

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 August 2005 (04.08.2005)

PCT

(10) International Publication Number
WO 2005/070534 A1

- (51) International Patent Classification⁷: **B01J 20/08**, 20/04, B01D 15/00, C02F 1/28
- (21) International Application Number: PCT/IN2005/000022
- (22) International Filing Date: 19 January 2005 (19.01.2005)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 51/CHE/2004 22 January 2004 (22.01.2004) IN
- (71) Applicants (for all designated States except US): **INDIAN INSTITUTE OF TECHNOLOGY** [IN/IN]; IIT P.O., Chennai 600 036, Tamil Nadu (IN). **AQUAMALL WATER SOLUTIONS LIMITED** [IN/IN]; No. 7-2-1851/1, Fatehbaugh, Sanathnagar, Hyderabad 500 018, Andhra Pradesh (IN).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **SREEKUMARAN NAIR, Appukuttan, Nair** [IN/IN]; Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Chennai 600 036 (IN). **PRADEEP, Thalappil** [IN/IN]; Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Chennai 600 036 (IN).
- (74) Agents: **NAIR, R., R.** et al.; DePenning & DePenning, 31 South Bank Road, Chennai 600 028, Tamil Nadu (IN).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ADSORBENT COMPOSITION, A DEVICE AND A METHOD FOR DECONTAMINATING WATER CONTAINING PESTICIDES

(57) Abstract: This invention relates to novel adsorbent compositions for adsorbing pesticides like chlorpyrifos and malathion. This composition consists of nanoparticles of gold/silver supported on activated alumina or magnesia in powder or other forms. This invention includes a device and a method for decontaminating water contaminated with pesticides. This device consists of a housing provided with an inlet and an outlet. The housing is loaded with nanoparticles of gold/silver supported on activated magnesia. Contaminated water is allowed to pass through the housing while pesticides are adsorbed by the composition. Decontaminated water flows out through the outlet.

WO 2005/070534 A1

5 **Adsorbent composition, a device and a method for decontaminating**
 water containing pesticides

TECHNICAL FIELD OF THE INVENTION:

Majority of water bodies in the developed and developing countries are contaminated with organo-halogen and organo-sulphur pesticides as a result of their wide spread use in agriculture. Clean-up of such contaminated water bodies impose colossal financial burden on governmental and non-governmental organizations. Most developing countries do not have an effective system for removing pesticides from water. As a result pesticide-free drinking water is still a distant dream for most of the countries. A cheap and widely acceptable technology for removing pesticides from water for the production of safe drinking water has been a long-felt need in both the developed and developing countries. Our invention relates to adsorbent compositions consisting of nanoparticles of silver and gold supported on activated alumina, magnesia and other suitable substrates, which are found effective in removing most common pesticides like chlorpyrifos and malathion chemically known as 0,0-Diethyl-O-(3,5,6-trichloro-2-pyridyl phosphonothioate and S-1,2-bis(ethoxycarbonyl)ethyl 0,0-dimethyl phosphorodithioate, respectively from flowing and static water. The method is also applicable for the removal of other chlorine and sulphur containing pesticides from water in addition to those mentioned above. This invention also relates to a device particularly attachable to on-line supply of drinking water and a method for decontaminating water containing pesticides.

5 **BACKGROUND OF THE INVENTION:**

Pesticide removal from drinking water is a vital issue that concerns many in both the developed and developing countries. Attempts have been made to degrade and remove a wide variety of halocarbon pollutants with bare metal nanoparticles of silver and gold. Metal halides and amorphous carbon are the products of such degradation. These bare metal nanoparticles are also found to be useful in detecting and extracting endosulfan, yet another widely used pesticide. Further, nanoscale iron particles and palladized iron nanoparticles are used to degrade a wide variety of halogenated organic pollutants. Nanoscale iron particles are also used in degrading two most common pesticides in water, namely DDT and lindane. TiO₂ nanoparticles have also been used to degrade harmful agrochemicals.

Activated carbon powder and carbon block have also been used to remove sediments and pesticides from water.

20 **OBJECTS OF THE INVENTION:**

Ability of bare metal nanoparticles of silver and gold to bind to organic molecules containing chlorine and sulphur has been further exploited to develop commercially viable, cost effective and long lasting adsorbent compositions to remove harmful pesticides like chlorpyrifos, malathion and other organo halogen/sulphur pesticides from flowing and static water. This effort led to the production of silver and gold nanoparticles having sizes up to 150 nm supported on activated alumina and/or magnesia or a combination of these materials with activated carbon. Studies have shown that pesticide removal from contaminated

5 water with the help of these adsorbent compositions meet a long-standing requirement.

This invention relates to adsorbent compositions containing silver or gold nanoparticles having sizes up to 150 nm, deposited on activated alumina and/or magnesia or a combination of these materials with
10 activated carbon.

This invention also includes a device for decontaminating water contaminated with chlorpyrifos and malathion or other organo halogen/sulphur pesticides, which comprises a housing loaded with gold/silver nanoparticles supported on activated alumina and/or
15 magnesia or a combination of these materials with activated carbon, the said housing provided with an inlet connectable to the water supply source, and an outlet for the decontaminated water, with the said outlet being provided with regulating means. This invention also relates to a method for decontaminating water comprising the steps of allowing
20 contaminated water to flow through a bed of silver/gold nanoparticles supported on activated alumina and/or magnesia or a combination of these materials with activated carbon to adsorb pesticides like chloropyrifos, malathion or other organo halogen/sulphur pesticides and collecting decontaminated water flowing out of the bed.

25 This invention also includes a process for preparing the novel adsorbent compositions having silver/gold nanoparticles deposited on activated alumina and/or magnesia or a combination of these materials with activated carbon. The said nanoparticles can be supported on any suitable substrate for the intended purpose.

5 **BRIEF DESCRIPTION OF THE INVENTION:**

Raw materials required for the present invention are AgNO_3 , $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, trisodium citrate, activated alumina, activated magnesia, activated carbon and triply distilled water. Gold and silver nanoparticles are synthesized by known methods. In a preferred embodiment, 25 mL
10 (1 mL in the case of gold) of 0.005 M silver nitrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in the case of gold) in water was diluted to 125 mL for Ag (19 mL for Au) and heated until it begins to boil. 5 mL of 1% sodium citrate solution (1mL of 0.5% for Au) was added and heating continued till the colour of the solution turned to pale yellow for silver (wine red for Au). The silver
15 and gold nanoparticles synthesized by the method have sizes up to 150 nm. The synthesized colloidal nanoparticles will be described as Ag@citrate or Au@citrate in the subsequent discussions. Bare nanoparticles of silver and gold synthesized in aqueous medium by alternative methods like sodium borohydride reduction can also be used.

20 The next step in the process involves incorporation of these nanoparticles on activated alumina or activated magnesia.

To one litre of the above Ag@citrate or Au@citrate, half a Kg of activated alumina or activated magnesia globules were soaked and kept with intermittent stirring for a minimum period of 6 hours to ensure
25 saturable adsorption of nanoparticles. The saturable adsorption on nanoparticles' surface was ensured by measuring absorbance of the solution at periodic intervals. No decrease in absorbance of the solution was observed after the period thus indicating that saturable adsorption has taken place on the oxide surface. More nanoparticle solutions were
30 added and stirring continued if saturation did not occur. Intake of

5 nanoparticles per alumina globule is high, about 0.116 mg per globule on an average. After completion of deposition, the globules were washed with distilled water repeatedly and air-dried. In a modification of the procedure, nanoparticles may be loaded on to activated alumina powder (neutral) in which case the intake of nanoparticle is very high.
10 250 g of activated alumina powder can load the nanoparticles in 6 L of the above solutions. These compositions may be described as $\text{Al}_2\text{O}_3 @ \text{Au}$ or $\text{Al}_2\text{O}_3 @ \text{Ag}$. In yet another modification of the procedure, the above nanoparticles (adsorbed on activated alumina) are baked with activated carbon at 120°C . Activated magnesia powder or magnesia
15 globules can be used in place of alumina.

BRIEF DESCRIPTION WITH REFERENCE TO THE DRAWINGS:

The device used by the inventors is a column. It consists of a housing having an inlet and an outlet. The inlet is connectable on-line to
20 a water supply source. The housing is filled with either $\text{Al}_2\text{O}_3 @ \text{Au}$ (powder or globule) or $\text{Al}_2\text{O}_3 @ \text{Ag}$ (powder or globule) or combination of them with activated carbon adsorbent composition. There is a sealant provided at the base of the housing and a regulating means for regulating flow of water through the outlet.

25 In a preferred embodiment, 250 g of activated alumina powder saturated with nanoparticles was filled in the column. In a modification of the embodiment, activated alumina globules saturated with nanoparticles or a combination of with them with activated carbon was also used. 10 L of 50 ppb chlorpyrifos or malathion solution in water
30 was made and used for the experiments. 1 L of the above water solution

5 was taken as blank and chlorpyrifos in it was extracted thrice with 150
mL n-hexane. This was then concentrated to 2 mL in a rotavapour and
made up to 10 mL in a standard flask using n-hexane. The amount of
chlorpyrifos in it was quantitated using UV-visible spectroscopy and gas
chromatography. The remaining pesticide containing water solution was
10 passed continuously through the column containing the adsorbent
composition and each 1L of the outgoing solution was collected, and the
pesticide content in it was extracted as above with n-hexane and
analyzed by UV-visible spectroscopy and gas chromatography.
Experiments were conducted with ppm level concentration of
15 chlorpyrifos and malathion in water.

The same device was tested for over three months and with little
or no reduction in the efficiency in pesticide removal.

DETAILS OF STUDY ARE SHOWN IN THE FIGURES
20 **ACCOMPANIED HEREWITH IN WHICH:**

Fig. 1 shows graphical representation of pesticide adsorption on the
nanoparticles' surface in solution state in a time dependent manner.

25 Fig. 2 shows graphical representation of removal of 1 ppm chlorpyrifos
from water using silver nanoparticles supported on alumina.

Fig. 3 shows graphical representation of removal of 1 ppm malathion
from water using silver nanoparticles supported on alumina.

Fig. 4 shows graphical representation of removal of 1 ppm malathion
from water using gold nanoparticles supported on alumina.

5 Figs. 5 and 6 shows graphical representation of gas chromatogram indicating the complete removal of chlorpyrifos from water using supported nanoparticles of silver.

Figs. 7 and 8 shows graphical representation of infrared spectra indicating pesticide adsorption on nanoparticles' surface.

10

Figure 1 refers to the time dependent UV-visible spectra showing the adsorption of chlorpyrifos on Au nanoparticles. Trace a is the absorption spectrum of 2 mL of Au@citrate (as prepared above, after diluting with equal volume of water) showing the absorption maximum at 522 nm. Trace b was taken 20 minutes after the mixing of 2mL of 2 ppm chlorpyrifos (in water) with it. After 40 minutes, the plasmon excitation absorption at 522 nm decreases in intensity and another broad absorption feature emerges at longer wavelength (trace c). At this stage the solution turns pale blue in color. This can be attributed to the adsorption of chlorpyrifos on Au nanoparticles' surface and their subsequent aggregation. With further passage of time, the plasmon absorption at 522 nm decreases in intensity and that at longer wavelength gains in intensity accompanied by further red shift. This is due to the time dependent adsorption of chlorpyrifos on the nanoparticles' surfaces. Subsequent traces were recorded at 20 minutes intervals thereafter. After 4 hours (trace cc), the completely blue particles begin to precipitate due to aggregation.

Figure 2 refers to the time dependent UV visible spectra showing the adsorption of 1 ppm chlorpyrifos on Al₂O₃ @ Ag. Trace a is the absorption spectrum of 1 ppm chlorpyrifos and b is the absorption spectrum of the solution, 20 minutes after soaking the supported

5 nanoparticles in the pesticide solution. The subsequent traces (c-r) were taken at 20 minutes intervals thereafter. Small increase in background and a minor hump are also visible in the traces (c-r), possibly due to the formation of small quantities of Ag^+ in solution. Trace s was taken after 10 hours showing the complete disappearance of chlorpyrifos from
10 water. The inset shows decrease in absorbance vs. time from the absorption spectroscopy data for the traces (a-s). The dotted line in the inset shows a fit of the exponential decrease in absorbance with time.

Figure 3 refers to the time dependent UV-visible spectra showing
15 the adsorption of 1 ppm malathion on $\text{Al}_2\text{O}_3 @ \text{Ag}$. Trace a is the absorption spectrum of 1 ppm malathion having an absorption maximum at 267 nm and b is that of the solution taken 20 minutes after soaking the supported nanoparticles in the pesticide solution. The subsequent traces (c-p) were taken at 20 minutes intervals thereafter.
20 Trace q was taken after 10 hours showing the complete disappearance of malathion from water. The inset shows the decrease in adsorbance vs. time for the reaction for the traces (a-q). The dotted line in the inset shows a fit of the exponential decrease in absorbance with time.

25 Figure 4 refers to the time dependent UV-visible spectra of the reaction between 2.5 ppm malathion and $\text{Al}_2\text{O}_3 @ \text{Au}$. Trace a is the absorption spectrum of 2.5 ppm malathion. Trace b was taken 20 minutes after soaking the globules into the pesticide solution. Subsequent traces (c-p) were recorded at 20 minutes intervals. The
30 gradual decrease in the absorbance of solution is due to the adsorption of

- 5 malathion on the nanoparticles' surface. Trace q was taken after 10 hours showing the complete disappearance of malathion from water.

Figure 5 shows the gas chromatogram of 1 L of the 50-ppb chlorpyrifos solution extracted thrice with 150 mL of hexane, evaporated to nearly 2 mL in rotavapor and made up to 10 mL using hexane. The peak at 2.933 min is that of chlorpyrifos (labeled CP) and that at 2.14 min is that of the solvent. Figure 6 is the chromatogram of the chlorpyrifos solution (same concentration as above) after passing through the column loaded with $\text{Al}_2\text{O}_3@\text{Ag}$, extracted with hexane and made up to 10 mL as above. The absence of the peak at 2.993 min in Figure 6 implies the complete removal of chlorpyrifos from water. The sensitivity of the detection for chlorpyrifos was estimated to be 1 ppb.

Figure 7 refers to the IR spectra of pure pesticides and those adsorbed on the nanoparticles' surface. In Figure 7, trace a is the IR spectrum of chlorpyrifos and b, is that adsorbed on Ag nanoparticles' surface. A careful comparison of the two spectra reveals that all IR features of chlorpyrifos are seen in trace b too, with reduced intensities accompanied by broadening and shifting due to changes in the symmetry as a result of binding on the nanoparticles' surface. Similarly Figure 8 shows the IR spectra of pure malathion (a) and that adsorbed on the Ag nanoparticles' surface (b). The shift and broadening of the infrared features of the pesticide due to adsorption on the nanoparticles' surface are clearly visible from the traces. The additional peaks observed in the b traces of Figure 7 and Figure 8 are due to the citrate impurity.

5 CLAIMS:

1. Adsorbent compositions for removing pesticides like chlorpyrifos, malathion and other organo halogen/sulphur pesticides comprising gold/silver nanoparticles having a size upto
10 150 nm deposited on activated alumina and/or magnesia.
2. Adsorbent compositions as claimed in claim 1, which is prepared by loading silver and gold nanoparticles on activated alumina and/or magnesia.
15
3. Adsorbent compositions as claimed in claim 2, wherein said activated alumina or other substrates are in the various forms such as globules and powder.
- 20 4. Adsorbent compositions as claimed in claim 2, wherein the silver and gold nanoparticles are used along with activated carbon in all compositions.
- 25 5. A device for decontaminating water contaminated with pesticides like chlorpyrifos, malathion or other organo halogen/sulphur pesticides which comprises a housing loaded with gold/silver nanoparticles having a size upto 150 nm supported on activated alumina and/or magnesia, said housing provided with an inlet connectable to water supply source and an outlet for
30 decontaminated water, said outlet being provided with regulatory means.

- 5 6. A method of decontaminating water by removing pesticides such
as chlorpyrifos, malathion or other organo halogen/sulphur
pesticides comprising the step of allowing contaminated water to
flow through a bed of gold/silver nanoparticles having a size upto
150 nm supported on activated alumina and/or magnesia to
10 adsorb said pesticides and collecting decontaminated water
flowing out of said bed.

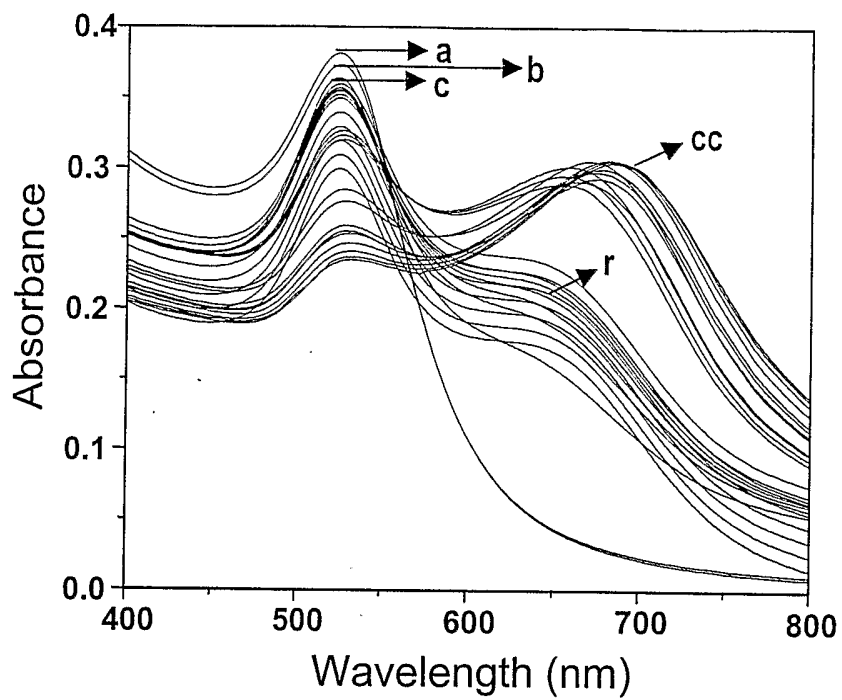


FIGURE 1

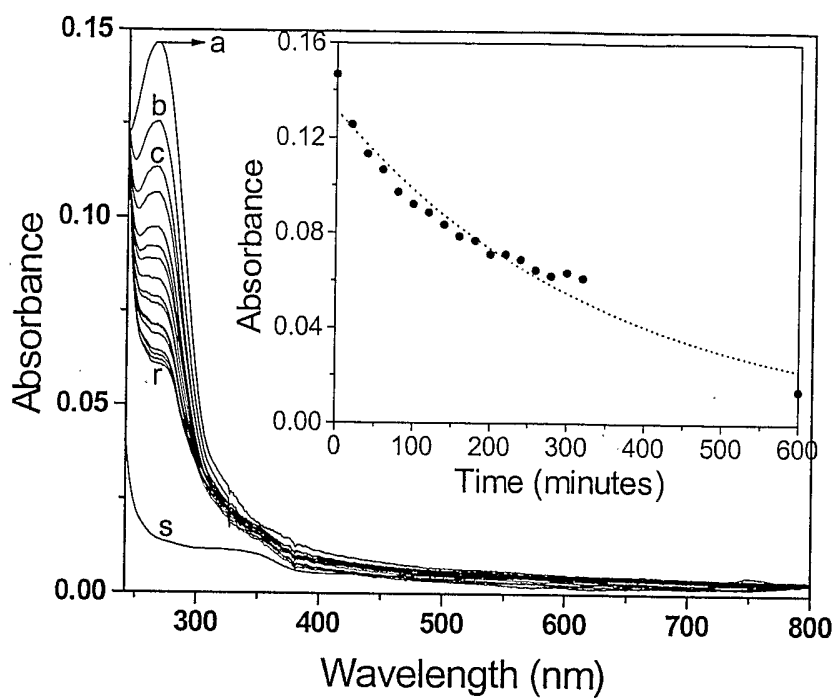


FIGURE 2

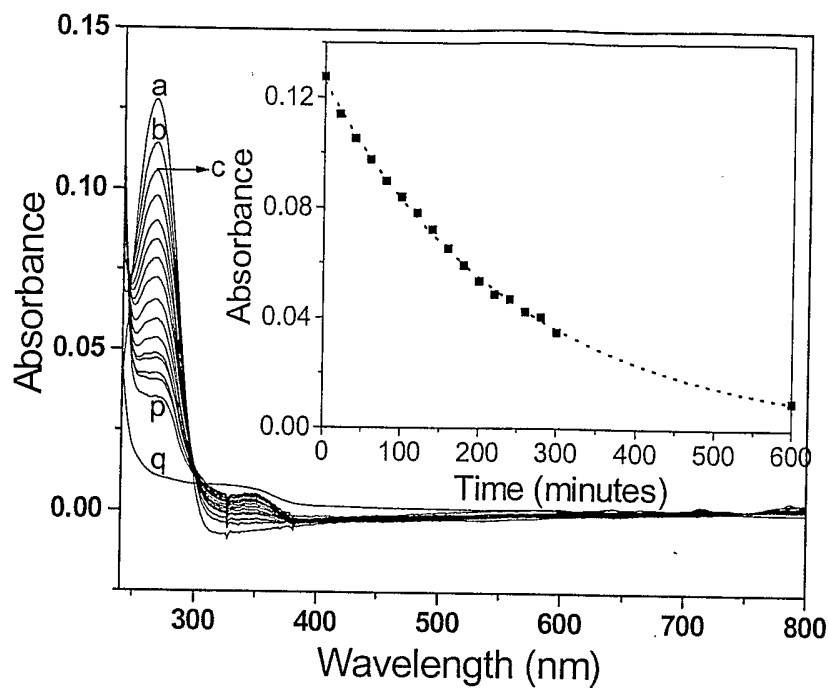


FIGURE 3

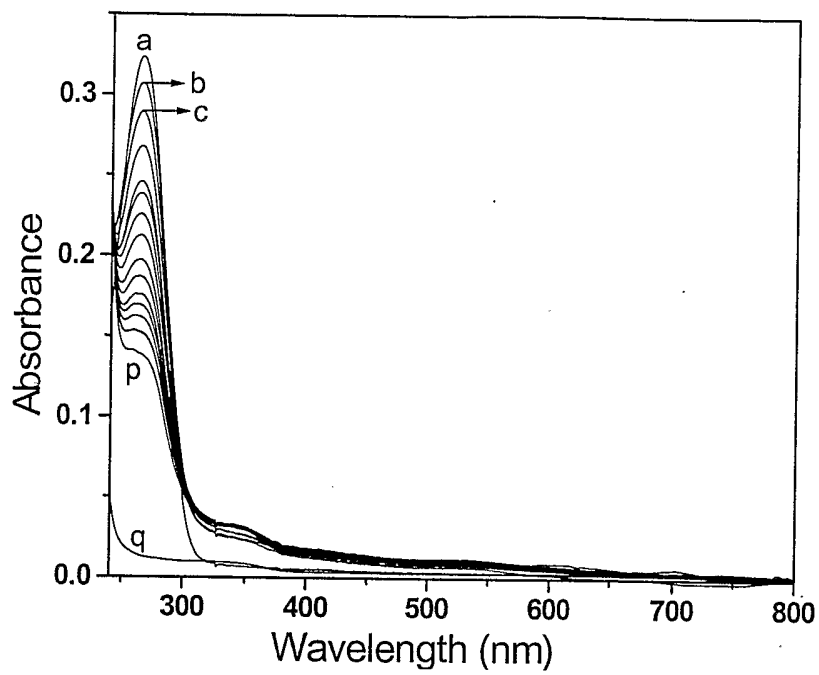


FIGURE 4

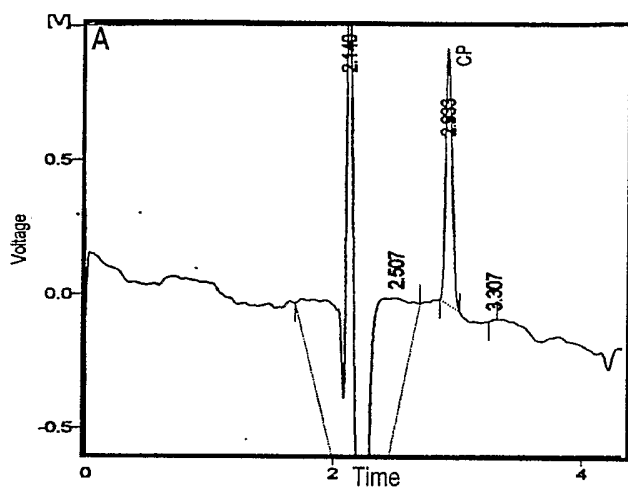


FIGURE 5

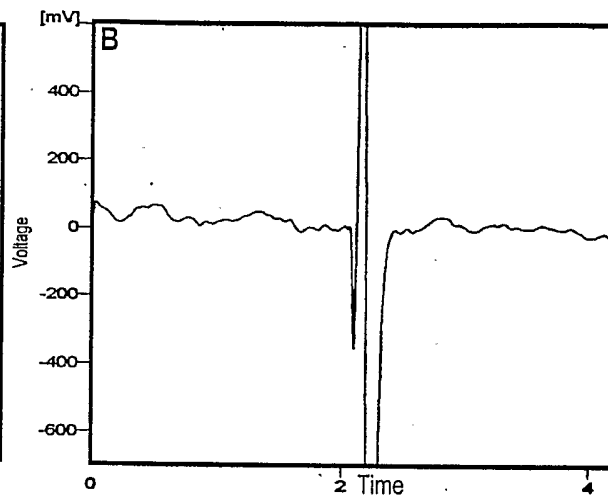


FIGURE 6

FIGURE 7

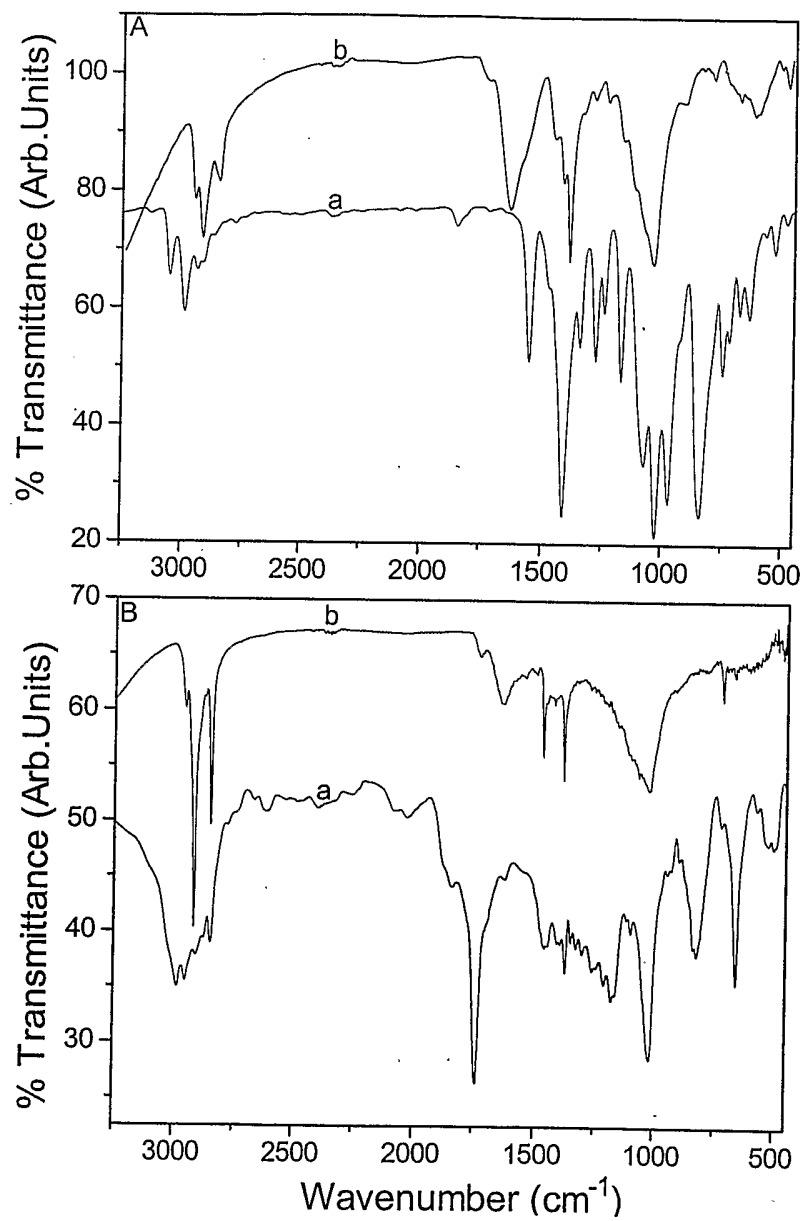


FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN 2005/00022

A. CLASSIFICATION OF SUBJECT MATTER IPC ⁷ : B01J 20/08, B01J 20/04, B01D 15/00, C02F 1/28 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC ⁷ : B01D, B01J, C02F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched -		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPOCOC, WPI, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 2221031 A (GOTTFRIED REUTER GmbH) 15 November 1973 (15.11.1973) <i>claims 1-5&7; page 4, line 27 - page 5, line 6; examples.</i>	1-3,5,6
Y	--	4
Y	WO 2004/056709 A1 (KAZENOV A. et al.) 8 July 2004 (08.07.2004) (abstract) World Patent Index [online]. London, U.K.: Derwent Publication, Ltd. [retrieved on 2005-03-09]. Retrieved from Questel/Orbit, France. DW 0447, Accession No. 04-500276 [47].	4
	--	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 9 March 2005 (09.03.2005)		Date of mailing of the international search report 4 April 2005 (04.04.2005)
Name and mailing address of the ISA/ AT Austrian Patent Office Dresdner Straße 87, A-1200 Vienna Facsimile No. +43 / 1 / 534 24 / 535		Authorized officer PUSTERER F. Telephone No. +43 / 1 / 534 24 / 311

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN 2005/000022

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5360547 A (COCKETT et al.) 1 November 1994 (01.11.1994) <i>claims 1,14&15; column 4, line 64.</i>	1-6
	--	
A	US 5256300 A (COCKETT et al.) 26 October 1993 (26.10.1993) <i>claims 1&2; column 2, lines 49-52.</i>	1-6
	--	
A	WO 1999/065826 A1 (ORIDIO AB) 23 December 1999 (23.12.1999) <i>claim 1.</i>	1-6
	--	
A	WO 2002/083297 A1 (IMS LLC) 24 October 2002 (24.10.2002) <i>claims 1,2,11,19,20&31.</i>	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/IN 2005/000022

Patent document cited in search report			Publication date	Patent family member(s)		Publication date	
DE	A1	2221031	1973-11-15	none			
US	A	5256300	1993-10-26	ZA	A	9208529	1994-05-05
				JP	A	6007672	1994-01-18
				AU	A	2818492	1993-05-06
				EP	A1	0541358	1993-05-12
				BR	A	9204276	1993-05-11
US	A	5360547	1994-11-01	JP	A	7284657	1995-10-31
				ZA	A	9302169	1994-09-26
				BR	A	9301336	1993-10-05
				AU	A	3549693	1993-10-07
				ES	T3	2112964T	1998-04-16
WO	A	19990658 26		none			
WO	A	20020832 97		none			
WO	A1	20040567 09	2004-07-08	none			