

CHAPTER FOUR

The SEM microgram in 4.16A shows silver nanoparticles immobilised on track-etched PET membrane which are spherical in shape and the corresponding histogram shows a nanoparticle size range of 28 to 44 nm. The histogram for sample 10-AgPET is asymmetric, skewed to the right and has a high frequency of silver nanoparticle sizes between 36 and 40 nm. The average size of the silver nanoparticles was 37.5 nm for sample 10-AgPET which was immobilised for 10 minutes.

The SEM microgram in 4.16B shows silver nanoparticles immobilised on track-etched PET membrane which are spherical in shape and the corresponding histogram shows a nanoparticle size range of 40 to 62 nm. The histogram for sample 20-AgPET is symmetric and has a high frequency of silver nanoparticle sizes between 48 and 54 nm. The average size of silver nanoparticles was 51.4 nm for the 20 minutes of immobilisation (20-AgPET).

The SEM microgram in 4.16C shows silver nanoparticles immobilised on track-etched PET membrane which are spherical in shape and the corresponding histogram shows a nanoparticle size range of 54 to 68 nm. The histogram for sample 30-AgPET is asymmetric, partially skewed to the right and has a high frequency of silver nanoparticle sizes between 60 and 64 nm. The average size of the silver nanoparticles was 62 nm for sample 30-AgPET which was immobilised for 30 minutes.

The results in Figure 4.16 show that the morphology of silver nanoparticles was mostly spherical in shape. The size of silver nanoparticles increased relative to the increase in the time of immobilisation of silver nanoparticles on the surface of track-etched PET membrane. The SEM results are in agreement with the ultraviolet-visible (UV-vis) spectroscopy results of the silver-coated membranes in Figure 4.12. The silver nanoparticle size was noted to increase with the time of immobilisation during reduction of silver nitrate by trisodium citrate. The SEM micrograms also show that silver nanoparticles on the track-etched PET membrane were not uniformly immobilised which complements ultraviolet-visible (UV-Vis) spectroscopy results presented in Section 4.3.2.1. The increase

in size and variation in the shape of silver nanoparticles on the surface of the modified track-etched PET membrane concur with the broad plasmonic peaks and red shift of the plasmonic peaks in Figure 4.12, which was also reported by Reznikova *et al.*, (2014). The SEM micrograms also show that silver nanoparticles on the PET membrane were not uniformly immobilised which complements UV-Vis spectroscopy at different points of the same sample. The histograms in Figure 4.16 show size distribution of the silver nanoparticles immobilised on the surface of amine-modified track-etched PET membrane. The results showing that as immobilisation time was increased, the nanoparticle sizes also were increased are in agreement with literature reviewed (Solove'v *et al.*, 2007).

4.4 Additional characterisation of the physical properties of track-etched polyethene terephthalate membrane and silver nanoparticles

Additional characterisation was done to investigate changes in the properties of the track-etched polyethene terephthalate (PET) membrane as a result of exposure to the wet chemistry reaction and high temperature. Therefore, thermogravimetric analysis and contact angle measurements were carried out. The thermogravimetric analysis technique was carried out to determine the thermal properties of the amine-modified track-etched PET membrane, silver-coated track-etched PET membrane and the unmodified track-etched PET membrane. The contact angle measurement was conducted to investigate wettability of the surface of the modified track-etched PET membrane in comparison with the unmodified membrane. The modification of the track-etched PET membrane would affect the filtration capabilities of the track-etched PET membrane if the surface became more hydrophobic.

4.4.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to determine and compare changes in the thermal profile of the polyethene terephthalate (PET) membrane samples. The analysis was used to quantify the weight loss relative to applied temperature

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gradient and quantify the silver nanoparticle loading. The comparison was amongst unmodified (CO-APET), amine-modified (75A-PET) and silver-coated amine PET membranes (30-AgPET), in order to monitor any thermal degradation as a result of the modification process. The samples 75A-PET and 30-AgPET were chosen because they were obtained under optimised conditions and CO-PET as a baseline sample. The TGA characterisation was carried out as described in Section 3.5.6 of Chapter 3. The samples that were characterised are 30-AgPET, 75A-PET and CO-APET which were prepared as described in Section 3.2. The conditions under which samples were prepared are described in Table 4.4. The results of the thermal profile of the samples 30-AgPET, 75A-PET and CO-APET are presented in Figure 4.17

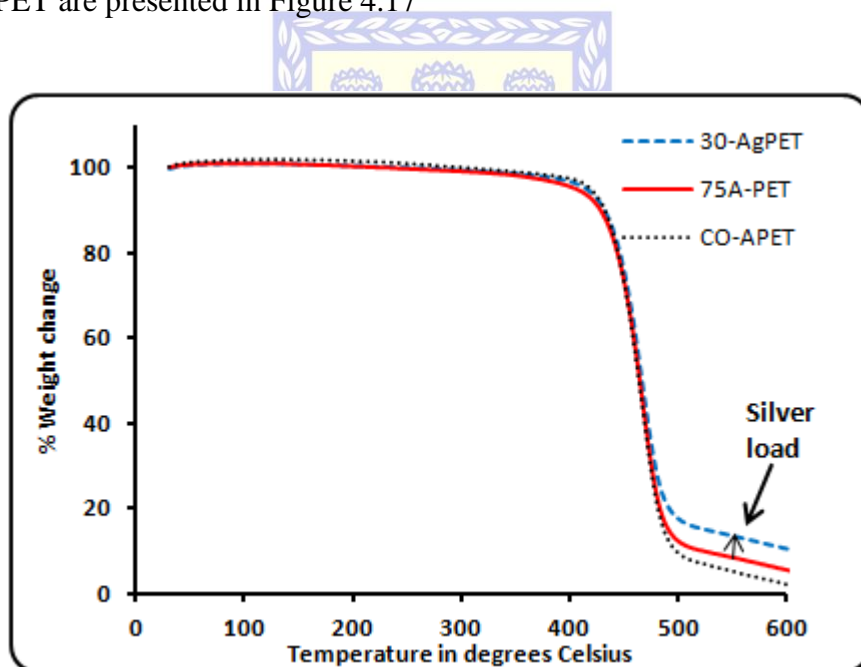


Figure 4.17: Thermogravimetric analysis graph showing the thermal profile of unmodified track-etched PET (CO-APET), amine-modified track-etched PET (75A-PET) and silver-coated track-etched PET (30-AgPET) membrane

The thermal profile in Figure 4.17 shows that all the membranes (30-AgPET, 75A-PET and CO-APET) are stable, without weight loss up to 300 °C where only a 2.5% weight loss is observed until reaching a temperature of 390 °C. After 390 °C the high percent weight loss was observed till reaching 490 °C. In between 390 °C and 490 °C range, the weight loss was 87.5% for unmodified track-etched PET and 83.5% for amine-modified track-etched PET, and 77.5% for silver-

coated track-etched PET. The results indicate that after 490 °C, most of the polymer was lost and the remaining residue was mainly elemental carbon for samples CO-APET and 75A-PET and elemental silver and carbon for sample 30-AgPET which is silver-coated amine-modified track-etched PET membrane. The different profiles after 490 °C arose from different elemental compositions of residue which is made up of carbon and silver. At a temperature of 500 °C the silver-coated track-etched PET membrane sample coded 30-AgPET shows a 20% weight remaining, which is 10% more than CO-APET sample (unmodified track-etched PET membrane) and 6% than sample 75A-PET (amine-modified track-etched PET membrane). The difference in weight of 10% between 30-AgPET and CO-APET is due to elemental silver and additional carbon contributed by diethylenetriamine which was present as a residue after 490 °C. The 4% difference between sample 75A-PET and CO-APET would arise from carbon in diethylenetriamine that has been functionalised on the PET membrane surface. It can therefore be inferred that of 6% silver loading shows the amount of silver that was immobilised on the amine-modified track-etched membrane. This observation correlates with Figure 4.2, which shows a loss of ethylene glycol (two carbon atoms) that is replaced by four carbons from diethylenetriamine functionalised on the surface of PET.

The next section presents results of the contact angle measurements of the modified and unmodified surface of polyethylene terephthalate membranes.

4.4.2 Contact angle measurements

The contact angle measurements were conducted in order to understand changes made to surface structures of the amine-modified and silver-coated track-etched polyethylene terephthalate (PET) membrane. The measurements of contact angles were carried out using distilled water at ambient conditions as described in Section 3.5.8 of Chapter 3. The contact angle measurements were carried on samples CO-APET (unmodified track-etched PET membrane), 75A-PET (amine-modified track-etched PET membrane) and 30-AgPET (silver-coated track-

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etched PET membrane). The results of contact angle measurements are presented in Table 4.7.

Table 4.7: Contact angles measurements of CO-PET, 75A-PET and 30-AgPET samples.

PET membranes	Average Contact angle (degrees)
CO-APET	88.5
75A-PET	46.4
30-AgPET	53.7

The results in Table 4.7 show a decrease in average contact angle following modification of the PET membrane by diethylenetriamine (DETA). The average contact angle decreased from 88.5° for sample CO-APET which is unmodified track-etched PET membrane to 46.4° for amine-modified track-etched PET membrane (sample 75A-PET). The introduction of amines on the surface improved the wettability of the sample 75A-PET, the amine-modified track-etched PET membrane surface. The membrane surface became more hydrophilic as the track-etched PET membrane was modified with diethylenetriamine which bears ionisable groups, the amines (NH₂). The amines were introduced onto the surface of track-etched PET membrane as shown in reaction mechanism Figure 4.2. The observation agrees with the literature that ionisable functional groups on the surface of membranes improve hydrogen bonding between water molecules and ionisable moieties on the surface of the membrane (Goddard *et al.*, 2007). The contact angle increased upon immobilising silver nanoparticles on the surface due to loss of ionisable moieties (nitrogen) which has been partly hindered by the silver nanoparticles.

The next section presents the summary of the chapter.

4.5 Summary of chapter

The achievements described in this chapter are the successful chemical modification of the track-etched polyethylene terephthalate (PET) membrane via a wet chemistry method involving a solid/liquid interface reaction, resulting in the immobilisation of silver nanoparticles on the track-etched PET membrane surface. This type of track-etched PET membrane surface modification using diethylenetriamine and then immobilisation of silver nanoparticles on the surface has not been reported in literature. The results have shown that the ester bond scission and formation of amide bond occurred at the solid/liquid interface of diethylenetriamine solution and surface of the track-etched PET membrane. Wet chemistry modification of the track-etched PET surface was confirmed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR). The immobilisation of silver nanoparticles on the surface of the track-etched PET membrane during reduction of silver nitrate by trisodium citrate was confirmed by scanning electron microscopy (SEM), ultraviolet-visible (UV-vis) spectroscopy and XPS. Transmission electron microscopy (TEM) was used to confirm the shape and size of colloidal silver nanoparticles while SEM was used to show shape of silver nanoparticles that were immobilised on track-etched PET membrane surface. The chapter linked results of different characterisation techniques in ascertaining modification of the surface of track-etched PET membrane, finding the optimum conditions for synthesis of silver nanoparticles then reports immobilisation of silver nanoparticles. The initial characterisation of the modified track-etched PET membrane caused more challenges as the FTIR results gave very little observable changes in the absorbance spectra. The presence of silver was therefore determined with XPS showing the amount in percentage of elemental silver immobilised on the surface. Further size distribution and concentration of silver nanoparticles on the amine-modified track-etched PET surface was confirmed by SEM and UV-vis spectroscopy respectively. ImageJ software was used to calculate the size of nanoparticles immobilised on the surface of amine-modified track-etched PET membrane from the SEM and TEM monograms.

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The use of the surface-enhanced Raman spectroscopy (SERS) for the detection of acetaminophen using the silver-coated track-etched polyethylene terephthalate membrane is presented in the next chapter. The next chapter also discusses the characterisation of silver-coated track-etched PET membranes using Raman spectroscopy in order to determine the silver-coated track-etched PET membrane sample which would serve the purpose as a platform for SERS application.



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CHAPTER FIVE

Applications

5 Introduction

This chapter presents results and discussion of the detection of acetaminophen on a modified surface of track-etched polyethylene terephthalate (PET) membrane that was fabricated as outlined in chapter three. The chapter also lays out the results and the applicability of surface-enhanced Raman spectroscopy using silver-coated surface of track-etched PET membranes (10-AgPET, 20-AgPET and 30-AgPET samples) for detection of acetaminophen,. The sample codes 10-AgPET, 20-AgPET and 30-AgPET are as defined in Table 3.3 and their fixed and variable experimental parameters are given in Table 4.4. The focus is on whether the silver-coated track-etched PET membranes would be able to enhance a weak Raman signal resulting from Raman scattering by acetaminophen molecules on the surface as reviewed in Section 2.5 of Chapter 2. The samples 10-AgPET, 20AgPET and 30-AgPET were prepared as described in Section 3.3 of Chapter 3. The samples were characterised by Raman spectroscopy as described in Section 3.5.7 of Chapter 3. A discussion of the challenges encountered to detect acetaminophen on the surface of both unmodified track-etched PET (Co-AgPET) and silver-coated track-etched PET membrane (10-AgPET, 20-AgPET and 30-AgPET samples) using the Raman spectrometer is also presented in the chapter.

The moieties of acetaminophen have specific vibration modes that produce a Raman spectrum specific to acetaminophen (Kauffman *et al.*, 2008). The chemical structure of acetaminophen is shown in Figure 5.1.

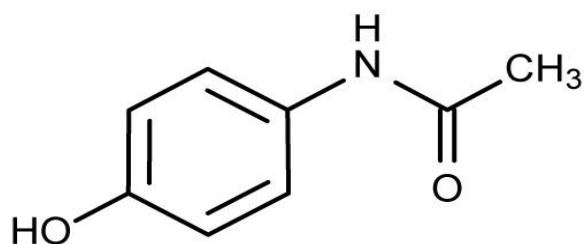


Figure 5.1: Chemical structure of acetaminophen

Acetaminophen has functional groups that have peaks in its Raman spectrum, which are also common to other chemicals. The functional groups are phenyl, amide, carbonyl and hydroxyl. Although acetaminophen has similar peaks to common functional groups, its overall Raman spectrum is specific to acetaminophen only, making the Raman spectrum, a fingerprint signature. The typical acetaminophen peaks identified in its spectrum are outlined in Table 5.1 (Kauffman *et al.*, 2008).

Table 5.1: Peaks in Raman spectrum of acetaminophen.

Proposed bond	Spectral peak cm^{-1}
C-O	854, 861, 1170
C-N	1245, 1281, 1328
C=C	1557, 1565, 1576
C=C	1608, 1615, 1623
C=O	1646, 1650

The peaks of the Raman spectrum in Table 5.1 were used to ascertain the presence of acetaminophen on the prepared surfaces of unmodified track-etched PET membrane (CO-AgPET), silver-coated track-etched PET membrane (30-AgPET) and a control surface made of silver nanoparticles sputtered on a glass support (Quartz).

5.1 Preparation for Surface-enhanced Raman Spectroscopy platform

The platform for the performance of surface-enhanced Raman spectroscopy (SERS) for detection of acetaminophen was fabricated as described in Section 3.3 of Chapter 3. The characterisation of the silver-coated surface is discussed in Section 4.3.2 of Chapter 4 of the thesis. The silver nanoparticles were coated on the surface of modified track-etched polyethylene terephthalate (PET) membranes as surface-enhanced Raman spectroscopy active materials to intensify the weak Raman scattering signal with an aim of detecting acetaminophen molecules on the surface. The immobilisation of silver nanoparticles was done at different times in order to find the best conditions that would suppress the polyethylene terephthalate Raman signal. The conditions and sample codes are as presented in Table 3.4. Figure 5.2 shows the Raman spectra of the silver-coated track-etched PET membranes (10-AgPET, 20-AgPET, 30-AgPET) and the unmodified track-etched PET membrane (Co-AgPET) as a baseline (control sample).

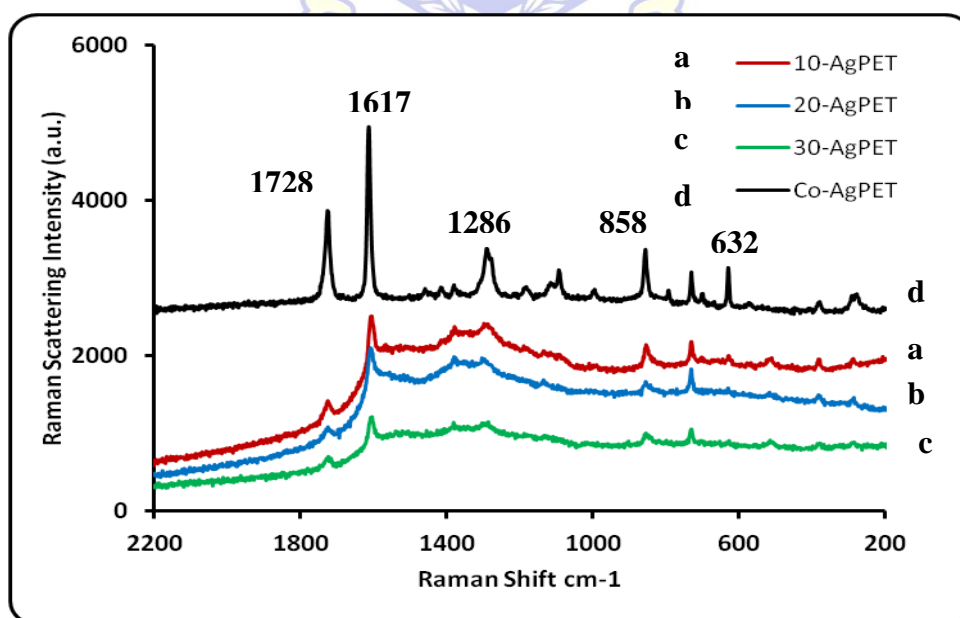


Figure 5.2: Raman spectra of silver-coated track-etched PET membranes at reaction times (a) 10 minutes (10-AgPET), (b) 20 minutes (20-AgPET), (c) 30 minutes (30-AgPET) prepared at 90 °C using 2 mL of 1% trisodium citrate and unmodified PET membrane (d) control (CO-AgPET).

The results for Raman spectra in Figure 5.2 show that as the time of silver nanoparticle immobilisation increased, the intensity of the peaks relating to the PET membrane were reduced with the lowest signal at 30 minutes as shown by the spectrum of 30-AgPET in Figure 5.2. The Raman spectra of silver-coated track-etched PET membranes (10-AgPET, 20-AgPET, 30-AgPET) show suppressed peaks relating to the polyethene terephthalate membrane and these peaks were not as prominent as for the unmodified track-etched PET membrane (Co-AgPET). The Raman spectra peaks of silver-coated track-etched PET membranes show that as the silver nanoparticle immobilisation time was increased from 10 minutes to 30 minutes, the PET peaks' intensities were suppressed. The reduction in the PET peaks' intensities follows the trend of size of silver nanoparticles immobilised on the surface of amine-modified track-etched PET membranes as discussed in Section 4.3.2.3. The trend observed in Section 4.3.2.3 showed that as the time of reduction reaction increased, so did the size of silver nanoparticles immobilised on the surface of PET. The silver-coated track-etched PET membrane coded 30-AgPET was therefore chosen as the most suitable platform for detection of acetaminophen using surface-enhanced Raman spectroscopy. The Raman spectrum of sample 30-AgPET was chosen as baseline because this sample of silver-coated track-etched PET membrane showed the minimum peak intensities of the PET membrane itself. The cut-off point of immobilising silver nanoparticles on modified track-etched PET membrane was set at 30 minutes because the size of silver nanoparticles of sample 30-AgPET, as observed in Section 4.3.2.3, fell within the average range of 58 nm as stated by Taurozzi and Tarabara, 2007.

5.2 Detection of acetaminophen using fabricated silver-coated track-etched polyethene terephthalate membrane.

Similar to Fourier transform infrared spectrum, a Raman spectrum comprises wavelength distribution of peaks equivalent in character to molecular vibrations specific to the analyte being characterised (Ferraro *et al.*, 2003). Surface-enhanced Raman spectroscopy (SERS) as an advanced Raman spectroscopy

technique was used to detect acetaminophen using silver nanoparticles as SERS active materials to enhance the Raman signal.

The detection of the molecules of acetaminophen on the silver-coated track-etched polyethylene terephthalate membrane was carried out at ambient conditions as described in Chapter 3 under the Raman spectroscopy Section 3.5.7. A solution of 20 μL of 1.51 mg/L aqueous acetaminophen was dropped and dried on the surfaces of the selected samples. The Raman spectra of acetaminophen detected on the surface of silver-coated track-etched polyethylene terephthalate (PET) membrane (30-AgPET), unmodified track-etched PET (Co-AgPET) and Quartz, a silver-coated glass surface (non-porous) as described in Section 3.1 are shown in Figure 5.3.

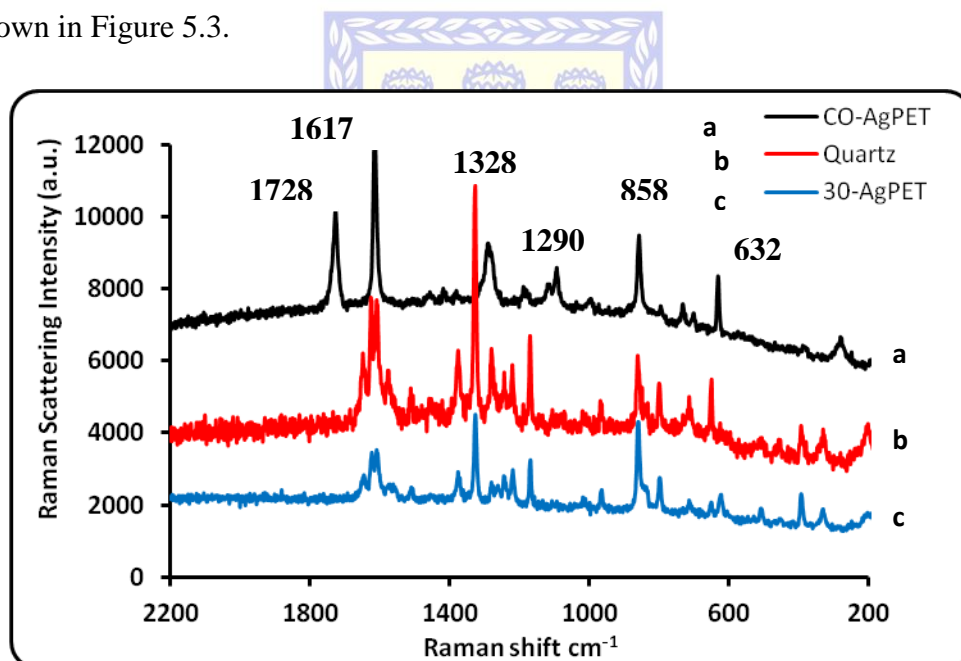


Figure 5.3: Raman spectra of 1.51 mg/L of acetaminophen on the surface of (a) Co-AgPET (unmodified track-etched PET) membrane (b) Quartz (Non-porous) and (c) 30-AgPET (silver-coated track-etched PET membrane).

Figure 5.3 shows that the peak intensities are higher for the sample coded Quartz (a non-porous silver-coated glass) than that of 30-AgPET, the track-etched silver-coated track-etched PET membrane. In the case of the control sample, Co-AgPET, which is unmodified track-etched PET membrane, no characteristic peaks of acetaminophen could be observed among the overall prominent peaks of polyethylene terephthalate membrane. This could be attributed to lack of SERS

signals on the surface of sample Co-AgPET membrane to enhance the Raman signal of acetaminophen. Therefore it is inferred that the lack of silver nanoparticles is the main cause of the lack of acetaminophen peaks for the sample Co-AgPET. When comparing the Raman signal intensity of acetaminophen on sample Quartz (a non-porous SERS surface) against 30-AgPET (a track-etched silver-coated track-etched PET membrane), most of the acetaminophen vibrational bands on 30-AgPET are rather weak. The limited SERS intensity and the low spectral intensities could be due to the loss of some molecules of acetaminophen that may leach through the pores.

5.3 Concentration studies for detection of acetaminophen

Concentration studies were carried out using a silver-coated track-etched polyethylene terephthalate (PET) membrane sample 30-AgPET for detection of acetaminophen in different concentrations as described in Section 3.4. Acetaminophen solution was prepared using distilled water. The following concentrations were prepared 15.10 mg/L, 1.51 mg/L and 0.151 mg/L which were coded Acet-100, Acet-010 and Acet-001 respectively. Acetaminophen solution of volume 20 μ L for each concentration was dropped and dried on the surface of 30-AgPET. Figure 5.4 shows the Raman spectra for the concentrations of the acetaminophen at 15.1 mg/L, 1.51 mg/L and 0.151 mg/L detected from the surface of 30-AgPET membrane.

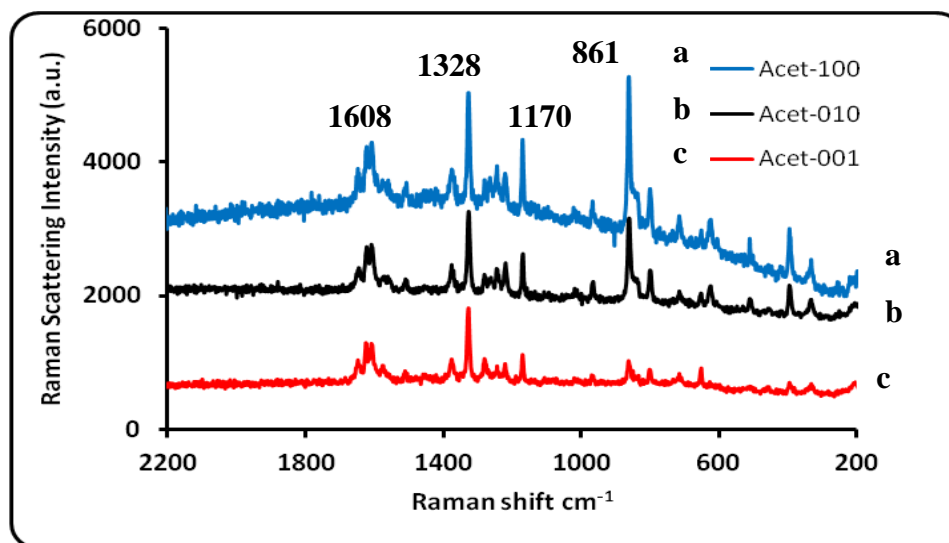


Figure 5.4: Raman spectra showing variations in intensity of different concentrations of acetaminophen in aqueous media (a) 15.1 mg/L, (b) 1.51 mg/L and (c) 0.151 mg/L.

Figure 5.4 shows that the intensity of the Raman peaks increased with an increase in acetaminophen concentration. The trend agrees with what was reviewed in the literature that Raman peak intensity is a function of the concentration of analyte (Taurozzi and Tarabara, 2007). Sample Aceta-100 which is 15.1 mg/L has its acetaminophen peak intensity greater than those of lower concentration (Aceta-010 and Aceta-001) which were 10 and 100 times more dilute, respectively. The changes in the intensity of the peaks of the acetaminophen spectrum are consistently changing with change in concentration. This finding of detecting acetaminophen upon the surface of silver-coated track-etched PET membrane using surface-enhanced Raman spectroscopy has not been reported in literature.

Theoretically, when there is a higher number of molecules on the surface-enhanced Raman spectroscopy surface hot sites, there is a greater chance of observing medium to strong Raman signals (Strachan *et al.*, 2007). This is also shown in peaks of the spectra in Figure 5.4. When more acetaminophen molecules covered the surface of silver-coated track-etched PET membrane, the possibility of observing a strong to medium Raman signal was greater. The SERS effect is provided by the localised surface plasmon of silver nanoparticles. The higher Raman scattering intensity could be as a result of SERS contributions

from both electromagnetic effects and chemical effects (charge transfer) arising from adsorption of acetaminophen molecules on the silver nanoparticles. There is a greater probability for the acetaminophen to be adsorbed on the surface if it exists in high concentration on the surface.

5.4 Application of spectral peaks for quantification

Theoretically, quantification of an analyte in a sample is possible with Raman spectroscopy since the Raman scattering is proportional to the concentration of the analyte. The intensity of Raman scattering of a particular vibration mode is directly proportional to vibrating moieties' concentration (Strachan *et al.*, 2007). Raman spectra analysis could be used to extract information from the peak height or area, and/or use the ratio of peak height or area to quantify the analyte. This could be possible only if spectral peaks do not overlap, and all analyte samples are exposed to the same conditions so as to be affected equally by undetected interferences. In reference to Figure 5.4 showing Raman spectra of concentrations 15.10 mg/L, 1.51 mg/L and 0.151 mg/L represented as Acet-100, Acet-010 and Acet-001 respectively, Figure 5.5 shows the trend in specific Raman intensity peak height relative to concentration of acetaminophen.

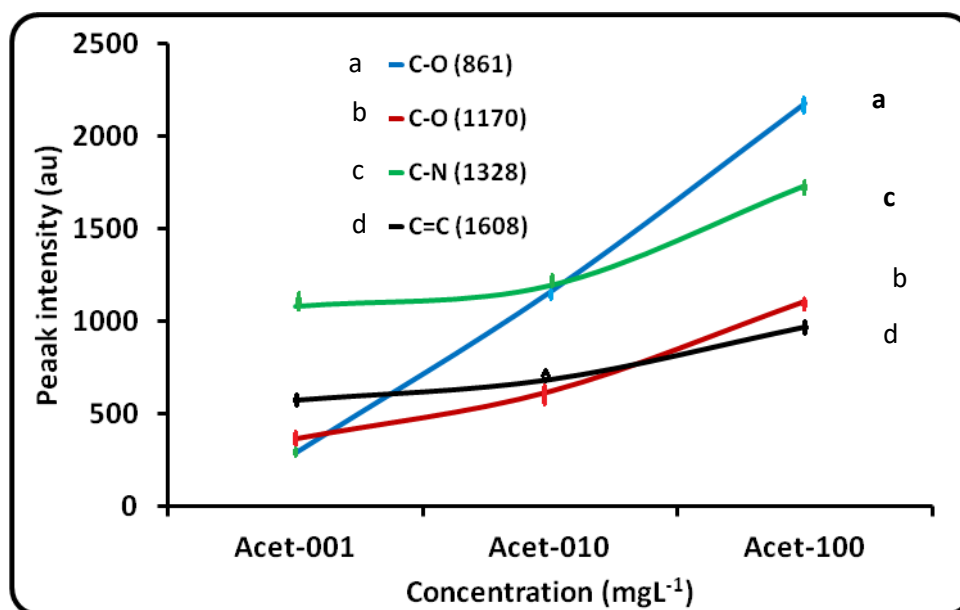


Figure 5.5: Graphical presentation of relationship between concentration of acetaminophen and trends in Raman intensity peak height at specific bond vibrations (a) C-O (861), (b) C-O (1170), (c) C-N (1328) and C=C (1608)

The general trend in Figure 5.5 shows that as the concentration increased so did the peak intensity height. The difference in the trends is observed when comparing the rate of change amongst the specific bonds. For instance the rate of change of C=C (1608) and C-O (1170) are not correlated, but rates of change for C-O (1170) and C-N (1328) have a similar trend. The peak intensity trend for the C-O (861) vibration shows a linear response. The linearity of peak intensity of the C-O bond versus the concentration has the best correlation of the two factors. The other bond vibrations C-O (1170), C-N (1328) and C=C (1608) show no linearity and if extrapolated towards zero concentration they cross the peak intensity axis instead of the concentration axis. The linear correlation line of C-O (861) when extrapolated would give a limit of detection of approximately 0.0755 mg/L. The challenge with the peak intensity heights is that the proportionality does not seem to be the same for all peak intensity heights, that is the peak intensity increases were not the same for all spectrum peaks. The finding has not been reported anywhere else in literature and therefore this is the first observation to have been made by this study.

The detection of acetaminophen on the surface of silver-coated track-etched polyethylene terephthalate (PET) or unmodified track-etched PET was faced with some challenges. The Raman spectrometer used for detection had limited options, for instance it was limited to one laser option of excitation wavelength of 532 nm, and lacked software to calculate peak heights and areas.

5.5 Summary of the chapter

The chapter has covered in detail the results and characterisation of using the silver-coated track-etched polyethylene terephthalate (PET) membrane as a platform for the detection of acetaminophen by surface-enhanced Raman spectroscopy (SERS). The quartz platform was used as control to compare the detection using the surface-enhancement of silver nanoparticles of the silver-coated track-etched PET membrane against unmodified track-etched PET membrane. Silver nanoparticles were found to have enhanced the Raman signal of acetaminophen. Further Raman characterisation of the PET membranes that were immobilised with silver nanoparticles at different times showed how effective the amount of silver nanoparticles and their size suppressed the polyethylene terephthalate signal. The chapter also made comparison of concentrations of acetaminophen which showed increase in peak height of spectra with an increase in concentration.

The next chapter presents the conclusions and recommendations of the research aims and objectives, findings and achievements in the thesis.

CHAPTER SIX

Conclusion and Recommendations

6 Introduction

The chapter presents an overall conclusion of key findings and achievements of this study. This chapter also presents suggestions in the form of recommendations for further research as a result of the key findings accrued in this study.

6.1 Conclusion

The study outcomes have shown that the surface of a track-etched polyethylene terephthalate (PET) membrane can be modified with diethylenetriamine (DETA) via aminolysis, a wet chemistry technique. The modified track-etched PET membrane surface was characterised by the ester bond scission and formation of an amide bond (C-N). This was confirmed by Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) spectra. The surface of track-etched PET membrane was successfully modified with DETA. The surface modification brought about changes in terms of wettability of the surface as evidenced by the contact angle measurements outcome. The chemistry of the surface was also changed by the introduction of amide bond and changes in chemical states of carbon (C1s) following ester bond scission and formation of amide bonds which resulted in a percentage increase of C1s in C-C chemical state and a decrease in the percentage in O-C=O chemical state as shown in XPS data. The observance of an amide II absorbance in FTIR spectrum of amine-modified track-etched PET membrane at 1578 cm^{-1} was complementary to XPS data.

The silver nanoparticles were successfully synthesised by reducing silver nitrate with trisodium citrate that served as a reducing and stabilising agent. The colloidal silver

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nanoparticles were found to be stable following their zeta (ζ) potential values of more than minus 20 mV. The transmission electron microscopy images of colloidal silver nanoparticles showed that they were of spherical shape with an average size of 46 nm for sample 20-AgNP. The plasmonic peaks of silver solution and silver-coated track-etched PET membranes were observed between 400 and 420 nm which is typical of silver nanoparticles synthesised via reduction by trisodium citrate. The scanning electron microscopy (SEM) images of the silver-coated track-etched PET membranes showed successful immobilisation of silver nanoparticles on the surface. The SEM images showed silver nanoparticles sizes ranging between 28 nm and 68 nm for silver nanoparticles immobilised between 10 minutes and 30 minutes. The SEM results were also in agreement with transmission electron microscopy (TEM) results regarding the spread in size of the silver nanoparticles as measured by ImageJ software. The SEM results also showed a trend in the increase of silver nanoparticles size with an increase in the time of immobilisation. Furthermore, the XPS results complemented the SEM results and UV-Vis results regarding the number of silver nanoparticles immobilised on the surface where XPS data showed an increase in the percentage from 2.53 to 5.20% of silver ($\text{Ag}_{3d_{5/2}}$) relative to the increase in time of immobilisation from 10 minutes to 30 minutes. The thermal properties of the track-etched PET membrane was found not to have been affected by aminolysis of the surface and immobilisation of silver nanoparticles at 90 °C. The thermogravimetric analysis (TGA) showed that at a temperature of 550 °C, the silver-coated track-etched PET membrane still had 20% of its original weight, which was calculated to be 6% more than the amine-modified track-etched PET membrane. and 10% than unmodified track-etched PET membrane. The 6% weight of silver-coated track-etched PET membrane which was over and above amine-modified track-etched PET membrane weight was due to residual silver nanoparticles that were immobilised on the surface. The Raman spectra of the silver-coated track-etched PET membrane confirmed immobilisation of a layer of silver nanoparticles that suppressed the Raman signal of polyethylene terephthalate. The more silver nanoparticles that were

immobilised on the surface of PET membrane, the more the reduction of interference was observed by suppression of the PET scattering signal. This was found to be of importance as any analyte on the surface could be detected without interference from PET membrane spectrum.

The silver-coated track-etched PET membrane was successfully used to detect acetaminophen as low as 0.151 mg/L (parts per million). In comparison to a quartz platform which was non-porous, it was observed that the spectra of acetaminophen detected from the surface of silver-coated track-etched PET membrane were of lower intensity. This was attributed to the loss of some of the acetaminophen molecules that leached through the pores of the track-etched PET membrane. The unmodified track-etched PET membrane did not show any peaks of acetaminophen in the Raman spectrum obtained. The Raman spectrum obtained was mainly of polyethene terephthalate monomer of the track-etched PET membrane itself. In the concentration studies of detecting acetaminophen, the Raman peak intensities of acetaminophen decreased with a decrease in concentration of acetaminophen. The correlation of the Raman peak intensity heights and concentration of acetaminophen for C-O bond vibrations at Raman shift of 861 cm^{-1} had a linearity response. The other bond vibrations C-N at 1328 cm^{-1} , C=C at 1608 cm^{-1} and C-O at 1170 cm^{-1} showed no linearity response. The best correlation from the peak when extrapolated gave 0.0755 mg/L as limit of detection for acetaminophen using a track-etched PET membrane that was amine modified with 75% DETA for 24 hours and immobilised with silver nanoparticles for a duration of 30 minutes.

The fabricated silver-coated track-etched PET membrane was successfully used as a platform to detect acetaminophen.

6.2 Recommendations

The results obtained in this study inspire further research in order to ascertain some parameters that led to the above conclusions in section 6.1. The observed reduced Raman spectra of track-etched PET membrane could further be studied by using PET

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membranes of different pore densities and pore sizes, mainly targeting smaller pore sizes and lower pore densities for improved pre-concentration. This is to observe if there could be an improved Raman scattering intensity, on the fact that less analyte would leach through the PET membrane. The silver nanoparticles were found not to be uniformly immobilised in a monolayer arrangement and this could either have created SERS hot spots or reduced the number of hot spots on the surface. Therefore, there is need to explore this further. The other area of interest generated from the findings of this study is the size of nanoparticles that would enhance the Raman signal. It would be of greater scientific importance to find out how the sizes of silver nanoparticles affect the enhancement of Raman signal when immobilised on the surface of PET membrane. Therefore further research could be explored with much smaller nanoparticles. As regards quantification of analyte from the Raman spectra intensity, further investigations could be explored to focus on the relationship between concentration and Raman intensity of prominent peaks in the spectra for different compounds. This could lead to a calibration curve of Raman scattering intensity versus concentration of an analyte as is done in chromatography studies.

The surface-enhanced Raman spectroscopy technique could be modified and combined with another quantitative analytical technique. This could also be explored in the future research. The SERS technique should be part of the hyphenated technique where compounds are isolated by before analysis as is done in gas chromatography and high performance liquid chromatography.

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