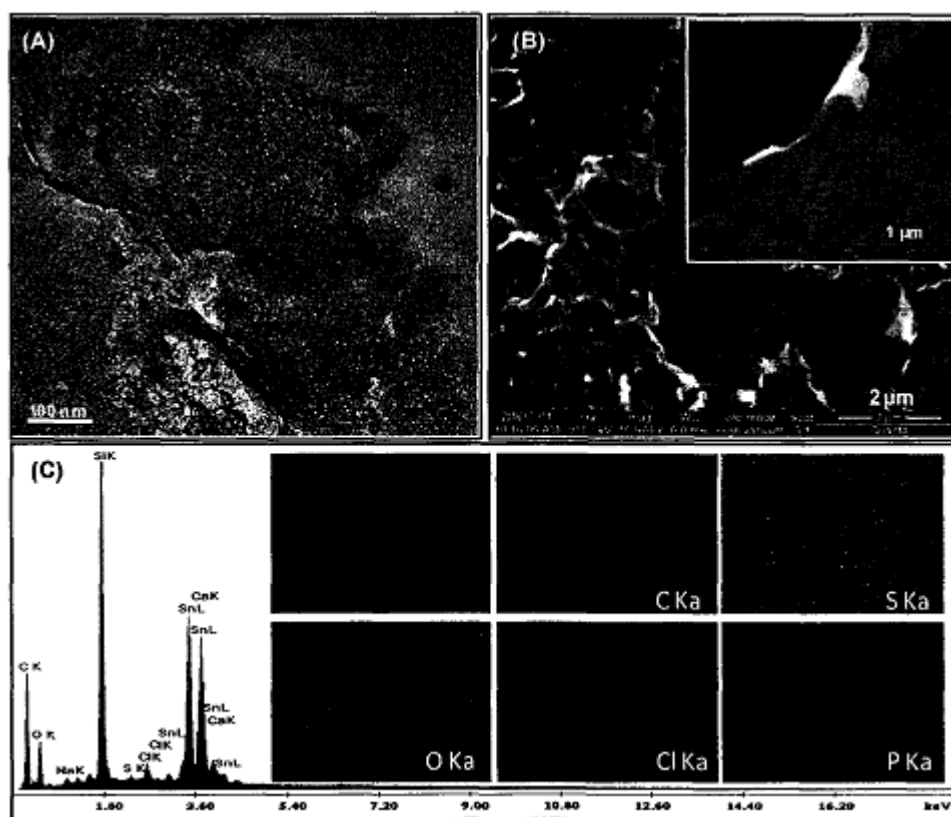


Figure 11

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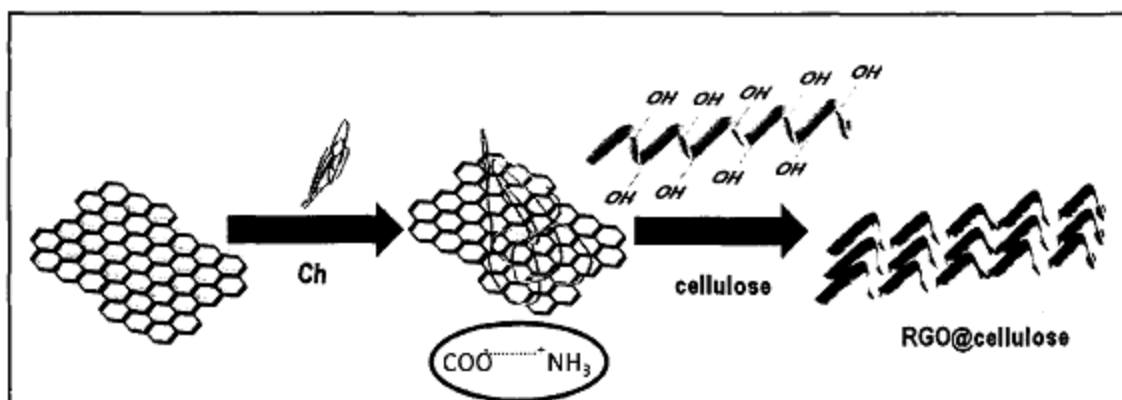
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Figure 12

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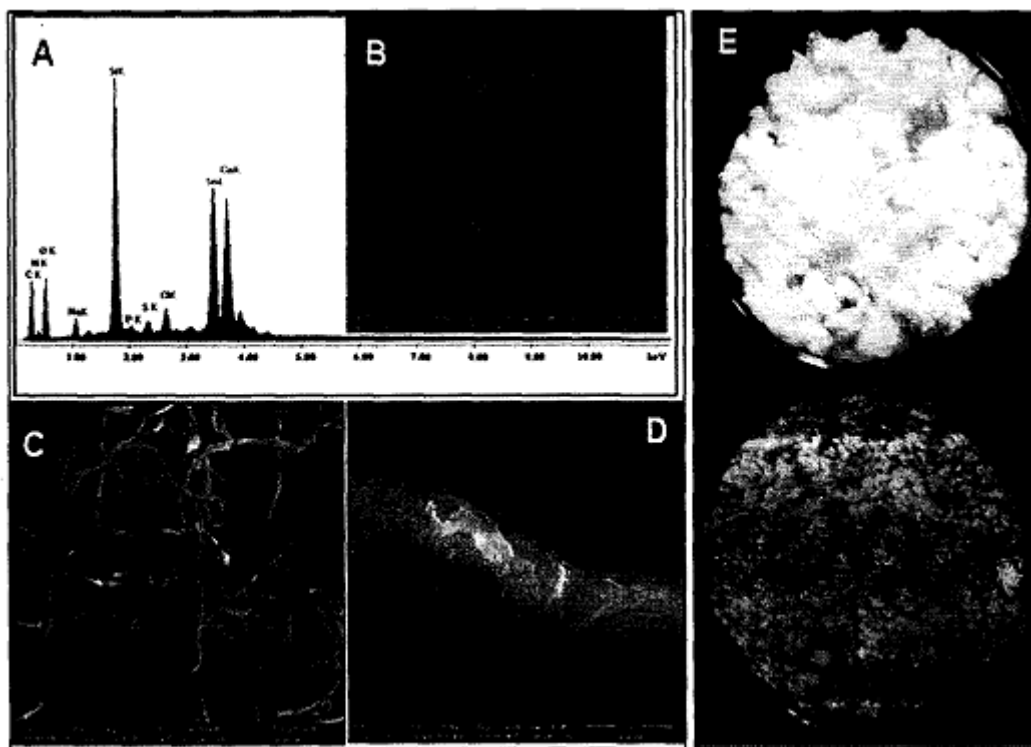


Figure 13

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Advocate & Patent Agent
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