FABRICATION OF TiO_2/WO_3 FOR TREATMENT OF CARWASH WASTE WATER

By

Amna Anam Durrani

684-FBAS/MSES/S18

Department of Environmental Sciences

Faculty of Basic and Applied Sciences

International Islamic University Islamabad

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Chromium pollution

Tetrachloroethylene

Poly aromatic

Sulfur removal

Tungsten tetrachloride

بسم الله الرحمن الرحيم

Department of Environmental Sciences

International Islamic University Islamabad

Dated: _____

FINAL APPROVAL

It is certificate that we have read the thesis submitted by Ms. Amna Anam Durrani and it is our judgment that this project is of sufficient standard to warrant its acceptance by the International Islamic University, Islamabad for the M.S Degree in Environmental Sciences

COMMITTEE

External Examiner
Dr.Rohama Gill
Associate Professor
Department of Environmental Sciences
Fatima Jinnah Women University, Rawalpindi

Internal Examiner
Dr.Rukhsana Tariq
Assistant Professor
Department of Environmental Sciences
International Islamic University, Islamabad

Supervisor
Dr. Maliha Asma
Assistant Professor
Department of Environmental Sciences
International Islamic University, Islamabad

Incharge, DES
Dr.Maliha Asma
Department of Environmental Sciences
International Islamic University, Islamabad

DEDICATION

To Almighty ALLAH and the Holy Prophet Muhammad (P.B.U.H)

&

My Loving Ami, Abu

DECLARATION

I hereby declare that the work present in the following thesis is my own effort, except where otherwise acknowledged and that the thesis is my own composition.

No part of the thesis has been previously presented for any other degree.

Date _____

Amna Anam Durrani

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Amna Anam Durrani

LIST OF ABBREVIATIONS

CW	Carwash
WW	Wastewater
COD	Chemical oxygen demand
BOD	Biological oxygen demand
TOC	Total organic compound
DO	Dissolve oxygen
CA	Cellulose acetate
BDD	Boron Doped Diamond
VOCs	Volatile Organic compounds
TDS	Total dissolved solids
TSS	Total suspended solids
VSS	Volatile suspended solids
PBR	Packed bed reactor
EPA	Environment protection agency
PAH	Poly aromatic hydrocarbons
SEM	Scanning electron microscope
LV	Low vehicle
HV	High vehicle
UV	Ultraviolet

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ABSTRACT

Carwash industry wastewater contains many obnoxious pollutants which need to be removed to achieve EPA standard. Almost 100 liters of water consumed to clean a car which goes to sewage after washing. Major components are oil, grease, diesel, detergents and solid particles which become source of many carcinogenic organic compounds that need to be removed before discharging into sewage lines. This type of wastewater requires treatment for effectively removal of contaminants. TiO_2 have been the most promising chemical for treating contaminants. In this study Tungsten trioxide (WO_3) and titanium dioxide (TiO_2) composite decorated on commercial available stainless steel mesh by chemical deposition and dip coating. The SEM images shows the clear chemical deposition on mesh. SEM images were taken before and after application of mesh. WO_3 and TiO_2 particles bounded with each other due to high temperature. And therefore attached on laser etching area while the chemical deposition was weak at the area which is without laser etching. The pollutants from waste water retained by laser etched area of mesh because of proper and uniform coating of TiO_2 and WO_3. The stainless steel mesh after laser etching and dip coating be recommended as perfect filter for car wash waste water treatment.

Key Words:- Car wash waste water, Titanium di oxide, tungstate tri oxide, poly aromatic hydrocarbons

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1IMPORTANCE OF WATER FOR LIFE

Water is cause of life on earth. As water is the one of basic needs of life. It is essential component for all reactions and processes like chemical or biological.it is an essential element in human body as well as for all other living organisms. For plants water is basic component of food factory. Water uses are more than any other compound. As water used more therefore its pollution rate is also high. Due to growing rate of population and its multiple usages it become scarce day by day. To overcome its shortage it is important to treat the water and makes it pollution free.

1.2WATER DISTRIBUTION ON EARTH

Water is universal solvent. It is rapidly distributed on earth. 96.5% water is in oceanic form, 0.93% is in ground water form, 0.0062% of water is in lakes, and 2.5% is fresh water among total water percentage present on earth. From 2.5% of fresh water 68% is in polar ice form, 0.037% is in atmospheric water form, 0.33% marshes form, 0.97% is in other ice forms. Water consumption is higher whether it is present in saline lakes, glaciers or as a soil moisture. Human being dependency on water is 90% and consumed high ratio of water in either forms (Bossu,2006). Water usage is high in industrial sector like agriculture, irrigation, chemical, pharmaceutical, and carwash industry.

1.3WATER AVAILABILITY IN PAKISTAN

Water is available in massive quantity on earth. It becomes shorter and unapproachable just because of its misuse. As water is life so its accessibility is necessary for basic purposes. As Pakistan is agriculture country so it depends on water resources for 90% of its food. Pakistan Water and Power Development authority give percentage of water table. That is 12.9% of canal area had a subsurface table of water between 0 to1.5 meters. Due to industrialization, economic activity, urbanization, increasing rate of population and water pollution cause scarcity of fresh water (Aijaz 1992).

Pakistan strategic Country published report of Environmental Assessment in 2006 that per capita water availability has decreased from 5000 to 1100 m^3y^{-1}. This shortage is due to water pollution and inaccessible of fresh water (SOE,2005). Fresh Water availability become less day by day up to 700 cubic meter per head (Pak-SCEA, 2006). Majority of cities in Pakistan used groundwater resource which become polluted by different contaminants.

Pakistan province Punjab has 80% fresh water as a ground water resource which is contaminated by industrial pollutants. 30% ground water in sondh is fresh all other resources are contaminated. In Balochistan and KPK most water resources are saline (Pak-SCEA, 2006).

1.4WATER USAGE IN INDUSTRY IN PAKISTAN

Water used in industries for different reactions and purposes. WWF presented a factsheet in 1993 that in Paksitan 23% water is consumed in industries this percentage is far greater

now.Industrial wastewater contained toxic elements, hazardous substances and different pollutants. There are many industries in Pakistan which discharged their waste water into nearby rivers, lakes and canals untreated. Like Faislabad, Karachi, Sialkot contribute major part in this water pollution (Saleemi, 1993).

1.5WATER USAGE IN CARWASH INDUSTRY

As water is a prime source of all chemical and biological reactions. In industry specifically in carwash industry it is a main source of washing automobiles. Carwash industry consume liters of gallons for washing vehicles and discharge this water untreated. Carwash industry now a days is major cause of water pollution (Bhatti.et.al, 2010).

Water is primary source of this business industry and need of every human being to wash their cars. In Belgium 100 liter of fresh water is consumed per car. It means 400 liters of fresh water can be consumed just for washing 400 cars (Bossu, 2006). In developed world 10 gallons of fresh water consumed per minute. It means that 50-60 gallons consumed in 5-6 minutes. And wastewater which discharged untreated is about 150-200 gallons (Green,2002).

1.6 REUSE OF CARWASH WASTEWATER

As population rate increases, public demand for water also increases. There are many areas worldwide which are unable to access fresh water even for drinking. On the other hand car washing activity consumes 1000 liter of fresh water just for washing purposes, and fresh water become wastewater. To overcome basic public needs it is necessary to treat and reuse carwash waste water for same purpose. Many researchers treated carwash waste water,

there are some conventional methods like gravity filtration, activated carbon adsorption, bag filtration and bag filtration and particulate filtration (Chelton,1978). And it was also treated by chemically and through deionizing method (Lahti, 2000). Some other techniques like oil water separator, and some filters were also projected (Odwani,2007). For treating carwash waste water some researchers proposed Membrane processes (Bossu,2007). Bossu also worked on nanofilater techniques for treating and reusing carwash waste water (Bossu,2008). While Panizza treated carwash waste water by anodic oxidation using lead dioxide and boron doped diamond anodes. She treated carwash waste water and reuse it for same purposes (Panizza, 2010).

1.7 ROLE OF NANOTECHNOLOGY IN TREATMENT OF WASTE WATER

Now a days it is very necessary to control water scarcity by saving water and reusing waste water. For overcoming water pollution problem one of emerging technique known as Nano technology is proposed to be best. Beside other treatment technologies like coagulation, flocculation, electrochemical methods and ion exchange method Nano technology has worldwide consideration for treating waste water (Chella, 2016).Many Nano materials and Nano particles are discover to date for treating waste water. Researchers obtained significant results after treating with Nano materials. There are many Nano materials like Nano metal oxides, Nano zero valent iron and cellulose nanomaterial were discovered for treating waste water (Venugopal, 2016).

1.8 ROLE OF NANOTECHNOLOGY IN TREATMENT OF CAR WASH WASTE WATER

Nano technology have applicability in almost all field of science. Nano technology due to its smaller size and high efficiency gained worldwide attention. And it is used to remediating environment. Due to its high efficiency many researchers used Nano materials for treating oily and greasy car wash waste water. In 2006 Bossu and Kindts treated car wash waste water with hydrophilic and hydrophobic Nano filtration membrane. From which waste water were passed on after 15 min rinsing and oil and grease from waste water were left on membrane (Bossu,2006). Recycling the carwash waste water by Nano filtration membranes result in less fouling (Karakulski, 2003). In 2015 Kiran explored that poly membrane made from cellulose acetate effectively remove the turbidity and COD of car wash waste water (Kiran,2015). Lau in 2013 examined that nano membrane with hydrophilic negative charged NF270 can significantly reject the total dissolved solids, suspended solids and COD from carwash waste water (Lau,2013). Alinne in 2017treating carwash waste water with micro and ultra-filtration membrane and found that these membranes have very good capacity to retain suspended solids and organic materials (Alinne,2017).

1.9 POLLUTANTS IN CARWASH WASTEWATER

Carwash industries consumed a lot of water for cleaning vehicles interiorly and exteriorly. Wastewater of carwash industries contain a lot of pollutants surfactants, detergents, petroleum, hydrofluoric acid, phosphates, ammonia, fats, volatile organic compounds, hydrocarbons, oil, grease and other chemicals which remain untreated and discharged into

rivers, streams and lakes. Due to pollutants present in carwash wastewater, turbidity, COD and BOD level of lakes and streams increases, which become hazardous for aquatic life.

The carwash waste water not only affect the quality of surface water but also destroy the ground water sources and make drinking water impure (Brasino,2007). These hazardous pollutants destroy the food chain also. Even increasing level of dissolved oxygen is fatal for aquatic species, and high toxic compounds which are found as causative agents for abnormalities in fish growth and behavior (Dengler, 2007)

Oil and greasy waste water contains many harmful hydro carbons including poly aromatic hydrocarbons (PAH). These hydrocarbons are carcinogenic in nature and cause cancer to living organism (Gryta, 2001). The untreated carwash waste water having PAH when enters into seas and nearby water bodies becoming part of aquatic food and ultimately pass on to the whole food chain (Milinkovitch, 2011). United state Environmental Protection agency (USEPA) and European Union (EU) declare these PAH as carcinogenic and toxic organic pollutant for all living organism (Khalil,2012) therefore it is necessary to treat carwash waste water before discharge into nearby water bodies.

1.10 SIGNIFICANCE OF STUDY

For removing these toxic PAH from carwash waste water my research study propose to treat the waste water by Titanium dioxide and tungsten trioxide composite pasted on mesh which act as a filter for these Poly aromatic hydrocarbon.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 DIFFERENT TREATMENT TECHNOLOGIES USED FOR CARWASH WASTEWATER

As carwash wastewater is one major cause of water pollution, and due to Increasing scarcity, competition, and inaccessibility of water all over the world it is necessary to treat reuse and conserve the water. Developed countries have already legislative to reuse treated water from carwash stations but there is need for developing countries to become conscious about wasted fresh water. It is time now for developing countries to plan for reuse of wastewater.

As water is life so it is required for different purposes but due to shortage of water and misuse of fresh water rural areas didn't approach to water even for sanitation purposes. To fulfill these basic requirements it is necessary to conserve the water by saving it or treated it. After treatment it would be able to reuse. To approach this facility and overcome water pollution issue and to conserve water many countries has used different techniques for the treatment of carwash wastewater.

2.1.1 ELECTROCHEMICAL METHOD BY ANODIC OXIDITATION

Panizza in 2010 used electrochemical method by anodic oxidation with diamond and lead dioxide anodes. The lead dioxide and born doped diamond anodes used for car wash waste water treatment. These anodes were fixed in an electrolytic flow cell. Due to Galvano static

electrolysis COD was effectively removed from carwash waste water. High level of COD is due to oil and grease present in waste water. It was found that COD removal increases as applied current and flow rate rising (Panizza, 2010). But in this experiment energy consumption was too high that is 1A to 3A so it is not used practically and commercially.

2.1.2 ELECTROCHEMICAL COAGULATION METHOD

From Panizza's previous work in which only anodic oxidation method was used. In this work Panizza et.al used integrated electrochemical coagulation and electrochemical oxidation method by making it twostep process. In electrochemical coagulation iron anodes were used and in electrochemical oxidation boron-doped diamond anode were used for the carwash waste water treatment. From this method COD removal rate was 75% with low energy consumption. While the complete removal of COD was attained after two step process (Panizza, 2010). In comparison with previous work energy consumption for two step process is low than only anodic oxidation method. From this twostep process complete COD removal was attained up to 97% in 100 min of treatment by using only 12 kWh. So this method could be applied in carwash service stations.

2.1.3 MICRO AND ULTRAFILTRATION METHOD

In 2017 Alinne investigated Micro and ultrafiltration hydrophilic membranes for carwash wastewater treatment. Carwash waste water has high turbidity due to total solids present in it, in both organic and inorganic form. Initially car wash waste water has 85 NTU turbidity, total organic and inorganic carbon were 4.1 and 58 mg/L respectively. In addition with hollow fiber polyetherimide membranes these membranes showed good retention for solids, organic matter, turbidity and COD. After treatment total organic and inorganic

carbon decreases up to 2.7 and 35.4 mg/L respectively. And Turbidity removal rate were up to 98.6%. Due to effective reduction of parameter make the micro and ultra-membranous technology suitable for waste water treatment. (Alinne,2017).

2.1.4 INTEGRATED TREATMENT WITH CHEMICAL OXIDATION

In 2011 Bhatti.et.al performed experiment and investigated that car wash waste water contains petroleum, hydrofluoric acid, ammonium bifluoride products, paint residues, rubber, phosphates, oil, grease and volatile organic compounds (VOCs). Two step process were designed, in primary step extra scum, oil and grease were removed by aeration. And due to coagulation by alum 93% and 97% reduction of COD and turbidity respectively was observed. While during secondary treatment hydrogen peroxide was used, which further 71% and 83% COD and turbidity respectively were removed. This integrated treatment system effectively treat the oil content up to 96%. Due to reduction of oil contents, turbidity and COD this integrated treatment system were recommended to use on commercial scale (Bhatti, 2011).

2.1.5 ELECTROOXIDATION WITH FENTON

In 2018 Soliu and his colleagues investigated alternative technique that is electrochemical advanced oxidation process. Electro oxidation with hydrogen peroxide and electro-Fenton process used for removal of anionic surfactants and organic matters from car wash waste water. The experiment was performed on real car wash waste water at current of 500mA. After 6h of electrolysis COD removal and total decay of organic matter were observed.

Electrochemical treatment technology found to be a good alternative for decaying of organic matter and anionic surfactants present in carwash waste water. Some other organic compounds like carboxylic acids, oxalic, malonic, formic, glyoxylic, and acetic acid were identified as a byproduct at the end of reaction (Soliu,2018).

2.1.6 CELLULOSE ACETATE METHOD

In 2004 Hamada proposed a cellulose acetate, hollow fiber ultrafiltration membrane with flocculation and activated carbon treatment. Experiement was done with membrane area of 32 m^2 and 48 m^2 with pressure of membrane 20 kPa. This method was used with cellulose acetate for more than 6 months. And COD, BOD was not effectively decreased but its oil and grease components which forming sludge were treated (Hammada, 2004).

2.1.7 COMPARISON OF BUS WASHING COMPANIES

In 2010 in Brazil Almedia compared three bus washing system for analysis of water consumption. On daily working days 15,064 vehicles were washed and yearly transport companies consumed 2,200,000 m^3 of fresh water. Two bus washing companies used the washing system which is conventional and common that after washing effluent can be discharged into public network or near water bodies. While the third company used rainwater catchment and treatment plant system for reusing purposes. This method was environment friendly and cost effective. Therefore it was suggested that installation of treatment system within the companies showed environmental friendly outcomes as well as recycle the waste water for reuse purposes (Almeida et al. 2010).

2.1.8 FLOCULATION COLUMN FLOTATION

Zaneti in 2011 proposed a technique made up of flocculation-column flotation, sand filtration and at last chlorination. In this study waste water was treated by flocculation method and at the end its chlorination was done. By which in waste water fecal count and total coliforms were analyzed both in waste water and after treatment of waste water. And its cost analysis showed that 8 weeks were required to update and set this flocculation system for washing 30 cars per day. This technique was effective enough to be applicable as commercially (Zaneti et al. 2011).

2.1.9 MEMBRANE BIOREACTOR METHOD

In 2016 Ida and et.al investigated that many membrane technologies were proposed and effectively remove COD, BOD but car wash waste water also contain organic and inorganic solids which are contaminants. They proposed Membrane bioreactor ozonation technique which effectively treated the suspended solids along with COD and turbidity. Ozonation was method which effectively treated particular pollutants. Due to high efficiency removal rate of COD and suspended solids up to 97 and 98% respectively this technique was recommended for reusing purposes. From ozonation and coagulation method membrane bioreactor technique is good option for using in car wash industries for treating waste water and reuse it on same service station (Ida, 2016).

2.1.10 ELECTROCOAGULATIONMETHOD

Z.Beril in 2017 proposed the study on electrochemical treatment. Car wash waste water was treated with electrochemically using electrocoagulation process with Fe and Al electrodes. In this study COD, oil-grease, and chloride removal were detected. It was found that at pH 8 and current density 3mA for Fe and at pH 6 current density 1 mA for Al electrodes removal efficiency for COD was 88%, oil-grease was 90% removed and chlorides was 50% removed for Fe. While COD was removed 88%, oil-grease was removed 68% and chlorides was removed 33% for Al electrodes. After the treatment sludge was produced which was determined by FTIR spectroscopy and zeta potential for both electrodes. Due to efficient removal of COD and oil-grease pollutants this technology was recommended for car wash waste water treatment (Z.Beril, 2017).

2.1.11 NANOFILTRATION MEMBRANE METHOD

In 2006 Bossu used nanofiltration membrane technique for treating car wash waste water in Belgium. In this study the hydrophilic (NF270) and a hydrophobic (NFPES10) membrane were used. For this experiment waste water was collected at two different stages These membranes were used as comparison and found that hydrophilic membrane NF270 show high water permeability and retain organic and inorganic components up to 95%. Nanofiltration membrane immediately should be cleaned after filtration. Physical parameters were observed after treatment like BOD, COD and conductivity which were effectively treated (Boussu et al. 2006)

2.2 INTRODUCTION TO NANOTECHNOLOGY

Different researchers used different membranous separation techniques such as microfiltration, reverse osmosis, ultra-filtration, and electrochemical techniques for treating car wash waste water. These techniques were efficient for removing physical parameters like COD, BOD, turbidity, organic and inorganic components but none of them address the oil and greasy component of waste water. Car wash waste water contains oil and grease in high amount which is essential to remove. Now a days Nanotechnology is emerging technology for treating oil and grease from different waste waters.

2.2.1 APPLICATION OF NANOMATERIALS

Chella and et.al in 2016 reviewed the literature that nanomaterials have wide variety of application for treating waste water. Organic/inorganic pollutants were effectively removed by nanomaterials. Nanotechnology have high potential to use as an alternative treatment technology to conventional treatment technologies. Different nanomaterials have adsorption properties, some are used as a chemical photocatalytic activity. Nanomaterials are commercially not available but can be prepared accordingly and used for different applications (Chella, 2016).

2.2.2APPLICATION OF NANO COMPOSITES

Liuhua in 2015 make Fe_3O_4/PS composites and experiments were designed as a comparison to analyze magnetic properties of composites and oil absorption on composite

surface. These Fe_3O_4 composites combined with unsinked, highly hydrophobic and superleophilc in nature. The Fe_3O_4 nano composite absorb diesel oil and other organic solvents present in waste water. From this study it is shown that composite of nanoparticles effectively treated the waste water contaminants especially oil and grease. And recommended for safe use and are environment friendly (Liuhua,2015).

2.2.3 APPLICATIO OF TITANIUM DIOXIDE

Bo Wang in 2018 coated the stainless steel mesh with Tungsten trioxide (WO_3) and titanium dioxide (TiO_2). This chemical deposition on mesh with Nano materials were used to separate the oil water emulsion. Emulsion were prepared in laboratory and tested for oil treatment. The prepared membrane have high efficiency of oil removal. Due to WO_3/TiO_2

Coatings oil was adhere on the surface of mesh. It can be recommended that the stainless steel mesh fabricated with Titanium and tungstate composites used for oily water for oil water separation (Bo Wang, 2018).

2.3 POLY AROMATIC HYDROCARBONS

Nano particles effectively used for treating oil water separation. The carwash waste water contains many obnoxious pollutants including oil and grease and many Poly aromatic hydrocarbons. Poly aromatic hydrocarbons (PAHs) are carcinogenic group of organic compounds which are present in high quantity in untreated car wash waste water (CWWW). When CW WW discharged into nearby lakes these PAHs entered directly into the aquatic environment and disturbs whole food chain. Zahir and Sardar in 2017 investigates these PAHs in Car wash waste water near Peshawar. This study compares the

amount of PAHs present in low vehicle wash station and high vehicle wash stations. Both pyrogenic and petro genic sources were observed (Zahir, 2017).

Table:- 1 PAH diagonastic Ration (Zahir.2017)

PAHs diagnostic ratio			This study		
	Pyrogenic origin	Petrogenic origin	LVWS	HVWS	Sources
Ph/Ant	<10	>15	1.00	1.87	Pyrogenic
Chr/BaA	<1	>1	1.08	1.53	Petrogenic
Flu/Pyr	>1	<1	1.04	1.16	Pyrogenic
Flu/(Flu + Pyr)	>0.5	<0.5	0.51	0.54	Pyrogenic
LMW/HMW	<1	>1	3.83	4.97	Petrogenic

2.3.1 STRUCTURES OF POLY AROMATIC HYDROCARBONS

According to Poly aromatic Hydrocarbons (PAHs) diagnostic ratio pyrogenic compounds are phenanthrene/anthracene,fluoranthene,pyrene, and fluoranthene and petrogenic compounds are chrysene/ benz(a)anthracene. These pyrogenic and petrogenic compounds have 2 rings, 3 rings, 4 rings and 5 rings structure. According to their ring structures they have different melting and boiling points (Abiodun).

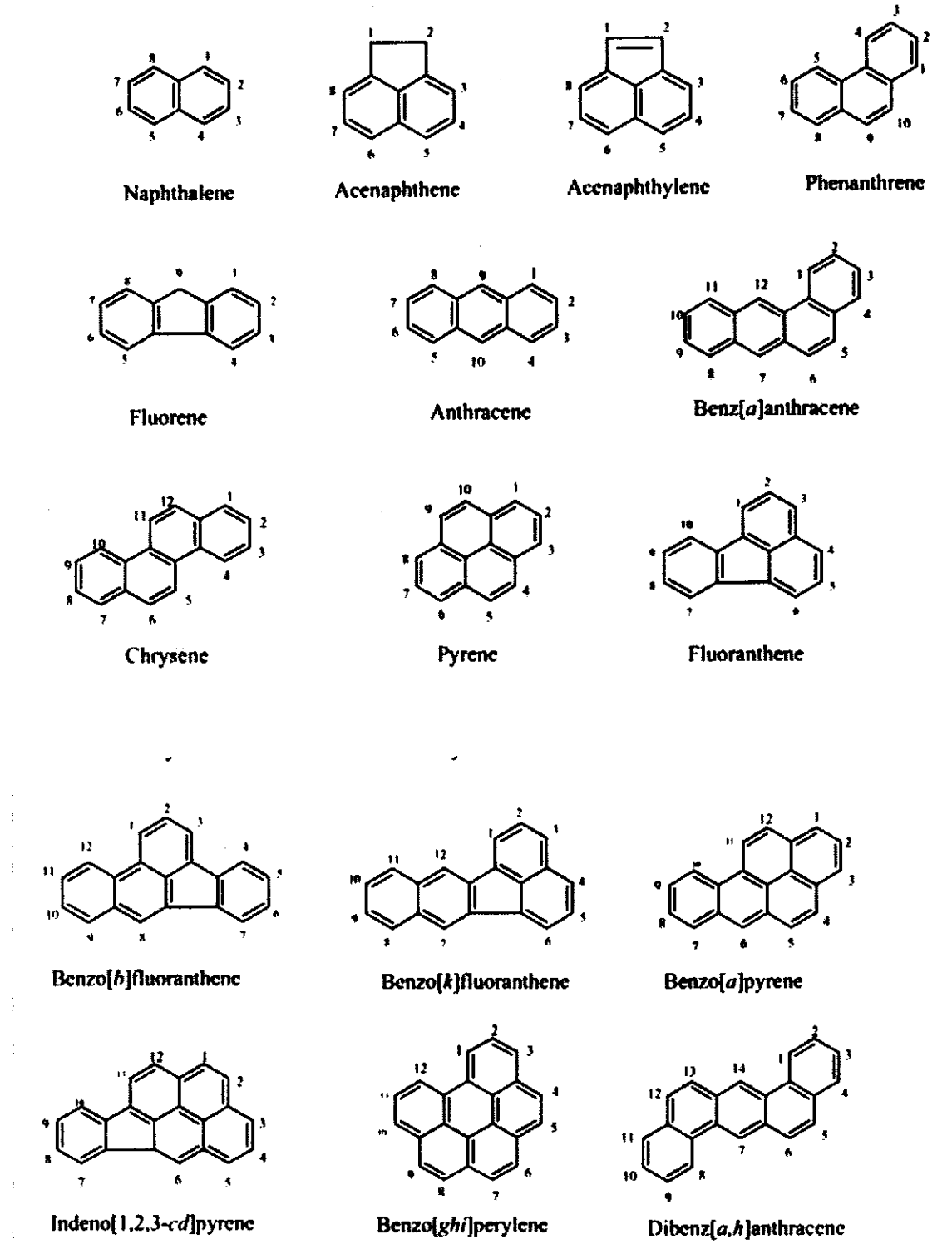


Fig:- 1 Structures of PAHs (Abiodun)

2.3.2 PYSIOCHEMICAL PROPERTIES OF POLYAROMATIC HYDROCARBONS

Table:- 2 Physiochemical properties of PAHs (Abiodun)

PAHs	Chemical formula	Molecular weight (g/mol)	CAS number	Ring number	Melting point (°C)	Boiling point (°C)
Naphthalene	$C_{10}H_8$	128	91-20-3	2	80.2	218
Acenaphthylene	$C_{12}H_8$	152	208-96-8	3	92.5	280
Acenaphthene	$C_{12}H_{10}$	152	83-32-9	3	93.4	279
Fluorene	$C_{13}H_{10}$	166	86-73-7	3	115	295
Phenanthrene	$C_{14}H_{10}$	178	85-01-8	3	99.2	340
Anthracene	$C_{14}H_{10}$	178	120-12-7	3	215	340
Fluoranthene	$C_{16}H_{10}$	202	206-44-0	4	108	384
Pyrene	$C_{16}H_{10}$	202	129-00-0	4	151	404
Benzo[a]anthracene	$C_{18}H_{12}$	228	56-55-3	4	167	435
Chrysene	$C_{18}H_{12}$	228	218-01-9	4	258	448
Benzo[b] fluoranthene	$C_{20}H_{12}$	252	205-99-2	5	168	481
Benzo[k] fluoranthene	$C_{20}H_{12}$	252	207-08-9	5	217	480
Benzo[a]pyrene	$C_{20}H_{12}$	252	50-32-8	5	177	495
Dibenzo[a,h]	$C_{22}H_{14}$	278	53-70-3	5	270	524
Indeno[1,2,3-cd] pyrene	$C_{22}H_{12}$	276	193-39-5	6	164	536
Benzo[g,h,i]perylene	$C_{22}H_{12}$	276	191-24-2	6	278	550

2.3.3 HEALTH EFFECTS OF POLY AROMATIC HYDROCARBONS

Zahir and et.al in 2017 investigated 16 PAHs in car wash waste water in Peshawar district. PAHs were released from low vehicle and from high vehicles in high amount. PAHs released in high quantity can exceed their limits (Zahir, 2017).

Table:-3 PAHs quantity from low vehicle and high vehicle

PAHs	LV	HV
Nap	204	808
Acy	19.38	37.62
Ace	13.03	47.09
Fl	16.28	52.88
Ph	11.29	65.35
Ant	11.27	34.89
Flu	11.43	27.94
Pyr	10.99	24.00
BaA	8.55	15.25
Chr	9.27	24.83
BbF	5.17	31.87
BkF	6.88	26.20
BaP	3.54	21.57
D[*ah*]A	8.47	11.02
InP	3.96	12.60
B[*ghi*]P	3.66	15.11
∑16PAHs	347	1256

Poly aromatic hydrocarbons are carcinogenic in nature when they release untreated they create hazardous effects on aquatic environment and enter into food chain. PAHs interacts with living beings from three pathways dermal, inhalation and ingestions and cause toxicity (Neff, 1979; Weast,1968). PAHs compounds also fix to DNA of living beings can interrupts the enzyme functioning, and cause cell damage (Orecchio, 2010).

CHAPTER 3

MATERIALS AND METHODS

3.1 BACKGROUND OF AREA

For this study service station from G 13 Islamabad were selected. The area is very rush area and included in urban side of Islamabad. Islamabad is a region of mixed communities. The ratio of urban population is continuously increases since last few years. And this population rate is exceeding due to its natural beauty and pleasant season over the year, most tribes can migrate from different regions of Pakistan to Islamabad. By increasing population rate at Islamabad also increasing the competitions among resources consumption. Which enhance the pollution rate in this beautiful city. Water pollution is one of major problem of Islamabad because water is universal solvent and due to water pollution clean water accessibility is not difficult but impossible for the local population of Islamabad.

As water is consumed in all aspects of life, for domestic purposes, for agricultural purposes, irrigation and also in industries especially carwash industries consume a lot of water because its main purposes is cleaning and washing. So a lot of fresh water is consumed in service stations which become hazardous and discharge untreated in lakes and streams. For conservation of water it is necessary to treat that wastewater and reuse it for same purpose. By treating and reusing that wastewater we can conserve almost 1000 gallons of water daily from carwash industry.

3.2 SITE ASSESMENT

The service station named Alfalah Service station was selected from G 13 area Islamabad for sampling, because of its location and working hours. Service station operated via three bays for washing cars at one time. The time taken washing one car is 30 minutes. At

carwash station hand pipes are used with hydraulic lifting system for bracing the car. The washing materials were detergents and shampoos, and for greasing waste mobile oil are used. Daily almost twenty to thirty cars are washed at this station only. There is one storage tank where fresh water is stored and untreated wastewater is discharge into sewage lines or channels.

3.3 SAMPLE COLLECTION

Samples were collected in plastic containers from service station, containers were cleaned with distilled water twice before sample collection. Samples were collected during January and brought to laboratory for analysis. Before treating and analysis of that wastewater sample was remain for 3 hours for natural sedimentation and aeration.

Fig 2: Sampling of car wash waste water

3.4 LASER ETCHING OF MESH

Stainless steel mesh SSM 304 was cut into 52mm diameter and etched by laser machine, from National Institute of Lasers and Optronics (Nilop). The laser etching was done on mesh with wavelength of 1064nm, it was twice exposed to 1000 shots of laser with exposure time of 10 Hz and 330 J/P energy.

During the process of laser etching, the cover layer of material is vaporized, producing little depth. The process is like cutting, except only the top layer is vaporized. Laser etching works well on materials with two or more layers, like coated metals, stainless steel materials and anodized aluminum (trotec, laser marking, etching and engraving).

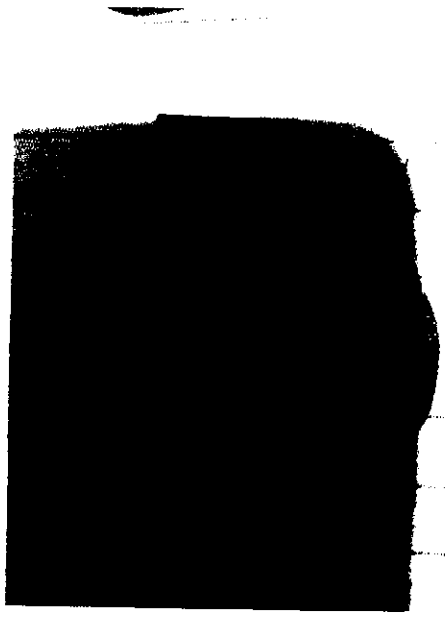


Fig 3: Laser etching of Mesh

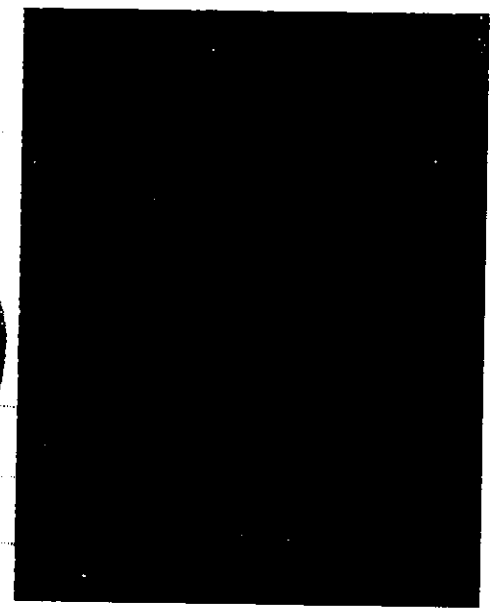


Fig 4: Laser etched area

3.5 PREPARATION FOR COATING A MESH

After Laser etching the stainless steel mesh was coated with different solutions. Firstly, sulfuric acid was added to the water with a solution of 25% concentration and the mesh was immersed in it for 5 min at 40 °C. Then, it was purged with alcohol and dried in the oven for 10 min at 60 °C. Secondly, Sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) 4.5g, Sodium citrate dehydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) 3.6g and Ammonium Sulfate ($(NH_4)2.SO_4$) 2.7g were dissolved in distilled water (100 mL) into A solution. After 2 h later, 20 mL of A solution was poured into 250 mL beaker and H2SO4 (1 mL), H2O2 (0.5 mL), N2H4 (0.2 mL) were added in it respectively under stirring, this was called B solution. The pretreated SSM 304 was immersed in B solution at 40 °C in the thermostat water bath for one hour and dried in the oven for 30 min at 60 °C after rinsing with deionized water. Thirdly, Titanium isopropoxide ($C_{12}H_{28}O_4Ti$) 4ml, Ethanol (C_2H_6O) 14.8ml, Acetyl Acetone ($C_5H_8O_2$) 0.8ml and Distilled Water 0.4 ml were mixed into C solution under quickly stirring for 5 h at room temperature, and then set aside for one day before using. The deposited SSM 304 was dip-coated in C solution for 5 min and was lifted vertically, then it was dried in the oven for 20 min at 80 °C.

During the process of making solutions, there were some chemical reactions occur. Solution A was transparent and WO_4^{2-} was present in A solution. As H_2SO_4 was added in A Solution it produced yellow precipitate known as tungstic acid. Which proceed following reaction.

$$WO_4^{2-} + 2H^+ = H_2WO_4 \qquad \text{eq 1}$$

Due to tungstic acid, Solution lack its deposition capability. But when H_2O_2 and reductive agent N_2H_4 were added in it under stirring then solution become clear and gain strong capacity of deposition. Actually tungsten was changing its oxidation state from +8 to +6.

$$H_2O_2+H_2WO_4= 2H^+ + WO_5^{-2} + H_2O \qquad \text{eq 2}$$

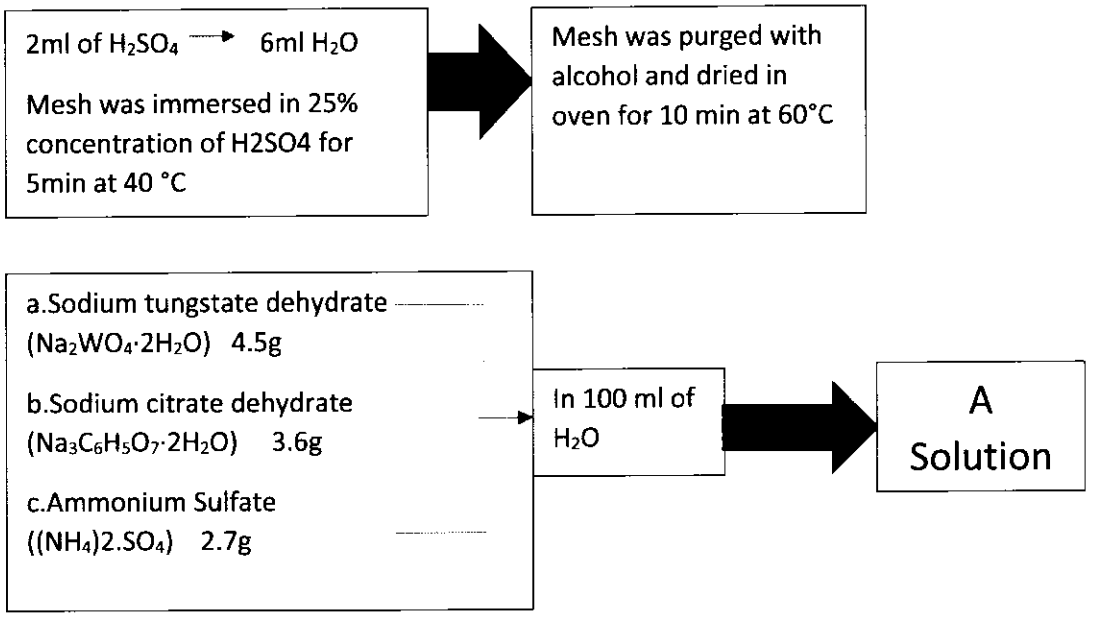
After this reaction stainless steel mesh were immersed in it for 1 hour and Fe changes its state

$$Fe=Fe^{+2} +2e^- \qquad \text{eq 3}$$

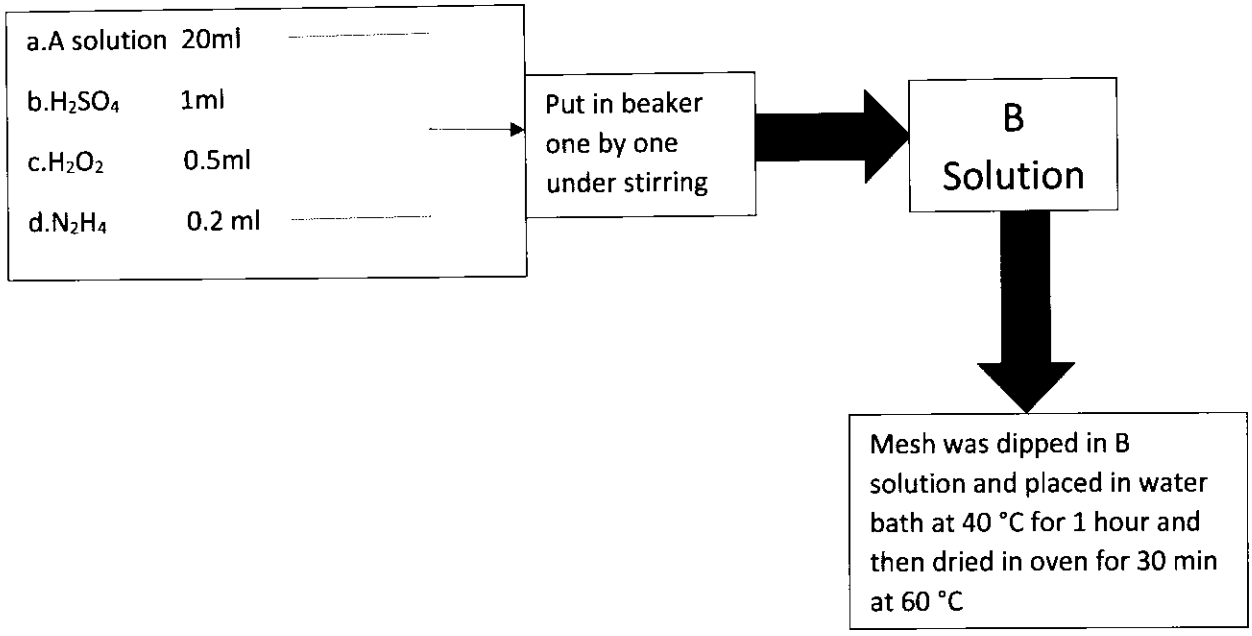
Then the overall reaction occurs like this

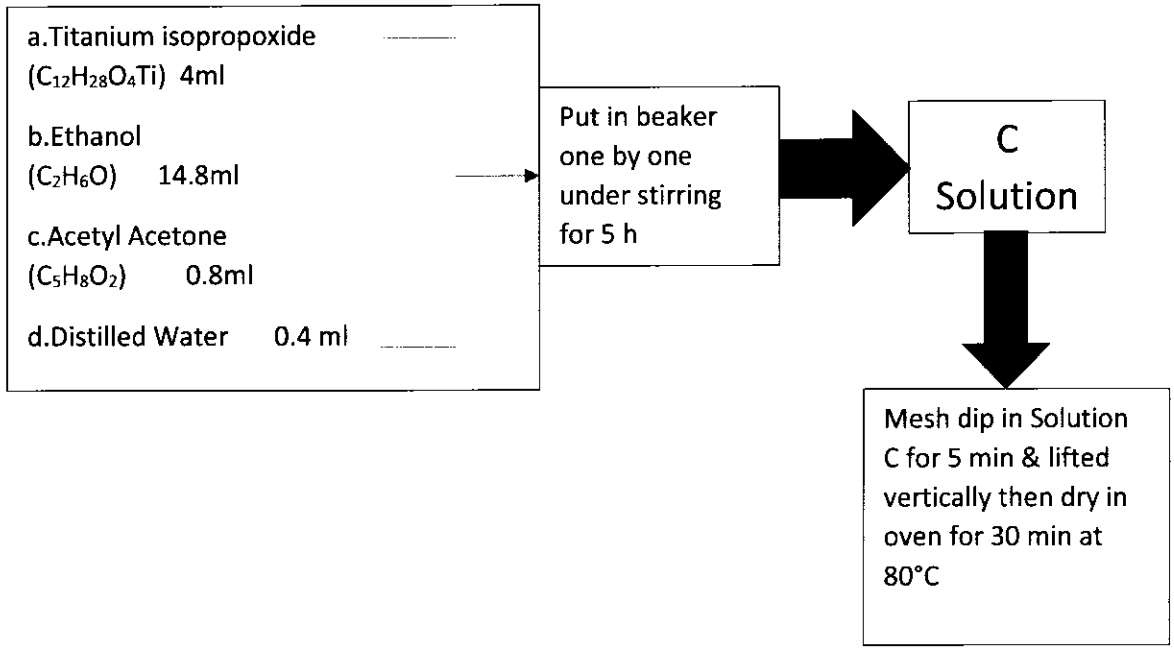
$$Fe + N_2H_4 + 4H^+ + WO_5^{-2} = Fe^{+2} + N_2 + WO_3 + 2H_2O +2H_2 \qquad \text{eq 4}$$

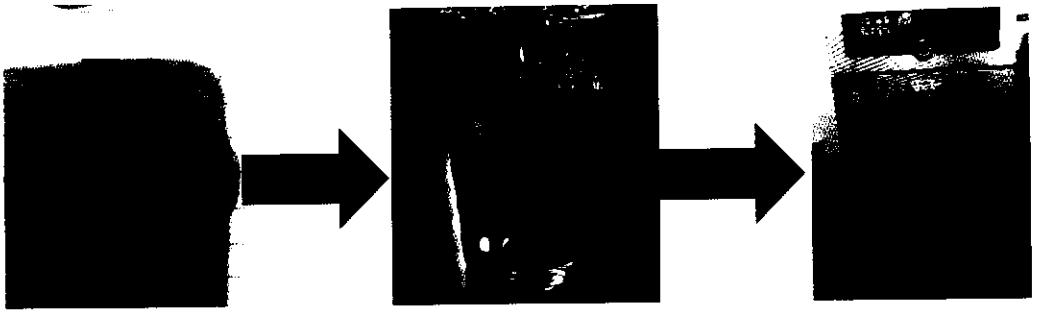
This reaction shows that WO_5^{-2} changed into tungsten oxide, which became able to deposit on mesh and stick there (Bo Wang, 2018).



After 2 hours







Laser etched Mesh

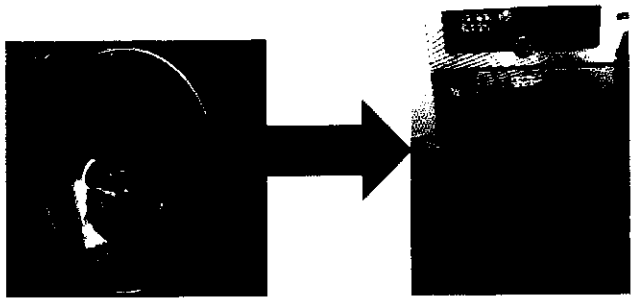
Dipped in 25% H_2SO_4 Solution

Drying in Oven

Fig 5: Mesh

Fig 6: Dipped in solution

Fig 7: Drying in oven

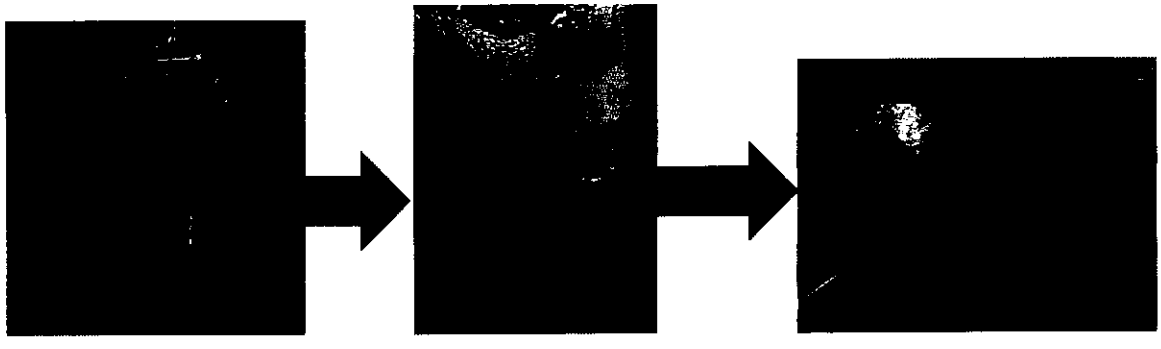


Purged with alcohol

Dry in Oven

Fig 8: Purging

Fig 9: Drying in oven



Solution A

Mesh dipped in Solution B

Placed in Water Bath

Fig 10: Solution A

Fig 11: Dipping in Sol B

Fig 12: Water bath

Again Dry in Oven

Fig 13: Drying oven

Solution C

Fig 14: Sol C

Mesh dipped in Solution C

Fig 15: Dipping in sol C

Lifted vertically

Fig 16: Lifted vertically

Again Dry in Oven

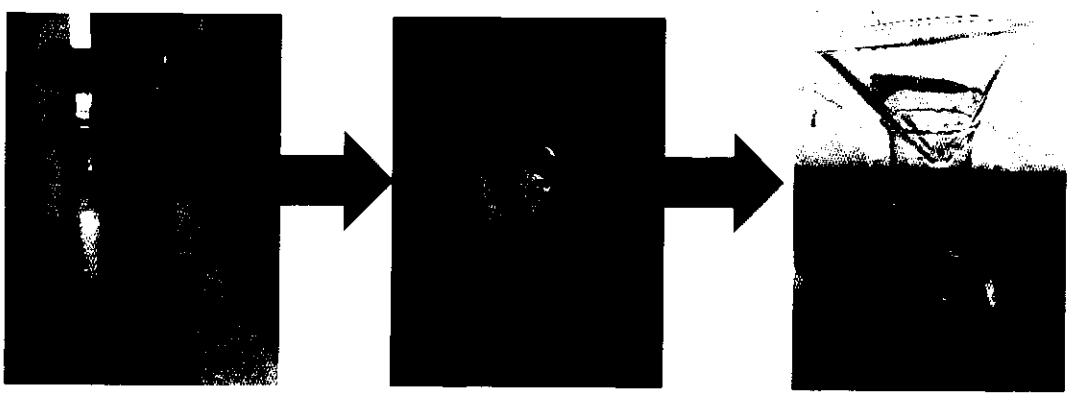
Fig 17: Dry oven

3.6 SCANNING ELECTRON MICROSCOPE (SEM) OF SSM 304 MESH

After preparation of coated stainless steel mesh it was sent for SEM. Coated mesh SEM was done before using mesh and after using mesh. And taken as comparison that after treatment waste material deposited on mesh. The scanning was done by Scanning electron microscope model number, KYKY EM6900.

3.7APPLICATION ON CARWASH WASTE WATER

The car wash wastewater was brought to laboratory and after 3h sedimentation it was passed from coated mesh. Mesh was lifted vertically and samples were passed from mesh turn by turn and collected separately.



Waste water Sample

Fig 18: WW Sample

Coated mesh in funnel

Fig 19: Mesh in funnel

Passing Waste Water From Mesh

Fig 20: Passing WW

Passing Waste Water From Mesh

Fig 21: WW from Mesh

Treated Water collected separately

Fig 22: Treated Water

3.8 DETECTION BY ULTRAVIOLET

UV detection method was used for detection of aromatic hydrocarbons. Before treating waste water and after treatment, water was collected and detected on UV for analysis. As it was water so its solvent were water and run against distilled water in UV spectra.

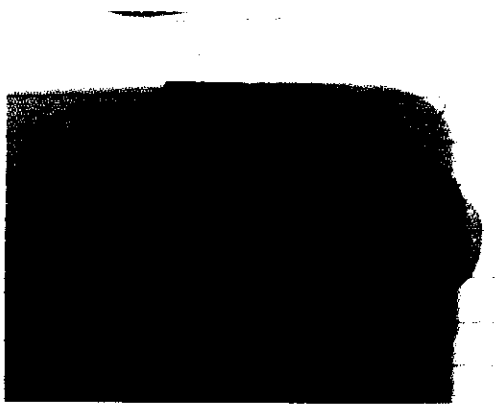
CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

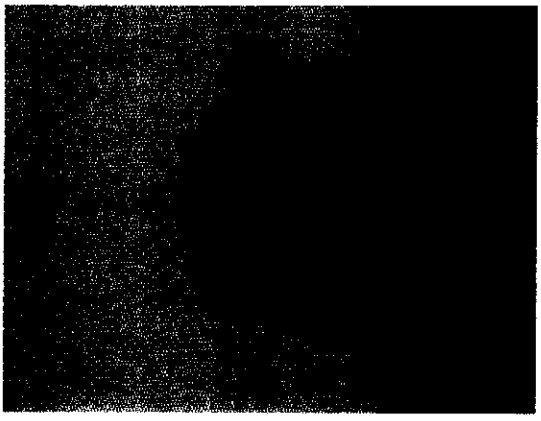
The present study was on preparation of stainless steel mesh by Nano composites. Nano composites tungsten trioxide and titanium dioxide was prepared and coated on SSM 304 stainless steel mesh. The coated mesh were used for treating waste water of car wash. Carwash waste water contains many pollutants like surfactants, detergents, petroleum, hydrofluoric acid, phosphates, ammonia, fats, volatile organic compounds, oil, grease and other chemicals which increase COD and BOD of waste water.

The stainless steel mesh were coated with TiO_2/WO_3 composites. And changes happening on mesh were clearly visible by naked eye. Mesh was first coated with 25% H_2SO_4 and dried in oven at 60 °C. Then it was coated with composites and changes were shown clearly.



Before Coating

Fig 23: Before Coating



After Coating

Fig 24: After coating

4.1 SCANNING ELECTRON MICROSCOPE (SEM)

The scanning electron microscopy develops images of specific sample after sampling by using a focused beam of electrons. Various signals are produced when the electrons of microscope interact with electrons in the sample. Microscope detects the electrons that contain information about the sample's surface topography and composition. The Fig shows the stainless steel mesh in original view. In original view mesh surface is seen smooth before chemical deposition.

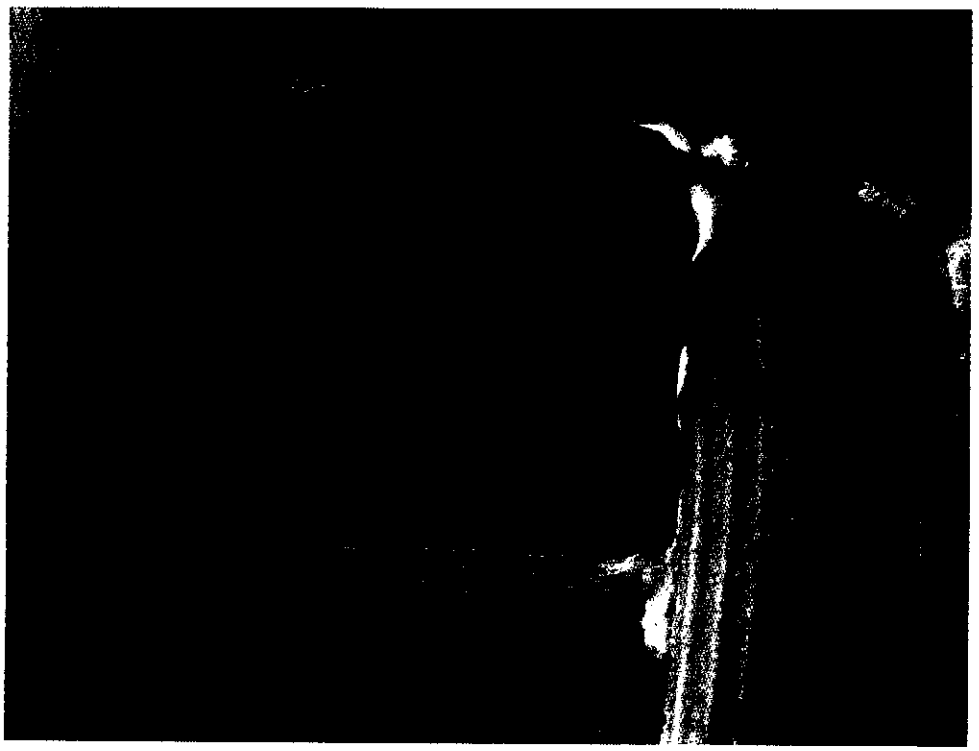


Fig 25: SEM image of mesh before deposition

4.2 SEM AFTER DEPOSITION

The coated mesh then imaged by SEM. The Fig shows the coated mesh image. It clearly indicates that the changes occur in morphology of mesh after process. Dipping of mesh in composite solutions for different timings, properly deposited TiO_2/WO_3 on surface of mesh (Bo Wang, 2018). After the chemical deposition mesh surface become rough. Actually the tungsten particles properly deposited on inner surface of mesh and covered all the spaces.

Fig 26: a. SEM after deposition on laser etched area

The area which properly deposited with composites are etched area by laser marking machine. There are different size particles of titanium and tungsten, like micro and nano sized which are all uniformly deposited on surface of mesh. Fig shows that topography of mesh which is uniformly dispersed by composite. The reason of behind smooth dispersion

of composite on mesh is that the tungsten trioxide fully bounded by titanium dioxide at given temperature (Bo Wang, 2018). The uniformity of composite dispersion can reduced the smoothness of mesh.

Fig 27: b. SEM after deposition on Laser etched area

4.3 DEPOSITION ON WITHOUT LASER ETCHED AREA

The area which was not etched by laser marking machine show some different image than laser etching. Without laser etching the composite deposition were not proper and uniform. The area on mesh which was etched with laser have strong deposition than without etching area.

Fig 28: SEM of deposition without laser etching area

4.4 APPLICATION

After efficient deposition on stainless steel mesh its application was done in laboratory. The collected waste water from service station was passed through from stainless steel mesh. After 3 hours of sedimentation the waste water was passed through slowly. After passing, the treated water was collected in separate coil. After application again SEM image of stainless steel mesh were analyzed.

The results shows that pollutant particles stuck on mesh in a long chain. The stainless steel mesh retain the pollutants due to uniform dispersion of tungstate particles. The contaminants stuck on area of mesh which were laser etched and it's nearby in a form of long chain.

Fig29: a. SEM image of Mesh (laser etched area) treatment of CWWW

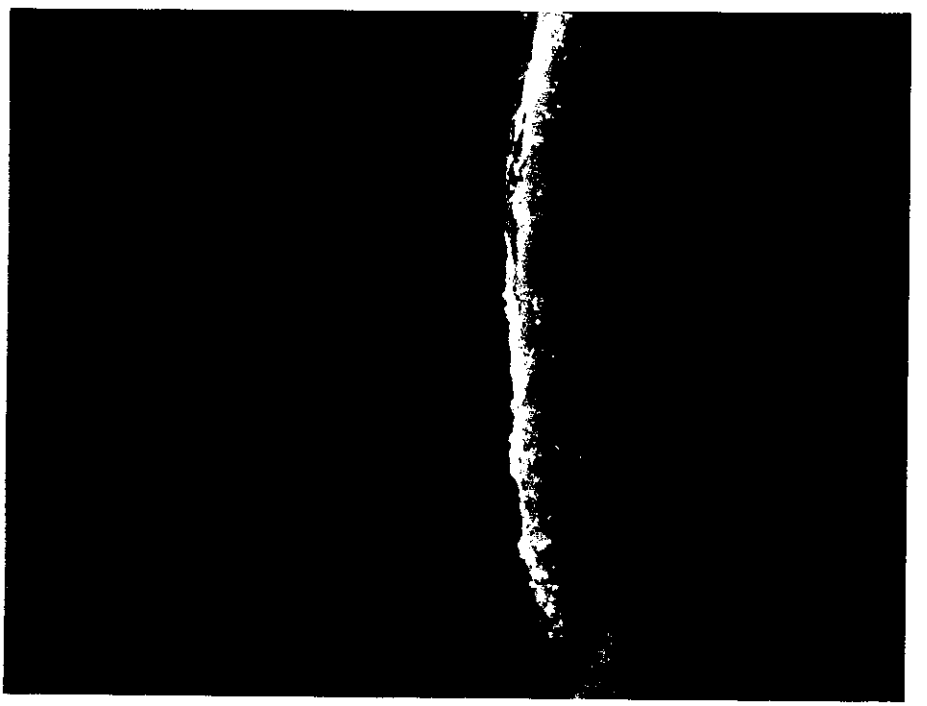


Fig 30: b SEM image of Mesh (laser etched area) treatment of CWWW

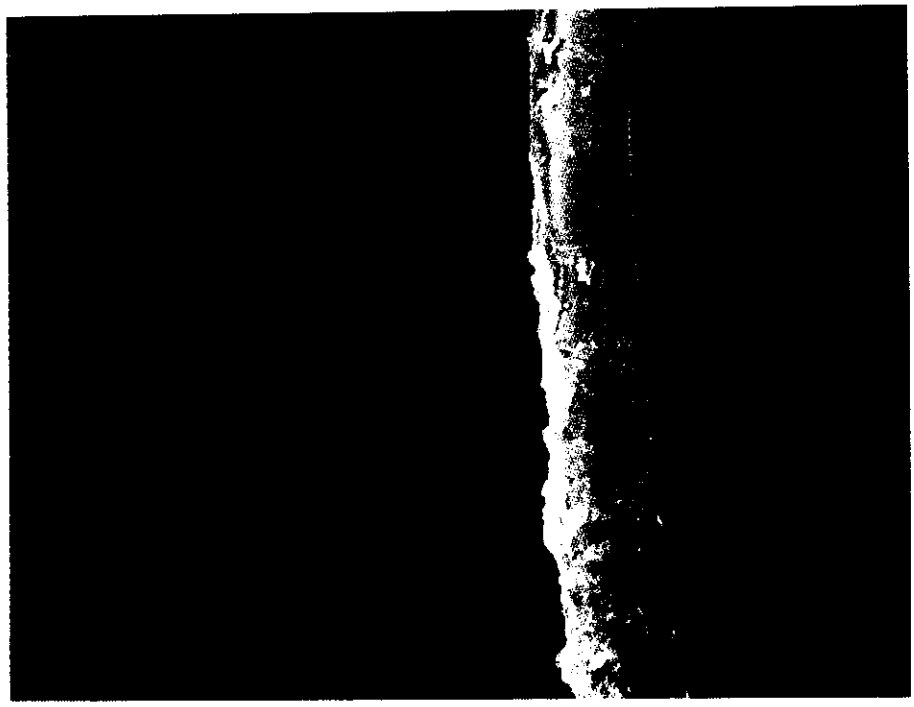


Fig 31: c SEM image of Mesh (laser etched area) treatment of CWWW

The area on mesh which were without laser etching and have not uniform deposition on it are unable to retain pollutants on it. The contaminants were not retain on it because it doesn't have uniform deposition of tungstate and titanium composites. Therefore it not shows proper retention for pollutants.

Fig 32: a. SEM image of Mesh (without laser etched area) treatment of CWWW

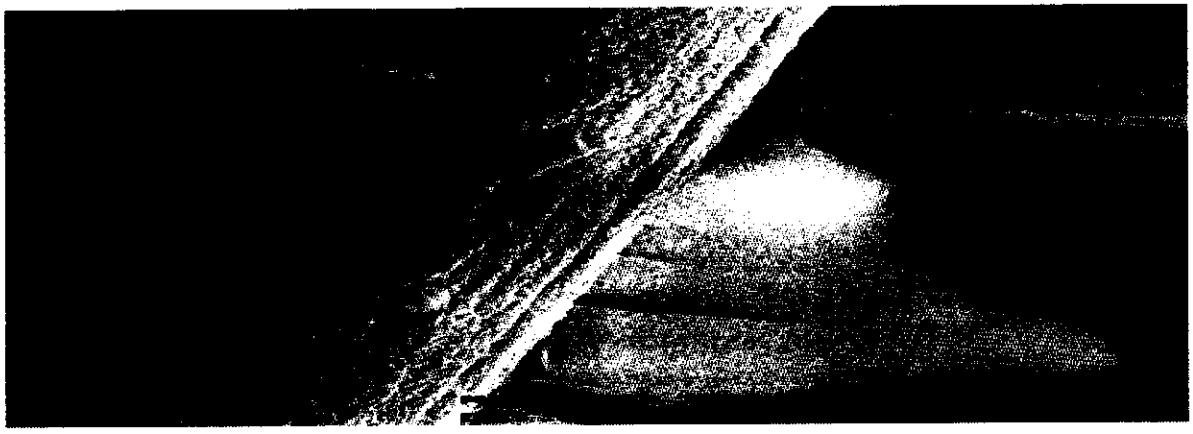


Fig 33: b SEM image of Mesh (without laser etched area) treatment of CWWW

4.5 PAHs DETECTION

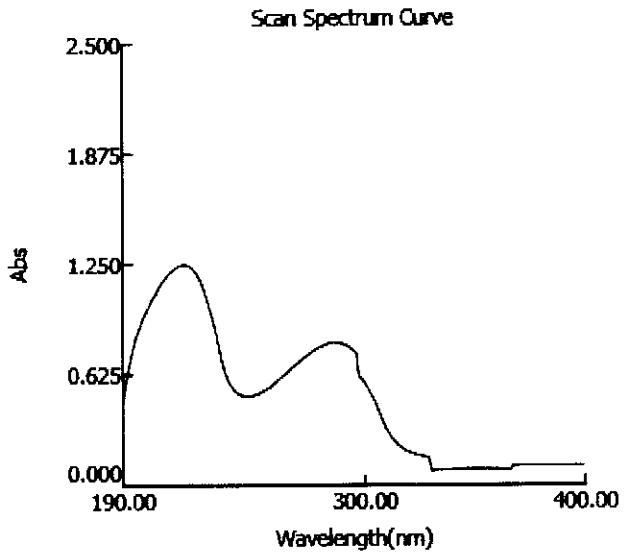


Fig34: Polyaromatic hydrocarbons

The waste water were analyzed on UV Visible spectrophotometer for identification of Polyaromatic hydrocarbons. The results clearly indicate that PAHs obtained on different wavelength that is naphthalene indicated on 220 nm, 2methylnapthalene on 276 nm, fluorine on 207 nm and acenapthene on 249 nm, 2,3 dimethylnapthalene on 276 nm, flouranthene on 356, pyrene on 391, 2-3 benzoflourene on 202, chrysene on 268nm. These PAHs are double and triple ring structures (Macromini, 1987). The highest peak shown between 190 to 220 nm which indicates that naphthalene, acenapthene have larger absorbance that is between 0.625- 1.250. And smallest absorbance shown between 300 to 400nm. It might be flouranthene and pyrene which show absorbs between 0.001 to 0.005.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this study WO3/TiO2 were firmly coated on SSM 304 stainless steel mesh by chemical deposition and dip coating. Chemical deposition of Tungstate and titanium was occurred in micro and Nano size particle. Chemicals particles were adhere on mesh surface due to strong bonding between tungstate and titanium at high temperature. And results shows that laser etched area on mesh have strong deposition of tungstate and titanium particles while the area without laser etching didn't show strong deposition. Laser etched area become rougher and can easily adhere and adsorb particles on it. While the area without laser etching was not able to adsorb particles on it. After chemical deposition waste water was passed through from mesh and found that the area with laser etching and strong chemical deposition retain the pollutants more than the area without laser etching. The waste water sample and treated sample were analyzed by UV spectrophotometer for detecting different organic pollutants.

5.2 RECOMMENDATIONS

The following are some recommendations for further studies

- Further detailed characterization of stainless steel mesh will required after chemical deposition.
- Further applications of stainless steel mesh will be explored.
- For making the stainless steel mesh a perfect filter for waste water further analysis will required

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