Porous Polysulfide Polymer in Removing Perfluorooctanoic acid from Water and Extracting Gold

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Acknowledgments

Table of Contents

List of Figures

List of Tables

Abbreviations

PFOA	**Perfluorooactanoic acid**
STA	Simultaneous Thermal Analysis
IR	Infrared
SEM	Scanning electron microscopy
EDS	Energy dispersive X-ray spectroscopy
XRD	X-ray diffraction
ICPOES	Inductive coupled plasma optical emission spectroscopy
CMC	Concentration micelles confirmation
F NMR	Florine nucleus
EPA	Environment protection agency

Declaration

I, the undersigned, hereby declare that the work in this thesis was carried out in the College of Science and Engineering at Flinders University, South Australia under the supervisor of Dr. Justin Chalker.

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does contain any material previously published or written by another person except where due reference is made in the text.

Salah Alboaiji

November 2017

Project Summary

The aim of this project was to synthesis a porous polysulfide polymer from sulfur and canola oil. Sulfur is an industrial by-product and waste, canola oil is a cooking oil and renewable product. Porous surface is made by adding NaCl to the reaction of polysulfide polymer. This project has two sections. In the first section, porous polysulfide polymer will be used for removing PFOA from water for environmental remediation. Water that is free from toxic compounds is necessary everywhere, at all times. PFOA is persist in the environment, therefore using inexpensive technology to eliminate toxic compounds such as PFOA from ecosystem is beneficial. In the second section the binding of Au(III) to the porous polysulfide polymer was examined. Artisanal and small scale gold mining collect huge amounts of gold, but uses mercury to capture the gold from ore. Mercury methods pollute communities and badly effects miners and their families. Small scale gold miners are in need of inexpensive technology that have gold binding properties. Porous polysulfide polymer is a safe technology and mercury-free method to be used to extract gold from ore in small scale gold mining, therefore the dangerous technique will be replaced by porous polysulfide polymer eliminating pollution, increasing safety for miners and being to remediate our environment. Several techniques and instrument will be used to characterise the data. Instruments includes SEM, EDS, ^{19}F NMR, ICPOES, XRD, and STA.

Introduction

The environment is continuously being polluted with toxic compounds during the production of materials that are considered as an essential to our current life-styles such as Teflon cooking product and in mining to extract valuable gold. Toxic compounds are also introduced into the environment from lifesaving technologies including firefighting foam.

The big challenge is how we then remove these dangerous materials form the environment in a cheap and environmentally friendly. The goal of green products is not only to eliminate waste and wipe out toxic by-products, but also to produce a useful product from waste material to clean-up environment from toxic waste in cheap processing. Government regulates the pollution to minimise any pollution that put a risk on people's lives and/or environment[1]. The laws have helped to reduce the severity of the issue but it has not resolved the issue completely[2].

An example of a pollute that is still being introduced into the environment and endangering our health is perfluorooctanoic acid (PFOA). PFOA is used in the production of Teflon products, in firefighting form and in surfactant use[3]. PFOA has negative impacts on environment and people health[3-6]. The main reason for persist to environment is because C-F bond is very strong[7]. Long chain alkyl fluorinated compound were phased out USA due to toxicity, however its negative effects are still around[8].

The most inexpensive technology is a technology that uses waste from other processes as the raw materials in the production of a new product preferably without use of expensive and wasteful solvents. An example of this type of technology is the synthesis of a polysulfide polymer by simply mixing molten sulfur with canola oil. About 70 million tonnes of sulfur is produced annually as a waste material from petroleum refineries[9], left sitting unused. There is huge amounts of sulfur around refineries in Canada [9-12]. Canola oil is a natural resource and an abundant renewable product[13]. The polysulfide polymer has been shown to be efficient in capturing mercury[10]. A porous polysulfide polymer can be made by adding NaCl during the synthesis of the polymer. Washing the polysulfide polymer with water removes the NaCl giving the polymer porosity[10]. An increase in the weight percentage of NaCl used in the polymer synthesis leads to an increase in the porosity. The percent of porosity in the polysulfide polymer might make different in the ability of the polymer to capture PFOA from soil and water ways.

The properties of PFOA are very hardly degradation at normal condition and F-C bond is very strong[14]. These properties make PFOA as persist in environment[7-15]. The

Environmental Protection Agency (EPA) listed PFOA as an emerging materials that needs to be removed from the environment[1]. There are several methods for capturing PFOA from water. Commonly seen in Japan it the use of activated-carbon[3, 15-16]. Activated- carbon has a limited shelf-life for removing PFOA. The limited shelf- life is one year, which makes Active-carbon is useless after one year[3, 15-16]. Porous polysulfide polymer would be tested for its ability to remove PFOA from our environment.

Artisanal small scale gold mining is other major pollution to environment and health risk to people. Heavy metals from mining or deep sea mining last with negative impact on globe, harmful effects on people health and badly influence on next generation. Demand for gold is high due to increasing in gold price. The value of gold makes people and companies are less aware regarding any toxic compounds may leach into environment. Amalgam is a solvent extraction of gold by burning amalgam, then leading into vaporise mercury to recover gold as a metal[2, 10]. Vapour mercury causes several diseases including brain damage[2]. It is affect workers and people who live in same area. Mercury classified as a pollute compound an either metallic mercury or vaporous mercury. Metallic mercury sweep into rivers, when then would be eaten by fish which increase bioaccumulation level[2]. Cyanidation process for gold recovery is other undesired method that has a negative impact on environment[17]. Cyanidation process is used because it is simple method and selective technique[17]. The highly cost of transport is other issues for deep sea mining industries[18]. Scientist proves that sulfur highly likely bound to gold[19]. The structure be RS-Au-RS in the alkyl sulfur, however in polysulfide polymer case might be different as polysulfide polymer is stable at room temperature condition and polysulfide polymer starts for degradation at 230 °C, with 9% free sulfur in polysulfide polymer [10]. Porous polysulfide polymer that has large surface area is excellent choice for using in mining field. Porous polysulfide polymer is made by using sulfur and canola oil as inverse vulcanizing with adding NaCl during raction to increase surface area, then NaCl wash by DI water to make porousness in polysulfide polymer[10]. Increasing large surface area leads to increase effectiveness of binding gold to the porous polysulfide polymer. Using porous polysulfide polymer in mining industries benefits all parties, environmental agencies by reducing waste materials, and benefits mining companies by using inexpensive products, and workers in mining field by using safe sorbent. Using porous polysulfide polymer is considered as a green product. Then green product has a significant advantage in getting sustainable globe[20]. The advantages of synthesis of polysulfide polymer are not only a green product but also no solvent is required and the raw materials are entirely waste. The green product is needed in our globe weather using waste

materials such sulfur or renewable sources such as canola oil. Polysulfide polymer has shown effectiveness in capturing mercury and the color of polysulfide polymer changed into black color as soon as the mercury bound to it[10]. In this study porous polysulfide polymer will be used to capture PFOA from water and then concentration of PFOA be reduced to minimum level. Other test will be to examine if aqueous gold (III) bound to porous polysulfide polymer.

Synthesis and characterisation of the porous polysulfide polymer

Sulfur (5.0 g) was stirred and heated to 180 °C in a round bottom flask using a hotplate. At 120 °C the sulfur became orange in colour. After the sulfur had melted canola oil (5.0 g) was added drop-wise to the stirring sulfur ensuring to maintain a temperature around 180 ℃. Then, ground NaCl (23.5 g) was added portionwise to the mixture. The reaction was stirred until it solidified, forming a rubber (~ 45 minutes total reaction time) before cooling to room temperature. The polymer was removed from the flask and milled in a blender to give particles between 0.5-3.0 mm in diameter. The polysulfide polymer was stirred in a beaker with 800 mls DI H_2O for 2 hours to remove the salt. Vacuum filtration was used for isolation of the polymer before being placed in an open tray in the fume hood to dry. A constant mass indicates that the polymer is dry and ready for use. In the cases where NaCl is still present on top of the polymer, it was washed and dried again.
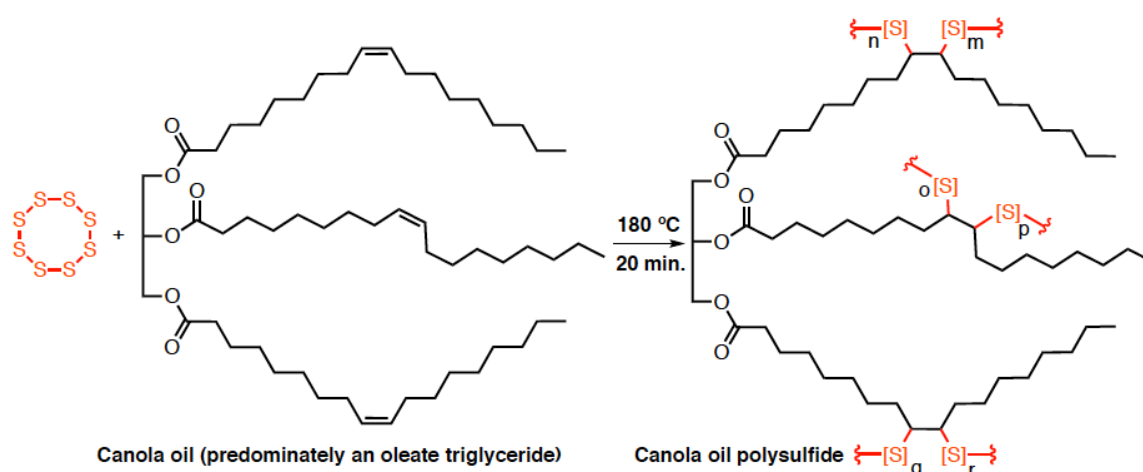
Figure 1: Structure and synthesis of the polysulfide polymer[10].

Figure 1 shows the reaction of synthesis of polysulfide polymer that heating up sulfur. Heating the sulfur breaks the S-S bonds forming sulfur radicals. These radicals can then react with the alkenes in canola oil, with the process continuing until the polymerisation terminates

when either the sulfur radicals bind to themselves or all sulfur radical have reacted with an alkene.

Figure 2: Image for porous polysulfide polymer This particle was isolated with a sieve with a 2.5 mm cut-off.

Images shown in figure 2 is porous polysulfide polymer. The porosity can be seen on the surface of the polymer. The porosity increases surface area of porous polysulfide polymer.

IR Analysis
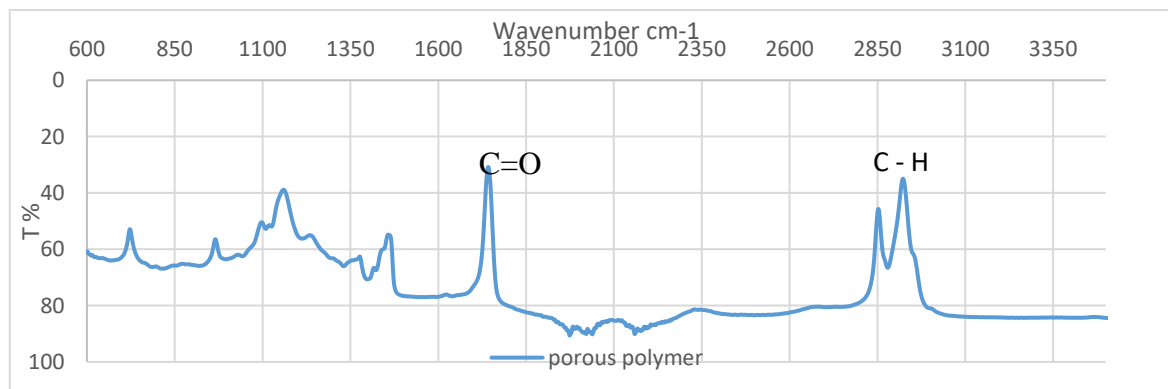
Figure 3: IR spectra of the porous polysulfide polymer.

IR spectra reveals the absence of C=CH and C=C peaks and shows C-H at wavelength 2850 and C=O peaks which is consistent with literature[10]. The absence of C=C and C=CH means that all double bond is reacted. The literature reports that the absence of peaks C=CH and C=C is an evidence for radical sulfur reacts with alkyne that are in canola oil.

5

Simultaneous Thermal Analysis (STA)

Simultaneous thermal analysis (STA) was conducted on to the porous polysulfide polymer. The initial temperature was set to 30 ºC, heat flow rate to 20 ºC/ min and the final temperature was set to 600 ^{0}C holding for 2 minutes. STA disclosed two mass losses during the thermal analysis, one at 270 °C and another at 580 °C. The reported data that sulfur degraded at 270 ºC at this temperature, the volatile and malodourous gas is released. Canola oil is degraded at 580 ºC. The canola oil domain breaks down in the second stage[10].
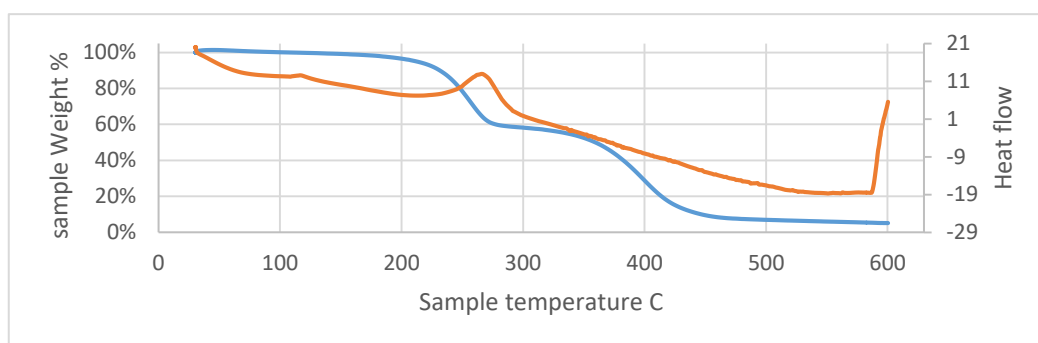
Figure 4: STA data for porous polysulfide polymer. Data for isothermal analysis

The data indicates that there two stages of thermal degradation for the polymer. The polysulfide polymer is made by two materials which are sulfur and canola oil, therefore the isothermal data indicated that the first stage degraded at 48% of total weight of polysulfide polymer (probably S-S bond degradation)[10].

Scanning Electron Microscope (SEM) Analysis

The SEM images were obtained by placing a carbon tube on a stub, then a small particle size of porous polysulfide polymer was placed on the carbon tube. Using sputter coater, the sample was coated with 5 nm of Cr and placed inside the SEM chamber. A 20 kV was found to provide higher quality images than 5 kV.
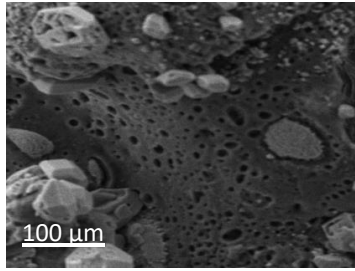
Figure 5: SEM image for porous polysulfide polymer showing the porosity. It looks sponge –

like. Scale is 100 μm.

Perfluorooactanoic acid

Introduction

PFOA is classified as a toxic compound and has emerged as a health risk and threat to our environment[21], having being identified by the EPA in many countries including Australia and the USA[1]. In addition to the toxicity of PFOA, it is also persistence and stays in the environment for long periods of time after its introduction. One major problem with PFOA is that the degradation process is very slow. The strong C-F bond[7] resulting from the high electronegativity of the fluorine atom[7, 22-23].
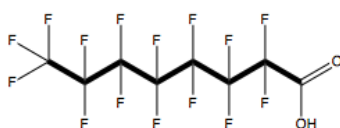
Figure 6: PFOA structure

Another problem is the spread of PFOA in the environment, is able to be transport up to 2 miles[23]. This transport of PFOA means not only the adjacent area will be affected, but the other side of land might be affected also.

Although long chain of alkyl fluorinated banned in most countries, PFOA it is still widely used in our world and has several applications being used in firefighting foam, insecticide, and surfactant[3-4, 15-16, 21-22, 24-28]. Firefighting in fire station is still having some firefighting form but is not used for training. Therefore, PFOA products are still in aquatic land or even in the fire station.

In general, a surfactant is an amphiphilic compound, one which has both hydrophilic heads and hydrophobic tails, PFOA also amphiphilic[7, 29]. Dissolving surfactants such as PFOA in water forms micelles[29].

Our environment has been contaminated by waste PFOA products with most being discarded into our water ways[1, 6, 22, 25, 30]. Waste PFOA is challenging for ecosystem due to the very slow degradation process and persistence in the nature. There are some applications that are being used to capture PFOA such activated carbon, however this has a limited shelf-life for capturing PFOA. It is essential that an effective technology using cheap and non-toxic materials is developed to help in the removal of PFOA from groundwater.

The Chalker lab has developed an inexpensive, green polysulfide polymer from the waste material sulfur and canola oil. Both these raw materials are cheap and also renewable. This polysulfide polymer meets the requirement for a desired material for PFOA capture. It is made from cheap, waste products, is made via an easy process containing no solvents, and produces no by-products [9-11]. This low cost process plays an important role in cleaning up the environment as converts waste materials into purposive products. Recycling waste products in addition to the low cost process is required in our world. The inexpensive process is an essential for encourage companies.

The polysulfide polymer is classified as a green product and is made using a low lost process. Polysulfide polymer becomes more attractive for industries because the sources are abundant and cheap. However, this technology needs to be able to reduce the quantity of PFOA down to the EPA limits which is 70 ng/L[21].

A improved porous polysulfide polymer has also being synthesized by the Chalker lab (reference here) using salts in the production increasing the surface area[10]. Using NaCl during the synthesis of polymer creates pours throughout the polymer contain the NaCl crystals. This NaCl can then be removed simply by washing the polymer with water leaving being channels throughout the polymer. This creates a porous polysulfide polymer with a higher surface area. Using this cheap and green polymer to remove toxic compound such as PFOA has two major advantage for our environment. First it eliminates waste product, sulfur and cooking oil, forming a useable product. Second, the polymer can remove toxic compound from our environment.

In this study, the porous polysulfide polymer is tested for its effectiveness in removing or reducing PFOA from water with the aim of reducing it to below the limits set by EPA (70 ng/L). If achieved the water becomes more healthy and free of PFOA.

Aim

PFOA is found as a toxic compound in environment. There are several applications that become sources of PFOA wastes because PFOA is a main raw material. The applications are including firefighting form, surfactants and Teflon products. Those applications are essential in our current life-style. PFOA is a very unaffected with normal conditions. Porous polysulfide polymer that was made by waste and by-product sulfur and renewable product canola oil will be used for removing PFOA from water and environment.

Materials

PFOA purchased from Sigma Aldrich 5 g, DI water, sulfur, canola oil and NaCl. The porous polysulfide polymer was prepared as previous described.

Results and discussion

<u>^{19}F NMR PFOA concentration limit:</u>

A 2 mg/ml solution of PFOA was prepared by added PFOA (50 mg) to a 25 ml volumetric flask and filling with DI H_2O. Serial dilutions were performed to create solutions of concentrations 1, 0.5, 0.25, 0.125, 0.0625 and 0.03125 mg/ml. Each concentration sample was analysed by ^{19}F NMR. The NMR sample was prepared by adding 60 μL of D_2O spiked with trifluoroacetic acid (TFA) (5.4 mg/ml) to 600 μL of the PFOA solution.
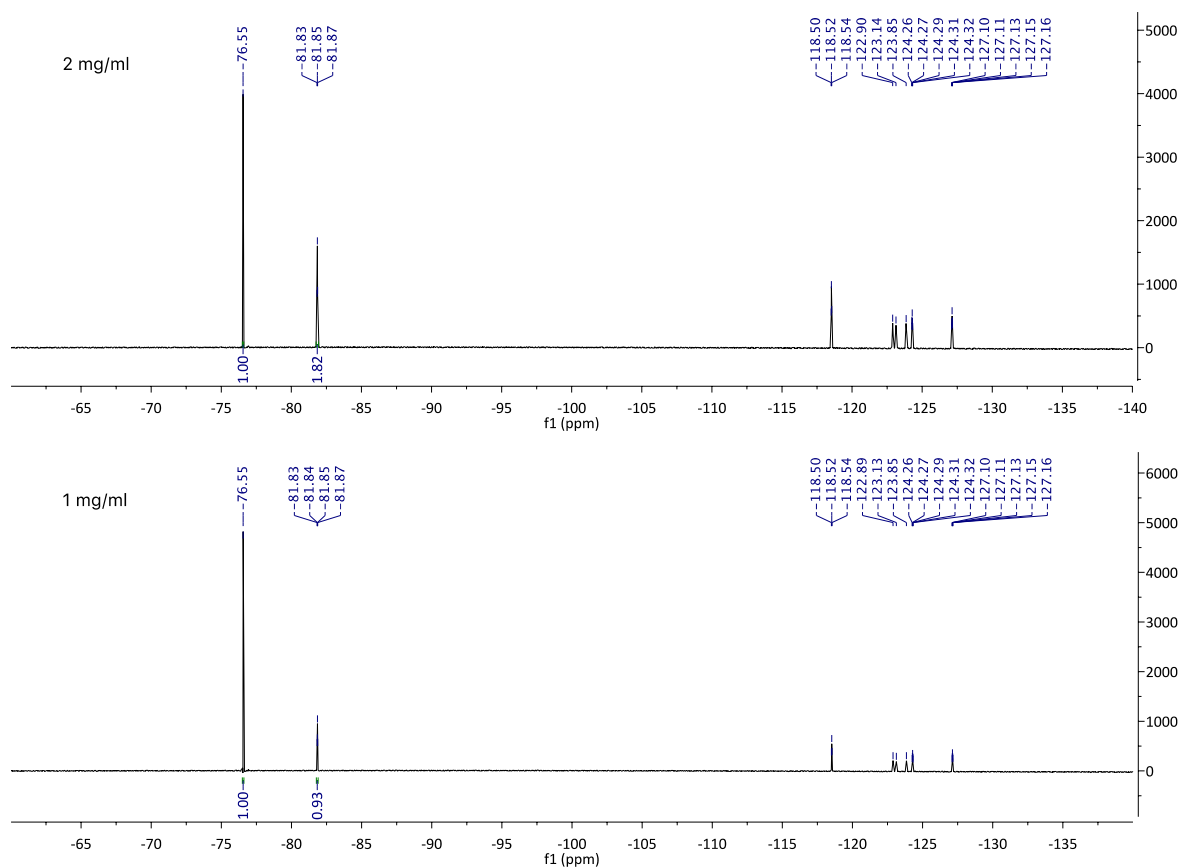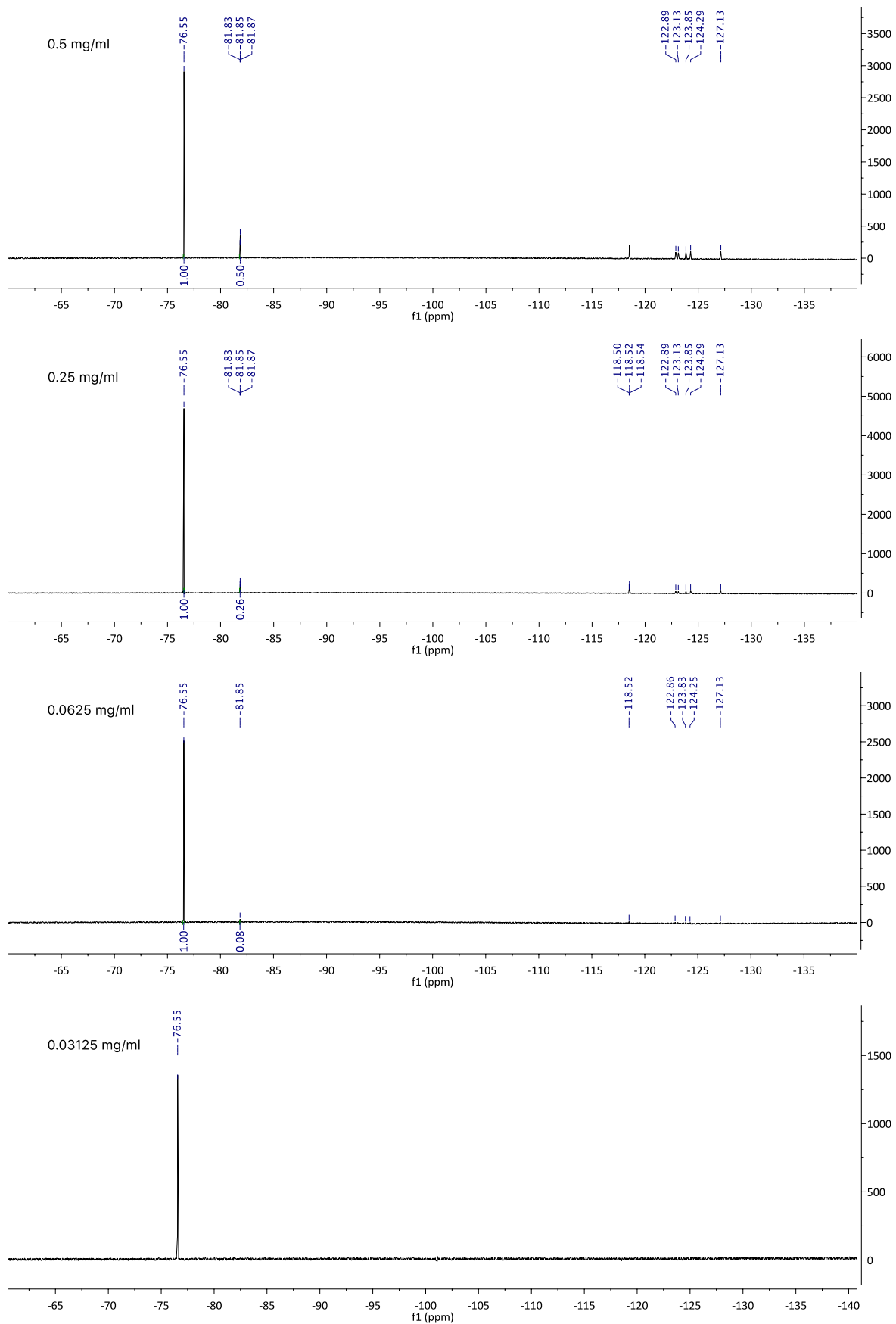
Figure 7: ^{19}F NMR of 2, 1, 0.5, 0.25, 0.125, 0.0625 and 0.03125 mg/ml PFOA solutions.

At a concentration of 0.0625 mg/ml small signals can be seen in ^{19}F NMR spectrum, the error in integration is high. As such, the limit of detection for this study was determined to be 0.25 mg/mL. Data was plotted on figure 8, the data performed straight line with R^2 value is 0.9998.

PFOA in water (NMR control):

A 9.5 mg/mL (saturated) solution of PFO was prepared by added PFO (953 mg) to a 50 ml volumetric flask and filling with DI H_2O. It was analysed by ^{19}F NMR at 24 hours. The NMR sample was prepared by adding 60 μL of D_2O spiked with TFA (5.4 mg/ml) to 600 μL of the solution from the vial in a NMR tube.
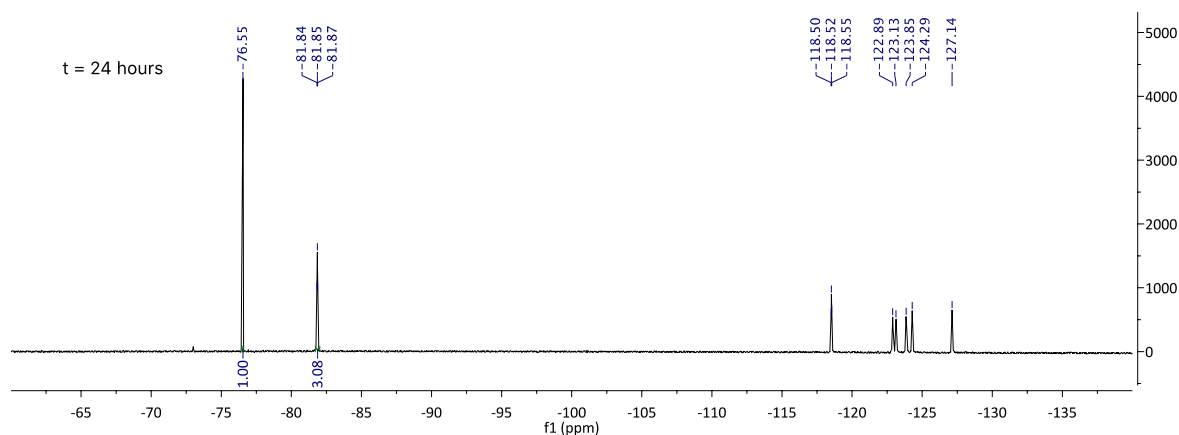
Figure 8: ^{19}F NMR for PFOA [9.5mg/ml] control sample at 24 hours.

The ^{19}F NMR has a signal for TFA at -76.55 ppm and PFOA at -81 ppm. The signal for TFA represents three fluorines (CF_3COOH) as does the signal for PFOA ($CF_3C_6F_{12}COOH$). As such TFA can be used as an internal standard for determining the amount of PFOA in solution. For this reason, TFA is a good internal standard and excellent comparing standard for PFOA.

Removing PFOA from water:

A solution of PFOA (5 ml, 9.498 mg/ml in H_2O) was added to a glass vial containing the porous polysulfide polymer (2.00 g). After 24 hours the sample was analysed by ^{19}F NMR. This experiment was repeat in triplicate. The NMR sample was prepared by adding 60 μL of D_2O spiked with TFA (5.4 mg/ml) to 600 μL of the solution from the vial in a NMR

tube.

Figure 9: ^{19}F NMR for PFOA absorption of the porous sulfur polysulfide at 24 hours (Replicates 1, 2 and 3).

The change in the ratio of PFOA to the internal standard with and without the polymer indicates some absorbance by porous polysulfide polymer of PFOA.

PFOA absorption non-porous polysulfide polymer:

A solution of PFOA (5 ml, 9.498 mg/ml in H_2O) was added to a glass vial containing the non-porous sulfur polysulfide (2.00 g). After 24 hours the sample was analysed by ^{19}F NMR. This experiment was repeat in triplicate. The NMR sample was prepared by adding 60 μL of D_2O spiked with TFA (5.4 mg/ml) to 600 μL of the solution from the vial in a NMR tube.

Figure 10: ^{19}F NMR for PFOA absorption of the sulfur polysulfide (non-porous) at 24 hours (Replicates 1, 2 and 3).

The non-porous polysulfide polymer was found to be less efficient than porous polysulfide polymer at removing PFOA from water. The main differing feature between the porous and non-porous polysulfide polymer is that the porous polymer has a higher surface area. The ratio for control sample is 3.06 PFOA to 1 TFA, and the ratio of PFOA when using porous polysulfide polymer is 2.1 PFOA to 1 TFA, but the ratio of PFOA when using non-porous polysulfide polymer is 2.21 PFOA to 1 TFA. The low ratio of PFOA to TFA is less for using porous polysulfide polymer. The table below reveals the difference in removing efficiency between porous and non-porous polysulfide polymer.

Table 1: The difference in removing PFOA from water with the porous polysulfide polymer and the non-porous polysulfide polymer.

	control	PFOA removed %	Porous	PFOA removed %	Non-porous	PFOA removed %
	3.06	0%	2.15	29%	2.16	29%
	3.06	0%	2.13	30%	2.23	27%
	3.06	0%	2.02	34%	2.24	27%
Average	3.06	0%	2.1	31%	2.21	27%

SEM/EDS of the polymer after capture of PFOA:

The porous polysulfide polymer that had been treated with aqueous PFOA [9.5mg/ml] was filtered by vacuum filtration and placed in fumehood to dry. This sample analysed using SEM. The sample was coated with 5 nm platinum because polysulfide polymer is non-conductive polymer and SEM requires conductive material.
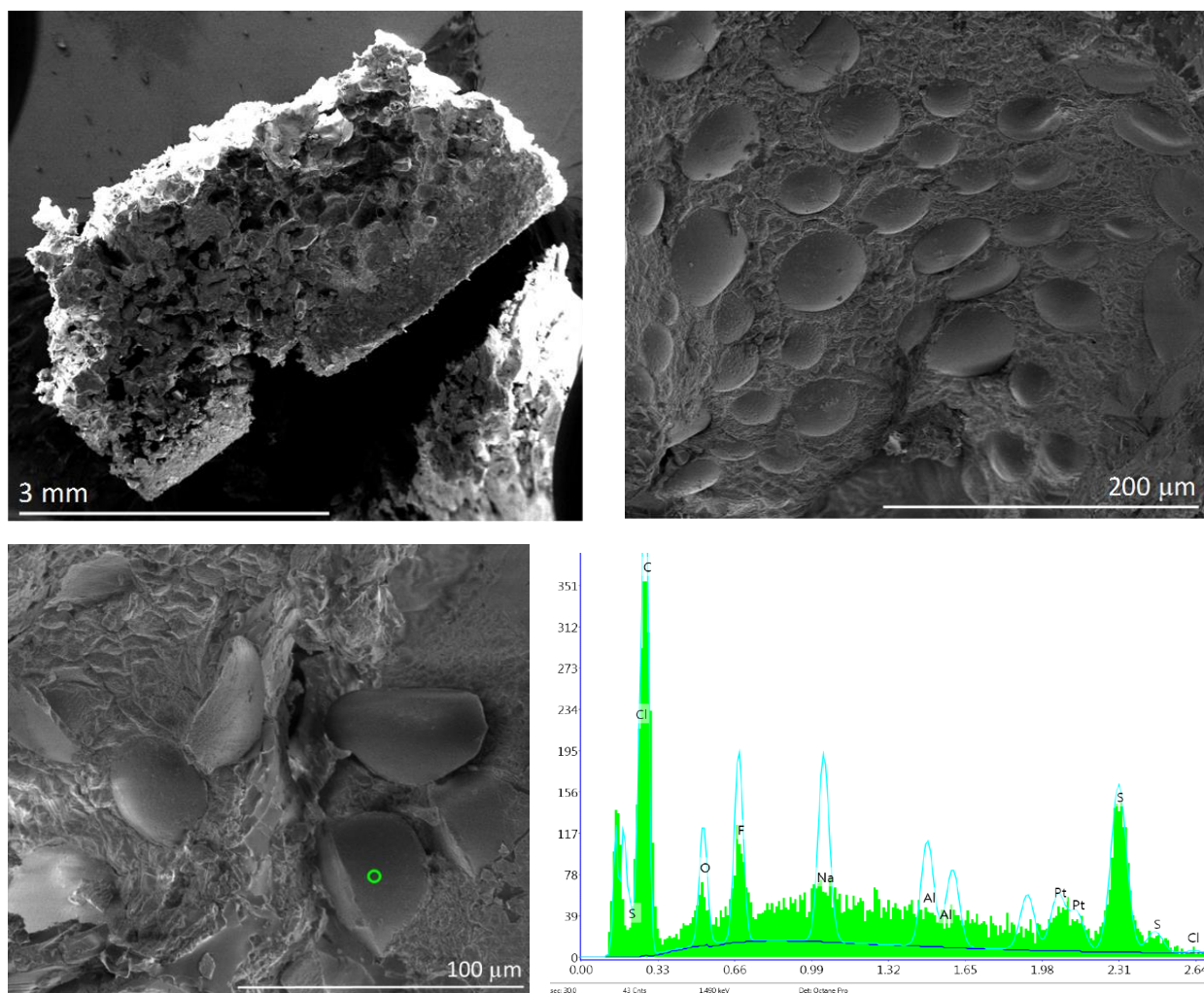
Figure 11:SEM images and EDX spectra of porous polymer after incubation with PFOA.

SEM (in figure 12) images shows hemi-micelles on surface of porous polysulfide polymer. As mentioned above that PFOA has hydrophobic tail and hydrophilic head. Porous polysulfide polymer is hydrophobic material. EDS confirms the fluorine availability on surface of porous polysulfide polymer.

PFOA absorption with varying quantities of porous polysulfide polymer:
A solution of PFOA (5 ml, 9.498 mg/ml in H_2O) was added to four glass vial containing the

porous polysulfide polymer (vial 1 contained 0.5 g, vial 2 contained 1 g, vial 3 contained 1.5 g and vial 4 contained 2 g). After 24 hours the sample was analysed by ^{19}F NMR. The NMR sample was prepared by adding 60 µL of D_2O spiked with TFA (5.4 mg/ml) to 600 µL of the solution from the vial in a NMR tube.
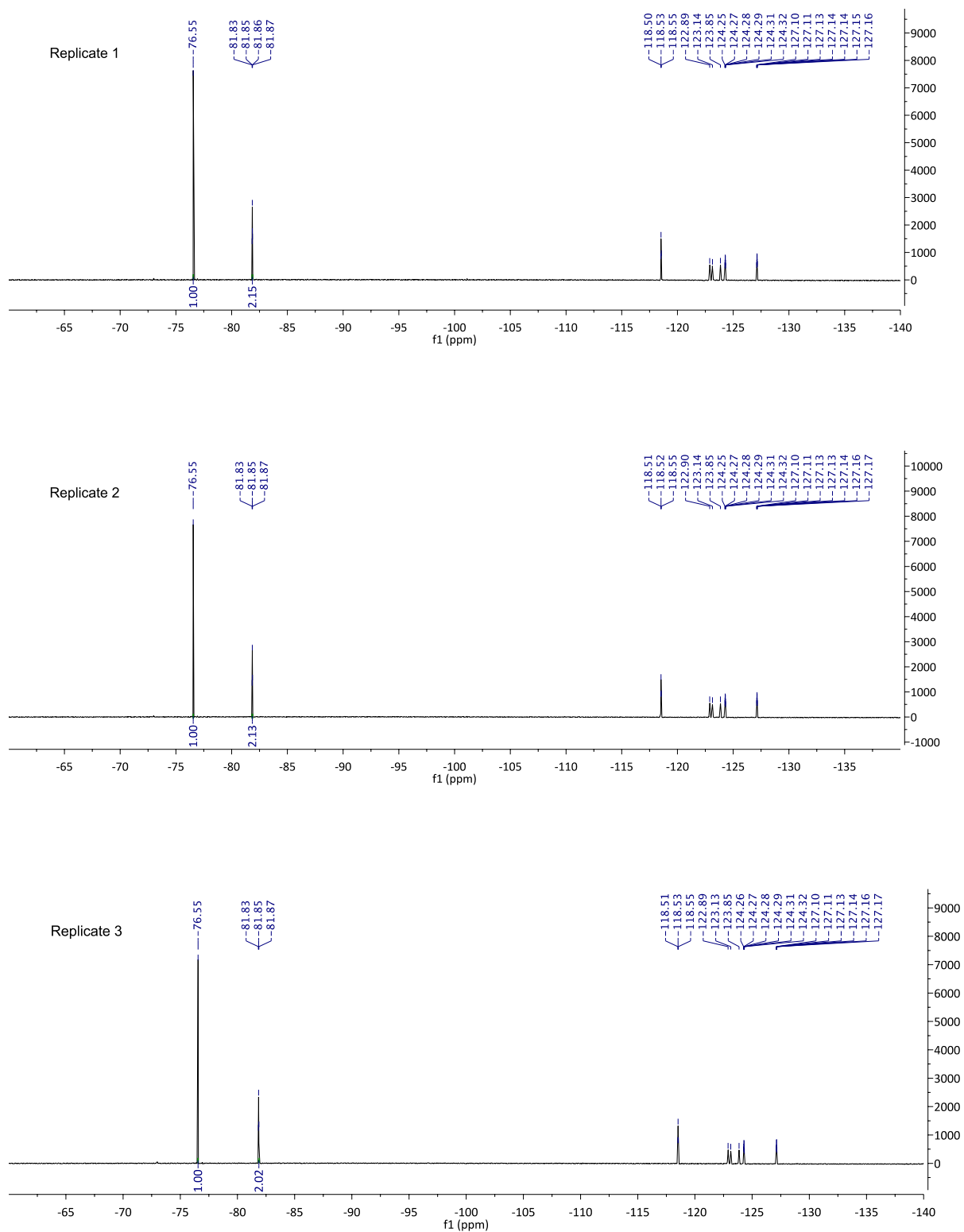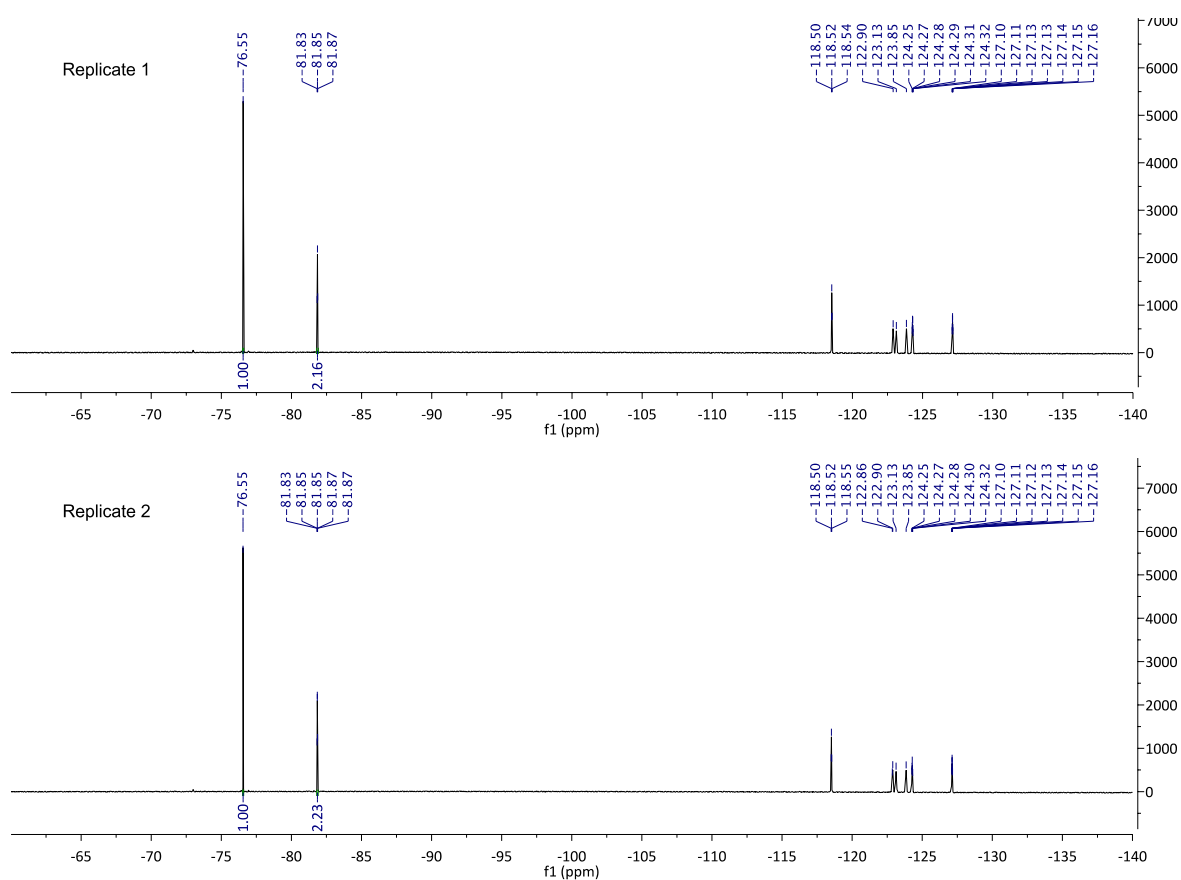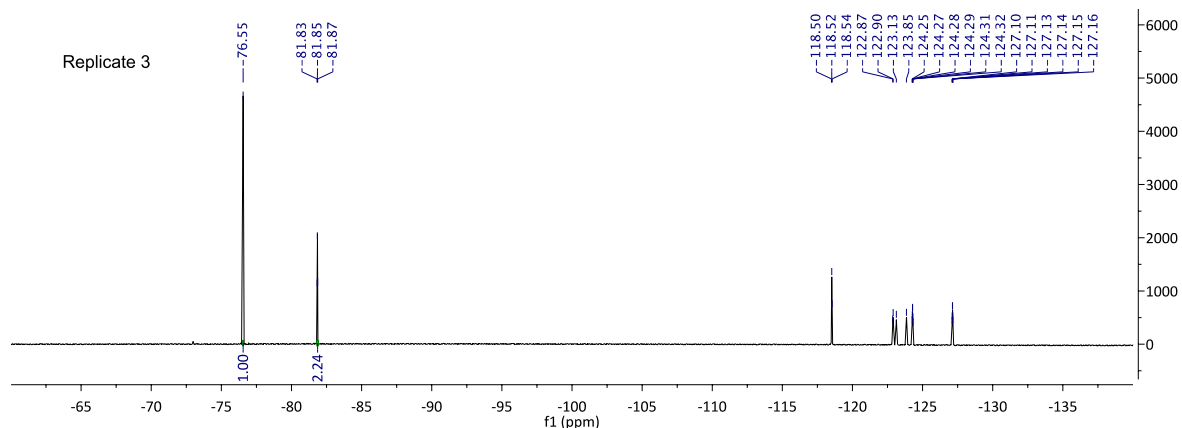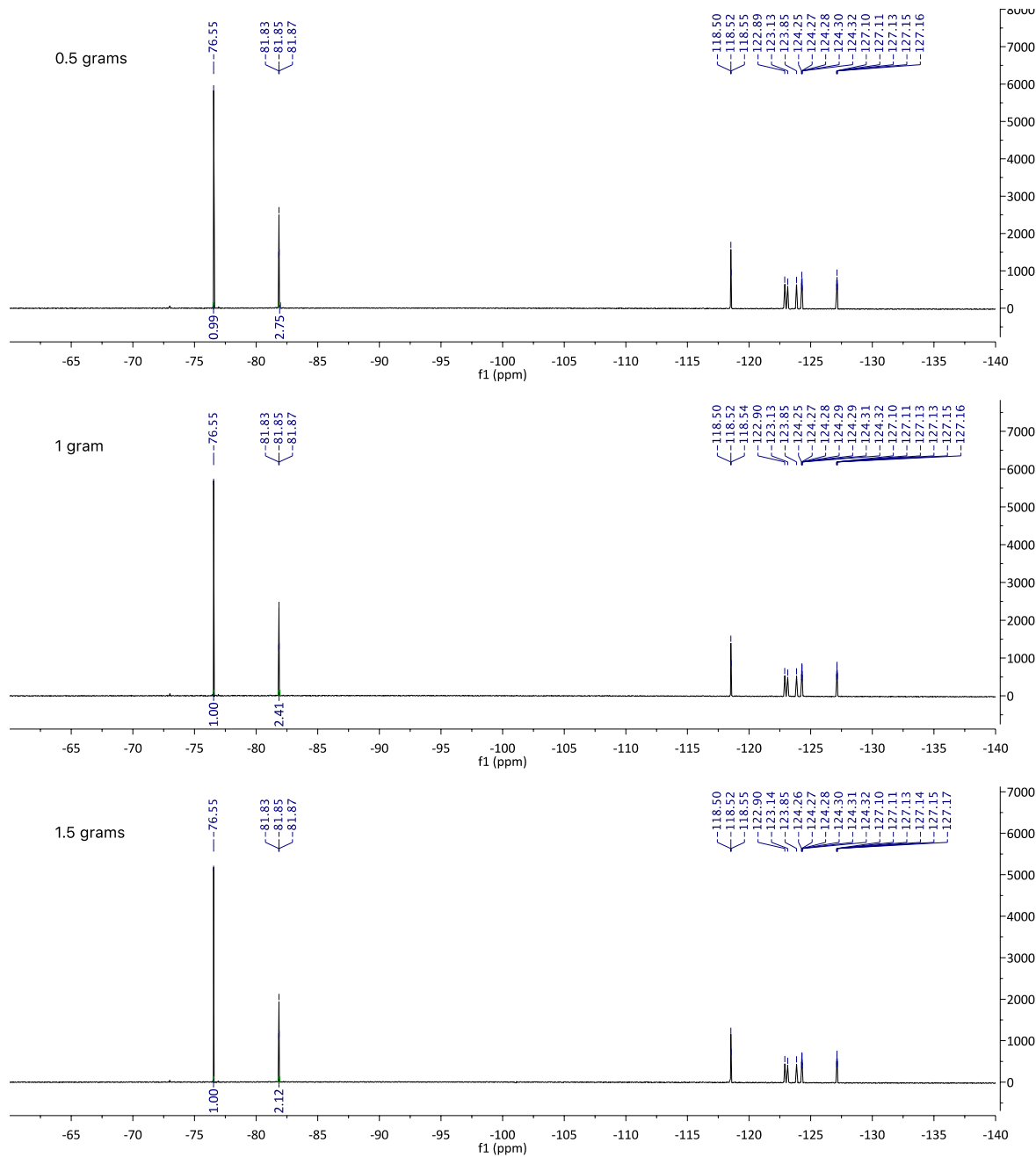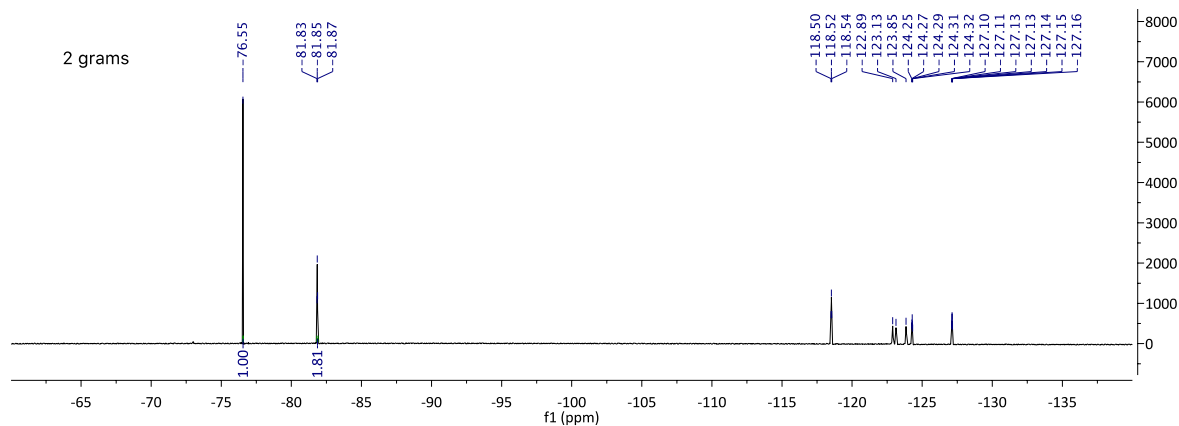
Figure 12: ^{19}F NMR for PFOA absorption of 0.5, 1, 1.5 and 2 grams porous sulfur polysulfide at 24 hours.

The ^{19}F NMR shows that the absorption of PFOA by porous polysulfide polymer is constant. High mass of porous polysulfide polymer leads to the highest removal of PFOA form water. Each 0.5 g porous polysulfide polymer can absorb about 13% of the PFOA in a 9.5 mg/mL solution. The ratio of PFOA concentration reduced 13% when mass of porous polysulfide polymer increased from 0.5 g to 1 g. The same ratio is constant for other mass of porous polysulfide polymer. The results have proved that the porous polysulfide polymer is able to remove aqueous PFOA, and ability of absorbance increases with mass of porous polysulfide polymer increase.

Dissolve PFOA in cold DI H$_2$O:

DI water was placed in ice-bath until the thermometer read 6 $^{\circ}$C, then added 50ml of cold DI water to the weighed 24.6mg of PFOA in volumetric flask (50ml). the final concentration is 0.492mg/ml aqueous PFOA. In a glass vial, porous polysulfide polymer was weighed 2 g, and added 5ml aq. PFOA. In other glass vial, made a control sample by adding only the aq. PFOA prepared in cold water.
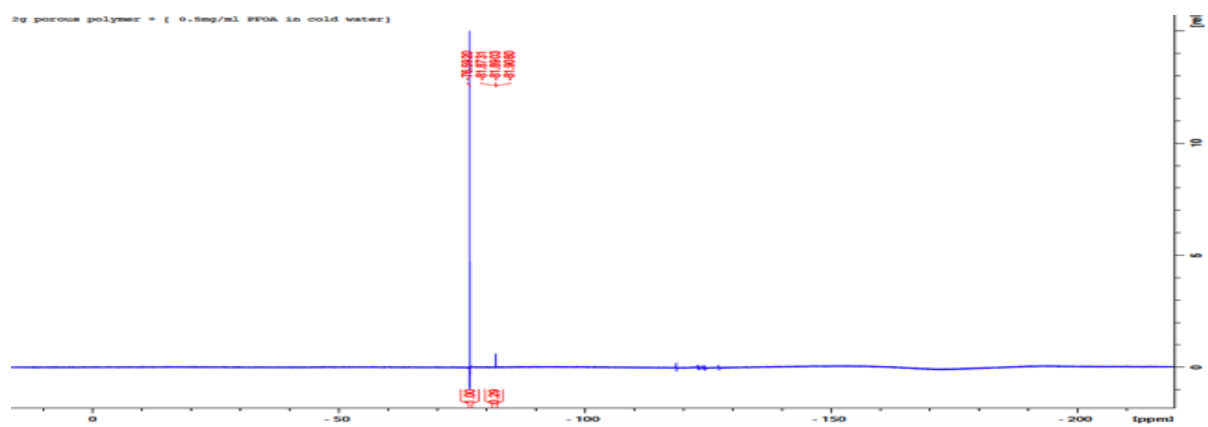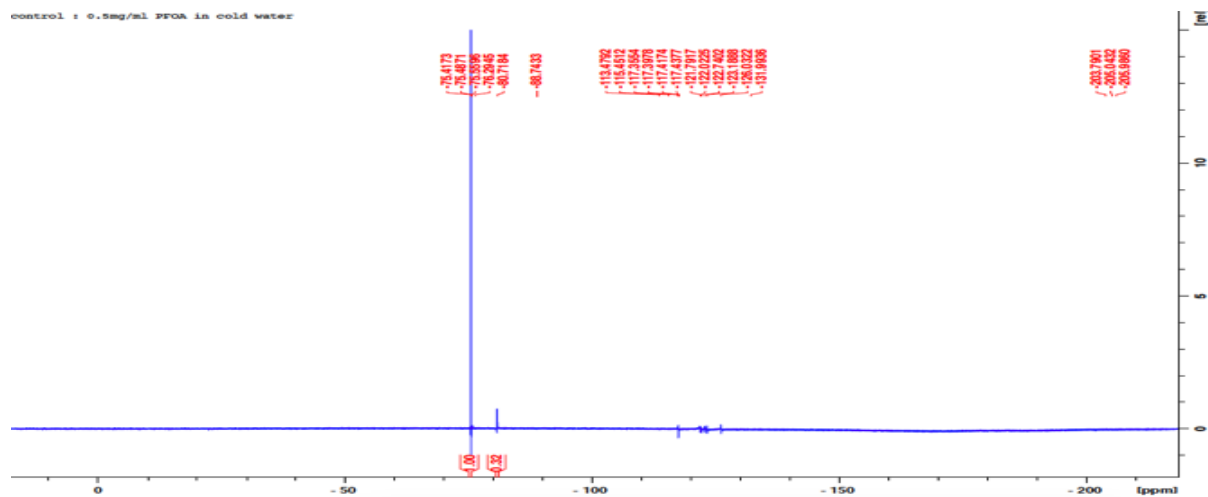
Figure 13: ^{19}F NMR spectrum for low PFOA dissolved in cold water and then mixed with 2 g porous polysulfide polymer.
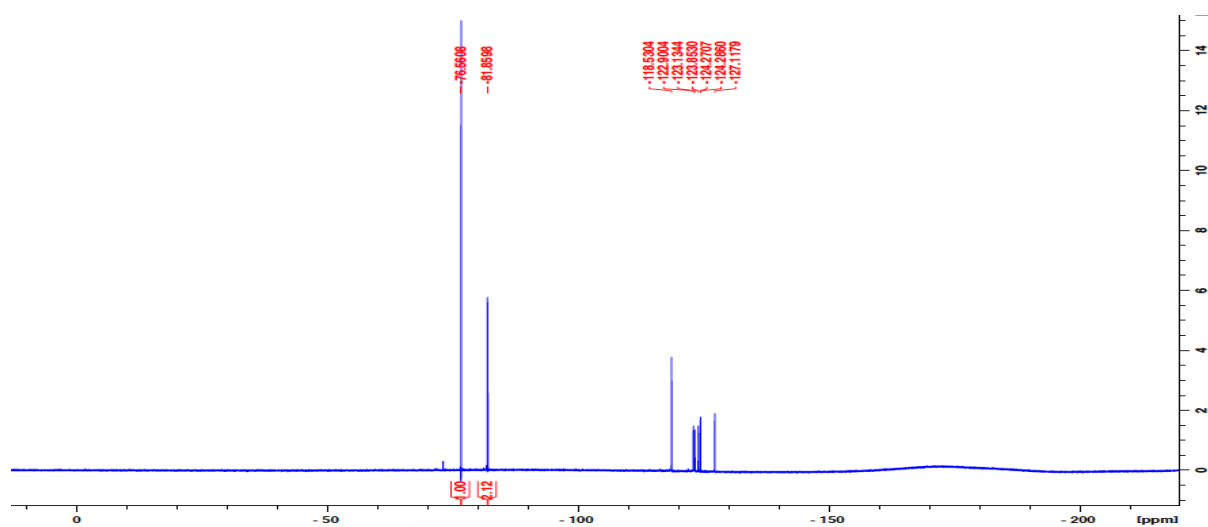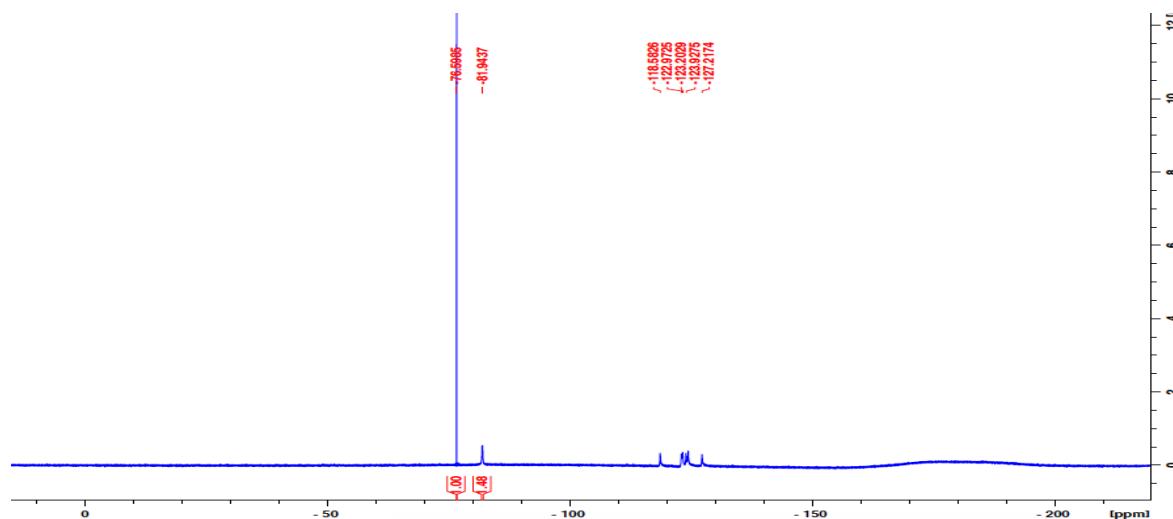
Figure 14: ^{19}F NMR spectrum for high concentration of PFOA dissolved in cold water and then mixed with 2 g porous polysulfide polymer.

PFOA is hydrophobic and when dissolved in water forms hemi- micelles. Micelles are effected by several factors including temperature, concentration and pH of the solvent. In this experiment the use of cold water was to find out if confirmation of micelles does effect, then absorbed by hydrophobic porous polysulfide polymer. aqueous PFOA makes micelles in water and it naturalize with hydrophilic media which make a challenge to be absorbed by hydrophobic polysulfide polymer. The results show some PFOA be absorbed by porous polysulfide polymer but the very low amount of PFOA was absorbed, therefore it is hard to conform that cold solvent prevent micelles from been formed. The results repeated with high concentration of aqueous PFOA in cold DI water and compare the results with normal temperature of water that PFOA was dissolved in and also compares with low concentration of aqueous PFOA that was dissolved in cold water. At low concentration of PFOA that dissolved in cold water, only 10 % was absorbed but at high concentration of PFOA that dissolved in cold water about 30% was absorbed by porous polysulfide polymer.

Conclusion

Porous polysulfide polymer is lipophilic and PFOA is hydrophobic. PFOA in water forms hemi-micelles which neutralizes with water. The hemi-micelles forms on Porous polysulfide polymer. porous polysulfide polymer may need pre-treatment to be able to destroy micelles and then absorbs PFOA, since micelles is stable. Although stability of micelles, porous polysulfide polymer is capable to absorb some amount of PFOA. The future work will be

used very dilute nitric acid with porous polysulfide polymer for charging surface of porous polysulfide polymer then when it becomes dry, add it to the aqueous PFOA. The positive charge might attract negative charge that on hemi-micelles. Since the point is to charge positively surface of porous polysulfide polymer. Other future experiment is that the polysulfide polymer does not need to wash out the NaCl from it, once polysulfide polymer places with aqueous PFOA, NaCl would be washed leaving porosity behind and increase pH of the media and it might destabilize hemi-micelles formation.

Gold

Introduction

Mining industry is a major economy for some countries[18]. The gradual increase in the commodities market recently and the benefit of mining business are leading to expand mining either in land or even in deep sea mining. Tailing disposal becomes more attractive for business due to the rise in the price of mineral. The long term of tailing disposal makes the tailing has high concentration in metals which are investable for companies and due to the costly technology, the companies faces obstacles for cost reduction of mining. In addition, the long term of disposal into deep sea, accumulates and increases the concentration of unwanted metals and as a consequence of high concentration, it discharged into coast [4]. The technology that is required for separation valuable metals from invaluable metals is cost time and money. Scientists are developing a technology that low cost for separation and adsorbs metal and in the same time it is save for workers and environment. The reliable technology needs to meet the diverse of conditions such as safe for environment, economic benefit for companies, and low risks for workers.

Despite the laws, there are several issues that preventing companies from applying the laws of protecting environment. The matters are overlap and laws are varying from region to another[31]. The current process for gold mining either contains health risks or is a complicated process and/or has a high cost. The high cost means in other side a low profit for businesses. In Artisanal small scale gold mining (ASGM), 10% to 15% of gold mining worldwide using amalgam process which are using bare hand then burns mercury for obtaining gold metal[10]. Small-scale gold mining is contributed about 25% of global production of gold[32].The high demand for gold mining leads to exploration of gold even in deep sea[18]. Deep sea mining (DSM) has become a target for mining industries [18]. Deep sea mining is tailing that was disposed from tailing ore. In addition to the industries, small-scale gold mining is conducting by people at their home. Miners are using excessive mercury to form amalgam, amalgam is able remove gold from ore. Mercury method that is using in ASGM contributes 37% of mercury pollution in world annually [32]. In other hand, by using clean technology that is replaced mercury leads to reduction of mercury pollution to 37%. The Instead of applying new laws which may make the life more complicated, finding new green technology that ease the life of people and prevent pollution and also clean –up waste materials. sulfur is waste product of petroleum industries which is underused[9]. Sulfur is highly produced every year

and it is very cheap[12]. It is major feedstock for sulfuric acid[9]. Canola oil is renewable source and non-toxic[10-11]. The synthesis of polysulfide polymer is made by two materials which are sulfur and canola oil, and the reaction run without any solvent. This process meets the most principles of green chemistry. In addition, the use of green technology for reducing health risks and increases benefits of miners and also clean up the ecosystem would be great impact. Polysulfide polymer is made by sulfur and canola oil. Synthesis of polysulfide polymer is needless catalyst or solvent. In addition, the synthesis of polysulfide polymer has no by-product. The technology is entirely used waste materials which are sulfur and canola oil. Both raw materials are cheap and waste materials. Polysulfide polymer has a positive impact for nature in two ways. The first way is a cheap technology that able to clean-up the nature from waste material and the second way is that can capture toxic waste. In this thesis, polysulfide polymer is proofed for binding gold and after scientific analysis. In this thesis, gold chloride is used as an aqueous solution and mix with polysulfide polymer. Gold chloride bound to polysulfide polymer within one hours, then the gold chloride recovers as metal gold at the end. Gold metal is aim for mining sector. By using cheap, renewable, green technology of producing polysulfide polymer, the pollution becomes less, the health risks become fewer, and the benefit of gold miners will be huge by cost reduction. By applying this technology, it benefits all including mining sector people by using cheap technology with abundant sources, and benefits people by reducing all toxics materials and furthermore polysulfide polymer advantages environments by recycling waste materials.

Aim

The aim of this research is synthesising renewable materials that are entirely from waste materials and by-product with no catalyst and no solvent is required. The material will be used in mining sector for binding gold. The material is Polysulfide polymer. Polysulfide polymer technology has several value either for gold mining companies, environment, or workers at mining sector. The low cost of polysulfide polymer will lead Gold mining companies to obtain extra benefits and the abundant sources for the technology that are sulfur and canola oil. The polysulfide technology is a polymer that is made from sulfur and canola oil. Polysulfide polymer technology is aiming to use for gold mining to bind gold and then recover gold as metal. There are several techniques will be used to for characterisation of the research. The instruments are ICPOES for initial concentration, SEM analysis to find polysulfide polymer before mixing with gold and after mixing with gold for any different.

EDS technique is an excellent instrument to detect the gold on polymer and recovered gold. XRD during the bound of gold on polymer and examine the recovered materials. UV-vis spectroscopy and STA also will be used.

Materials

Polysulfide polymer technology is a simple technology that is no catalyst, or reagent or solvent is required. The two main raw materials are sulfur and canola oil. Sulfur is a by-product material, cheap waste, underused material. Some petroleum industries sell it in negative price. The second raw material is canola oil. It is vegetable oil which are renewable product. $AuCl_3$ is using as a source of gold.

Results and discussion

Au (III) calibration curve:

Aqueous $AuCl_3$ was prepared by weighing 500 mg $AuCl_3$ in a 100ml volumetric flask, then added DI water to the mark. The volumetric flask was placed in a sonicator. After that, series dilution was prepared from 5 mg/ml $AuCl_3$, 2.5 mg/ml $AuCl_3$,1.25 mg/ml $AuCl_3$, 0.625 mg/ml $AuCl_3$, 0.312 mg/ml AuCl3 were prepared and used to construct a calibration curve based on the absorbance at 314 nm. The calibration curve is shown below. This calibration curve was used to monitor removal of Au (III) in subsequent experiments.
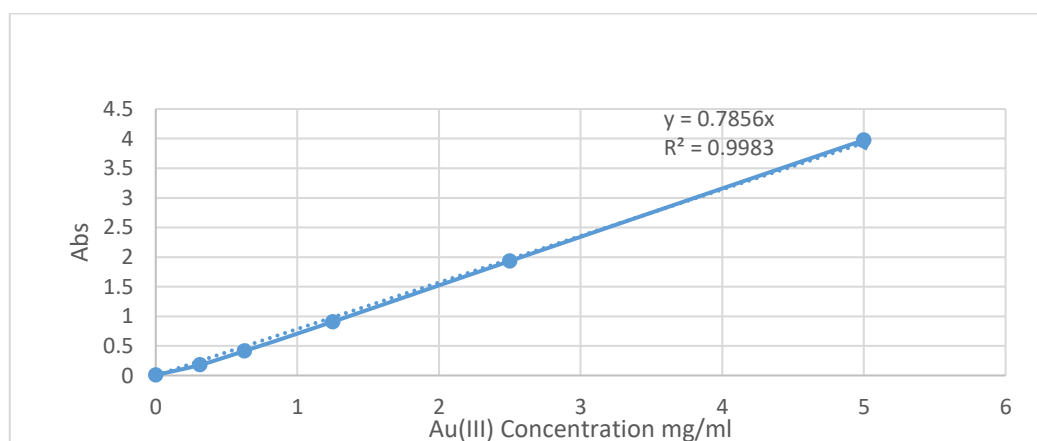
Figure 15: calibration curve for aqueous gold(III).

Au (III) removal from water using porous polysulfide:

A 20 mL aqueous of the 100 mg/L $AuCl_3$ solution was added to each of 4 centrifuge tubes (50 mL tube). One sample served as a control experiment in which no porous polymer was

added. To the remaining samples,0.25 g, 0.5 g, 0.75 g and 1.0 g of the porous polysulfide was individually added in each tubes. All samples were then placed on a rotating mixer (25 RPM) at room temperature. The concentration of Au (III) was monitored for all samples by taking a 3 mL aliquot and removing any solids using a bench top centrifuge (Stennick Scientific, 50-60Hz, 110-240V, HB3A004622). The absorbance at 314 nm was then recorded for the sample of different mass over zero time, 60 minutes and 180 minutes. The concentration of Au (III) in the solution over time is shown below.

Table 2: Concentration of Au(III) with different mass of polysulfide polymer over t = 0, 60 and 180 minutes.

gold (0.1mg/ml) mixed with porous polymer								
	0.25 g		0.5 g		0.75 g		1 g	
time	Abs	% Con. Of Au(III)	Abs	% Con. Of Au(III)	Abs	% Con. Of Au(III)	Abs	% Con. Of Au(III)
0	0.4003	100%	0.4003	100%	0.4003	100%	0.4003	100%
60	0.1717	43%	0.0186	5%	0.0255	6%	0.0244	6%
180	0.0397	10%	0.0186	5%	0.025	6%	0.0244	6%
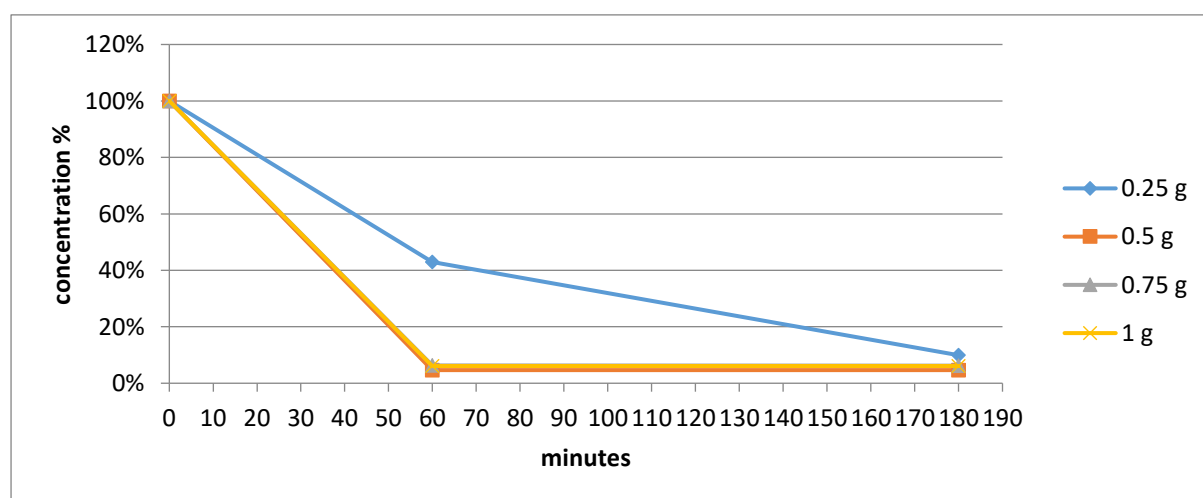
Figure 16: the concentration of Au(III) with different mass of polysulfide polymer over t = 0, 60 and 180 minutes.

<u>Finding the difference between different particles size of porous polysulfide polymer for removing Au(III) solution:</u>

The particle size plays important role for removing Au(III) from water. Small particle size is more efficient than larger particle size. The porous polymer was isolated by using different size of sieve to separate small particle size from large particle size. 5ml of aliquot of $AuCl_3$ was added into 8 different small plastic vails. 0.25 g porous polysulfide polymer with different particle size weighted into the small plastic vails. The particles size is varying from very fined particle size, particle size between 1mm and 2.5mm, and particle size larger than 5mm. The samples placed in mixer at room temperature for 90 minutes. Then after 90 minutes, the solution was draw to avoid any particles into a new small plastic vial. This step was repeating for all samples. All small plastic vials were placed in a benchtop centrifuge. Then all samples were analysed by UV instrument and data recorded at 314 nm.

Table 3: table shown differences between several particle sizes. the range between very fined particle sizes, 2.5mm>sample particle size>1mm, sample particle >5mm.

comparing between different particle size for faster gold absorbing			
particle size	concentration in mg/ml	% of gold in solution	difference
control sample (no polymer)	5.332		0.027
control sample (no polymer)	5.264		-0.027
average	5.298	100%	
very fined particle	0.086		-0.0006
very fined particle	0.088		0.0006
average	0.087	2%	
2.5mm>particle>1mm	0.098		-0.00135
2.5>particle>1mm	0.101		0.00135
average	0.099	2%	
particle >5mm	2.239		0.04945
particle>5mm	2.113		-0.04945
average	2.176	41%	

ICP experiments with gold and manganese:

Noteworthy to mention that manganese was used in this thesis for different reasons. First, it was part of collaboration with Prof. Claire Lenehan. Second, it aims to found out how porous polysulfide polymer selective for gold over manganese, in this case any metal available in mining might be used. 1g porous polymer was weighed in a plastic tube, and aqueous Au(III) was prepared as weighed 10mg $AuCl_3$ in volumetric flask 100ml, then added DI water to the mark. The final concentration is 0.1mg/ml. 20ml aqueous Au(III) was added to the 1g porous polymer and the plastic tube placed in the mixer for 90 minutes. Manganese Chloride was prepared by weighting 10mg $MnCl_2$ in volumetric flask 100ml, then added DI water to the mark to make final concentration 0.1mg/ml. Then 20ml of the aq. Mn2 solution was added to 1g porous polymer in a plastic tube. In the third section, 2 a plastic tubes have already 1g porous polysulfide polymer for each one, 10ml aq. Au(III) solution was added, and 10ml aq. Mn(II) solution was added to the same plastic tube. This addition makes 10 aq. Au(III) with 10ml aq. Mn (II) to total 20ml aq. Solution. After that, the plastic tubes placed in the mixer for 90 minutes. After 90 minutes, aqueous Au(III) solution and aqueous Mn (II) solution, and also from the mixture of Au(III) and Mn(II) were pipetted into a centrifuge tube, then added 2% (HCl 37%) to the total volume for preventing gold to stuck to the walls. The samples then centrifuged for 30 sec. the same process and steps were repeated for 120 minutes. All samples are triplicated and handled into Flinders analytical. The results were analyzed by suing Perkin Elmer Optima ICPOES 8000. All samples were diluted by 1 in 10 prior to analysis and acidified to 2% Aqua Regia.

Table 4: Data obtained by ICPOES for Au(III), Mn(III) and mixed between Au(III) and Mn(II) includes data for control samples.

Sample Id	Au (ug/L)	Mn (ug/L)
Au(III) + Mn(II) Control	20900	12000
Au(III) + Mn(II)	<LOQ	12000
Mn(II) Control	<LOQ	25000
Mn(II)	<LOQ	25000
Au(III) Control	48800	<LOQ
Au(III)	<LOQ	<LOQ
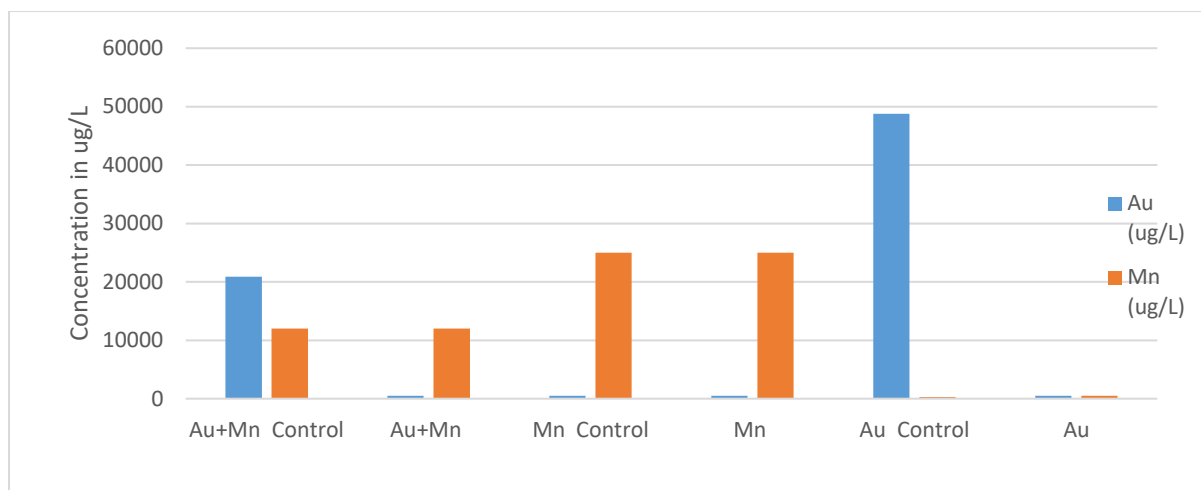
Figure 17: plot data for Au(III), Mn(II), and mixed Au(III) with Mn(II) includes control samples

SEM and EDS data for porous polysulfide polymer with gold:

Porous polysulfide polymer that was treated with aqueous Au(III) was filtered by vacuum filtration. The porous polysulfide polymer was placed in fume hood to dry. The dried sample was placed on SEM stub. The sample was coated with chromium 5 nm. Then the sample placed in SEM chamber for analysis.

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	37.91	69.55	1090.21	7.41	0.1212	0.7763	0.5955	0.4118	1.0000
O K	2.20	3.03	129.29	9.77	0.0073	0.7349	0.6023	0.4521	1.0000
S K	32.43	22.29	4339.03	1.70	0.2095	0.6666	0.6529	0.9620	1.0070
CrK	6.56	2.78	364.37	3.76	0.0429	0.6136	0.7218	0.9929	1.0735
AuL	20.90	2.34	151.23	11.96	0.1226	0.5009	0.9561	1.0265	1.1405

Figure 18: SEM images for porous polysulfide polymer. sample coated with Cr 5 nm. EDS data shows spot area and gold revealed gold peak.

Figure 19 revealed what polysulfide polymer contains as sulfur, carbon, and oxygen. In addition, gold peak appeared which indicates that the gold bound to polysulfide polymer. Figure 19 showed same dot are over all sample.

Porous polysulfide polymer treated with gold by STA:

By using STA technique, polymer is burnt and gold metal is recovered. The STA instrument is used for measuring the isothermal analysis of degradation of porous polysulfide polymer. The data is consistent with polysulfide polymer data published[10]. After 604 ºC, the weight of material that was unburnt is about 5% of original weight. The porous polysulfide polymer was mixed with aqueous A(III) with its concentration was 2.05 mg/ml. The sample was prepared for STA analysis by taking a small particle of porous polysulfide polymer, then the small particle placed in the crucible The program set as hold temperature on 30 ºC for two minute. Th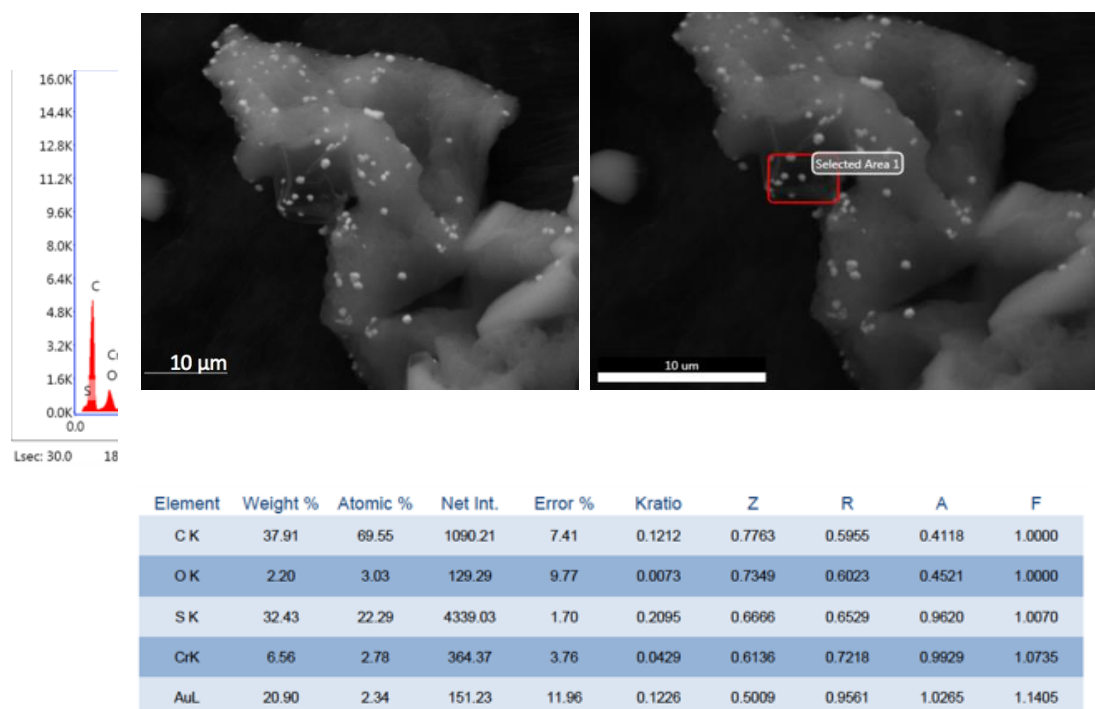en starting increasing heat flow from 30 ºC up to 600 ºC. then hold the temperature on 600 ºC for 3 minutes, and blow –up the sample with air to oxidise any unwanted left material that may oxidise by air. The program recorded the weight of the oxidized material.
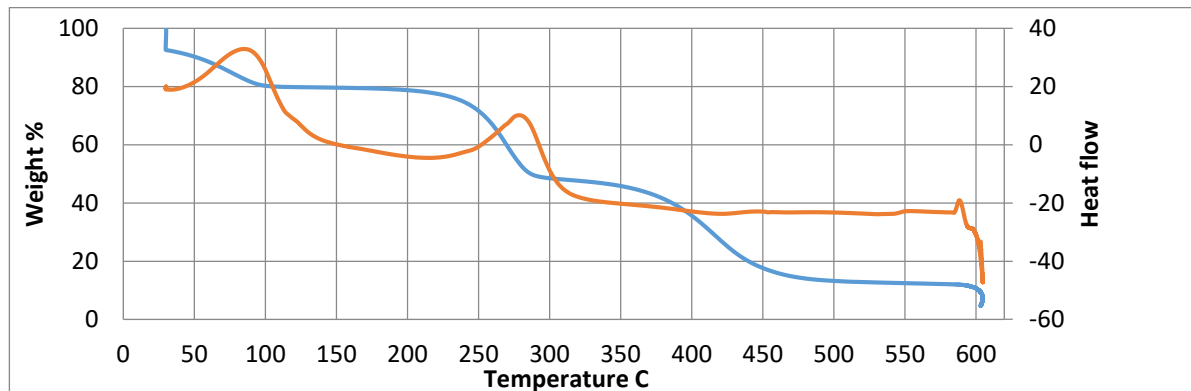
Figure 19: STA data porous polysulfide polymer that is already treated with Aqueous gold(III).

Isothermal analysis for polysulfide polymer that treated with gold reveals the breakdown of polymer in two stages.it is consistent with literature that was done by Worthington et al (2017)[10]. The first state of material is breakdown at about the 57% of total weight % of material. The polysulfide polymer made by 50% weight sulfur. In this case the isothermal is expected to be around 50%, but gold includes in the total mass of polysulfide polymer. Therefore, the isothermal calculation of material degradation is concluded the

weight of gold. After 605 ^{0}C, the polysulfide polymer was burnt and the gold metal is left. The percentage of remained gold is around 6% of the total mass of the material.

Recovered gold by burning off porous polysulfide polymer by using furnace and STA techniques:

Gold was recovered by using two different techniques. Both techniques are using same highest temperature which was 604 ℃. In furnace technique is able to use a large amount of porous polysulfide polymer, however, STA technique is only used 17mg. The recovered gold was imaged under microscope with magnification.
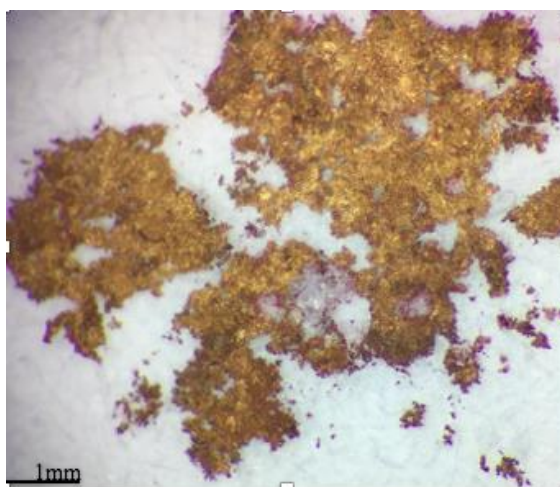
Figure 20: images of recovered gold by burning porous polysulfide polymer in a furnace, image was taken under microscope 10X.

STA technique is used as well to recover metal gold from porous polysulfide polymer. the program temperature was set at 604 ℃. the recovered material was gold and the image was taken under a microscope with magnification.
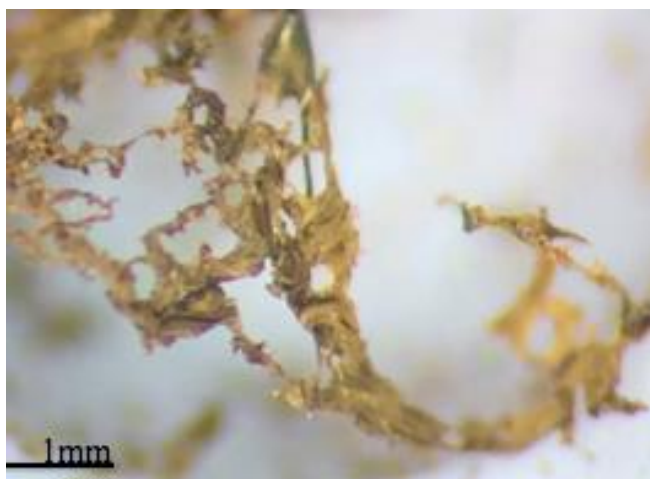
Figure 21: image for recovered gold by burning polysulfide polymer in STA, under microscope 10X.

SEM and EDS of gold recovered after STA:

Recovered gold was obtained after STA analysis. In STA analysis, the polysulfide polymer was burnt for 604 ℃ and gold recovered. For preparation of sample for SEM and EDS, carbon tube was placed on a stub. Then recovered gold placed on carbon tube. It is noteworthy that the sample was not coated at all. The stub including recovered sample placed inside SEM chamber. Then started the analysis of sample. The images were taken at different sizes. Then EDS was used to detect and find out the material on sample. The EDS revealed that gold is obvious percent of total weight of the sample.

Recover gold from burnt polymer:

The samples were analysed by XRD and compared with reference data base, the results matched gold synthesis as it shown in following figure. The sample was placed on XRD stub, and added acetone. Then placed it inside X-ray chamber.
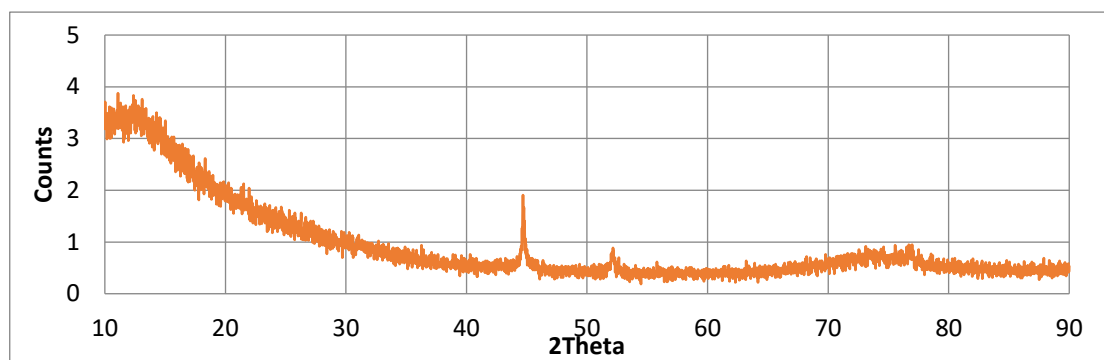
Figure 22: XRD data for recovered gold after burning polysulfide polymer in a furnace.

The chart shows only three peaks. The three peaks are matching with gold metal. The literature reported the same peak of XRD and it refers to gold nanoparticle. The second peak is about 50% of the first one, and the last peak is about 36% of the first peak [33]. Polysulfide polymer, that is treated with gold, was burnt by furnace up to 605 °C, then the recovered gold was analysed by XRD. Data is almost consistent with data for recovered gold by burning polysulfide polymer by STA. For recovered from burnt porous polysulfide polymer by using a furnace. 0.25 g of porous polysulfide polymer that is very fined particle size, weighed in a small plastic vail, then added 5 ml of aq. Au(III). The concentration of aq. Au(III) is 1.77mg/ml. The sample was leaving for 4 days. The solution was analysed by UV instrument, the data showed that porous polymer bound to 98% of gold. Two samples of this steps were done and filtered by vacuum filtration to have total weight of porous polymer 0.5 g. the dried porous polymer that treated with Au(III) and placed it in furnace. The program temperature was set for heating up to 605 °C. then after that the recovered gold was collected into a small plastic vial.
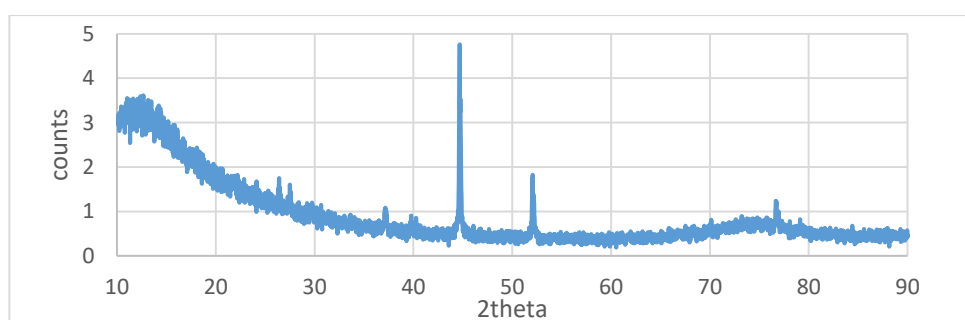

Figure 23: XRD data for recovered gold after burning polysulfide polymer in STA technique.

XRD data in figure 23, and figure 24 revealed same data with same 2theta value of peaks. The first peak shows intensity is much higher than other peaks. The peaks revels at 44.82^0,

31

52.02^0, and 76.65^0, respectively. According to Kannan,2008 the XRD pattern is crystal structure of gold nanoparticle. [34]

By using furnace is giving advantage over using STA instrument. the advantage is able to use a larger amount than in using STA instrument. However, STA instrument is more controlled burn. STA instrument is able to switch gas from nitrogen into air after the temperature reached 605 ^{0}C. air at 605 C might make an effect on purity of recovered gold. By comparing the two XRD data for recovered gold, there are some peaks appeared before the three peaks for gold metal.

SEM/EDS on recovered materials:

The material that was obtained after burnt polysulfide polymer. the weight of sample was remained is about 6% of started sample. SEM and EDS techniques were used to figure out the material. The sample was placed on carbon tape which are on stubs. No coating material was used at all. The result shows a large peak for gold. The weight of gold is about 98% of total weight of spot. There was some sulfur but it is about 6% of the total weight of material. The recovered gold that was obtained by burning polymer by STA is purer than recovered gold that was obtained by burning polymer by furnace. STA is a controlled technique. After the temperature of sample reached 600 ℃.
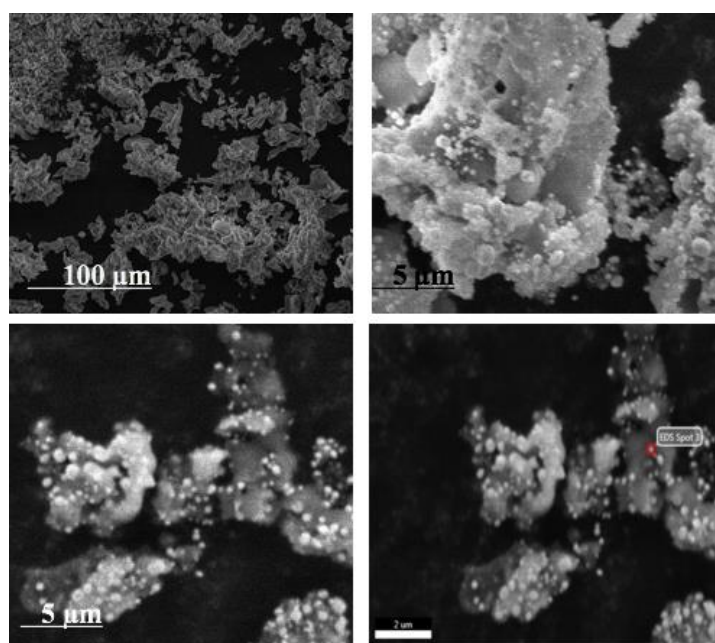
Figure 24: SEM images for recovered gold after burning by furnace at 604 ℃.

EDS data for recovered gold from porous polysulfide polymer that was treated with aq. Au(III). Porous polysulfide polymer burnt by Furnace

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	27.49	65.03	73.45	6.36	0.1886	0.8706	0.5180	0.7883	1.0000
O K	9.01	16.01	28.97	9.00	0.0530	0.8101	0.5225	0.7265	1.0000
NaK	6.27	7.75	21.61	9.66	0.0407	0.7276	0.5392	0.8905	1.0005
AuM	53.26	7.68	60.02	7.89	0.2696	0.4458	0.7633	1.1106	1.0227
S K	3.97	3.52	9.85	18.49	0.0278	0.7345	0.5859	0.9520	1.0007
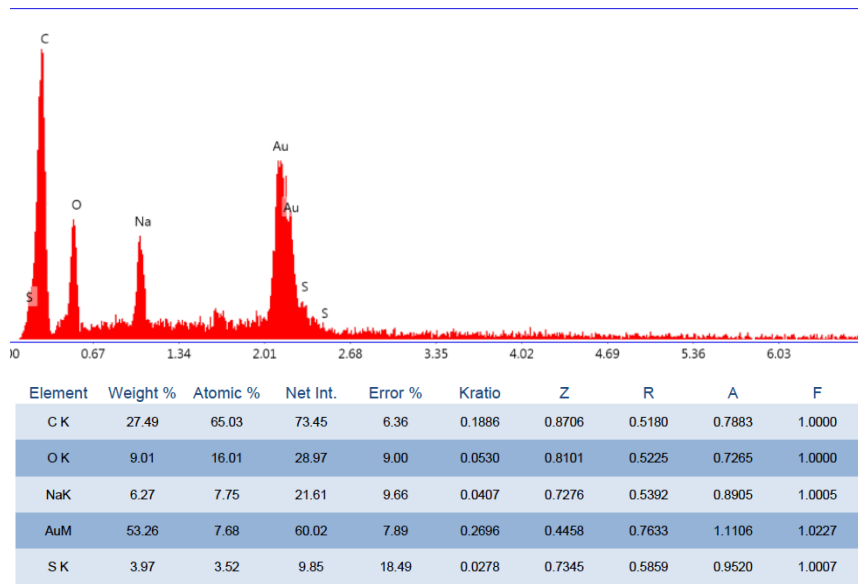
Figure 25: EDS data for recovered gold shown peak of gold and weight % of materials on spot area

The EDS data shows that the weight of gold among total weight is greater than 50%. The data shows that there are still small amount of carbon, sulfur and oxygen. It is noteworthy that the data was obtained without coating materials. it means that the material is conductive. Recovered gold after it burn by STA technique:

Figure 26: SEM images for recovered gold after burning by STA technique.

Recovered gold was placed on carbon tape then on a sub. No coating material added. SEM technique shows dots on a plate of material. Then EDS was used to figure out the dots and the shown material. EDS data as following:

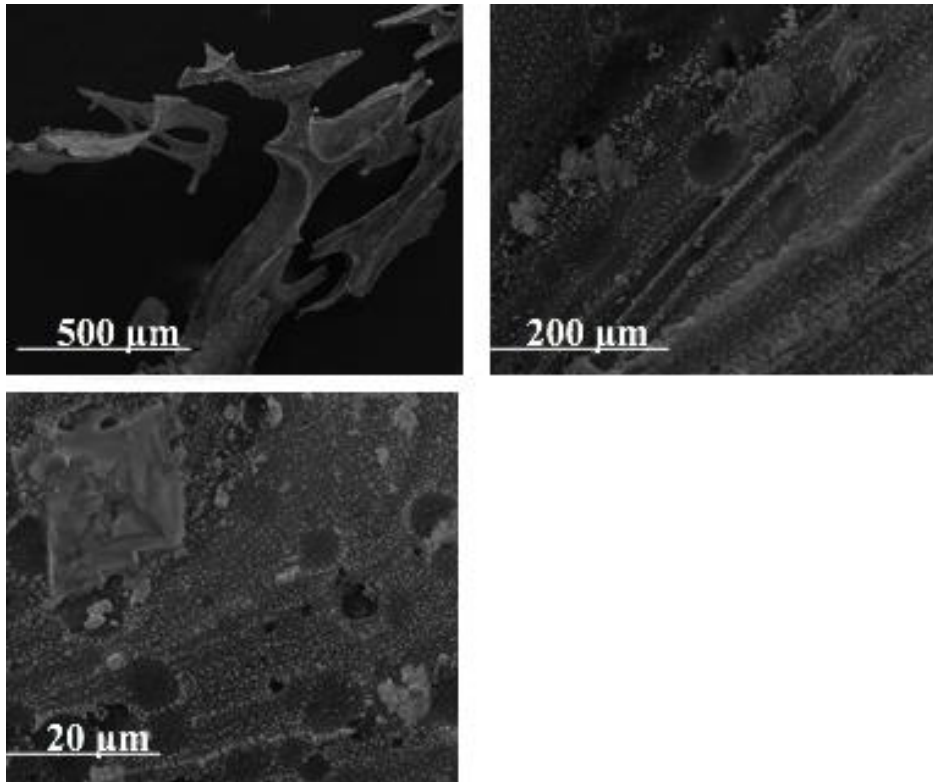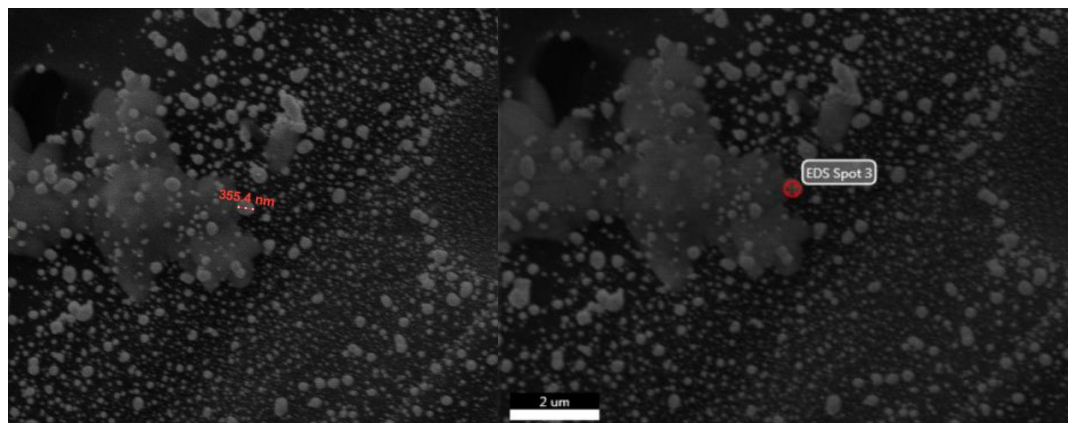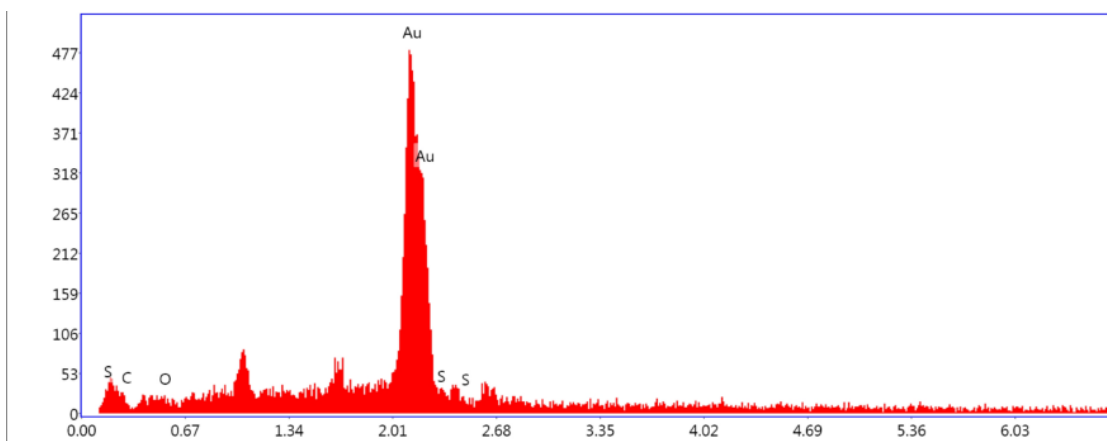| Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
C K	1.25	15.79	3.67	23.79	0.0098	1.1418	0.4023	0.6836	1.0000
O K	0.34	3.22	1.24	89.31	0.0023	1.0185	0.3905	0.6774	1.0000
AuM	97.11	74.82	123.03	6.10	0.5716	0.5382	0.5579	1.0745	1.0186
S K	1.30	6.17	3.54	64.19	0.0103	0.8852	0.4274	0.8934	1.0006

Figure 27: EDS data for recovered gold after burning by STA technique.

Recovered gold obtained by a controlled burning which are STA technique. STA technique provides purer recovered gold which is different from furnace that cannot exposure recovered gold to air while it is hot.

Conclusion

confirming by using several techniques, the cheap, renewable, green technology is proofed for binding gold. The technology is polysulfide polymer. Porous Polysulfide polymer shows the selective of gold(III) over Mn(II). The proof is confirmed by different techniques such as XRD, ICPOES, EDS, and UV. Polysulfide polymer bound to gold(III) and it recovers as gold. The metal that recovered after burn polysulfide polymer is gold metal and is confirmed by XRD, EDS. The future work is using porous polysulfide polymer with crushed ore that contains gold. Designing an experiment that convert gold from crushed ore into Au(III) by adding liquid sulfur or liver of sulfur with baking soda, then the mixture leave until the oxidation state takes place, then adding porous polysulfide polymer to the mixture to remove gold, then burn porous polysulfide polymer to recover gold. This project might collaborate with Prof. Claire Lenehan.

Future Directions:

For PFOA project experiment is that the polysulfide polymer does not need to wash out the NaCl from it, once polysulfide polymer places with aqueous PFOA, NaCl would be washed leaving porosity behind and increase pH of the media and it might destabilize hemi-micelles formation. The future work for gold project is using porous polysulfide polymer with crushed ore that contains gold. Designing an experiment that convert gold from crushed ore into Au(III) by adding liquid sulfur or liver of sulfur with baking soda, then the mixture leave until the oxidation state takes place, then adding porous polysulfide polymer to the mixture to remove gold, then burn porous polysulfide polymer to recover gold

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