



(11) **EP 1 715 947 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
22.08.2012 Bulletin 2012/34

(51) Int Cl.:
B01J 20/08^(2006.01) B01J 20/04^(2006.01)
B01D 15/00^(2006.01) C02F 1/28^(2006.01)

(21) Application number: **05703247.6**

(86) International application number:
PCT/IN2005/000022

(22) Date of filing: **19.01.2005**

(87) International publication number:
WO 2005/070534 (04.08.2005 Gazette 2005/31)

(54) **A METHOD FOR DECONTAMINATING WATER CONTAINING PESTICIDES**

VERFAHREN ZUR DEKONTAMINIERUNG VON PESTIZIDHALTIGEN WASSER

PROCÉDÉ DE DÉCONTAMINATION DES EAUX RENFERMANT DES PESTICIDES

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR

(30) Priority: **22.01.2004 IN CH00512004**

(43) Date of publication of application:
02.11.2006 Bulletin 2006/44

(73) Proprietors:
• **Indian Institute of Technology Tamil Nadu (IN)**
• **Aquamall Water Solutions Hyderabad 500 018, Andhra Pradesh (IN)**

(72) Inventors:
• **SREEKUMARAN NAIR, Appukuttan Nair Chennai 600 036 (IN)**
• **PRADEEP, Thalappil Chennai 600 036 (IN)**

(74) Representative: **Jansen, Cornelis Marinus et al Vereenigde Johan de Wittlaan 7 2517 JR Den Haag (NL)**

(56) References cited:
WO-A1-99/65826 WO-A1-02/083297
WO-A1-2004/056709 DE-A1- 2 221 031
US-A- 5 256 300 US-A- 5 360 547

EP 1 715 947 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**TECHNICAL FIELD OF THE INVENTION:**

[0001] 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 the use of adsorbent compositions consisting of nanoparticles of silver and gold supported on activated alumina, magnesia and other suitable substrates, which are found effective in a method for 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 may make use of a device particularly attachable to on-line supply of drinking water and a method for decontaminating water containing pesticides.

BACKGROUND OF THE INVENTION:

[0002] 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.

[0003] Activated carbon powder and carbon block have also been used to remove sediments and pesticides from water.

OBJECTS OF THE INVENTION:

[0004] Ability of bare metal nanoparticles of silver and gold to bind to organic molecules containing chlorine and sulphur has been further exploited to develop commer-

cially 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 water with the help of these adsorbent compositions meet a longstanding requirement.

[0005] This invention relates to a method according to claim 1

[0006] In a method of this invention 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 activated carbon may be used.

[0007] In a method of this invention also a device may be used 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 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. The method for decontaminating water comprises the steps of allowing 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 chlorpyrifos, malathion or other organo halogen/sulphur pesticides and collecting decontaminated water flowing out of the bed.

[0008] 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 is also disclosed herein. The said nanoparticles can be supported on any suitable substrate for the intended purpose.

BRIEF DESCRIPTION OF THE INVENTION:

[0009] Raw materials required for the present invention are AgNO₃, HAuCl₄. 3H₂O, 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 (1 mL in the case of gold) of 0.005 M silver nitrate (HAuCl₄. 3H₂O 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 (1 mL 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 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 nan-

oparticles of silver and gold synthesized in aqueous medium by alternative methods like sodium borohydride reduction can also be used.

[0010] The next step in the process involves incorporation of these nanoparticles on activated alumina or activated magnesia.

[0011] 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 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 added and stirring continued if saturation did not occur. Intake of 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. 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 globules can be used in place of alumina.

BRIEF DESCRIPTION WITH REFERENCE TO THE

DRAWINGS :

[0012] 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 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.

[0013] 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 was made and used for the experiments. 1 L of the above water solution 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 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 chlorpyrifos and malathion in water.

[0014] 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

ACCOMPANIED HEREWITH IN WHICH:

[0015]

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

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.

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.

[0016] 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.

[0017] Figure 2 refers to the time dependent UV visible spectra showing the adsorption of 1 ppm chlorpyrifos on $\text{Al}_2\text{O}_3 @ \text{Ag}$. 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 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 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.

[0018] Figure 3 refers to the time dependent UV-visible spectra showing 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. 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.

[0019] 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 gradual decrease in the absorbance of solution is due to the adsorption of malathion on the nanoparticles' surface. Trace q was taken after 10 hours showing the complete disappearance of malathion from water.

[0020] 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.

[0021] 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 in-

tensities 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.

Claims

1. 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 adsorb said pesticides and collecting decontaminated water flowing out of said bed.

Patentansprüche

1. Verfahren zum Dekontaminieren von Wasser durch Entfernen von Pestiziden wie Chlorpyrifos, Malathion oder anderer Organohalogene/Schwefelpestizide, umfassend den Schritt, der es erlaubt, dass kontaminiertes Wasser durch ein Bett von Gold-/Silber-Nanopartikeln mit einer Größe bis 150 nm fließt, getragen auf aktiviertem Aluminiumoxid und/oder Magnesiumoxid, um die Pestizide zu adsorbieren und das dekontaminierte Wasser, das aus dem Bett fließt, zu sammeln.

Revendications

1. Procédé de décontamination d'eau par élimination de pesticides, tels que chlorpyrifos, malathion ou autres pesticides organo halogénés/soufre, comprenant l'étape consistant à laisser de l'eau contaminée s'écouler à travers un lit de particules d'or/argent ayant une taille jusqu'à 150 nm supportées sur de l'alumine et/ou de l'oxyde de magnésium activé pour adsorber lesdits pesticides et à recueillir l'eau décontaminée s'écoulant à l'extérieur dudit lit.

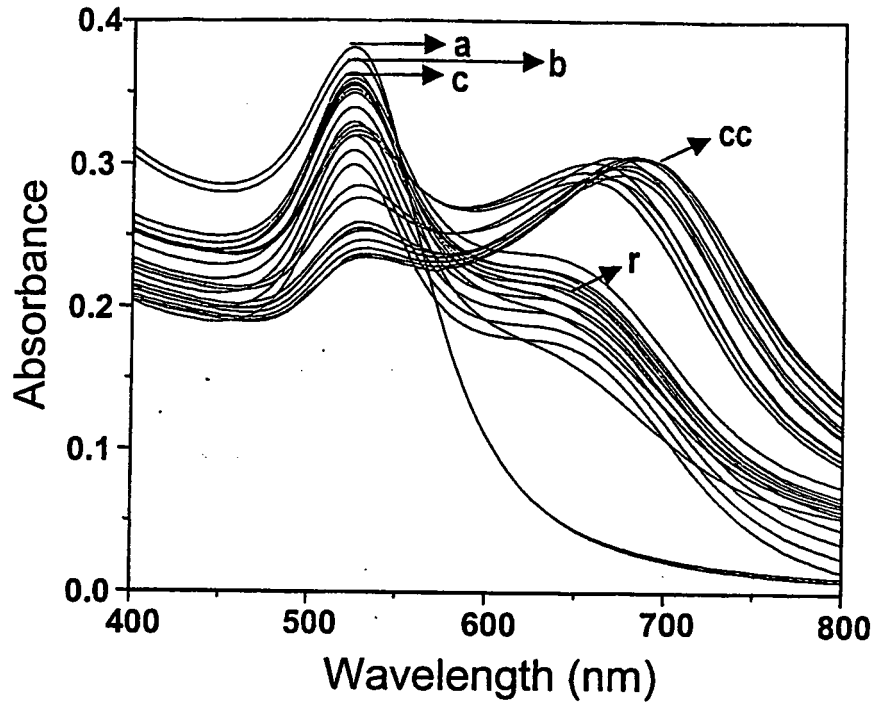


FIGURE 1

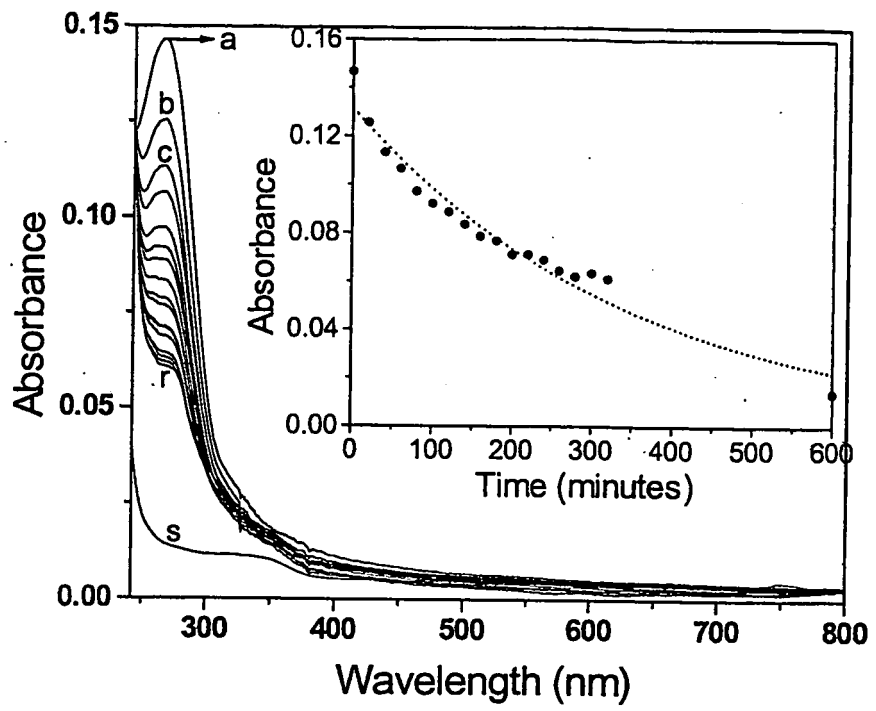


FIGURE 2

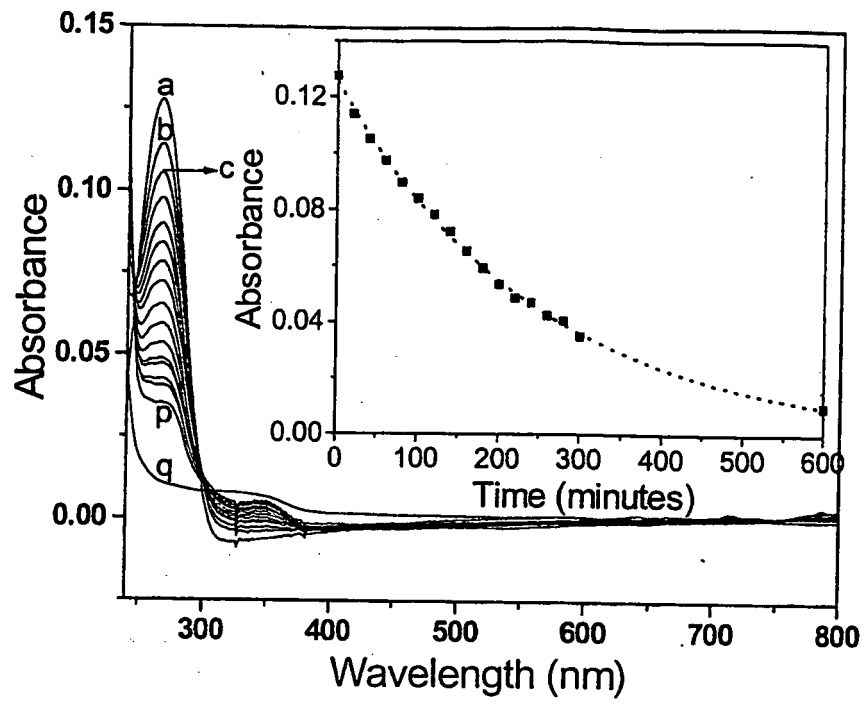


FIGURE 3

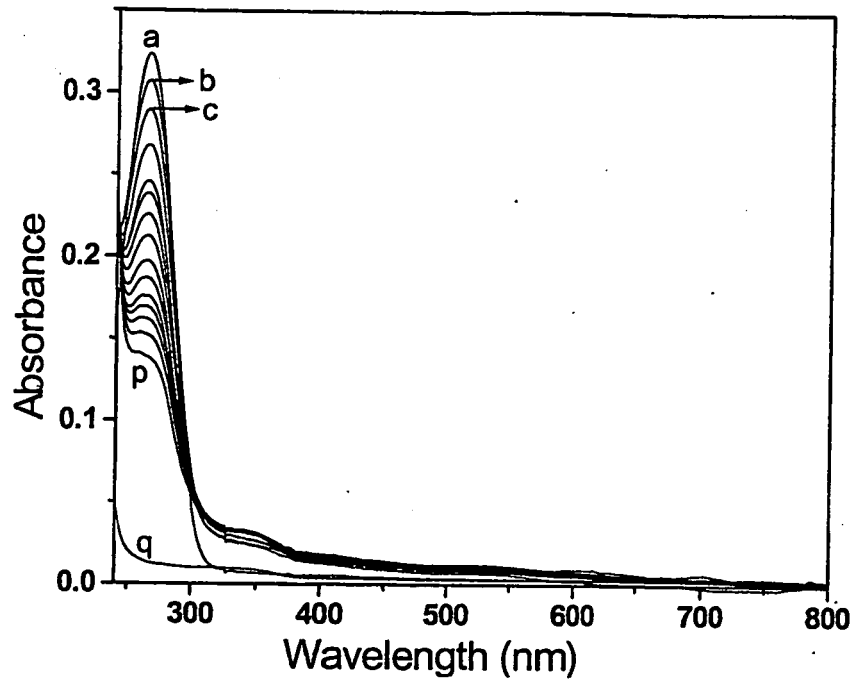


FIGURE 4

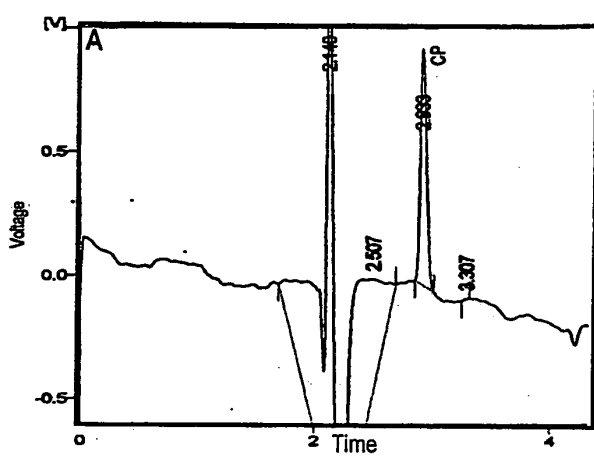


FIGURE 5

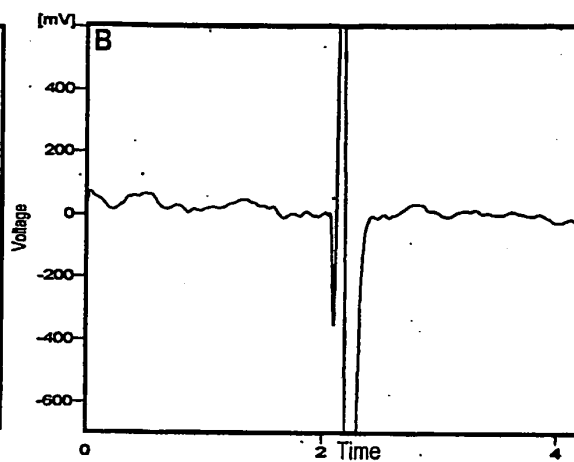


FIGURE 6

FIGURE 7

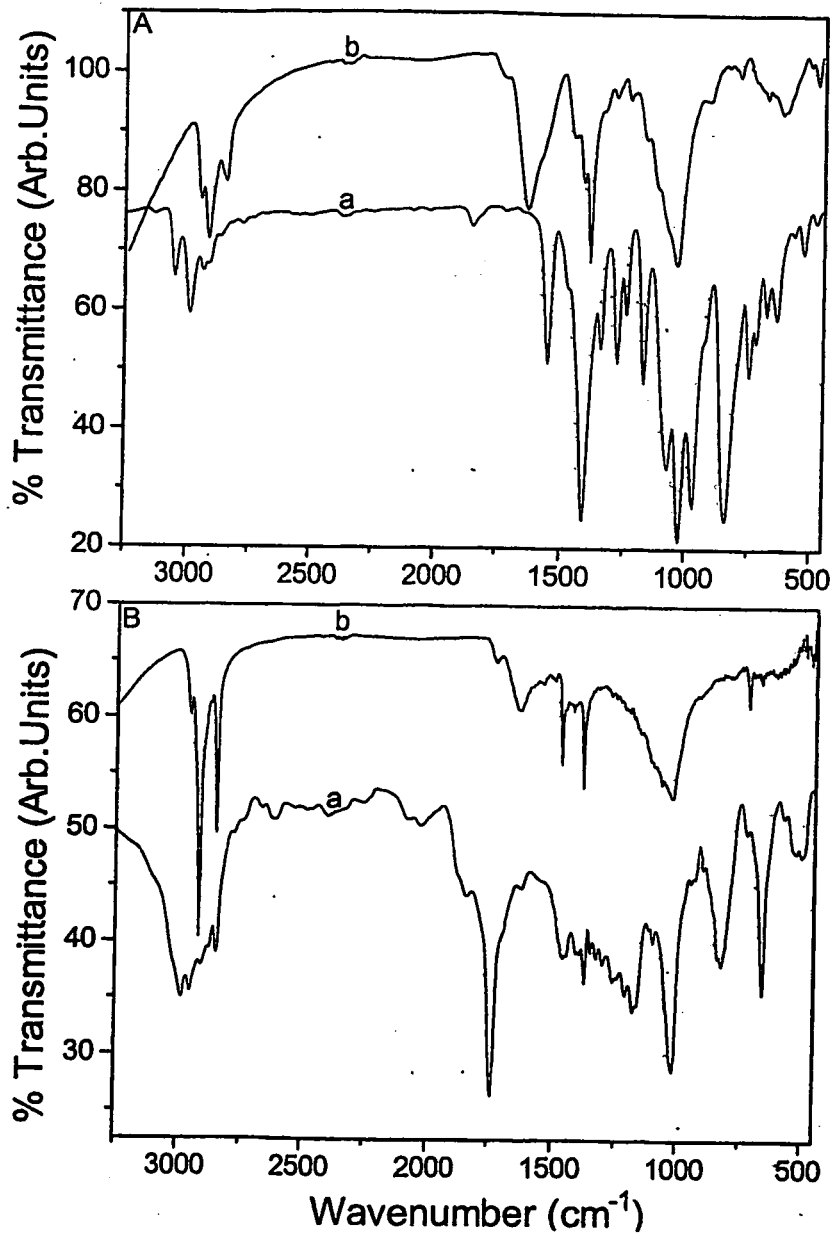


FIGURE 8