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Developing Nanoparticles as Mercury Eliminating Agents

By

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MASTER'S PROJECT

Submitted in partial fulfillment of the requirements

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ABSTRACT

The purpose of this study is to develop a unique Mercury filter system that is capable of removing both microparticulate and water soluble mercury from dental waste water in a dental office. The shavings from new fillings and the removal of old fillings make American dentistry one of the largest sources of mercury pollution in wastewater. EPA estimates that dentists discharge approximately 3.7 tons of mercury each year to POTWs [1]. EPA has stated that there are approximately 160,000 dentists working in over 120,000 dental offices that use or remove amalgam in the United States – almost all of whom discharge their wastewater exclusively to POTWs [1]. Numerous studies have shown that the removal of amalgam particulates using currently available filtration system can only sieve pieces bigger than 700 micrometer in diameter [2]. In addition, there is still a significant amount of mercury located in the dissolved or soluble fraction, and is high enough to violate local POTWs discharge limits [3]. This invention will help in mercury abatement by using gold nanoparticles incorporated in to a solid porous support. Affinity of mercury to gold is well-known since ancient times. Nanomaterials, the product of contemporary science are well-known for their large surface area. The effective removal mercury from dental waste water was achieved by amalgamation of mercury with gold nanoparticles.

INTRODUCTION

Mercury also known as quick silver is a heavy, silvery-white d-block element and is the only metal which is liquid at room temperature. Mercury commonly occurs in nature as sulfides and in a number of minerals. It is released from many natural and anthropogenic activities and is extremely volatile [4]. Mercury is released naturally from rocks and volcanoes, human activities have boosted its levels in the atmosphere. It is poisonous to humans as well as many other living organisms. Mercury is one of the most toxic substances commonly encountered, and according to Government agencies causes adverse health effects in large numbers of people in the U.S [4]. Mercury is used in a variety of industrial processes and commercial products which are eventually released back in to the atmosphere [4]. It is widely used mainly because of its special properties.

- Very dense (13.5 g/cc)
- The only heavy metal that exists as a liquid at room temperature
- Easily vaporizes in to air
- Good conductor of electricity
- Expands and contracts evenly with changes in temperature
- Alloys with other metals to form amalgams

Mercury is considered to be a global contaminant mainly because it is toxic, does not break down in the environment and can build up in living things. In its vapor or gaseous form, mercury can be carried long distances on wind currents, staying in the atmosphere for long periods of time. The health effects of mercury exposure depend on its chemical form (elemental or

inorganic mercury), route of exposure (inhalation or ingestion or skin contact), and level of exposure [4].

Elemental Mercury (Hg^0)

Elemental mercury or Metallic mercury is a heavy, odorless silver colored liquid. Because of its high vapor pressure, it easily evaporates in to air. Mercury vapor has a long half-life of two years. Inhalation is main source of toxicity. Long term exposure to mercury vapor can cause damage to mouth, respiratory tract and lungs, and can lead to death from respiratory failure [1]. Because of its unique property, uniform contraction and expansion with changes in temperature, it is used in thermometers, barometers and dental amalgams [5].

Inorganic Mercury (Hg^{2+} or Hg^+)

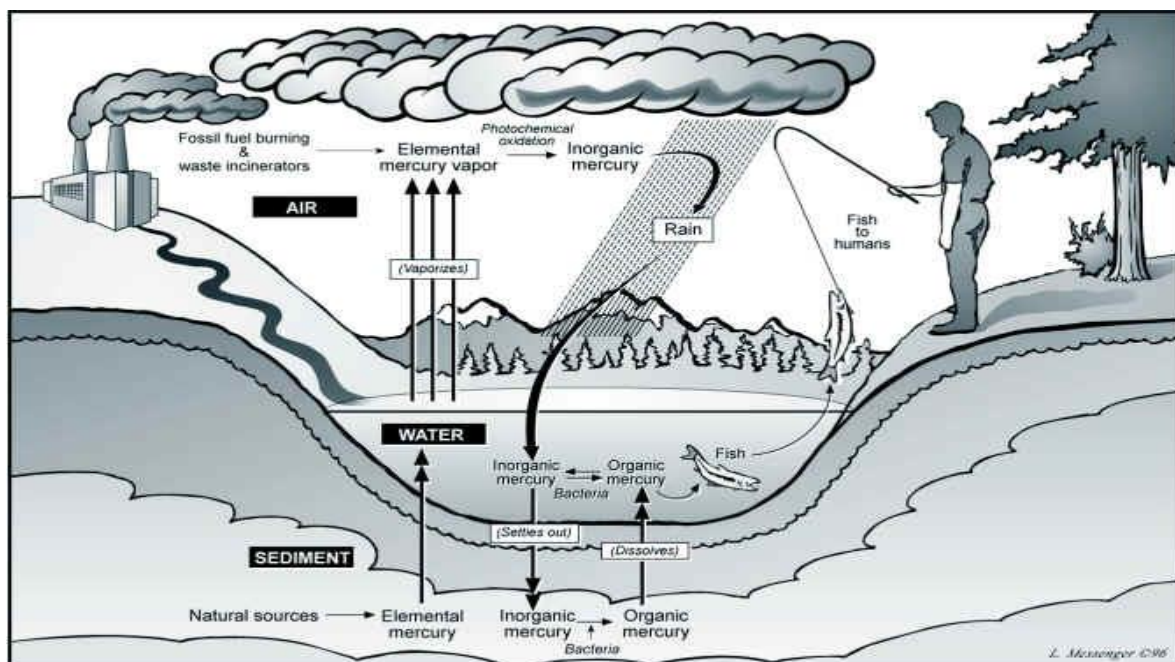
Inorganic mercury compounds are formed when elemental mercury combines with other elements like chlorine, sulphur or oxygen to form compounds known as mercury salts like Mercuric nitrate, Mercuric chloride. Ingestion of mercury salts are irritating and can cause blisters on lips and tongue. They are corrosive and can cause gastro-intestinal damage and kidney failure [5].

Organic Mercury ($R-Hg^+$ or $R-Hg-X$)

Elemental mercury combines with carbon to form organic mercury. It is formed when sulphate processing bacteria present in water convert the inorganic mercury in to more lethal organic mercury. Methyl mercury is considered to be the most lethal among all the three forms [5]. The rate of absorption is more when compared to the rate of elimination, thus leading to because of

its bio-accumulation. It is considered to be a potent neurotoxin. It is lipophilic in nature and can easily cross blood-brain barrier. It has a half-life of 50 days and stays in blood for longer time and accumulates in blood readily. It is absorbed through the digestive tract and is distributed throughout the body. It readily enters the brain, where it may remain for a long period of time causing brain and nervous system damage [5].

Figure 1: Mercury Cycle



Mercury is a concern to human health because it is a persistent bio-accumulative toxin. Mercury is released in to the atmosphere from many natural and anthropogenic activities. Once in atmosphere, elemental mercury vapor stays for long periods because of its long half-life, and is carried to long distances by wind currents and becomes widely spread. In the atmosphere, elemental mercury vapor may be converted in to inorganic mercury by photochemical oxidation, which reacts with the moisture in the atmosphere and returns to the earth's surface as rain. Mercury water gets deposited on to soil and water. In water, inorganic mercury is converted in to

mercuric sulphide which settles down at the bottom as sediment or may be converted in to more lethal organic mercury by the action of sulphate processing bacteria [6]. This sulphate processing bacteria may stick to planktons which may be consumed by the next higher level organism in the food chain leading to bio-accumulation and bio-magnification [7].

Mercury pollution

Mercury is an environmental pollutant released from coal-burning power plants, oceanic and volcanic emissions, gold mining, and dental waste and solid waste incineration [8, 9]. Methyl mercury poisoning significantly affects human health and hence there is growing pressure for the reduction of the discharge of mercury waste. Methyl mercury poisoning in Japan in 1956 was caused due to the discharge of industrial by-products containing organic mercury in to Minimata bay, contaminating fish and resulting in poisoning of local population via consumption of fish [8]. Industrial discharge has been markedly reduced; subsequently, increased attention has been focused on the uncontrolled discharge of mercury waste from dental clinics [10].

Nowadays everybody blames the coal-fired power plants for mercury (Hg) contamination of our aquatic system. However, according to the Mercury Policy Project (MPP), the dental industry is equally guilty. Dental industry is the third largest user of mercury, using over 45 tons of mercury per year. According to the 2002 Mercury Source Control and Pollution Prevention Program Final Report prepared for the National Association of Clean Water Agencies (NACWA), dental clinics are the main source of mercury discharges to POTWs. The exact amount of mercury released by each dentist is hard to estimate, however, several studies have been conducted over the past ten years and in general, dentist released an average of 56 to 270 mg of mercury per day into the wastewater stream [11].

Amalgam is an alloy containing mercury and dental amalgam is a dental filling material used to restore teeth that have cavities. Dental amalgam is composed of 50% of mercury and the rest half of it is made up of silver, tin and copper with a trace amount of zinc [11]. There are other alternatives to dental amalgams like composite resins, porcelain and gold alloys. People prefer mercury amalgams over alternatives because alternatives are highly expensive, less durable and take longer time for restoration. Mercury amalgams are still preferred in the dentistry owing to their economical, user friendly and durable nature and are generally regarded as safe.

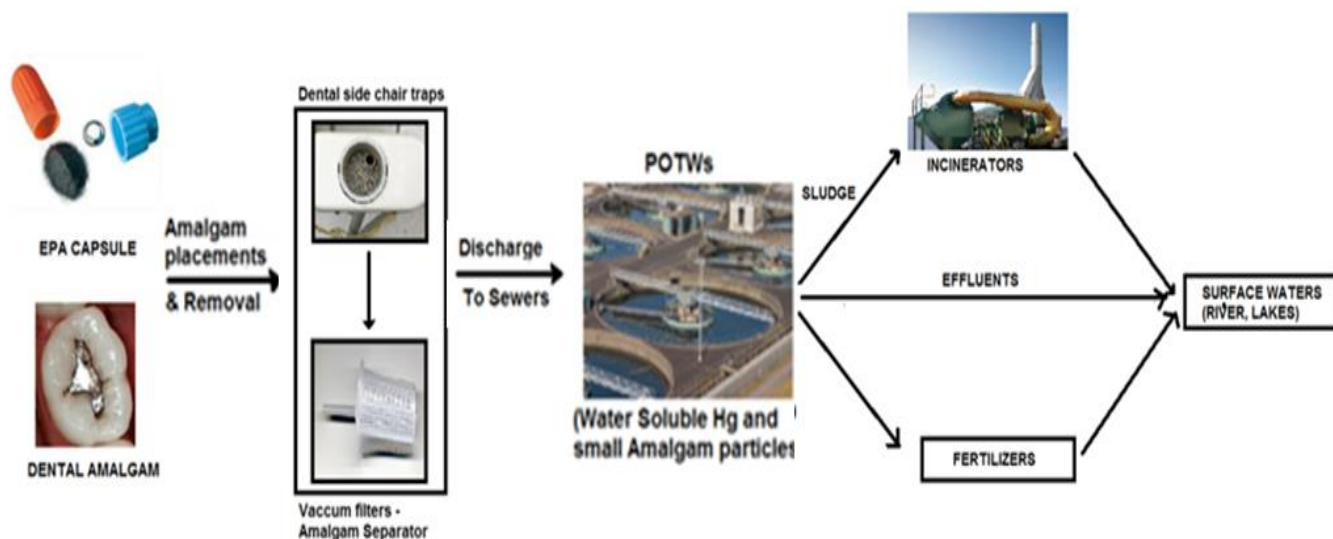
Dental procedures generate a heterogeneous waste mixture of liquids and particles. A major component of this waste mixture is amalgam particles, known also as contact amalgam, with sizes ranging from large visible particles to sub-micron colloidal size suspensions [6]. The American dental Association classifies the amalgam scrap in to [1]

Non-Contact amalgam scrap - Excess mix left over at the end of a dental procedure

Contact amalgam - Amalgam that has been in contact with the patient

When dental amalgam is released in to the environment, the mercury component in it is transformed in to methyl mercury by microbial action. Most dental offices dispose off their mercury waste in to municipal water systems without using an amalgam separator.

Figure 2 : Mercury pollution



The scrapings from amalgam placements and removal and waste water are initially trapped by the chair side traps in a dentist's chair which later passes through the amalgam separator. It is later discharged in to the sewers where it finally reaches the publicly owned treatment works. Municipal treatment plants separate waste water in to water and sludge.

Sludge from POTWs may be applied to agricultural land as fertilizer. Some of the mercury in the fertilizer may evaporate in to the atmosphere and through precipitation the airborne mercury eventually gets deposited into water bodies, land and vegetation. Sludge from POTWs may also be incinerated and once incinerated, the mercury may volatilize to the atmosphere and may then be deposited into lakes and streams via precipitation.

Amalgam - contaminated water is released from dental clinics, with a possible risk of adding significantly to the mercury burden in sludge, thus preventing recycling [12]. This problem can be solved relatively easily by installation of amalgam separating devices. Numerous studies have

shown that the removal of amalgam particulates using currently available filtration system can only sieve pieces bigger than 700 micrometer in diameter [2]. In addition, there is still a significant amount of mercury located in the dissolved or soluble fraction, and is high enough to violate local POTWs discharge limits [3].

The EPA recommends four specific actions to manage amalgam waste to reduce the contamination from dental offices [1].

- Gray Bag It - Discard excess amalgam wastes into a gray bag. Never dispose of dental amalgam wastes in medical red bags or in your office trash containers.
- Recycle It - Select a responsible dental amalgam recycler - who will manage your waste amalgam safely to limit the amount of mercury which can go back into the environment.
- Install It - Install an amalgam separator in the office to capture up to 95% of the mercury leaving a dental office through drains. This is the KEY to success.
- Teach It - Educate and train staff about the proper management of dental amalgam in the office.

According to MPP, there are only ten states in the United States that have mandatory mercury removal systems in dental offices. EPA expects to propose a rule in late 2011 and finalize in 2012 thus increasing the demand for a more efficient dental amalgam separator [1]. There is no filtration system on the market right now that has the ability to remove small or water soluble mercury. This invention improves the effectiveness of available technologies that is used in current commercial systems and is specially designed for removal of water soluble mercury and particulates less than 700 microns in the waste water.

Mercury is removed using methods like ion exchange, adsorption, membrane filtration, precipitation and nanotechnology [13]. Nanotechnology can be defined as the science and engineering involved in the design, synthesis, characterization and application of materials and devices whose smallest functional organization in at least one dimension is on the nanometer scale. Nanoparticles have size less than 100 nm. The properties of many conventional materials change when formed in to nanoparticles. This is typically because nanoparticles have a greater surface area per weight than larger particles; this causes them to be more reactive to certain other molecules. Nanomaterials are highly promising in the water purification process due to their unique properties like higher surface area per unit volume, ease with which they can be anchored onto solid matrices and the ability to functionalize with different functional groups to enhance their affinity towards target molecules [14]. Gold nanoparticles have special affinity towards mercury. The affinity of gold towards mercury can be explained as follows.

Atom	Average atomic mass	Ground state configuration
Au	196.9665	[Kr] 4d ¹⁰ 4f ¹⁴ 5s ² 5p ⁶ 5d ¹⁰ 6s ¹
Hg	200.59	[Kr] 4d ¹⁰ 4f ¹⁴ 5s ² 5p ⁶ 5d ¹⁰ 6s ²

Mercury has a unique electronic configuration with filled 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d and 6s subshells. The 6s electrons are close to the nucleus and this filled configuration strongly resists removal of an electron. Mercury forms weak bonds and thus easily melts solids. The stability of the 6s shell is due to the presence of a filled 4f shell. Metals such as gold have atoms with one less 6s electron than mercury. Those electrons are more easily removed and are shared between the atoms, forming relatively strong metallic bonds. Gold has only half-filled 6s

orbital. Accepting an electron into that low energy orbital will lower energy overall, and metal-metal bonding is expected to be strong as a result [15, 16].

EXPERIMENTAL METHODS

Synthesis of gold nanoparticles

Gold nanoparticles with pendant carboxylic acid and alcohol functional groups were synthesized and characterized using transmission electron microscopy (TEM) according to the literature [17]. To a solution containing 410 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 6 ml water, 200 mL of an ethanol solution containing 2.7 mmol 11-mercapto-1-undecanol and 0.3 mmol 16-mercaptohexadecanoic acid was added. After cooling the solution to 0 °C, 20 mL of a freshly prepared aqueous solution containing 380 mg of NaBH_4 was added dropwise with vigorous stirring. The resulting dark brown solution containing alkanethiol capped gold nanoparticles with pendant alcohol and carboxylic acid functional groups was stirred for 3 h, after which, the material was allowed to precipitate to the bottom of the flask. The particles were washed twice by dispersing them in 100 mL of 80% ethanol followed by centrifugation and decantation and the material was finally washed with 100 mL of ethanol containing ~50 μL of 1 M HCl solution. The washed material was dried under vacuum for 10 hrs [17]. Gold nanoparticles have affinity towards mercury. They form a complex in the ratio of 1:6. One gram of gold can hold about 6 gm of mercury.

Preparation of solid porous support

Hydroxyapatite is used in the formulations because of its large surface area. Cellulose is fibrous and forms crosslinking, which helps in incorporation of gold nanoparticles.

FORMULATION-I

0.2g polycaprolactone is dissolved in 2 ml of nitrocellulose and 2ml of acetone. To this solution 3 g of hydroxyapatite dissolved in 2ml of acetone and 0.3g of poloxomer dissolved in 2 ml acetone are added. Finally the binding agent, 0.1 gm of rosin and 0.014gm of linseed oil in about 1ml of acetone is added to the above mixture, with continuous stirring under low heat. The solution is mixed well and transferred to a mould and left for drying.

FORMULATION-2

3g of hydroxyapatite dissolved in 2ml of acetone is added to 1g of gelatin dissolved in 10 ml of water. 0.3g of poloxomer dissolved in 2 ml acetone is added to the above mixture with continuous stirring under low heat and finally transferred in to a mould and left for drying.

FORMULATION-3:

5gm of cellulose is added 10 ml of acetone and stirred to make a fine paste. To this 5 gm of hydroxyapatite and 0.5 gm of poloxomer are added with continuous stirring under low heat and finally transferred in to a mould and left for drying for 24 hrs.

FORMULATION- 4

5gm of hydroxyapatite is added to a mixture of 2ml of acetone and 2ml nitrocellulose, and is stirred continuously. To this mixture 0.2 g of cabopol and 0.2 g of poloxomer are added and mixed well. The mixture is transferred in to a mould and left for drying.

FORMULATION-5

4 g of hydroxyapatite, 5g of cellulose and 5 g of cement are taken in a beaker and mixed well. To this powder mixture sufficient quantity of water is added and mixed to form a fine paste. Approximately 0.2 g dissolved in 2 ml of acetone is added to the above mixture and mixed well. The mixture is transferred in to a mould and left for drying.

Incorporation of the gold nanoparticles on to the solid porous support

Gold nanoparticles can be incorporated in to the formulation in two ways.

- I. Directly mixing the nanoparticles with the formulation
- II. By coating the nanoparticles on the surface of filter cake.

Coating Material

- I. Dissolve 0.2 g of polycaprolactone 2.0 mL of acetone with constant stirring under very low heat.
- II. Add acetone drop by drop in the beaker until the polymer is totally dissolved.

Gold nanoparticles are added to the coating formulation and coating material is added to the filter cake and shaken for 12 hrs. On drying, the polymer forms a three dimensional network and holds the nanoparticles to the filter cake tightly.

Testing the filter cake

The filter cake is tested for the porosity and three dimensional network using SEM. The incorporation of goldnanoparticles is tested by EDX (elemental analysis) and X-ray scattering electron microscopy.

INSTRUMENTATION

Scanning Electron Microscopy

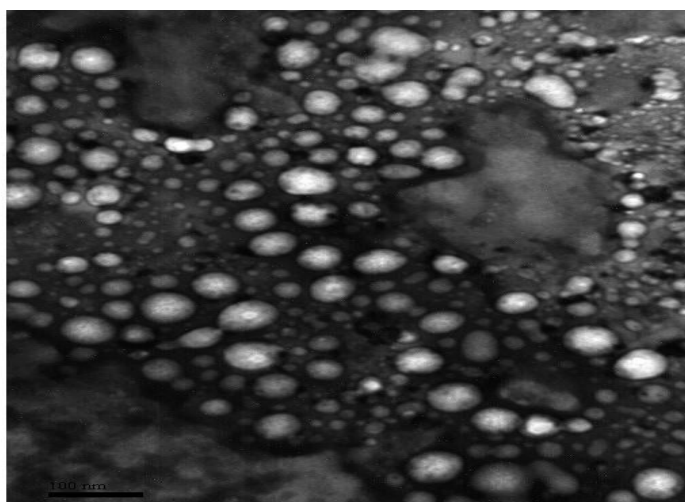
The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology, chemical composition, and crystalline structure and orientation of materials making up the sample [18]. These signals include secondary electrons, backscattered electrons, characteristic X-rays, visible light and heat. Secondary electrons are useful for showing morphology and

topography on samples and backscattered electrons are useful for illustrating contrasts in composition in multiphase samples. Characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam [18]. The SEM (model JEOL JSM-6610 LV) of the prepared formulations was conducted using high vacuum and low voltage on back scatter method.

RESULTS AND DISCUSSION

I. FIGURE 3

TEM of the synthesized gold nanoparticles



Specimen : 1_NegStain
Voltage : 30 kV
Indicated Magnification : X200000

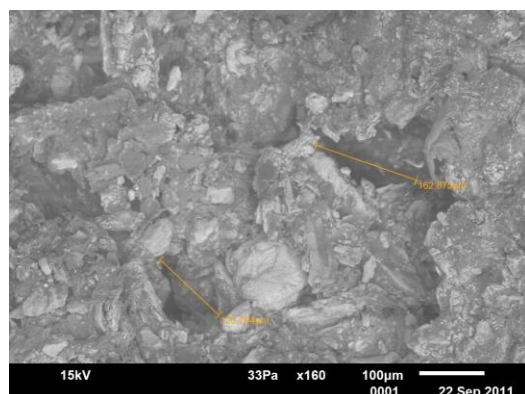
Total Magnification : X215000
Acquisition Date : 12/2/2010

Gold nanoparticles of size less than 50 nm were synthesized. The affinity of gold towards mercury is a well known fact since ancient times.

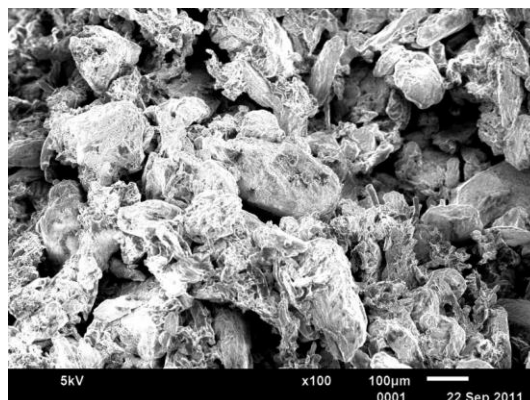
II. FIGURE 4

Formulation 1

TOP VIEW (Formulation 1)



SIDE VIEW (Formulation 1)

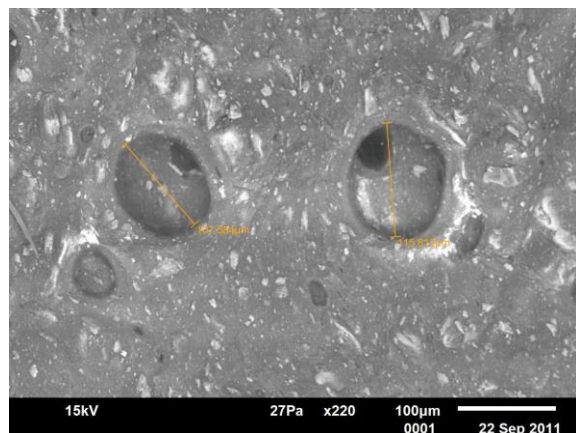


Water passage through the filter cake was very slow. The SEM clearly shows more surface area, grooves and porosity in to which the gold nanoparticles can be easily incorporated. Hydroxypatite didn't dissolve properly and can be seen as lumps. The filter cake was very dense and hence water didn't pass through it as desired. Filter cake was not very intact and broke easily.

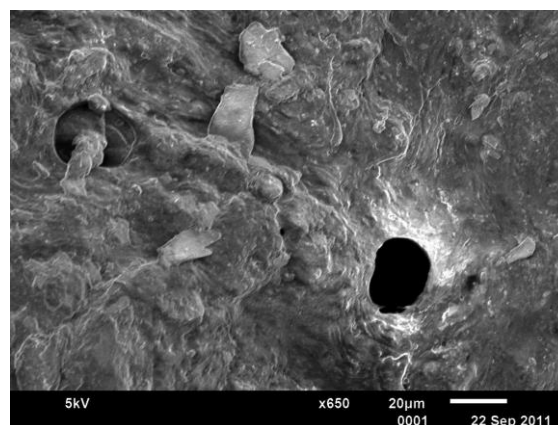
III. FIGURE 5

Formulation-2

TOP VIEW (Formulation 2)



SIDE VIEW (Formulation 2)



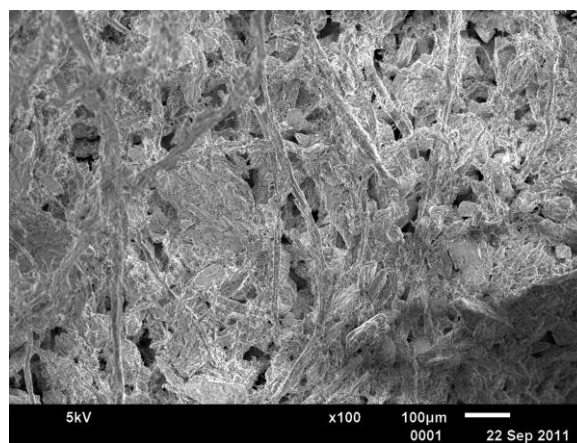
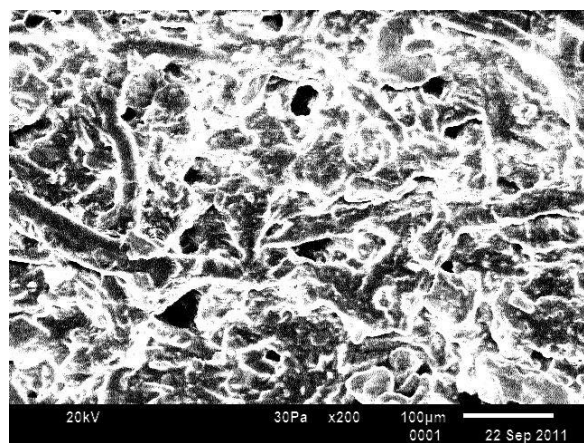
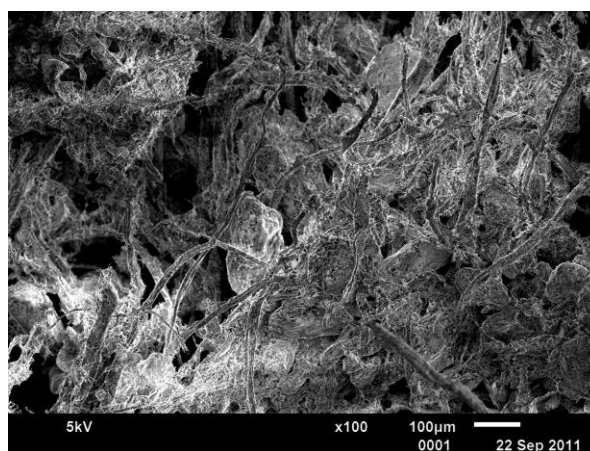
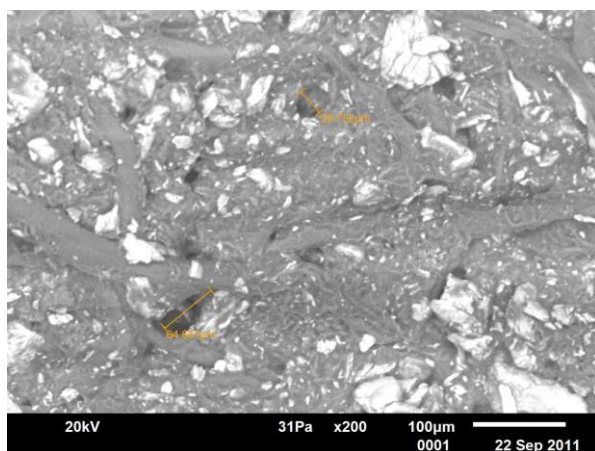
Here the SEM clearly shows the soft surface which is imperative of the poor surface area. Since the formulation is made of gelatin, water made the filter cake wet. Cross linking was absent and the filter cake was soft and broke easily.

IV. FIGURE 6

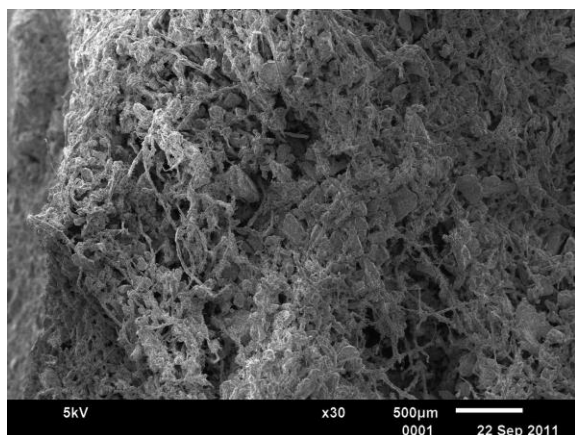
Formulation-3

This formulation was very good and had a very good absorption capacity. The surface area was more and the three dimensional network of the formulation can be seen. The pore size is around 65 microns which makes it possible to trap the microparticulate mercury.

TOP VIEW (Formulation 3)



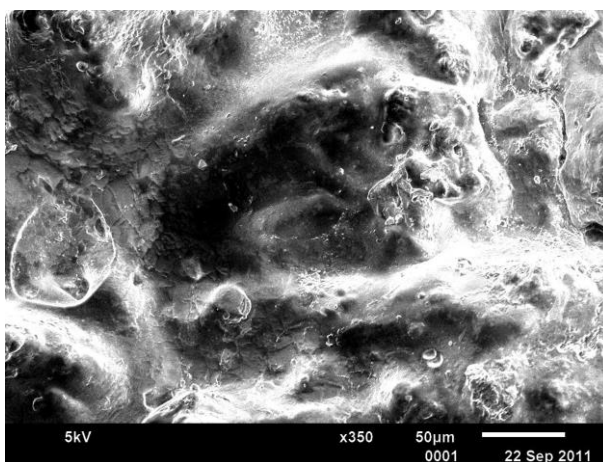
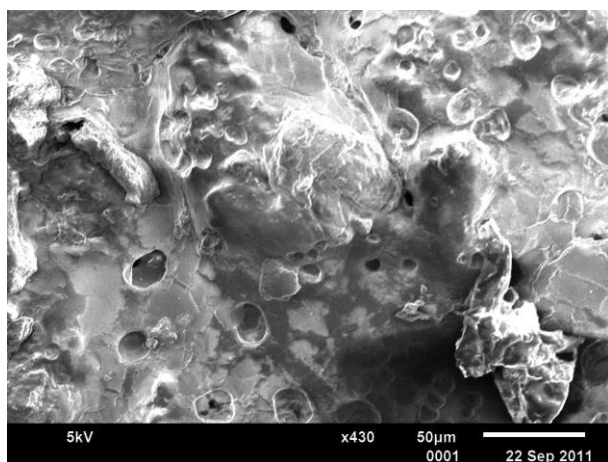
SIDE VIEW (Formulation 3)



The cross section shows good cross linking and the porous nature of the formulation. The only problem with this formulation was that the disc was deteriorating once the water passed through it.

V. FIGURE 7

Formulation-4



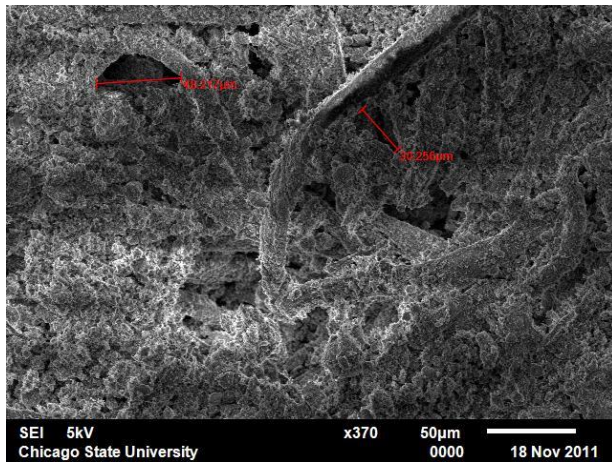
The filter cake was dense and the cross linking was absent. The surface showed grooves, but the cake was not porous.

VI. FIGURE 8

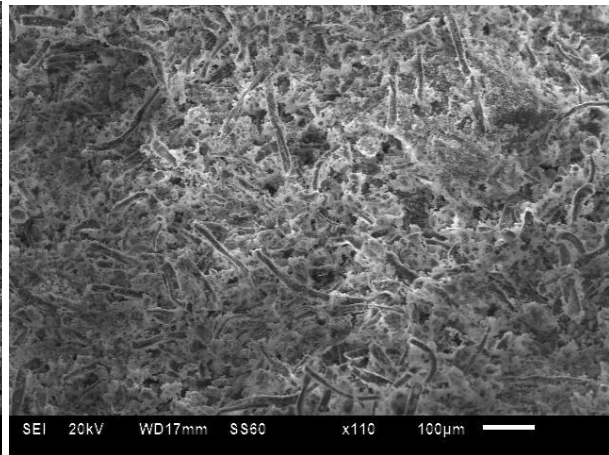
Formulation-5

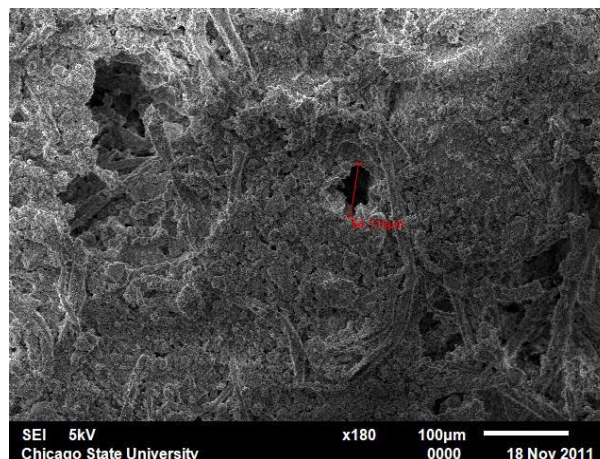
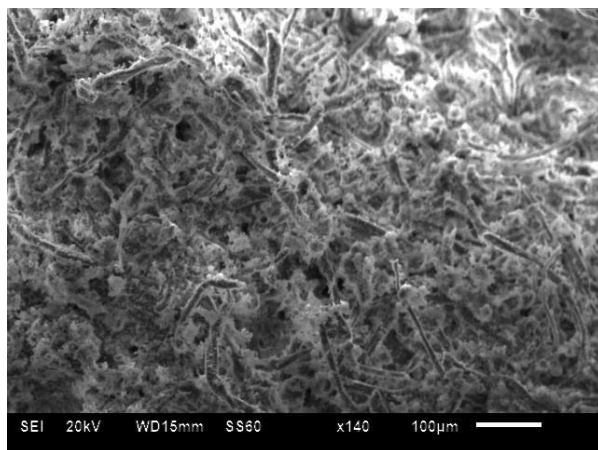


TOP VIEW (Formulation 5)



SIDE VIEW (Formulation 5)





The three dimensional network can be clearly seen in the SEM. The filter cake was porous and had good water absorbing capacity. Cement held all the ingredients together and hence the filter cake was hard and intact even when water passed through it. Cellulose fibers cross linked with each other to form a three dimensional network, which can hold the gold nanoparticles in it.

CONCLUSION

Mercury pollution has become today's top most priority, because of its severe consequences that it causes once it enters into the fish ecosystem. Dental amalgams are considered to be the most important contributor for the organic mercury into the POTWs, eventually into rivers, lakes and seas. We have found an efficient mercury filter system that is capable of removing both water soluble and microparticulate mercury from dental waste water. The filter cake shows mercury specific action, which acts chemically by trapping the water soluble mercury (about 6gm) into the "filter cake". The mercuric ions get removed by amalgamation and by complexation/adsorption with the gold nanoparticles incorporated on the porous filter support. The filter cake can custom fit all sorts of existing amalgam separators and is recyclable and

biodegradable. It being the first of its kind (US patent search), may well be the turning factor, in the effort to save the environment from the very harmful mercury poisoning.

FUTURE GOALS

Practical implementations of mercury filter system, by comparing the performance of mercury filter cake before and after treatment with mercury water. The residual mercury will be estimated in the output water using ICP-MS and Cold Vapor Atomic Fluorescence Spectroscopy to test for the efficiency of filter cake. To actually test the performance of filter cake on a dentist's chair in a dental office and test for its efficiency.

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18. Scanning Electron Microscopy

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