Ministry of Higher Education

and Scientific Research

Journal of Kufa for Chemical Sciences

A refereed

Research Journal Chemical Sciences

Vol.2 No.9 Year 2022

ISSN 2077-2351

Modifying the Polyvinyl Chloride Pipes Waste using Tannic acid as Sorbent for Crude Oil Spill Cleanup

Hawraa Ali Atwan and Hassan Thamir Abdulsahib

Chemistry Department , College of Science , University of Basrah

ABSTRACT

In the current study, waste polyvinyl chloride pipes were used as a basic material in the reactions, which are widely used Infor water supply and drainage system, where the waste pipes were prepared by cleaning them from suspended materials and grinding them into small particles, then reacting natural polymers from plant; Tannic acid .We have obtained modified polymer (PVC/Tannic acid) or PVC-Ta. The modified polymer have been grinded to obtain powder .Four techniques were used to characterize the properties of natural and prepared polymers: Fourier infrared spectroscopy (FTIR), scanning electron microscopy (SEM) , X-ray diffraction (XRD), and thermogravimetry (DTA-TG) . The study included the use modified polymers (PVC-Ta) to clean up the oil spill on the surface of the water by using the absorption phenomenon. This study included studying the effect of several conditions on the functioning of modified polymers, such as the amount of absorbent and time, for obtaining optimal conditions.

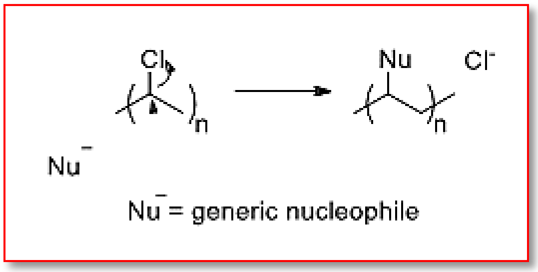
The study showed that the modified polymers possess a high efficiency in removing insoluble floating oil stains on the surface of water and dissolved petroleum materials, PVC-Ta recorded the highest percentage of insoluble oil stain removal with an oil absorption capacity of 5.55 g, an ideal weight of 0.4g and an ideal time of 4 hours. The modified polymers were recovered from the crude oil, and reused again with high efficiency. The physical and chemical method used in the present study of water treatment is mainly due to its simplicity, ease of use, low cost as well as excellent removal efficiency.

Keywords: *PVC , Tannic acid , Oil spills ,Cleanup, Absorption.*

INTRODUCTION

Water pollution is the contamination of water bodies, usually as a result of human activity, to the point when its authorized uses suffer damage [1] . A body's capacity to provide ecological functions that it could normally provide is reduced by water contamination. Water bodies include elements like lakes, rivers, oceans, aquifers, reservoirs, and underground. Contamination happens when pollutants are introduced into these sources of water. The four common causes of water contamination are sewage, manufacturing, agricultural, and civil drainage, including rainwater[2]. Aquatic ecosystems can suffer from the discharge of inadequately treated wastewater into natural waters, for instance. Drinking, bathing, washing, and irrigating with contaminated water increases your risk of getting sick from them. There are two types of sources of water pollution: point sources and non-point sources. Good example of point source pollution with a specific known cause are an oil leak, a sewage treatment center, and a storm drain. Non-point sources that are not confined to a single location such as agricultural runoff, are more diffuse [3] Contamination as a result of a prolonged cumulative influence.

Hazardous materials (e.g., oil, metals, plastics, pesticides, persistent organic pollutants, industrial waste products), harsh situations (such as pH shifts and hypoxia, stressful Types of pollutants include hot temperatures, high turbidity, offensive flavors or odors, saltwater changes, and harmful microorganisms. Pollutants include both organic and inorganic substances. Heat can be a contaminant, which is what the phrase "thermal pollution" alludes to. Thermal contamination is frequently caused by power stations and other industrial facilities using water as a coolant [3]. Oil Spills when a crude oil hydrocarbon is released into the environment, especially the sea environment, as a result of human activity, an oil spill occurs. The term typically refers to oil spills that happen in coastal or oceanic waters, though spills can also happen on land. Oil spills can be brought on by the release of crude oil from tankers, offshore platforms, drilling rigs, and wells, as well as the spilling of refined petroleum products (like gasoline and diesel) and their byproducts, heavier fuels used by huge ships, like bunker fuel, and any oily waste or reject [4] . PVC waste because of its long lifespan and numerous mechanical, electrical, chemical, thermal, and fire resistance qualities, polyvinyl chloride (PVC) has become third most popular plastic. Obtaining the desired qualities, however, necessitates the use of many additives, some of which contain dangerous compounds that pose various environmental and health hazards. PVC trash is anticipated to be generated as a result of the widespread use of the material in society. It's found in a variety of waste streams and is exposed to a variety of end-of-life treatments [5]. PVC pipes and fittings are necessary for sewage, drinkable water supply, irrigation systems, drainage and duct systems in buildings and facilities, and cable protection. 56 percent of total demand was met by buildings and facilities, followed by sewer (15 %), water supply (12 %), agriculture (4%), and cable protection (2%) [6,7]. PVC pipes and fittings placed underground could last for more than 50 years, essentially serving as semi-permanent fixtures[7]. PVC is presently one of the most widely recycled polymers in developed countries, owing to its suitability for virtually all recycling procedures. As a result, it receives a lot of attention in the recycling industry recycling of PVC. In this review, the following technological processes are discussed: Energy-recovery techniques , Mechanical recycling , Chemical recycling . Due of the comparatively simple chemical alterations that may be made to PVC's surface, it is also widely used in chemistry and materials engineering. PVC is a generally nonpolar material that yet has hydrophobic plasticizers that may diffuse throughout the structure and has strong nucleophilic substitution reaction reactivity with a variety of nucleophiles, including cross-linkers (scheme1) [8, 9].



Scheme (1) Generic substitution reaction of Cl with a nucleophile in PVC

Tannins are astringent polyphenolic macromolecules that bind to proteins and other organic substances such as amino acids and alkaloids and precipitate them. Leaves and acorn of a chestnut oak (Quercus Montana) . The plant is an important source of tannins. Tannin substances are extensively dispersed in a variety of plant species, where they may aid in controlling plant growth as well as serving as a form of defense against predators (including as insecticides) [10] . Unripe fruit, red wine, and tea all have astringent tannins that leave the mouth feeling dry and puckery after ingestion [11]. Structure and classes of tannins. There are three major classes of tannins.Shown below are the base unit or monomer of the tannin. Typically, tannin molecules require at least 12 hydroxyl groups and at least five phenyl groups to function as protein binders.[12]

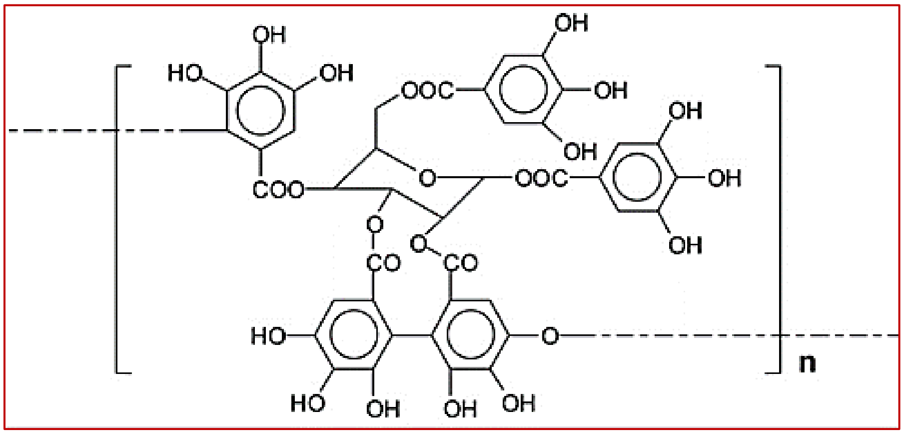


Figure 1: Schematic representation of the repeating unit of the ellagi-tannin of chestnut wood

The concept of employing tannin to purify industrial wastewater is based on polyphenols' inherent tendency to entrap metal ions, as well as the ease with which such a new product may be removed [13]. Today, tannins are increasingly used in tannin-modified adhesive formulations, as adsorbent materials for the pollution control of industrial effluent, and as flocculants due to their well-known scavenging behavior for many types of metal ions. They are secondary metabolites that naturally occur in the wood, fruit, leaves, and other parts of plants. There are several approaches, including chemical precipitation, coagulation and flocculation, sorption of vegetal trash and specialized processes like reverse osmosis or nanoparticle filtration [14].

Adsorption Mechanism :-

Adsorption is the result of interactions between ions, molecules, and the surface of the adsorbent. These interactions are influenced by the sorts of molecules or ions present as well as the kinds of adsorbent surfaces. The adsorbents are also either inorganic or organic, and the surfaces are one of these two. Highly polar in nature, inorganic surfaces typically have a positive or negative charge. The traditional

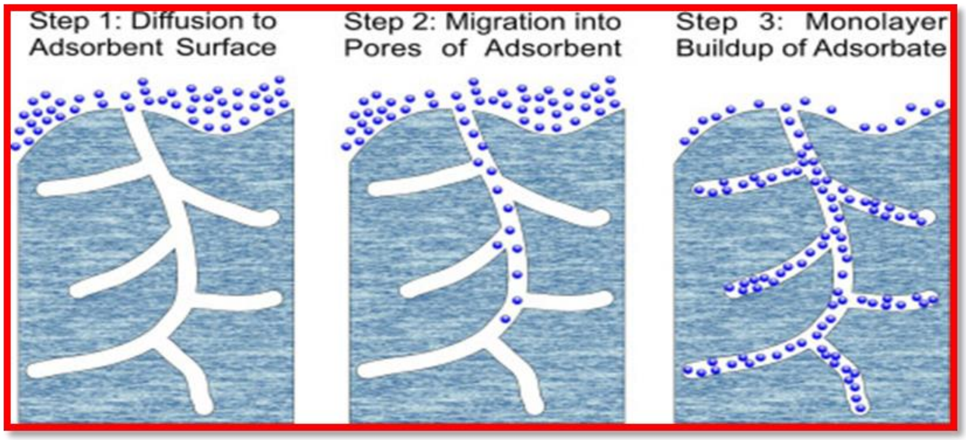


Figure 2: Three Steps of Adsorption Mechanism: a) Diffusion of Adsorbate to Adsorbent Surface b) Migration into Pores of Adsorbent c) Monolayer Build-up of Adsorbate on Adsorbent

adsorption method consists of three stages. (Figure.2): a) Adsorbate propagation to adsorbent surface. b) Movement into the adsorbent's pores. c) The formation of an adsorbate monolayer on the adsorbent. Figure. (2) explains the adsorbate distribution process. Adsorbate is diffused on the adsorbent surface in step 1 as a result of intra - molecular interactions between the two molecules. Adsorbate migrates into the holes of the adsorbent in the second step. Adsorbate particles are forming a monolayer of reacting molecules, ions, and molecules at the activity sites of the adsorbent during the last step, when they are distributed throughout the surface and have filled the volume of pores[15

The aim of this study finding the most **beneficial way of reusing** the waste PVC pipes through ground improvement which will contribute to sustainable development. The use of waste polymer as raw materials in the reaction instead of using pure chemicals. **Reducing pollution** that results from the accumulation of waste polymers Modification of PVC pipes waste by Tannins. **Characterization** the synthetic compounds by different technique. Using new compound those were prepared in **the different applications** such as Oil spill clean-up.

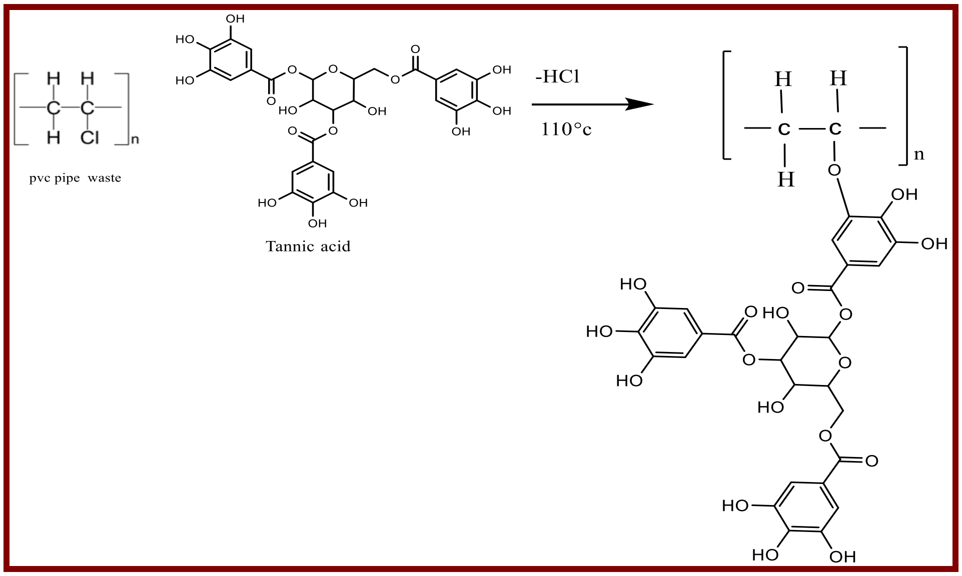
II. Materials and methods

- **PVC Pipe Waste** :-

PVC pipe waste were collected from Basra scrap site, Iraq. The PVC pipe were washed with water to remove dirt and were subsequently air dried. The cleaned pieces of the pvc pipe were cut into sections using very sharp knives to small pieces. The size of the PVC pipe waste were further reduced using an electric grinding machine.

- **Modifications of PVC with Tannic acid: -**

A (6.00 g) of the PVC pipe waste was (5.5g) of tannic acid (in the form of sodium phenoxide salts) and 25 ml of DMF were combined while stirring at 110 °C. The acidification with 10% v/v H_3PO_4 was carried out for one hour before the reaction was stopped. Cold ethanol was used to filter the product and precipitate it. Purification of the modified polymer was accomplished by using THF. Scheme (3) shows the chemical equation of the modification of PVC with Tannic acid [16].



Scheme (3) Chemical equation of the modification of PVC pipe with Tannic acid

- **Preparing Oil Spill :-**

The oil spill was made by first adding 50 mL of water to a glass beaker, followed by 1 g of crude oil, and swirling the mixture for five minutes to make the crude oil symmetrical on the water's surface.

- **Absorption experiments :-**

The spill oil clean up tests were carried out under the standard protocol U.S. American Society for Testing and Materials (ASTM) F726-06]. 0.5 g of modified polymer added to the oil spill with stirrer for 5mint to allow became homogenous surface. After one hour, the liquid was taken out and poured over a filter paper to catch any extra crude oil before being weighed on a scale. By dividing the weight of the absorbed oil by the weight of the dry materials at the beginning, the oil absorbency (g/g) was computed [17].

III. Characterization methods :-

Four methods were used for the characterization of the natural and prepared polymers: Fourier Transformed Infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) X-Ray diffraction (XRD) , and Thermo-gravimetry (DTA-TG)

- **Fourier Transformer Spectroscopy (FT-IR)** :-

The vibration frequency of the functional groups in the five distinct modified polymers was determined using Fourier transform infrared spectroscopy (FT-IR). An FT-IR spectrometer measured the spectra between 400 and 4000 cm^{-1} wave number. After completely combining the dry amount of polymers (approximately 0.1 g) with KBr and pressing the mixture into a pellet, the FT-IR spectra was captured.

- **The FT-IR spectrum of PVC :-**

The PVC FT-IR spectrum is displayed in Figure (3). The asymmetric stretching bond of C-H is seen by the peak at 2978.19 cm^{-1}, and the symmetrical stretching bond of CH_2 is shown by the peak at 2854. cm^{-1} the peak for the asymmetric stretching bond of CH_2 in phase is at 2908.75 cm^{-1} The -CH_2 aliphatic bending bond in phase is given to the peaks at 1489.10 cm^{-1}. The bending bond of -C-H near Cl is thought to be responsible for the peak at 1234 cm^{-1}. The PVC backbone chain's C-C stretching bond can be found between 1172.76 cm^{-1}. Finally, the C-Cl gauche bond is represented by the peak at 613.38 cm^{-1} [18,19].

- **FT-IR spectrum of Tannic acid :-**

The polyphenolic tannin compound exhibits a variety of features in different frequency bands. Figure (4) depicts the spectrum's FT-IR of tannic acid. The polymeric O-H group is responsible for the large peak at 3414 cm^{-1}; the dimer's

C=O stretching band is visible close to 1712.85 cm^{-1}. Additionally, at 1200,1450.52, and 1030.02 cm^{-1}, respectively,

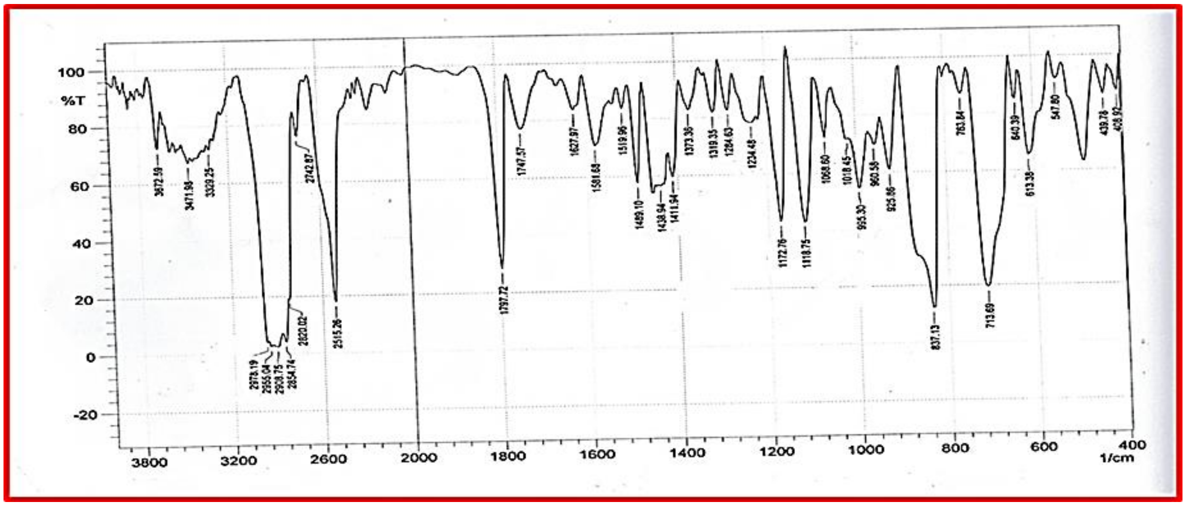


Figure (3) FTIR spectrum of pvc pipe waste

display the characteristic C-O stretching and in-plane and out-of-plane O-H bending bands. C-H stretching frequency corresponds to the band at 2928.04 cm^{-1}, while C=C is represented by the band at 1612.54 cm^{-1}. The medium to moderate C-H in-plane bending vibration 1323.21 cm^{-1} is more noticeable than the C-H aromatic stretching vibration. The effect of the distortion vibration of C=C in benzene rings is visible in the band at 759.98 cm^{-1}. The distinctive -D- glucose unit absorption may be seen in the absorption band at 871.85 cm^{-1} [20,21].

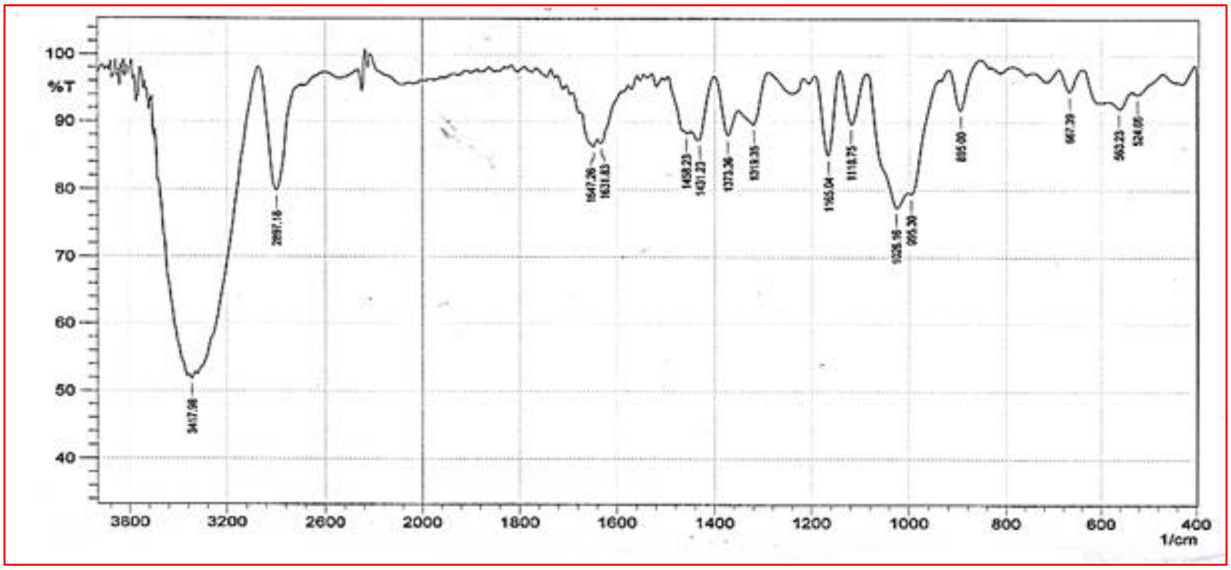


Figure (4) FTIR spectrum of Tannic acid

The compounds PVC-Ta was preparing by modification of pvc pipe waste as After that , this compound was characterized by FT-IR . FT-IR spectra are shown in figures (5), appear decrease in peak at 1724.42.13 cm^{-1} has been attributed to C=O, the band at 2970.48 cm^{-1} relates to C-H stretching frequency, the peak at 3421.83 cm^{-1} is credited to the polymeric O-H group, and the band at 1678.12 cm^{-1} can be associated to the existence of conjugated carbonyl groups. The band at 1774.57 cm^{-1} and the C-H bending frequency at 1330.39 cm^{-1} both provide evidence that the functional group C-O-C is present in tannic acid. It is possible to attribute a noticeable band at 1431.23 cm^{-1} to C-OH stretching. The finding exhibits distortion vibration of C=C in benzene rings at 759 cm^{-1}. Stretching vibrations of C-O groups can be seen in the spectrum about 1235.77 cm^{-1}. The characteristic absorption of a unit of -D-glucose is represented by the absorption band at 840.99 cm^{-1}. Table(1) shows the important characteristics FT-IR bands and their location for prepared compound PVC-Ta.

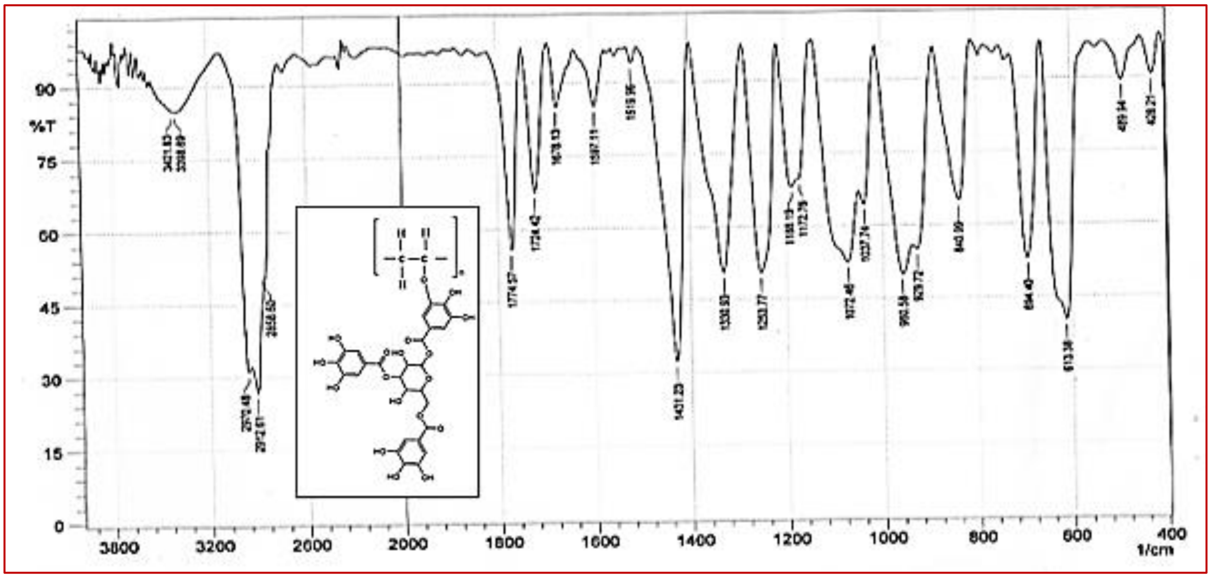


Figure (5) FT-IR spectrum of prepared compound PVC-Ta

Table(1) The important characteristics FT-IR bands and their location for prepared compound PVC-Ta.

Comp.	**OH (cm^{-1})**	**C-H Stretching and bending (cm^{-1})**	**C= O stretching (cm^{-1})**	**C-O (cm^{-1}) stretching**	**C-O-C (cm^{-1})**	**C-OH stretching (cm^{-1})**	**β-D- glu cose (cm^{-1})**	**C= C streching (cm^{-1})**
PVC-Ta	3421.83	2970.48 - 1330. 39	1724.42	1253.77	1774.7	1431.23	840.99	759

• Thermal gravimetric analysis (TGA) :-

Thermal gravimetric analysis (TGA) is one of the methods of thermal analysis techniques used to study the thermal stability of a wide variety of materials. TGA assesses the quantity and rate of change in a sample's mass as a function of time or temperature in an inert environment [22,23]. The primary purposes of those measurements are to ascertain the compositional and thermal properties of materials [24]. It is especially useful for studying polymeric materials. The thermal stability of polymers is defined as the resistance of polymers toward thermal and thermochemical degradation under isothermal or dynamic conditions. The generated thermograms were used in the current work to determine many of the thermal stability characteristics, such as the tangential decomposition temperature (initial decomposition temperature T_i). The degree of decomposition temperature at 50% weight loss of the sample (T_{50}), the final decomposition temperature (T_f), the amount of char at the conclusion of the decomposition process [25].

- **Thermal gravimetric analysis (TGA) of prepared compounds :-**

Concerning polymer PVC-Ta three stages of decomposition are shown in Figure 6. The post-curing, thermal reforming, initial oxidation stages, and removal of volatile fractions contributed to the first stage at 69.45°C (12.20 % wt.). The loss of methoxy molecules (49.84 %weight) from the cleavage of the methylene group is thought to be responsible for the second step at 311.93°C. a third stage is equivalent to (28.52% wt.). loss at 470.07 °C corresponds to condensation reaction, during which the **PVC-Ta** decompose and precipitate a large amount of H and a small amount of CH_4 with remains (9.44% wt.) of carbon . [13], [26] . Table (2) shows the TGA parameters for the synthesized PVC-Ta polymer .

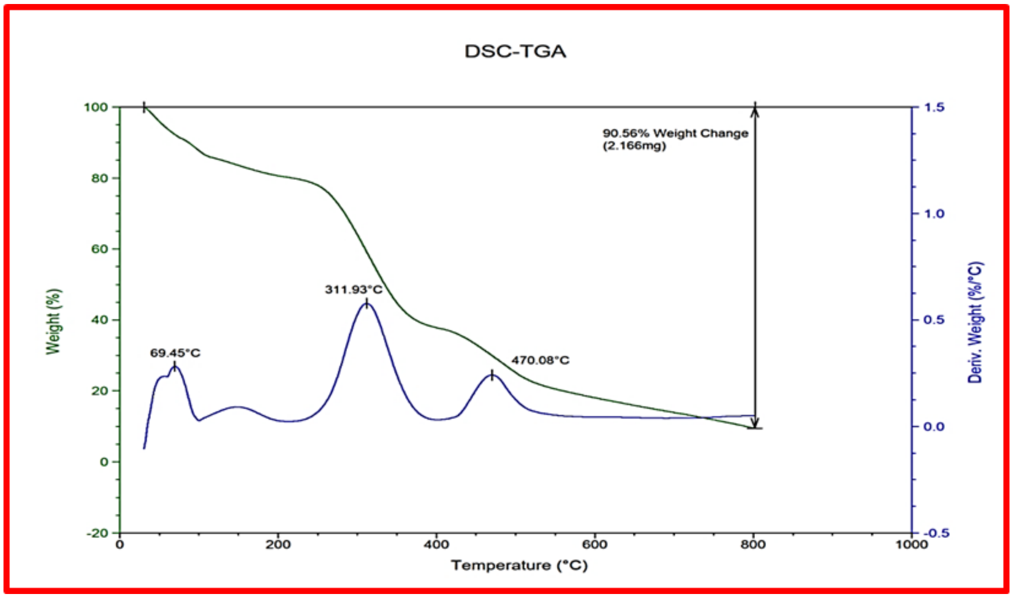


Figure (6)The TG/DTA curve of prepared compound PVC-Ta

Table (2) The TGA Parameters for the synthesized PVC-Ta polymer.

polymer	**TG/TGA**				**Mass loss %**	**Ruds. At C°**	**Total C°% Weight Loss**
	Decomposition Stage	T_i °C	Tm (max) °C	T_f °C			
PVC-Ta	First stage	45	69.45	110	12.20	800	90.56
	Second stage	290	311.93	385	49.84		
	Third stage	480	470.08	525	28.52		

- **X-ray Diffractometry :-**

Physically, diffraction is the result of electromagnetic radiation deflecting away from obstructions. As the atom plans are positioned at distances similar to X ray lengths, this phenomenon can be used to analyze materials. X rays are electromagnetic waves that resemble light but have a much shorter wavelength (= 0, 2 Å- 200 Å) [27].

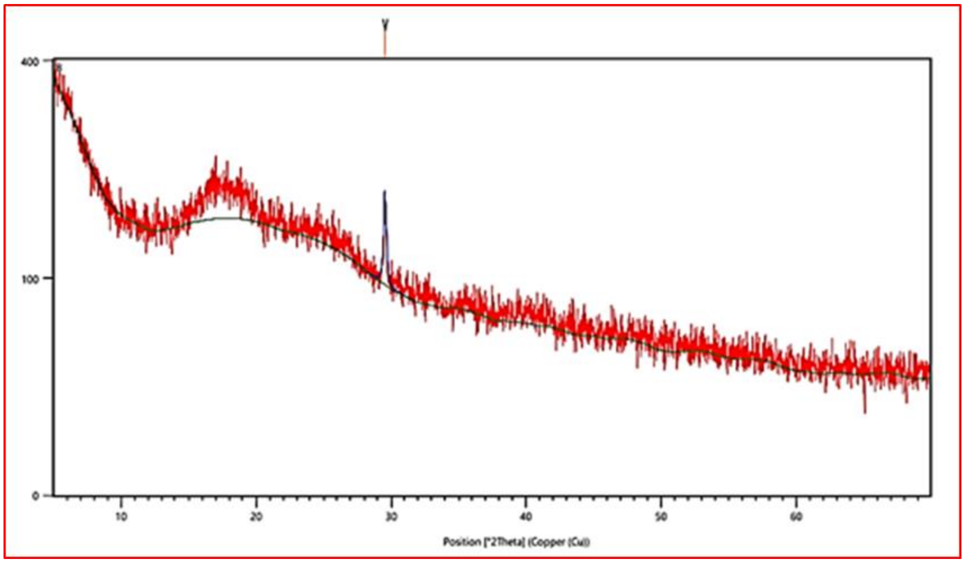
The way the material's atomic planes are arranged within the crystal lattices determines how much light is diffracted. The law describes the diffraction angle and the spacing between atomic planes in a crystal structure for a given wavelength of electromagnetic radiation. Typically, diffracted X-rays are found using a detector, then processed and counted to create diffracted or pattern beams. An unknown sample can be identified by converting diffracted patterns into d-spacing. Usually, the diffracted pattern beams are compared to numerous reference patterns in order to identify the materials [28].

The interplanar spacing d and the value of 2θ are described. The broad diffraction peaks from the obtained XRD patterns showed that the structure performed a semi-crystalline nature, which was defined by the location of the maximum 2θ of the broad peaks. The average values of d were determined using Bragg's equation ($2d\sin\theta = n\lambda$) [29] .

The molecular weight and crystallinity of polymers were the main determinants of their qualities. XRD The crystallinity index (CI), which is frequently used to gauge crystallinity, can be computed by X-ray diffract. I propose the following formula to calculate the crystallinity index (CI):

$$CI\ (\%) = [(Im - Iam)/ Im] * 100$$

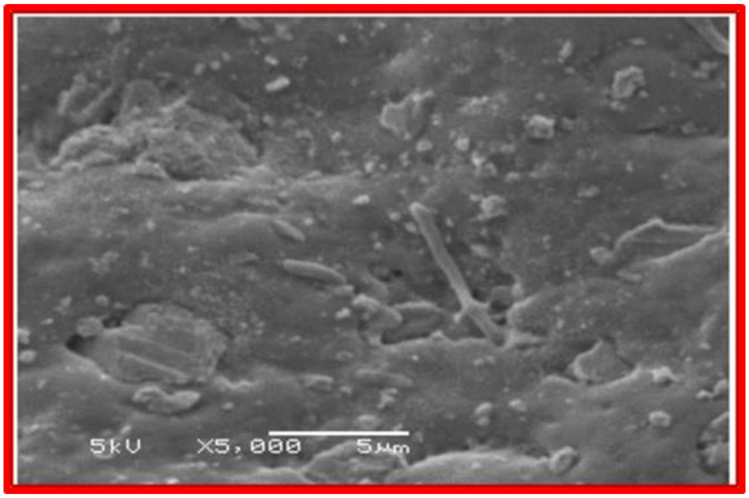
where Im is the crystalline peak's maximum intensity in arbitrary units, about 2θ, and Iam is the amorphous diffraction, in arbitrary units. The majority of the time, CI offers details regarding the crystal state. The area of the crystalline peaks could also be divided by the overall area under the curve in an X-ray diffractogram [30] to determine crystallinity. The typical PVC-Ta diffraction pattern, given in angle form figure (7) shows strong reflections at 2θ around 29.52°, however differently indexed crystalline peaks (100%).



Figure(7) XRD of PVC-Ta

- **Scanning Electron Microscopy (SEM)**:-

The surface morphology was investigated using SEM. A focused electron beam is used in scanning electron microscopy, a form of electron microscope, to produce images on the sample surface. The sample's atoms and electrons interact, resulting in a variety of signals that carry details on the surface's general composition and structure. [31-32]. The SEM micrographs of PVC figure (8) showed smooth and neat surfaces with a high degree of homogeneity [33].



Figure(8) SEM images of PVC

Figure (9) shows the SEM micrograph of PVC-Ta. The image appears as a single surface that contains fine cracks and pits that spread in huge quantities in the Nano form which see at 200 nm.

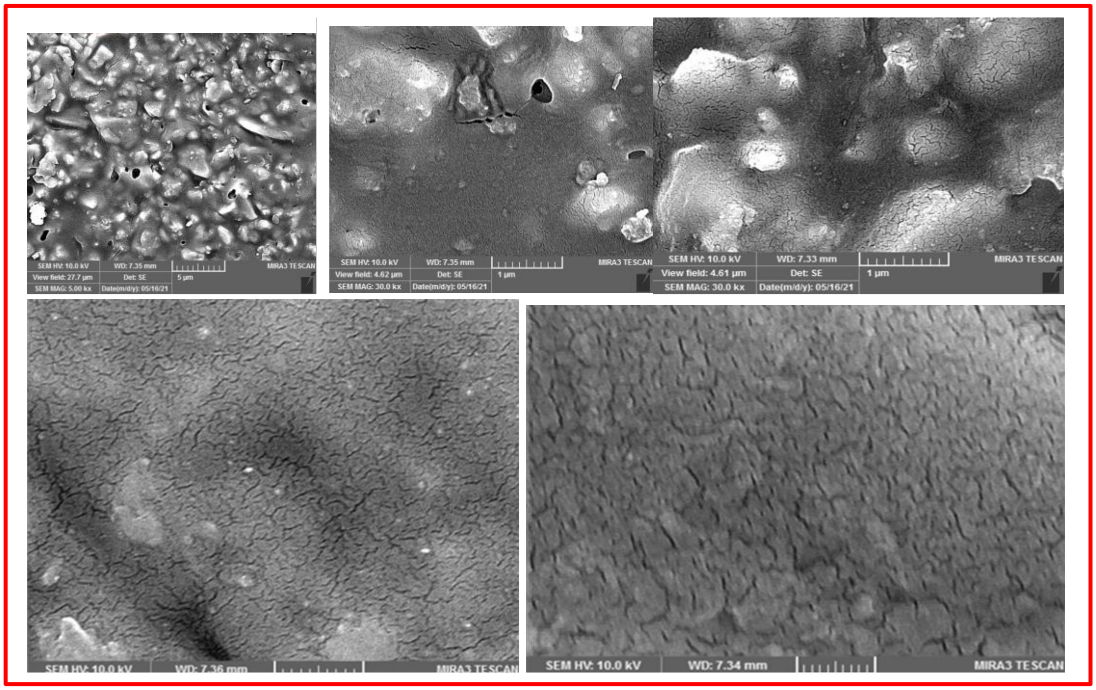


Figure (9) shows the SEM micrograph for PVC-Ta

VI. Absorption Studies :-

Products or substances known as sorbents have a strong capacity to absorb oil and resist water. They are also oleophilic and hydrophobic oil is let to absorb after the adsorptive substance has been applied to the stain. The material that has been saturated in oil is then taken, and depending on the adsorption process, it will either be safely thrown of or pressed to extract the petroleum and then redistributed. Recyclability, wettability, density, shape, sorption capacity, and sorption rate are all factors that affect how effective a sorbent is.

- **Oil Sorption Mechanisms :-**

The general sorption mechanisms in the current investigation include the absorption approach. Using crude oils, the oil absorption tests were carried out in accordance with the recommended procedure (American Society for Testing and Materials (ASTM) F726-06) [34] . The oil up take (g) for sorbent materials obtained from the following equation:

$$\textbf{Oil up take} = m_o - m_s$$

The following equation provides the oil absorption capabilities for these absorbents [35]:

$$Q = \frac{m_0 - m_s}{m_s}$$

Where Q represents the oil absorption capability (g/g), m_0 is the overall weight of moist absprbent following a 10-second oil drainage, and ms represents the mass of the absorbent prior to absorption (g). Then use a nipper, the moist absorbent was removed, and then it was weighed. The identical absorption time was tested three times individually for each sample, and the average value was calculated. All of the petroleum absorption tests were carried out at 27° C.

- **Study the Effect of Increasing the weight of Sorbent Materials on oil spill up take at constant Time:-**

Different weights of sorbent PVC-Ta, were used to study the effects of weight increase over a fixed period of time (1 hour) at room temperature (27).

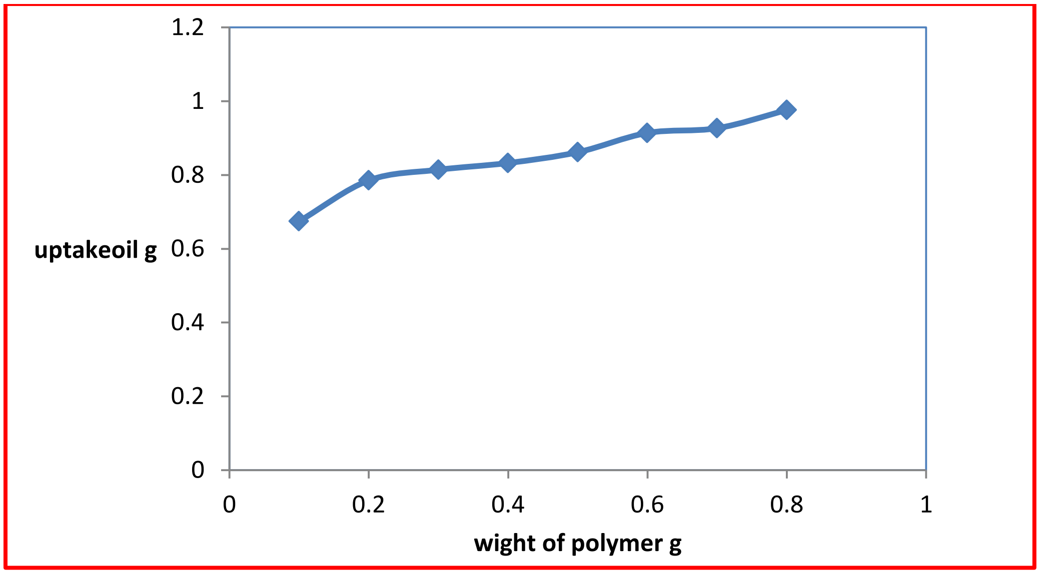


Figure (10) Effect of increasing weight on Oil Spill Cleanup for PVC-Ta

Equation was used to calculate the oil uptake value , According to figures (10), the q values of sorbent material increase as the sorbent material's weight increases. The q values have a linear relationship with an increase in the weight of the sorbent material when they reach their optimal values, as indicated in table (3). As weight rises, the uptake also does so by comes as a result of the surface area growing as the weight grows [36]. On the other hand, chemical modification techniques like and may greatly enhance sorption capabilities. The hydrophobicity of the surface of the material prevents water adsorption and hence increases oil sorption efficiency because there is no rivalry between the molecules of oil and water. Under practical circumstances, a number of variables interact to prevent the initial wetting of a surface, and they also frequently work against the retraction of fluid after wetting [37]. Real-world surfaces' heterogeneity and roughness can change wettability and contact angles at advancing and retreating spots on the surface. On the other hand, voids tend to stay loaded when a liquid has saturated a surface, which affects the interfacial force [37].

Table (3)optimum weight &optimum oil uptake of sorbent material.

Comp.	**Optimum Weight(g)**	**Optimum Oil uptake(g)**	**Oil absorption Capacity (g/g)**
PVC-Ta	0.4	0.83	2.07

- **Study Effect Increasing the Time on Oil Spill up take with Constant Weight of PVC-Ta :-**

The effect increasing time of absorption studied by using different times at constant weight (optimum weight) of sorbent material at room temperature(27C^o) for compound PVC-Ta.

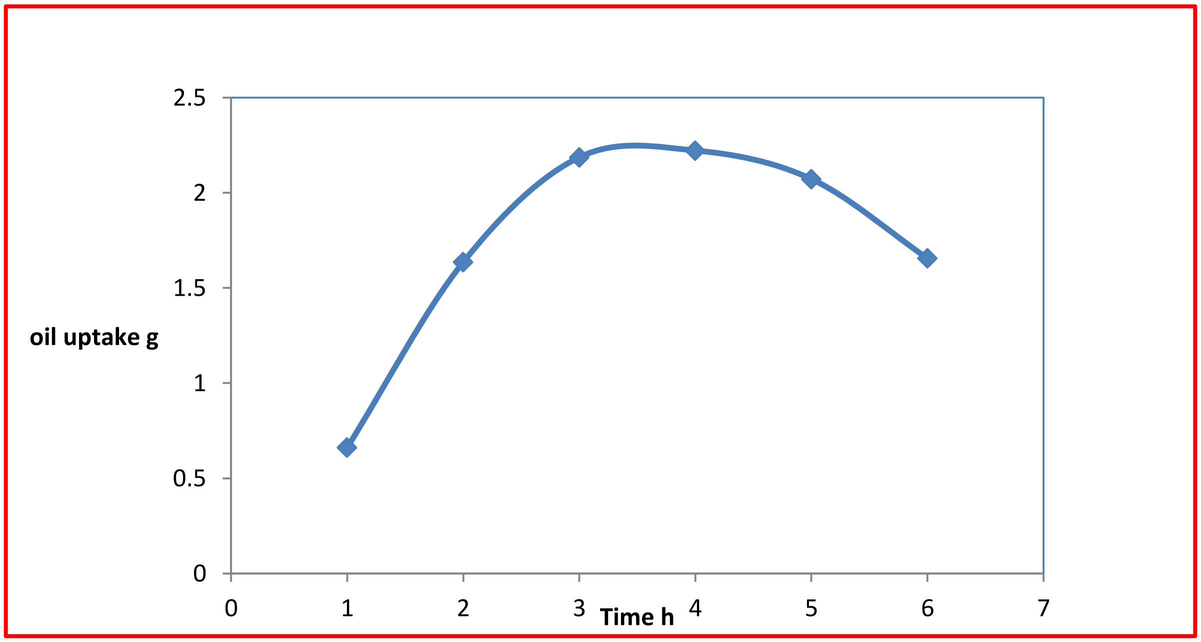


Figure (11) The impact of an increase in absorption time on oil uptake for PVC-Ta

Figures (11) we observe that compound PVC-Ta absorption increases to 4 hours before decreasing after that because it has begun to saturate and is no longer able to absorb oil. Due to the repellence forces between the oils in their bulk and in their phased-out forms, the adsorbent's internal pores were filled and all of the adsorption sites across its surface were consumed. Consequently, the adsorbent active sites' attraction for oil molecules decreased, which negatively impacted the oil-desorption process ,this causes a decrease in absorption . Table (4) Shows the optimum time and optimum oil uptake .

Table (4) optimum time & optimum oil up take of sorbent material

Comp.	Optimum Time(h)	Optimum Oil up take(g)	Oil absorption Capacity (g/g)
PVC-Ta	4	2.22	5.55

Because of the potential to collect and completely remove the oil from the oil spill scene, absorbent materials are appealing for particular applications. Oil recovery from absorbents, hydrophobicity and oleophilicity [38], high uptake capacity, high rate of uptake, retention over time, and reusability are all desirable characteristics of good absorbent materials. The oil absorption capacity depends on a number of factors, including the polymer's hole structure, the polar groups' hydrophilic and oleophobic properties, and the cross-linking density (which affects swelling ability). Lower cross-linking density results in higher swelling, lower cross-linking density in higher absorption capacity, and high-molecular-weight exhibits both of these properties . PVC-Ta polymer has a high oil absorption capacity due to its large molecular weight, high polar group, and lack of structural crosslinks or holes

- **Study Oil Spill Uptake Efficiency for Activated Compounds :-**

Following the treatment of an oil spill, the crude oil was recovered by dissolving it in toluene and filtering the sample (sorbent material loaded with crude oil). The precipitate (sorbent material) was then repeatedly washed with toluene and dried before being utilized again. To get rid of the solvent, the filtrate (crude oil) was put into a rotary oven.

After purification, section previous examined the oil uptake efficiency with time for compound (PVC-Ta) at constant weight. As a result of these findings, the purified compounds have demonstrated strong absorption potential to be employed as sorbent materials for additional oil spill cleanup, as illustrated in figures (12) The findings indicated that compound (PVC-Ta) has a greater capacity for absorption .

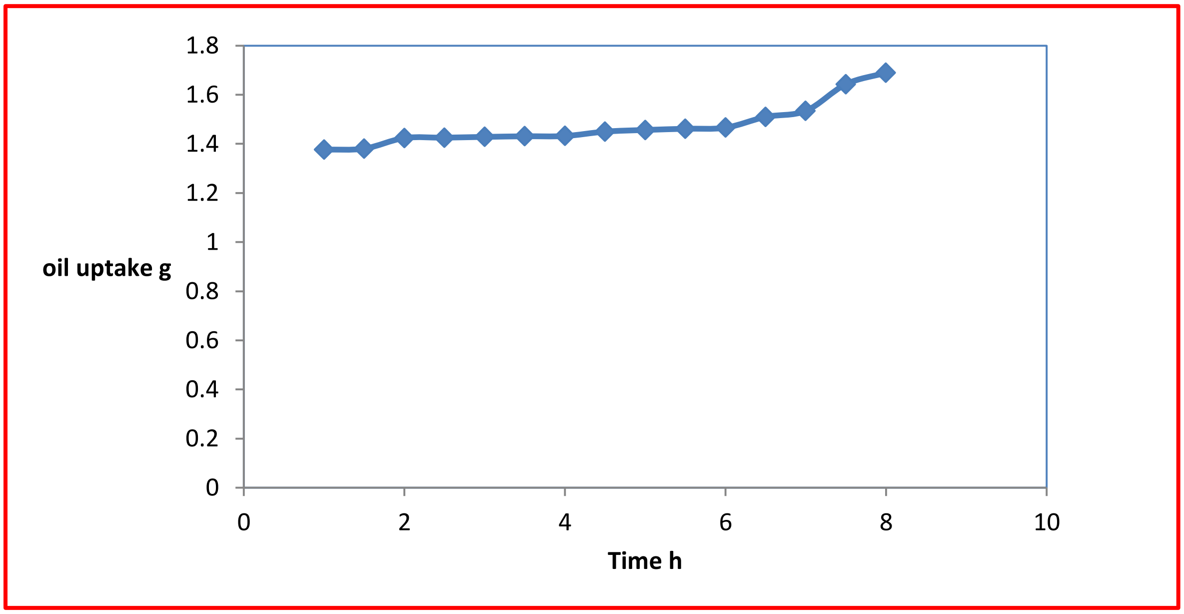


Figure (12) Oil Spill uptake Efficiency for activated Compound PVC-Ta

V-Conclusions:-

The present study leads to the following conclusions: the recycling polyvinyl chloride pipes successfully considered as raw material that may be reuses in different applications.Polymeric compounds prepared from waste polyvinyl chloride pipes were used , to remove oil spills, floating on the surface of the water, showed high efficiency. It is one of the green chemistry methods to reduce pollution

Acknowledgments

My sincere thanks and gratitude extend to the deanship of the College of Science, the presidency of the department of chemistry.

IV. References :-

1. V. Sperling"Wastewater Characteristics, Treatment and Disposal". IWA Publishing. , (2015). 6. doi:10.2166/9781780402086. ISBN 9781780402086.
2. W. Wesley Eckenfelder Jr. Kirk- Othmer Encyclopedia of Chemical Technology (1 ed.). John Wiley & Sons, (2000). Inc. doi:10.1002/0471238961.1615121205031105.a01. ISBN 978-0-471-48494-3.
3. M.Brian ,"Water Pollution by Agriculture". Phil. Trans. R. Soc. Lond. B(2008). 363 (1491): 659–666. doi:10.1098/rstb.2007.2176. PMC 2610176. PMID 17666391.
4. "Lingering Lessons of the Exxon Valdez Oil Spill". Commondreams.org. 2004-03-22. Archived from the original on June 13, 2010. Retrieved 2012-08-27
5. A. Fråne, J. M. Plepiene, Al. M. Almasi and A. K. Westöö «PVC waste treatment in the Nordic countries»TemaNord 2019:501
6. K. Ishizaki “Situation of recycling of the post use PVC pipes and fittings, the projection of the emissions, and issues to be addressed”, Construction Materials Recycling(2011), Winter, vol 54, p 16
7. “PVC pipes can last more than 50 years”, PPFA http://ppfa.gr.jp/02/index-a04.html (Accessed 14 Feb. 2015)
8. T. Kameda, M. Ono, G. Grause, T. Mizoguchi and T. Yoshioka,” Chemical modification of poly(vinyl chloride) by nucleophilic substitution”. Polym Degrad Stabil. (2009), 94, 107- 112 5

9. P. Jia, L. Hu, Q. Shang, R. Wang, M. Zhang and Y. Zhou, Self-Plasticization of PVC Materials via Chemical Modification of Mannich Base of Cardanol Butyl Ether.(2017),ACS Sustainable Chem. Eng. 5, 8, 6665-6673
10. S. Mole "The Systematic Distribution of Tannins in the Leaves of Angiosperms: A Tool for Ecological Studies". Biochemical Systematics and Ecology. (1993). 21 (8): 833–846. doi:10.1016/0305-1978(93)90096-A
11. Mc.G. ,Harold On food and cooking: the science and lore of the kitchen. New York: Scribner. (2004). p. 714. ISBN 978-0-684-80001-1.
12. "Notes on Tannins from PharmaXChange.info". Archived from the original on 4 January 2015.
13. G.Vazquez, , J.G. Alvarez, S. Freire, , M.L. Lorenzo and G. Antorrena "Removal of cadmium and mercury ions from aqueous solution by sorption on treated Pinus pinaster bark: kinetics and isotherms". Biores. Technol., (2002). 82, 247–251
14. H.T.Abdsahib. "Sythesis and charactarization of some polymer for the removal of some heavy metal ions and bentonite in waste water"(2015)1,67-68,
15. N. Wang, J. Feng, J. Chen, J. Wang, W. Yan, Adsorption mechanism of phosphate by polyaniline/TiO2 composite from wastewater, Chemical Engineering Journal, 316 (2017) 33-40.
16. Al-Majed. A., Adebayo .A. R. and. Hossain. M. E, “A sustainable approach to controlling oil spills”, Environmental Management (2012),113 , 213-227,.
17. Y.Turhan, , M. Doğan, & M. Alkan, Poly(vinyl chloride)/Kaolinite Nanocomposites: Characterization and Thermal and Optical Properties. Industrial & Engineering Chemistry Research, (2010). 49(4), 1503–1513.
18. H.A.Hijaj ,“Synthesis and Characterization of Polymeric Compounds from Waste Polyethylene Terephthalate and Polystyrene and studying its Efficiencies as Oil Spill Cleanup and Corrosion Inhibitors”. ,(2015) 4,76-94
19. S. Krim , M .Harrison M. Randall “Infrared Spectroscopy and polymer Structure .” Laboratory of Physics, University of Michigan, Ann Arbor, Michigan, U.S.A. 273,(1969)
20. B. Stuart , “ Infrared Spectroscopy: Fundamentals and Applications” 2004 John Wiley & Sons, Ltd ISBNs: 0-470-85427-8 (HB); 0-470-85428-6 (PB)

21. L. Falcão, M.E.M. Araújo, “Application of ATR–FTIR spectroscopy to the analysis of tannins in historic leathers: The case study of the upholstery from the 19th century Portuguese Royal Train, Vibrational Spectroscopy” , 74 (2014) 98-103.
22. A. Ricci, G.P. Parpinello, K.J. Olejar, P.A. Kilmartin, A. Versari, Attenuated ,“ Total Reflection Mid-Infrared (ATR-MIR) spectroscopy and chemometrics for the identification and classification of commercial tannins, Applied spectroscopy ”, (2015) 69 1243-1250.
23. P. Poddar, M.S. Islam, S. Sultana, H. Nur, A. Chowdhury, Mechanical and thermal properties of short arecanut leaf sheath fiber reinforced polypropyline composites: TGA, DSC and SEM analysis, Journal of Material Science and Engineering, (2016) 5 270.
24. C. De Blasio, Thermogravimetric Analysis (TGA), Fundamentals of Biofuels Engineering and Technology, Springer(2019), pp. 91-102.
25. M. Ahmad, R. Grössinger, M. Kriegisch, F. Kubel, M. Rana, Characterization of Sr-substituted W-type hexagonal ferrites synthesized by sol–gel autocombustion method, Journal of magnetism and magnetic materials, (2013) 332 137-145.
26. C.T. Chong, G.R. Mong, J.-H. Ng, W.W.F. Chong, F.N. Ani, S.S. Lam, H.C. Ong, Pyrolysis characteristics and kinetic studies of horse manure using thermogravimetric analysis, Energy conversion and management, (2019) 180 1260-1267.
27. X. Chen, X.A. Pizzi, E. Fredon,X. Zhou ,J. Li,C. Gerardin “‘Preparation and Characterization of Condensed Tannin Non-Isocyanate Polyurethane (NIPU) Rigid Foams by Ambient Temperature Blowing “Polymers (2020), 12(4), 750; https://doi.org/10.3390/polym12040750
28. J. Elena, M.D. Lucia, Application of X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods to the portland cement hydration processes, Journal of Applied Engineering Sciences, 2 (2012) 35-42.
29. R. Das, S. Bee Abd Hamid, M. Eaqub Ali, S. Ramakrishna, W. Yongzhi, Carbon nanotubes characterization by X-ray powder diffraction–A review, Current Nanoscience, (2015) 11 23-35.
30. Z. Li, K. Kou, J. Zhang, Y. Zhang, Y. Wang, C. Pan, Solubility, electrochemical behavior and thermal stability of polyimides synthesized

from 1, 3, 5-triazine-based diamine, Journal of Materials Science: Materials in Electronics, (2017) 28 6079-6087.

31. N. Herlina Sari, I. Wardana, Y.S. Irawan, E. Siswanto, Characterization of the chemical, physical, and mechanical properties of NaOH-treated natural cellulosic fibers from corn husks, Journal of Natural Fibers, 15 (2018) 545-558.
32. M.S.M. El-din, M.A. Ghafar, A. El GawadRabiea, H.A. Tieama, Novelpolyvinyl chloride-grafted-poly (ethylene imine) membranes for water treatment applications: Synthesis and membrane characterizations, American Journal of Applied Chemistry, 3 (2015) 13-21.
33. S. A. K. Ramesh, B. Vengadaesvaran, S. Ramesh, A.K. Arof, “Formulation and characterization of hybrid polymeric/ZnO nanocomposite coatings with remarkable anti-corrosion and hydrophobic characteristics”, Journal of Coatings Technology and Research, 13 (2016) 921-930.
34. Y. Lee, “An Evaluation of Microbial and Chemical Contamination Sources Related to the Deterioration of Tap Water Quality in the Household Water Supply System” Int. J. Environ. Res. Public Health(2013), 10(9), 4143-4160; https://doi.org/10.3390/ijerph10094143
35. X. Yuan and T. C. Mike Chung, “Novel Solution to Oil Spill Recovery: Using Thermodegradable Polyolefin Oil Superabsorbent Polymer (Oil−SAP)”, Energy Fuels, (2012). 26, 4896−4902
36. J. Lin , Y. Shang , B. Ding , J. Yang , J. Yu b and S. S. Al-Deyab,“Nanoporous polystyrene fibers for oil spill cleanup”, Marine Pollution Bulletin, (2012).64, 347–352,
37. Sayed, S A; El Sayed, A S; S M; Zayed, A,” M Oil Spill Pollution Treatment by Sorption on Natural Cynanchum Acutum L. Plant,” Journal of Applied Sciences & Environmental Management, Vol. 7, No. 2, Dec, 2003, pp. 63-73
38. Cassie, A.B.D.; Baxter, S. Wettability of porous surfaces. Trans. Faraday Soc. 1944, 40, 546
39. “Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties”, Journal of Porous Materials ,10, 159–170,(2003).