ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

Advanced Water Treatment Using Nano-Materials

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ABSTRACT: Cost effective water purification technology in developing countries like India is always welcomed.So this paper presents about cheap nanomaterials with high performance to treat water .Out of 4 main parts it consist,(i.e) first one is air cathode microbial fuel cell (MFC) which removes about 80% (COD,BOD)chemical and biological Oxygen demand. Secondly, Ultrafiltration(UF) membranes made of polysulphone and silver nano particles embedded into it,which filters out inorganic salts. Thirdly, photocatalysis part made of titania and graphene oxide which filters almost all organic contaminants but not inorganic salts. Last but not the least, biopolymer reinforced nano composite composed of aluminium-oxyhydroxide-- chitosan composite which filters all remaining traces of heavy metals and also mainly bacteria and viruses of less than 1 micron.

KEYWORDS: polysulphone, ultrafiltration, aluminium-oxyhydroxide—chitosan, graphene Oxide.

I. Introduction

Major problem in the world especially India is water polllution which takes the lives of millions of people every year.Its been reported that about 1.2 trillion gallons of untreated sewage,storm water and industrial waste are discharge into US waters annually.About 40% of America's rivers and 46% of America's lakes are too polluted for aquatic life.According to the report given by United Nations released on March 22,2010 on World Water Day says that water pollution kills more people than all other forms of violence including Wars.90 % of waste water discharged daily in developing countries contributes to the deaths of some 2.2 million people a year from diarrheal diseases.Atleast 1.8 million children younger than 5 die every year due to water-related diseases.Newdelhi's body of water is little more than a flowing garbage dump,with fully 57% of city's waste finding its way to the Yamuna.River Cooum,which is quite considered pure in 19th century is slowly dying due to unchecked pollution like the River Ganga.This motivated me to change the situation.

First in my project,I considered biosand filter,which is good in removing microbes due to biofilm at the top,but failed in turbid waters with more maintainance needed.Secondly,I utilized amla peel barks and plantain stems,which is also found good in removing pollutants.But Frequent replacement and frequent decay forced me to reject that too.Thirdly,I used rice husk ash,used tea leaves ,chitosan which is specific to a single contaminant like lead,chromium,etc.Similarly I used n no of natural materials to treat water but everything failed.So I finally gone for nanomaterials.Surfactant modified zeolite was the first one, i opted for.It is excellent in removic all cationic,microbes by permeability but on a long term basis,it also failed though it is not too costly(2.5$/kg).Finally I opted for biopolymer reinforced nanocomposite which works well for 1500l without reactivation with 120g of the composite for just about 2$/family.It gave me tremendous result on a smaller scale.

For a large scale basis,I added some other efficient nanofilters like microbial fuel cell(MFC),Polysulphone ultrafiltration technique and also photocatalysis,which I have opted not only due to their ability to treat water effectively but also to get current. The Present systems of water desalination involves cellulose acetate and other advanced membranes which is very difficult to process and also cost about several lakhs to install and maintain,which is bulky in countries like India,but its not the case for developed countries like USA,Canada,etc.Nano setup which consisting of polysulphone impregnated with silver nanoparticles which costs about RS.1000 and 2nd is air cathode microbial fuel cell and (titania-graphene oxide) filter which not only purifies water but also produces electricity and enough H_2,which is used for current production by passing it through H_2 fuel cell.Then finally in order to get water of good quality,it is passed through a biopolymer reinforced polymer composite which filters bacteria,virus and other

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toxic heavy metals and also very cheap(This filter ran up to 1,500 L with a bacterial input load of 10^5 CFU/mL without the need for reactivation).For effective extraction of lipids from algae,Natural nitrogen depletion is used which reduced the costs of transporting to N_2 depleted environment,which is used today for stressing to get biofuel from algae.Thus this setup is effective in performance as well as cost-wise.

II. MATERIALS AND METHODS

i. FILTRATION SETUP:

Fig.1 shows the total filtration setup where the waste water which contains organic compounds like glycerol,methanol,glucose,etc.are first passed through air cathode Microbial Fuel Cell(MFC) which removes about 80%COD,Bacteria,etc.Then it is passed through polysulphone ultrafiltration membranes coated with silver nanoparticles which improves biofouling resistance and virus penetration as present in current RO membranes.The effluent is then passed through titania coated graphene oxide on hexagonal mesh which oxidises organic pollutants and also produces H_2.Still if any pollutants like glycerol is present,it is hence finally passed through Aluminium oxyhydroxide-Chitosan composite,which filters bacteria,viruses,heavy metals,lead and arsenic.

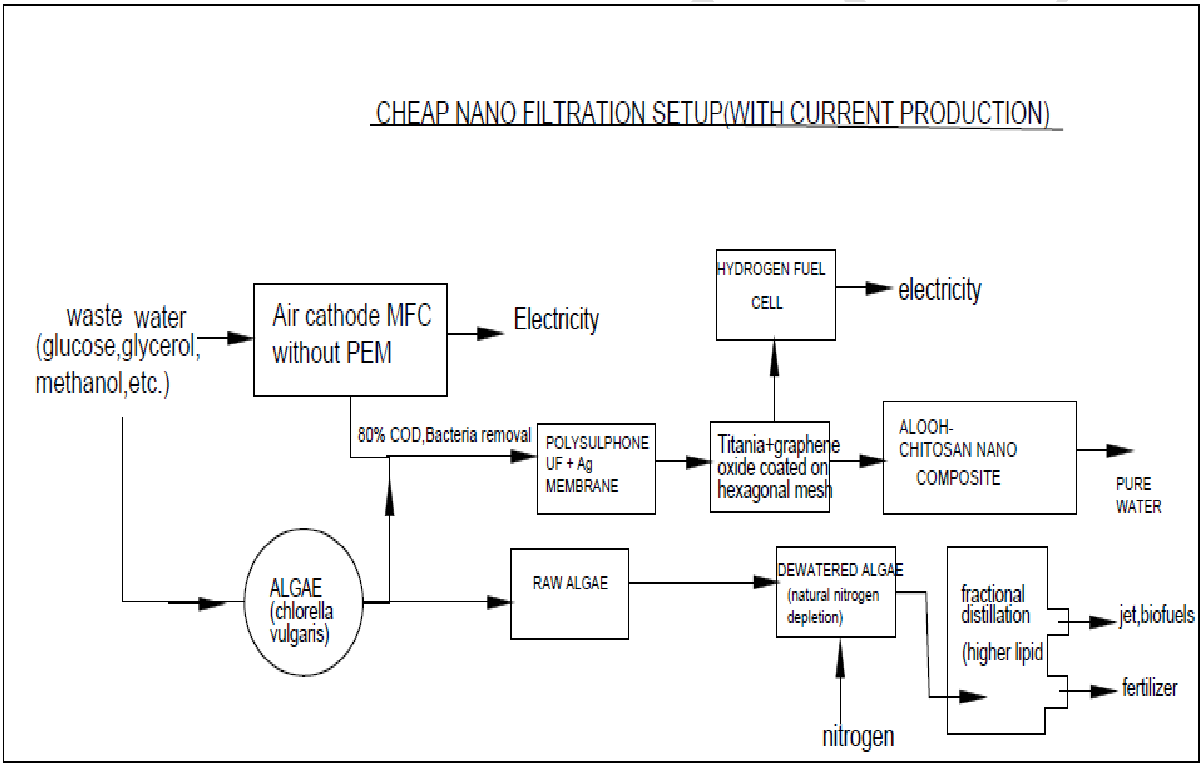

Fig. 1 Shows the total nano-filter setup with all the elements like MFC,biopolymer-nanocomposite,etc.

Lets see the description of each part in the total advanced economic water filtration setup.

a) MICROBIAL FUEL CELL(AIR-CATHODE)

For fuel production from algae,higher lipid content is needed.So by introducing N_2, through natural N_2 depletion,we get much higher yield of lipids(80%).We can also get electricity from microbial fuel cell depending upon hydraulic conditions at the inlet.Similarly at titania stage,we get enough H_2 by doping graphene oxide(GO) and Titania compared to ordinary titania as a photocatalyst.

Microbial fuel cells (MFCs) are typically designed as a two-chamber system with the bacteria in the anode chamber separated from the cathode chamber by a polymeric proton exchange membrane (PEM). Most MFCs use

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aqueous cathodes where water is bubbled with air to provide dissolved oxygen to electrode. To increase energy output and reduce the cost of MFCs, we examined power generation in an air-cathode MFC containing carbon electrodes in the presence and absence of a polymeric proton exchange membrane (PEM). Bacteria present in domestic wastewater were used as the biocatalyst, and glucose and wastewater were tested as substrates. Power density was found to be much greater than typically reported for aqueous-cathode MFCs, reaching a maximum of 262 ± 10 mW/m^2 (6.6 ± 0.3 mW/L; liquid volume) using glucose. Removing the PEM increased the maximum power density to 494 ± 21 mW/m^2 (12.5 ± 0.5 mW/L). Coulombic efficiency was 40−55% with the PEM and 9−12% with the PEM removed, indicating substantial oxygen diffusion into the anode chamber in the absence of the PEM. Power output increased with glucose concentration according to saturation-type kinetics, with a half saturation constant of 79 mg/L with the PEM-MFC and 103 mg/L in the MFC without a PEM (1000 Ω resistor). Similar results on the effect of the PEM on power density were found using wastewater, where 28 ± 3 mW/m^2 (0.7 ± 0.1 mW/L) (28% Coulombic efficiency) was produced with the PEM, and 146 ± 8 mW/m^2 (3.7 ± 0.2 mW/L) (20% Coulombic efficiency) was produced when the PEM was removed. The increase in power output when a PEM was removed was attributed to a higher cathode potential as shown by an increase in the open circuit potential. An analysis based on available anode surface area and maximum bacterial growth rates suggests that mediatorless MFCs may have an upper order-of-magnitude limit in power density of 10^3 mW/m^2.

b) POLYSULPHONE-AG COATED MEMBRANE

nAg incorporated into polysulfone ultrafiltration membranes (nAg–PSf) exhibited antimicrobial properties towards a variety of bacteria, including *Escherichia coli* K12 and *Pseudomonas mendocina*KR1, and the MS2 bacteriophage. Biofouling and virus penetration are two significant obstacles in water treatment membrane filtration. biofouling reduces membrane permeability, increases energy costs, and decreases the lifetime of membranes. in order to effectively remove viruses,nanofiltration or reverse osmosis (both high energy filtration schemes) must be used. Thus, there is an urgent demand for low pressure membranes with anti-biofouling and antiviral properties. The silver nanoparticles are deposited by the in situ reduction of silver nitrate on the cellulose fibers of an absorbent blotting paper sheet. it prevents silver leaching.The aim is to achieve inactivation of bacteria during percolation through the bactericidial sheet, rather than removal of bacteria from the effluent by filtration. Only pathogens smaller than the membrane's pore, 0.01 micron or 100 millionth of a metre in size,while trapping dirt, suspended particles, cysts, viruses, most types of bacteria including the dreaded E-coli, and other dissolved salts. Polysulphone is resistant to mineral acids and most chemicals likely to be found in water used for drinking, giving the membrane a life of three to five years. It also makes the candle (membrane) easy to clean with a bleach and maintain.A low pressure of .3 bar is enough to run without electricity.

c) SYNTHESIS OF SILVER NANOPARTICLES

The synthesis of Agcitrate was done according to the literature procedure. Briefly, the synthesis involves the following materials and methods: 25 ml of 0.005 M stock solution of silver nitrate in water was diluted to 125 mL and heated until it begins to boil. Then 5 ml of 1% sodium citrate solution was added; heating continued until the color was pale yellow. The solution was cooled to room temperature. The effect of silver-coated spacer on antimicrobial activity was more lasting. In the silver-coated spacer test, there was almost no multiplication of cells detected on the membrane during the whole testing period.

d) TITANIA COATED GRAPHENE OXIDE

Composite solution of TiO2 and GO (Graphene Oxide) - stirred@320K was prepared. After an hour in sunlight, the solutions had darkened,indicating GO reduction to Graphene.

Adding Methylene blue indicator solution then leaving in a shaded areafor an hour showed the effectiveness ofGrapheneOxide/ReducedGraphene Oxide doping.

Nano-powder cannot be directly applied in this device because it can be easily washed away and constant stirring is required (i.e. additional energy source is needed). Hence, I developed designs to solve this problem -from titania-coated beads to titania-coated membrane, I finally decided to use a hexagonal mesh coated with nano titania to increase the surface area of titania exposed to wastewater and light.It is also efficient in removing oilspills which is

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also a major threat,now-a-days.fig.3 shows hexagonal mesh coated titania with acrylic cover to prevent hydrogen gas leakage.

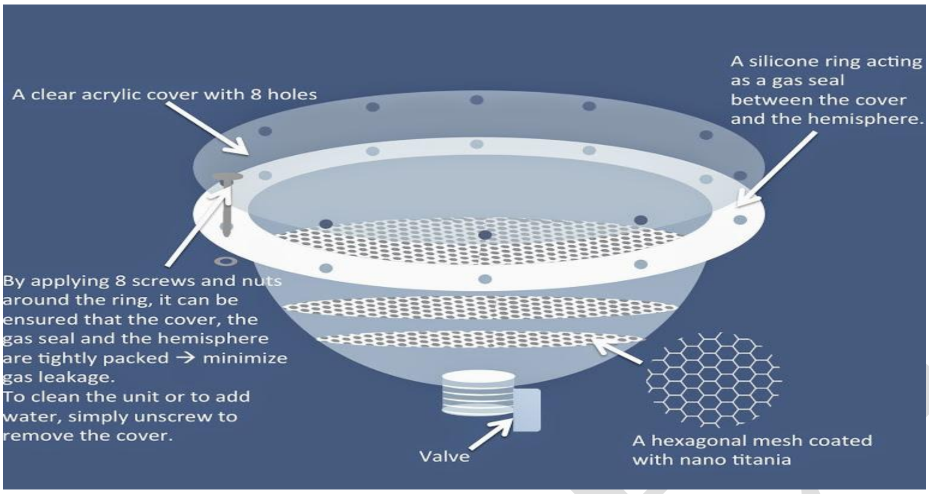

Fig.3 Shows the design of Grapheneoxide-titania coted with hexagonal mesh with valve for the purified water to pass through secondary filtration for household use.In my setup,it is then fed to AlooH-Chitosan composite.

e) **COMPOSITE COATED SPONGE**

I obtained a Graphene Oxide solution and a Titanium Dioxide microparticle powder. Despite Microparticles being less efficient,they are a lot cheaper and safer and coated it on the sponge.The oxidation of chemicals to useful products without using expensive catalysts or conditions. It also shows potential for usage in rural water purification, whilst demonstrating the coating's versatility. I squeezed the sponge's contents into the Tollen's test - the silver ions were being reduced by the presence of aldehydes to form a suspension of black particulates - proving that the catalyst coating (the preparation of which will be discussed in the method section) could be used to neutralise pollution in waterborne environments.

- **USES**

Abrasion resistant,more efficient in all light levels,cheaper,used on a wide variety of substrates,which makes it to degrade chemical/biological pollutants into CO2 and water - coat/ powder/sponge form.It can also be used for Air purification - similarly to conventional coatings, but more efficiently - neutralises air pollutants (NOx, SO2 etc) even in cloudy/low light conditions. Sponge/coat form (on outside of buildings etc).

f) **PRODUCTION PROCESS OF BIOPOLYMER-REINFORCED SYNTHETIC GRANULAR NANOCOMPOSITES**

Al3+-complexed chitosan solution (pH 0.8) was treated with an alkali . Alkali treatment initiates aluminum ion hydrolysis (leading to the formation of aluminum hydroxide nanoparticles) followed by chitosan precipitation (randomcoiled water-insoluble chitosan network).

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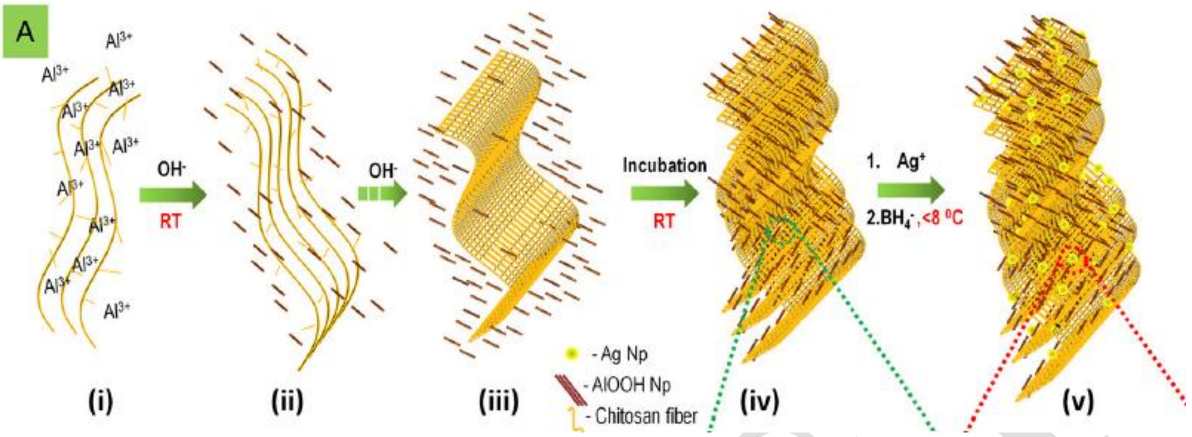

Fig 4 shows (i) Al3+ complexes with chitosan solution; (ii and iii) alkali treatment leads to formation of aluminum hydroxide nanoparticles and random coiled chitosan network; (iv) aluminum hydroxide nanoparticles bind to chitosan network,possibly through covalent sharing of oxygen, leading to the formation of aluminum oxyhydroxide; and (v) silver nanoparticles form on the aluminium oxyhydroxide–chitosan network.

For bacteria and virus removal, aluminium oxyhydroxide–chitosan nanostructure embedded with silver nanoparticles was synthesized.For Heavy metal removal, aluminum oxyhydroxide–chitosan nanostructure embedded with nano-Manganese dioxide particles and for arsenic and iron removal, iron oxyhydroxide–chitosan nanostructure was prepared individually and similarly for other toxic metals like mercury,etc.removal,respective metal ion precursors are individually prepared.

g) INCREASING LIPID CONTENT OF ALGAE

Algae is a promising source of lipid for biofuel. It is very efficient at producing oil at up to 5,000- 15,000 gallons per acre per year. Algae's lipid content can also be easily increased through stressing. Nitrogen depletion is one of the most common forms of stressing and involves depleting the amount of nitrogen in the media. With this technique maximum lipid yields of *Nannochlorpsis sp.* were 1,400 g/l or 0.7 ml/g. using current techniques for nitrogen depletion, the algae must be transferred from a nitrogen rich media to a nitrogen depleted media. This is cumbersome and costly.

An alternative way would be to let the algae deplete the nitrogen naturally through consumption, this is called natural nitrogen depletion. Natural nitrogen depletion involves adding a specific amount of nitrogen to the media. Because of the algae's consumption, the nitrogen ideally runs out before harvesting, allowing time for nitrogen depletion. With this method, nitrogen depletion can be used without having to harvest the algae to do so. It also still allows for growth in the early stages, increasing the cell counts in the later stages. This could be one of the needed growing techniques to reduce the cost of algal biofuels.

III. EXPERIMENTAL RESULTS

Fig. 5 shows the Composite solution of TiO2 and GO (Graphene Oxide) - stirred@320K was prepared. After an hour in sunlight, the solutions had darkened,indicating GO reduction to Graphene.

Adding Methylene blue indicator solution then leaving in a shaded area for an hour showed the effectiveness ofGrapheneOxide/ReducedGraphene Oxide doping. the blue colour has disappeared from the top and bottom cups but remained in the TiO2 cup.

Individual results are shown for each type of mixture composite. (1)

(1)Graphene oxide-TiO_2 mixed

(2) TiO_2 Dominant

(3)Graphene oxide -TiO_2 unmixed (2)

Graphene oxide and titanium dioxide mixed in (3) right proportions give the better result for degrading organic compounds.

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Fig.5 Shows methylene blue added was only decomposed in (1) and (3) but not(2)-TiO_2 dominant.

Fig. 6 Shows a mossy tile when sprayed with nano composite(mixed grapheme oxide and titanium dioxide),it removes algae on the surface.

Fig. 6 shows how algae has been decomposed and removed from the mossy tile surface. In this preliminary test, I sprayed the composite on a mossy tile, and found that it removed all the algae from its surface.

Fig.7 shows composite coated sponge for water purification. I obtained a Graphene Oxide solution and a Titanium Dioxide microparticle powder. Despite Microparticles being less efficient,they are a lot cheaper and safer and coated it on the sponge.The oxidation of chemicals to useful products without using expensive catalysts or conditions. It also shows potential for usage in rural water purification, whilst demonstrating the coating's versatility. I squeezed the sponge's contents into the Tollen's test - the silver ions were being reduced by the presence of aldehydes to form a suspension of black particulates - proving that the catalyst coating (the preparation of which will be discussed in the method section) could be used to neutralise pollution in waterborne environments.

(a) (b) (c)

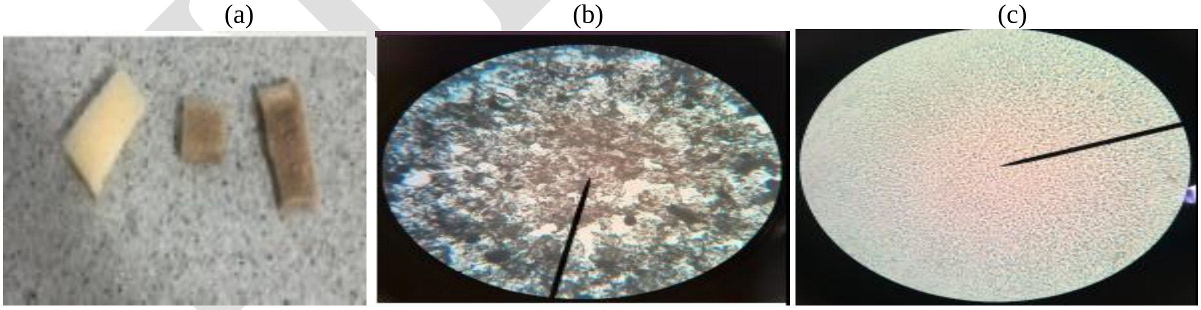

Fig. 7(a) shows composite coated sponge on the right.(b)SEM micrograph consisting of the 'normal' TiO2 coating - see excessive clumping of the microparticles and (c) The Graphene Oxide polymer composite; particles effectively distributed.

a) **CHLORELLA VULGARIS-HIGHEST LIPID CONTENT**

Chlorella sp showed maximal growth in municipal waste water at 30 ^{o}c, pH 8. Results presented in table 3 indicate that the free cells of this algae 20gm inoculums concentration without any additional nutrients could bring about more than 50percent reduction in COD and BOD after 96hrs. Whereas other two strains could reduce upto 49.5 and 48.3

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(Ulva sp) and 43.5 and 42.2 (Cladophora sp) for COD and BOD respectively under packed column. The antimicrobial composition consists of an aluminum oxyhydroxide–chitosan composite (referred to as BM) with silver particles of 10–20 nm diameter embedded in it and is capable of sustained release of silver ions[40 ± 10 parts per billion (ppb)] in natural drinking water over an extended volume of water passing through it, to achieve effective removal of microorganisms.

The antimicrobial composite (referred to as Ag-BM) is unique as it is made in water at near room temperature, using a biopolymer, and dried in ambient conditions to obtain water-insoluble granules, yielding Na_2SO_4 as the major by-product (>90%), thereby making it a green synthesis. The concentration of silver ion leached into drinking water from the prepared composite at relevant temperatures (5–35 °C) is significantly less than the maximum permissible limit of 100 ppb.These materials have been used to develop an affordable at US $2.5/y per family as it can run for about 1500l to purify water without reactivation of the composite(i.e)by regaining the ability to leach silver ions.

Fig.8 shows the comparison between 3 algal species like Ulva,Cladophora,chlorella species in removing both chemical and biological oxygen demand.

Variable	Contact time	Strain type		
		Ulva sp	*Cladophora sp*	*Chlorella sp*
COD	4	17.5	16.9	21.0
	8	19.2	18.7	24.2
	12	21.3	24.2	30.2
	24	25.6	28.3	35.6
BOD	4	5.5	6.3	7.8
	8	11.3	13.2	15.3
	12	16.7	18.1	23.1
	24	21.2	24.5	30.1

**Initial levels of COD-380mg/L, BOD186mg/L*

Fig. 8 shows algae species comparison for greater removal of oxygen demand.It can be seen that Chlorella sp. Achieved by removing 380 mg/L of COD(Chemaical Oxygen Demand) and 186 mg/L of BOD(Biological Oxygen Demand) to final 21 mg/L and 7.8mg/L of COD and BOD respectively.

b) **Ag-Bm Composite Result:**

The antimicrobial composition consists of an aluminum oxyhydroxide–chitosan composite (referred to as BM) with silver particles of 10–20 nm diameter embedded in it and is capable of sustained release of silver ions[40 ± 10 parts per billion (ppb)] in natural drinking water over an extended volume of water passing through it, to achieve effective removal of microorganisms.

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DOI: 10.15680/IJIRSET.2014.0311005

IJIRSET

ISSN: 2319-8753

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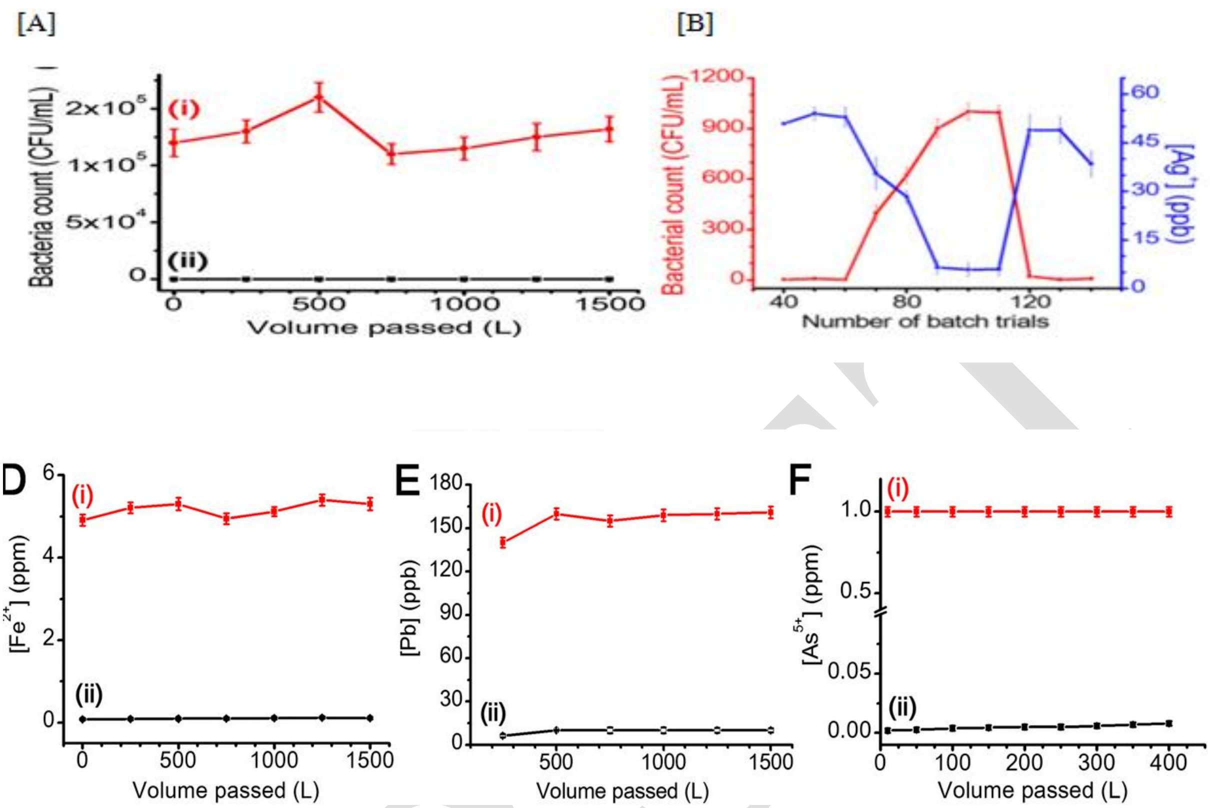

Fig. 9(A) shows Silver ion concentration measured by ICP-MS (blue trace) and corresponding bacterial count in CFU/mL for one of the cycles (number of trials: 40th–140th) (red trace) from batch measurements and remaining graphs shows the antimicrobial composition is used as granules and kept in the membrane filter. Carbon block is positioned just before the tap. Carbon block may also be used as a multilayer axial block, comprising adsorbents for specific regional contaminants such as arsenic, iron, and lead. (C–F) Column data for the removal of (B) E. coli, (C) Fe2+, (D) Pb2+, and (E) As5+. Input (i) and output (ii)concentrations are indicated in B–E.

IV. CONCLUSION

Thus the above evidence of each element implies the successful working of the above hypothesis of total cheap nano filtration setup.

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IJIRSET
ISSN: 2319-8753
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BIOGRAPHY

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I am pursuing my B.E(Mechanical engg) in Panimalar engg college.I am a critical thinker and hardworker.I would like to build a new nano ecofriendly engine which is useful for future generation automobiles.

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L.Abhishek
I am pursuing myB.E(Mechanical engg) in Panimalar engg college.I love to create a water purification for municipal water supply in our cities and my aim is to create a cheap filter for the poor.

Dr. Siva kumar. G
I am working as professor of Panimalar Engineering College, Chennai, India. My area of research is nanomaterials, and polymer nanocomposites. I would like to prepare new novel nanomaterials.