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Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy and Statistica Analysis of High and Low Pressure Coatings on Sediments Membrane for Stable and Efficient Wettability

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Abstract

In this paper, the Scanning Electron Microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) results of surface layers formed on sediments after low pressure (LP) and high pressure (HP) coating are analysed and validated by correlating with Statistica analysis software. This was to validate the coating pressure with efficient and more stable wettability properties. Different elements were revealed after different rounds of HP and LP coating by EDS and Statistica analysis software. Different thicknesses of coated fluorine (F) were also reported for HP and LP coated sediments. The maximum percentage of fluorine which gave optimal membrane surface smoothness was reported after 3rd round of HP coating. Different orientations of nanoparticles were observed to impact membrane wettability. Clusters were also observed on the membrane with more clusters observed in low pressure (LP) coating when compared with high pressure (HP) coating. The coated membrane surfaces were related to lotus effects and their surface roughness and smoothness was related to wettability and surface energy process. The 3nd round of HP coating gave optimal surface smoothness which enhances wettability. Correlation between SEM images, EDS and Statistica analysis software were done to validate obtained results in the current study. Keywords: Sediment, SEM, EDS, LP, HP, Coating and Nanoparticle

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1. INTRODUCTION

Ceramic and polymers have been used as membrane materials with poor stability and efficiency. The advantages of Ceramics used as fabrication materials are that ceramics have high chemical stability and mechanical strength [1-6]. Ceramic is also good since it offers better cleaning condition, long and reliable lifetime [1-8]. The main disadvantage of Ceramic is that it is quite expensive and very difficult to fabricate in good quantity due to its brittleness [2-4]. Ceramic also possess a great disadvantage of sealing pores when integrating in module, which causes major problem in efficient filtration process [1-6]. The membrane surfaces of ceramics are usually very rough and it is very difficult to obtain optimal wettability [1-6].

For polymeric membrane material the commonly used materials are poly (ether sulfone) (PES), poly (vinylidene fluoride) (PVDF), polyethylene (PE), polypropylene (PP) and polytetra fluorethylene (PTFE) [1- 6& 16]. All the listed polymers are hydrophobic except PES [16]. It should also be noted that PE, PP and PTFE are insoluble inorganic solvents specifically at room temperature, thereby making the manufacturing process very difficult [1-6& 16] for optimal wettability. The most commonly used porous membranes are based on PP and PTFE design that are usually produced by mechanical stretching of extruded films [1-6]. Membrane fouling is one of the biggest challenges in polymeric membranes because they are mostly hydrophobic [16].

Sediments are reported to have better thermal and mechanical stability when used as membrane materials in oil/water separation [1, 2 and 17]. Sediments are commonly used in wettability since they are friendly to water and also due to the fact that they are resistant to corrosion and rust when compared to other materials used in wettability process [17]. Sediments have lower surface roughness and higher thermal stability than ceramic, textile, polymers and glass materials which are commonly used in membrane wettability [1-17]. Since sediment material offers better thermal and mechanical properties than polymers and ceramics they are more recommended in filtration technology [1-9]. In this study sediment material was used as the main membrane materials used in oil/water separation. The main problem leading to membrane deficiency in sediment is the inability to determine optimal coating rounds with optimal nanoparticles coating surface distribution which offer optimal membrane wettability [1-17]. This is due to the fact that for optimal wettability the surface distribution of nanoparticle on the membrane surface must be homogenous [1-17]. The science of homogeneity and wettability was described by the lotus effect which stated that for efficient wettability the coated membrane surface must be homogenous [1-16]. Therefore the lotus effect is very possible in sediments material since their surfaces are better than ceramic material [1-6] when used as membrane materials for oil/water separation.

The major problem in sediment material for membrane technology is the inability to coat the membrane surface for optimal wettability [1-8]. Therefore there is a need for proper

investigation of optimal coating rounds with optimal nanoparticles coating surface distribution which offer optimal membrane wettability which is the main objective of the current studies. To achieve this research objective the SEM, EDS and STATISTICA (Data analysis software system) are employed in the study. These results are related to the lotus effects by analysing surface homogeneity after the different coating. The optimal coating rounds that gave optimal wettability during oil/water separation were produced. Wettability test was performed to validate the produced membrane in the current study.

2. METHODOLOGY

2.1. Nano4stone hydrophobic nanoparticles and spray gun were purchased for the experiment. The nano4stone materials were washed to remove foreign impurities such as dirt that could have prevented proper blending of nanoparticle on the sediment surface during coating (1-6 & 8-25). This was done with the help of a distilled water and pre-clean water. The washed sediments were allowed to dry for 24 hours under room temperature. The coating process was done using HP coating and LP coating. The jet spray gun used for coating was kept 5 cm away from the membrane surface at an angle perpendicular (90 degree). Before coating takes place, uncoated sample (sediment not coated and i.e. nano4stone not coated) was taken for microscopy analysis. The first, second and third rounds of coatings were done by LP and sample were removed for analysis after each coating round. Similarly first, second and third rounds of coatings were done at HP and (coated sediment material) were removed for microscopy analysis. The second and third rounds of coating were done in less than three minutes to prevent the membrane surface from becoming hydrophobic to the coated materials which will repel the second and third coating rounds. The first analysed samples were nano4stone (nano4sediment) control sample and sediment sample as shown in Fig.1.

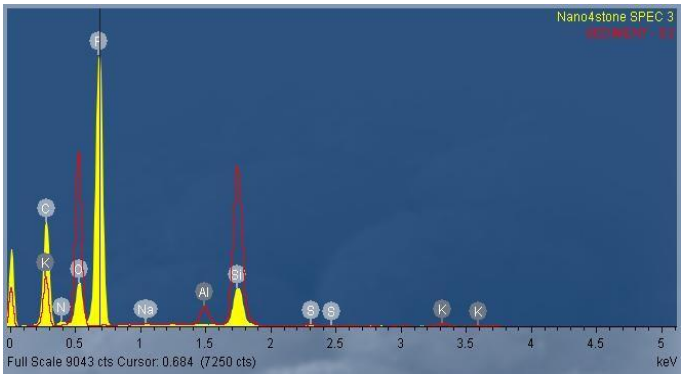


Fig.1 EDS results of nano4stone and sediment

Oxygen (O), K, Na, Al, S, and Si were observed in sediment control sample. The following element for nano4stone control sample as shown in Fig. 1, C, O, F, Na, Si and S. The nano4stone revealed unique elements of fluorine (F). Since the elements of both samples are known it was important to carry out the LP and HP coating for proper characterization process.

2.2 The samples preparation for SEM, TEM and EDS

2.2.1 The samples were not polished since the surface roughness of the coated hydrophobic nano4stone was the main parameter to be measured. The sample was embedded in epoxy resin blocks and later the thin section to be analysed was prepared. The holders in which the sediment sample were placed for microscopy analysis was 25mm or (1") diameter round. The sediment samples were electrically non- conducting during analysis and a conducting surface coated was applied to provide proper path for the incident electrons to flow to ground during analysis. Normally the coating material is vacuum-evaporated carbon (~10nm thick), having a minimal influence on X-ray intensities due to its low atomic number as specify for SEM sample so that it does not add unwanted peaks to the X-ray spectrum. To achieve higher resolution during SEM imaging, advanced detectors were used during SEM analysis. These were used to selectively detect the different location as indicated by spectrum 2 to spectrum 8 called site of interest where the lens was able to capture results as shown in SEM image in Fig. 2 (c). This was to ensure accuracy and elementary validation of findings on how particles were distributed on the membrane surface during coating as shown in Fig 2 (d). During the SEM analysis, the detector used was an In- Lens SE detector (Zeiss Supra 40, FE-SEM, Oberkochen, Germany). It must be noted that the In-Lens was only able to pick images in a straight path. Therefore the In-Lens was unable to pick images in curve section of the glass membrane and as such the sections were black in the SEM captured images. The nanoparticles sizes, shape, orientation, morphology and dispersion of lateral dimensions were measured. It should be noted that the STEM detector being placed under the samples was used to capture images in transmission mode in the SEM during experiment. This consists of sample holders which guide the transmitted electrons onto the electron multiplier in the form of a gold plate under the bright field. All the transmitted electrons are collected by the E-T detector. At the same time the screening ring being operated prevented the X-rays being emitted by the sample to reach the EDS detector and therefore it is important to remove the ring before an EDS analysis. More so a TEM grid transmission setup was used and the TSEM detector was able to analysed four samples on the holders and EDS analysis was carried out immediately.

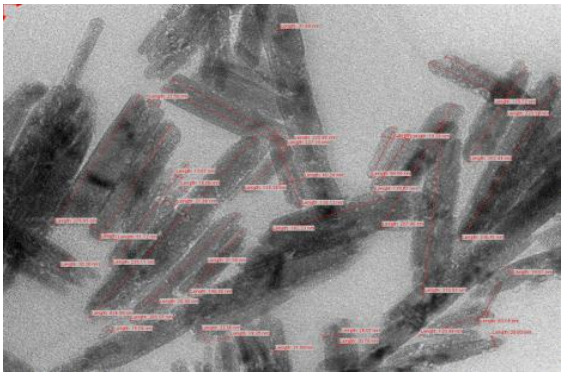
The various images of SEM and EDS configurations were captured for LP and HP. The coating thickness, surface spread, roughness, smoothness, contact angles, inter-separation distances, size, morphology, spatial distribution were observed and measured using SEM, image J particle analyser and energy dispersive X-ray spectroscopy. The viscosities of nanoparticle scattering were measured at room temperature using a rheometer (physica MCR301, Anton Paar Gmbh Graz, Austria). The densities of nanoparticles were also measured at room temperature with a densitometer (30 PX, Metler Toledo, Viroflay France). The surface tension were measured with a tensiometer (3 s GBX, Bourg de peage, France) using the wilhelmy plate method. To measure the contact angle drops of water were place on a flat coated membrane surface and the angle were measured with a goniometer (DiGi Drop Fast/60, GBX, Bourg de peage France). The thickness and inter-separation distances during nanoparticle coating depend on the

coating velocity and the physical properties (viscosity of scattering of nanoparticle). Due to these factors the thickness and inter-separation distances differs with velocity of nanoparticles coating for HP and LP during TEM and SEM observation. Bulk sample analysis in the SEM showed a conventional E-T detector which collected the SE/BSE electrons during the analysis. The SE electrons may also be collected using a high-resolution In-Lens SE detector during analysis. It is important to note that the large emission volume of X-rays can be collected by an EDS detector.

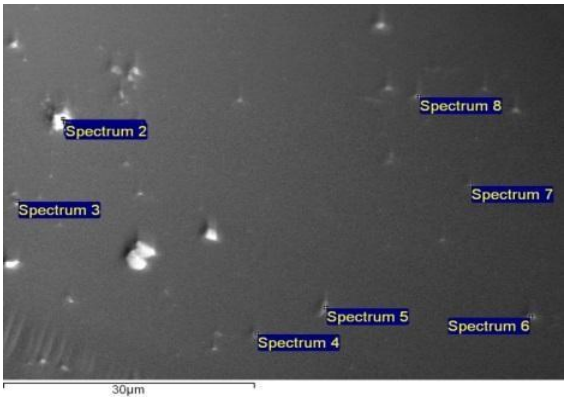
In the current study the following EDS detectors were used to analyze a 10 mm^2 sediment, coated sediment and hydrophobic nanoparticles (Thermo Scientific, USA), a 10 mm^2, SDD (Bruker, Germany), a 100 mm^2, SDD (Thermo Scientific, USA), with an annular 60 mm^2 Flat QUAD SDD (Bruker, Germany). The SDD annular is being inserted between the pole shoe and the experimental sample, to give a very large solid angle of the X-rays being emitted by the sample. For the TEM analysis the sample were not etched or polish since the coated nanoparticles was on the surface of the membrane. A standard TEM thin foil 3mm in diameter were prepared for analysis by electrolytic twin-jet (at −30°C, 30 V) in

Struers Tenupol 2 filled with 6% solution of perchloric acid in methanol. This observations were all carried out at 200 kV with JEOL JEM 2000FX microscope equipped with an X-ray energy dispersive spectrometer (XEDS) 53 LINK AN 10 000 (26). The diameter, length, orientation, angles, morphology, spatial distribution of the coated nanoparticles on the membrane surface was measured as shown in Fig.2 (b).

(a)



(b)



(c)

Figure 2 (a): Sediment material after hydrophobic nanoparticle coating (b) TEM measurement of length and diameter of control nano4stone (c) Spectrum lens location on the samples.

It was important to do a correlation with the EDS, Descriptive statistical analysis and SEM images during LP and HP coating. Before this correlation were done it was important to first analyze the control sample for sediment and nano4stone hydrophilic and their descriptive statistical analysis.

Project: SOB 2Project 1 Owner: INCA Operator Site: Site of Interest 1

Sample: SEDIMENT Type: Default

ID: SEDIMENT

Processing option: All elements analysed (Normalized).

All results in weight%

Table 1. Descriptive statistics of the amount of elements in the surface layer formed in sediment control sample

ESD setting

SOB 2Project 1	Project	Owner	Site:	Sample	ID
	SOB 2Project 1	INCA Operator	Site of Interest 1	Sediment control sample	Sediment control sample

Descriptive statistics

Spectrum	In stats.	O	Na	Mg	Al	Si	S	K	Ca	Total
SEDIMENT - S1	Yes	57.21	0.28	0.15	5.86	32.94	0.34	2.76	0.45	100.00
SEDIMENT - S2	Yes	56.46	0.27	0.19	1.97	39.85	0.41	0.49	0.35	100.00
SEDIMENT - S3	Yes	57.58	0.25	0.11	3.21	36.28	0.55	1.59	0.43	100.00
Mean		57.08	0.27	0.15	3.68	36.36	0.43	1.61	0.41	100.00
Std. deviation		0.57	0.02	0.04	1.99	3.46	0.10	1.14	0.05	
Max.		57.58	0.28	0.19	5.86	39.85	0.55	2.76	0.45	
Min.		56.46	0.25	0.11	1.97	32.94	0.34	0.49	0.35	

All results in weight%

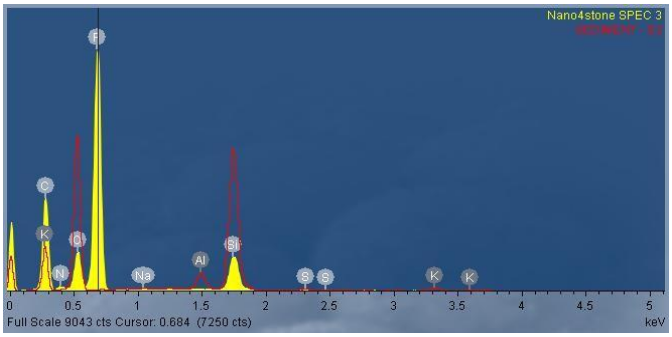


Fig. 3 Correlation between descriptive statistics of amount of elements in surface layer formed in sediment control sample and EDS of glass control sample

From Fig. 3, Both EDS and statistical analysis revealed eight elements that were found on the sediment control sample. The EDS shows the variation of intensity and kilo electrons volt electrons on a full scale during EDS analysis while the statistical analysis results revealed three site of interest (sediment control S1, sediment control S2 and sediment control S3) which data capturing were obtained. The statistical analysis revealed different mean, standard deviation, max and min which correspond to the varying peak, max spread, and min spread as shown in table 1. The observed elements in both EDS and statistical analysis that, eight elements existed as shown in table 1 in sediment control sample. These elements are oxygen (O), sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), Sulfur (F), Potassium (K) and calcium (Ca). The sediment control sample are reported to have very high content of O, followed by Si, Al, K, S, Ca and Na while Mg has the lowest content. Different mean, standard deviation, maximum and minimum proportion of elements were revealed for O, Si, Al, K, S, Ca and Na, which gave a total proportion of element to be 100%. The element with the highest mean, standard deviation, max and min was observed to be O, followed by Si, Al, K, Ca, Na and Mg was reported to have the lowest as shown in table 1. Good correlation can be seen between the results of EDS and statistical analysis. Oxygen was observed to have the highest peak intensity, followed by Si, Al, K, Ca, Na and Mg. It was also important to analyze the composition of sediment control sample shown in table 2.

Project: SOB 2Project 1 Owner: INCA Operator Site: Site of Interest 1

Sample: Nano4stone Type: Default

ID: Nano4stone

Processing option: All elements analysed (Normalized)

Table 2. *Descriptive statistics of the amount of elements in the surface layer formed in Nano4stone control sample*

ESD setting

SOB 2Project 1	Project	Owner	Site:	Sample	ID
	SOB 2Project 1	INCA Operator	Site of Interest 1	Sediment control sample	Sediment control sample

Descriptive statistics

Spectrum	In stats.	N	O	F	Na	Si	S	Total
Nano4stone SPECT 1	Yes	2.06	6.00	85.13	0.37	6.24	0.20	100.00
Nano4stone SPEC 2	Yes	1.26	7.34	83.05	0.23	7.87	0.25	100.00
Nano4stone SPEC 3	Yes	2.06	8.92	79.81	0.40	8.52	0.29	100.00
Mean		1.79	7.42	82.66	0.33	7.54	0.25	100.00
Std. deviation		0.46	1.46	2.68	0.09	1.18	0.05	
Max.		2.06	8.92	85.13	0.40	8.52	0.29	
Min.		1.26	6.00	79.81	0.23	6.24	0.20	

All results in weight%

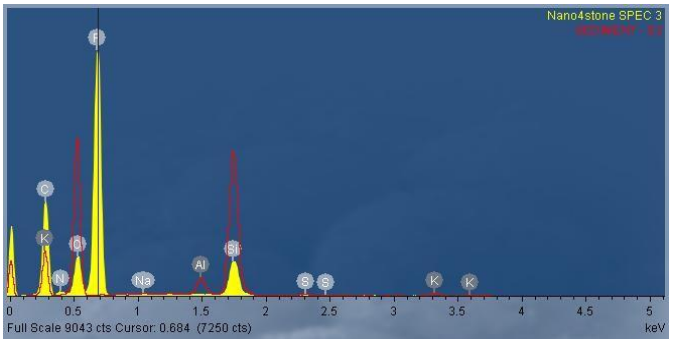


Fig. 4 Correlation between descriptive statistics of amount of elements in surface layer formed in nano4stone control sample and EDS of glass control sample

From Fig. 4 and table 2, Both EDS and statistical analysis revealed six elements that were found on the nano4stone control sample table of descriptive analysis results. The EDS shows the variation of intensity and kilo electrons volt electrons on a full scale during EDS analysis while the statistical analysis results revealed three site of interest (nano4stone control S1, nano4stone control S2 and nano4stone control S3) which data capturing were obtained. The statistical analysis revealed different mean, standard deviation, max and min which correspond to the varying peak, max spread, and min spread. The observed elements in both EDS and statistical analysis that, the six main elements are Nitrogen (N), oxygen (O), Fluorine (F), sodium (Na), silicon (Si), and Sulfur (S). It is observed as shown in table 2 that two new elements are reported which are Nitrogen and Fluorine (F) that are not found in sediments control samples shown in table 1. Nano4stone control sample was reported to have very high content of F, followed by Si, O, N, Na and S has the lowest content. Different mean, standard deviation, maximum and minimum element contents were revealed for N, O, F Na, Si, and S which gave a total element content of 100%as shown in table 2. Good correlation can be seen between the results of EDS and statistical analysis. Fluorine (F) was observed to have the highest peak intensity, followed by Si, and O.

SOB - Series 2 Project:

SOB - Series 2

Owner: INCA Operator Site: Site of Interest 1

Sample: SEDIMENT LP 2

Type: Default

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ID: SEDIMENT LP 2 Processing option: All elements analysed (Normalized)

Table 3: Descriptive statistics of the amount of elements in the surface layer formed in sediment 2rd round LP after PEO

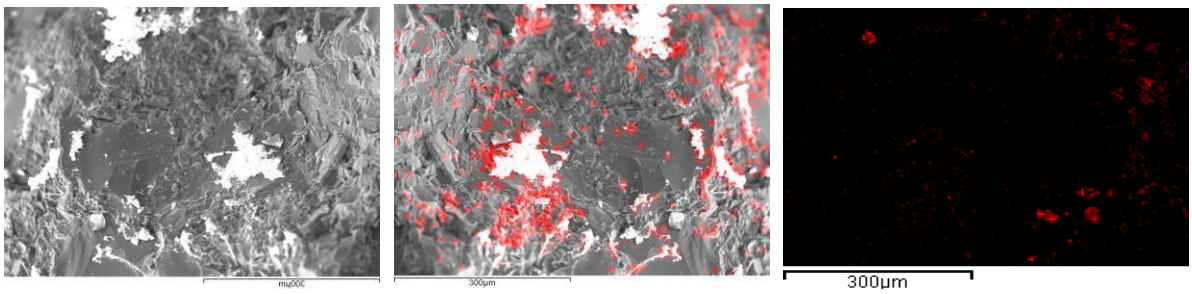
ESD setting

SOB 2Project 1	Project	Owner	Site:	Sample	ID
	SOB 2Project 1	INCA Operator	Site of Interest 1	SEDIMENT LP 2Type	SEDIMENT LP 2

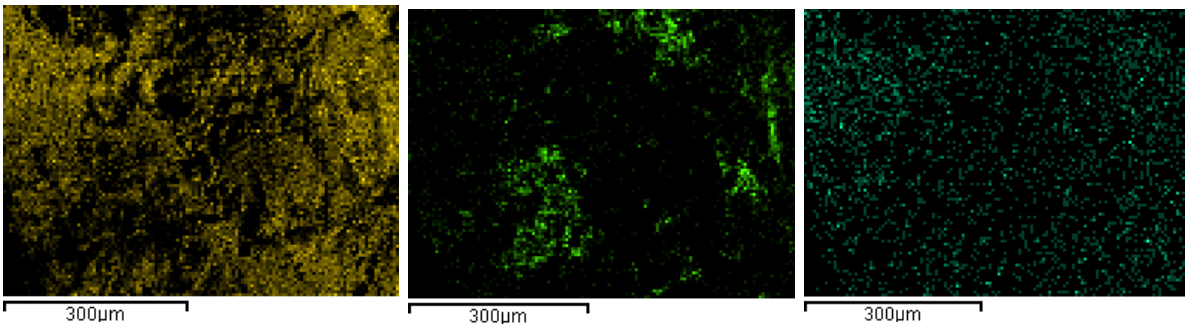
Descriptive statistics

Spectrum	In stats.	O	F	Na	Mg	Al	Si	S	K	Ca	Total
SEDIMENT 2-S1	Yes	54.65	4.02	0.33	0.14	0.80	38.76	0.85	0.10	0.36	100.00
SEDIMENT 2-S 2	Yes	49.46	2.92	0.35	0.04	14.85	24.79		7.42	0.17	100.00
SEDIMENT 2-S3	Yes	51.10	6.20	0.36	0.22	0.96	39.55	0.51	0.44	0.66	100.00
Mean		54.65	6.20	0.36	0.22	14.85	39.55	0.85	7.42	0.66	100.00
Min.		49.46	0.33	0.33	0.04	0.80	24.79	0.51	0.10	0.17	

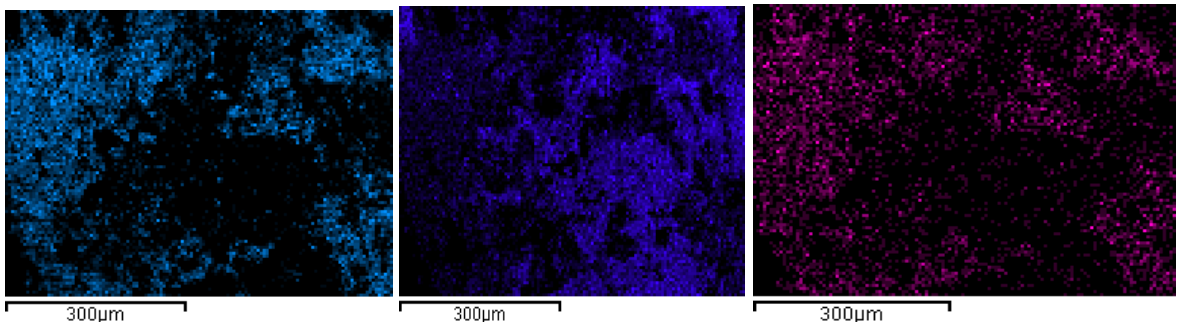
All results in weight%



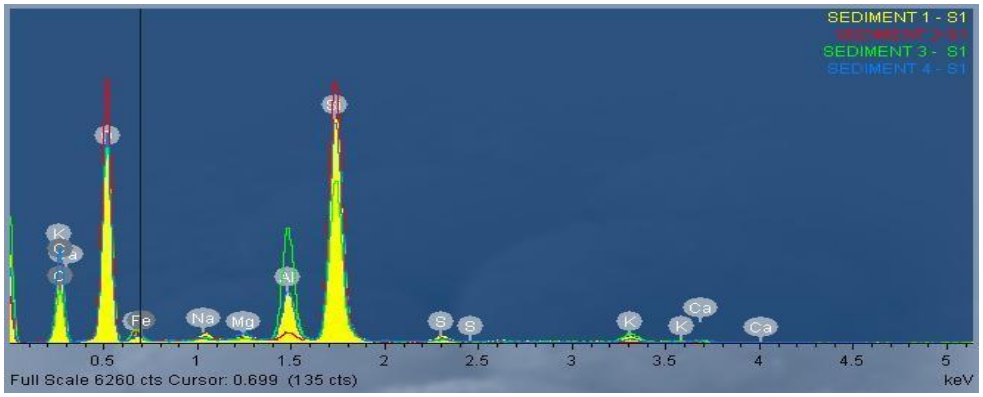
(a) **(b)** **(c)**



(d) **(e)** **(f)**



(g) **(h)** **(i)**



(j)

Figure 5 (a) Reference Sediment after 2rdround of LP coating (b) mix showing F element on the membrane surface (c) element C (d) element O (e) element F (f) element Na (g) element Al (h) element Si (i) element K and (j) energy dispersion X-ray spectroscopy

In Figure 5 and table 3, the SEM and EDS results of the membrane surface layer formed on sediment after 1st LP hydrophobic nanoparticle coating are presented table of descriptive analysis results. All SEM photos show different spread of surface density of F, O, Na, Mg, Al, Si, S, Ca and K on the sediment surface. Additionally, clusters were observed on the reference image and mix F element. The inter-separation distances are bigger and morphology, spatial distribution, orientation, sizes and shape of F keep changing. This may indicate high surface roughness which doesn't improvement membrane wettability when related to the lotus effect on surface wettability. The lotus effect on surface wettability stated that the coated membrane surface must be smooth as smooth surface enhanced wettability. The inter-separation is bigger in 2nd LP coating. The surface coated with hydrophobic nanoparticle revealed high O, Si, Al, K, C and F which can be correlated with the EDS and statistical analysis results as for 2nd LP coating. From the EDS it can be observed that the intensity or peak for O was the higher followed by Si, Al and K, while S was observed to have the lowest peak or intensity. A proper correlation is observed from the EDS results, statistical analysis and the SEM images. It was important to study the membrane surface after 3rd round LP of coating as shown in table 4.

SOB - Series 2

Project: SOB - Series 2

Owner: INCA Operator Site: Site of Interest 1

Sample: SEDIMENT LP 3

Type: Default

ID: SEDIMENT LP 3

Processing option: All elements analysed (Normalized)

Table 4. Descriptive statistics of the amount of elements in the surface layer formed in sediment 3rd round of LP coating

ESD setting

SOB 2Project 1	Project	Owner	Site:	Sample	ID
	SOB 2Project 1	INCA Operator	Site of Interest 1	Sediment LP 3rd	Sediment LP 3rd

Descriptive statistics

Spectrum	In stats.	O	F	Na	Mg	Al	Si	S	K	Ca	Fe	Total
SEDIMENT 3 - S1	Yes	47.16	6.16	0.48		14.45	27.49	0.51	3.74			100.00
SEDIMENT 3 - S2	Yes	34.15	3.76	0.43	0.40	8.87	42.11	1.29	4.31	1.60	3.06	100.00
SEDIMENT 3 - S3	Yes	48.68	1.33	0.18		2.56	45.32	0.37	1.57			100.00
SEDIMENT 3 - S4	Yes	57.02	4.95	0.31	0.29	5.36	30.88	0.44		0.76		100.00
Max.		57.02	6.16	0.48	0.40	14.45	45.32	1.29	4.31	1.60	3.06	
Min.		34.15	1.33	0.18	0.29	2.56	27.49	0.37	1.57	0.76	3.06	

All results in weight%

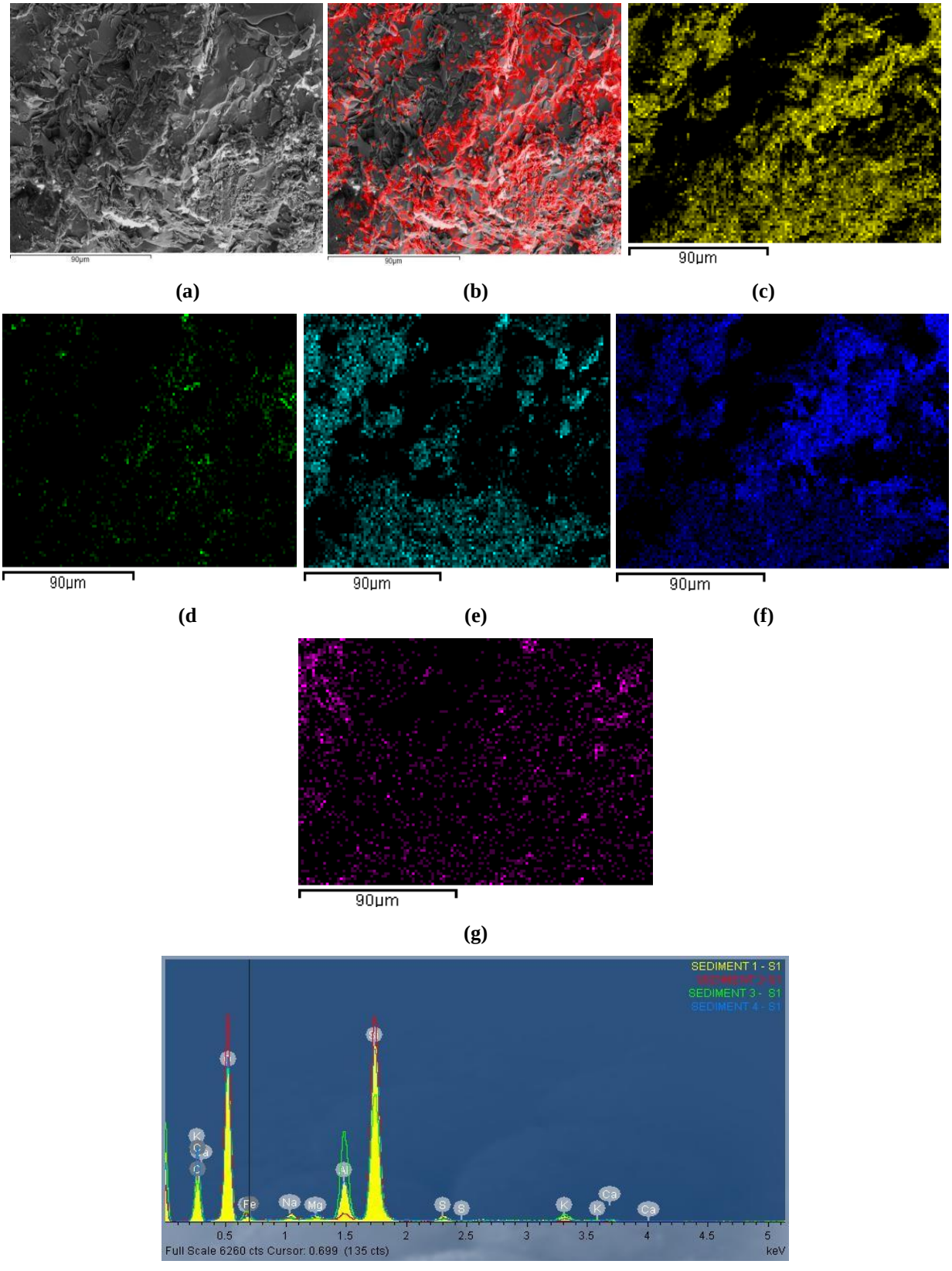


Figure 6 (a) Reference Sediment after 3rd round of LP coating (b) mix showing F element on the membrane surface (c) element O (d) element F (e) element Al (f) element Si (g) element K element and (h) energy dispersion X-ray spectroscopy

In Figure 6 and table 4, the SEM and EDS results of the membrane surface layer formed on glass after 3rd LP hydrophobic nanoparticle coating are presented table of descriptive analysis results. All SEM photos show different spread of surface density of F, O, Al, Si and K on the sediment membrane surface. Additionally, more clusters are observed on the reference image and mix F element when compared with and 2rd LP coating. On the coated hydrophobic nanoparticle mixed surface, the inter- separation distances are very small when compared with 2rd LP coating. The surface coated with hydrophobic nanoparticle have high O, F, Si, Al, and K which can be correlated with the EDS and statistical analysis results as for 3rd LP coating. The membrane surface appears with few clusters when compared with 2rd round of LP coating. Membrane clusters have significantly decreased with more F replacing the cluster with better orientation of F, morphology and spatial distribution of F. This increases the contact angles of water on the membrane surface which lowers the surface energy of water. The decrease in cluster increases surface smoothness which enhances wettability. The SEM images in Fig. 6 (c-g) revealed high distribution of O, Si and Al and a close validation of their intensity are shown in Fig. 6 (h).

The results in table 4 revealed membrane chemical compositions of sediment after 3rd coating by LP. Table 4 is compared with the control sample for nano4stone, sediment control sample and 2rd coating LP. When comparing 3rd coating by LP with control sample of nano4stone it is shown that F decrease and at the same time Na, Si and S increase. When comparing 3rd coating with sediment control it is shown that O and Si decrease and at the same time Na, Al, S and K increase. It was also noticed that Mg and Ca did not existed and there was a new element called Fe. When comparing 3rd coating and 2rd coating LP it is shown that O, Si and S decrease and at the same time F, Na, Al, S and K increase. However there was a new max element of Fe which was not found in 2rd coating LP sediment. There was a need to perform the analysis of 4th round of LP coating and observed their scattering on the membrane surface.

SOB 2Project 1

Project: SOB 2 Project 1

Owner: INCA Operator Site:

Site of Interest 1

Sample: SEDIMENT LP 4

Type: Default

ID: SEDIMENT LP 4

Processing option: All elements analysed (Normalized)

Table 5. Descriptive statistics of the amount of elements in the surface layer formed in sediment 4th round of LP coating

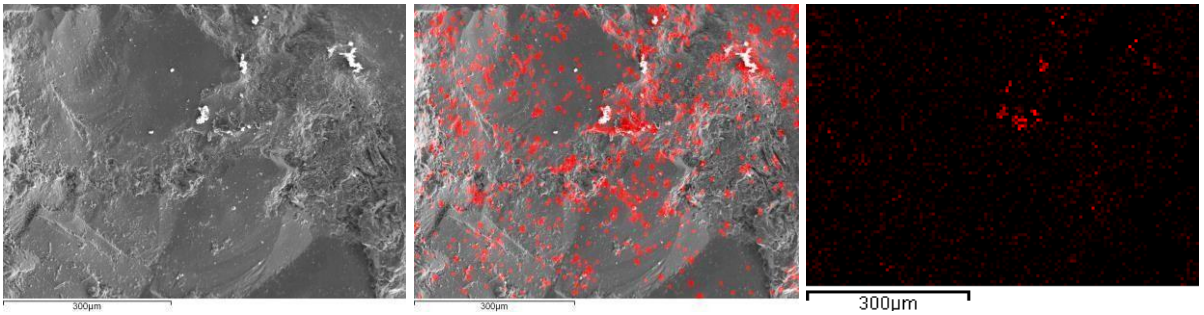
ESD setting

SOB 2Project 1	Project	Owner	Site:	Sample	ID
	SOB 2Project 1	INCA Operator	Site of Interest 1	Sediment LP 4th	Sediment LP 4th

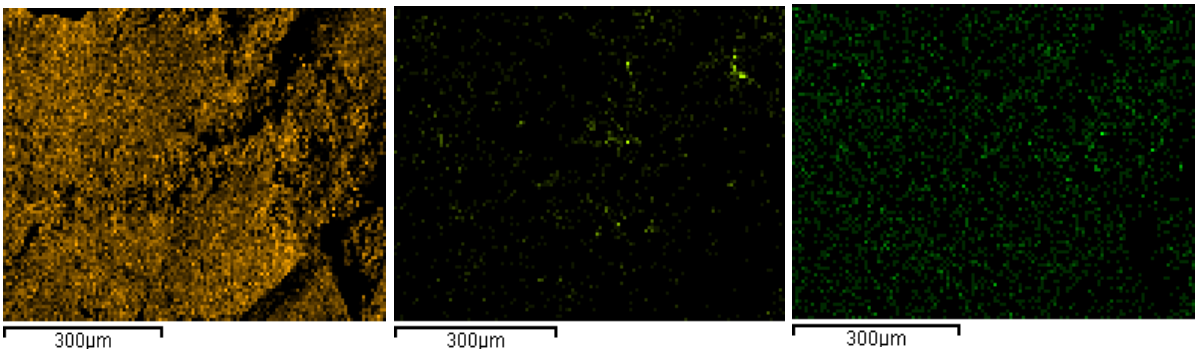
Descriptive statistics

Spectrum	In stats.	O	F	Na	Mg	Al	Si	S	K	Ca	Fe	Total
SEDIMENT 4 - S1	Yes	48.53	1.00	0.20	0.86	6.13	34.86	0.67	1.31	1.36	5.07	100.00
SEDIMENT 4 - S2	Yes	52.30	8.54	0.39	0.18	1.67	32.76	0.40	0.46	0.34	2.96	100.00
SEDIMENT 4- S3	Yes	54.49	2.80	0.28	0.19	3.72	32.62	0.45	0.77	0.27	4.41	100.00
Mean		51.77	4.11	0.29	0.41	3.84	33.41	0.51	0.85	0.66	4.15	
Std. deviation		3.01	3.94	0.09	0.39	2.23	1.26	0.14	0.43	0.61	1.08	
Max.		54.49	8.54	0.39	0.86	6.13	34.86	0.67	1.31	1.36	5.07	
Min.		48.53	1.00	0.20	0.18	1.67	32.62	0.40	0.46	0.27	2.96	

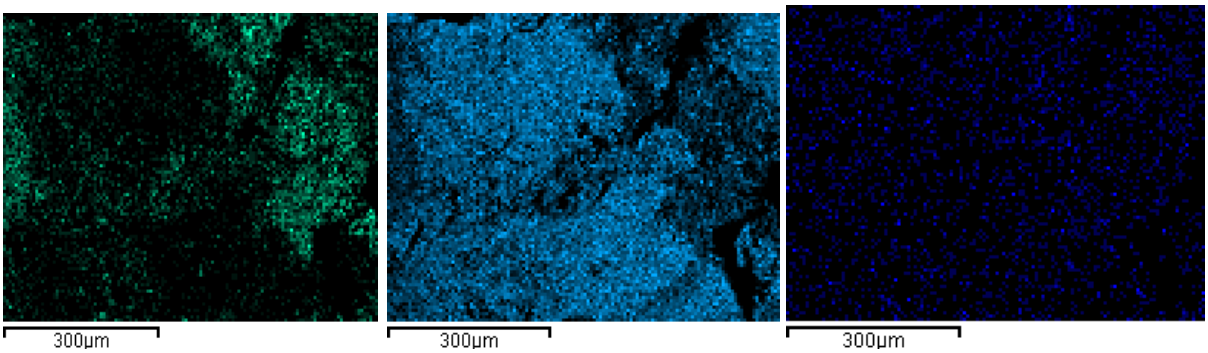
All results in weight%



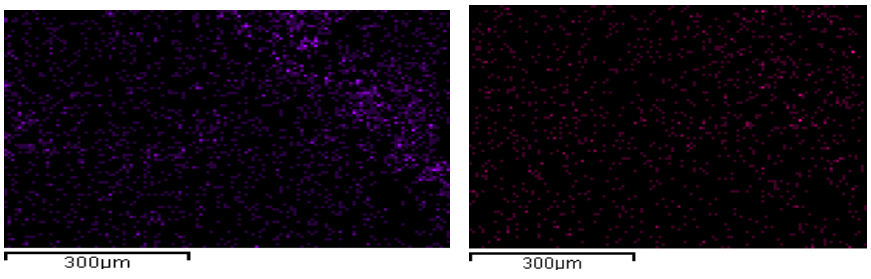
(a) **(b)** **(c)**



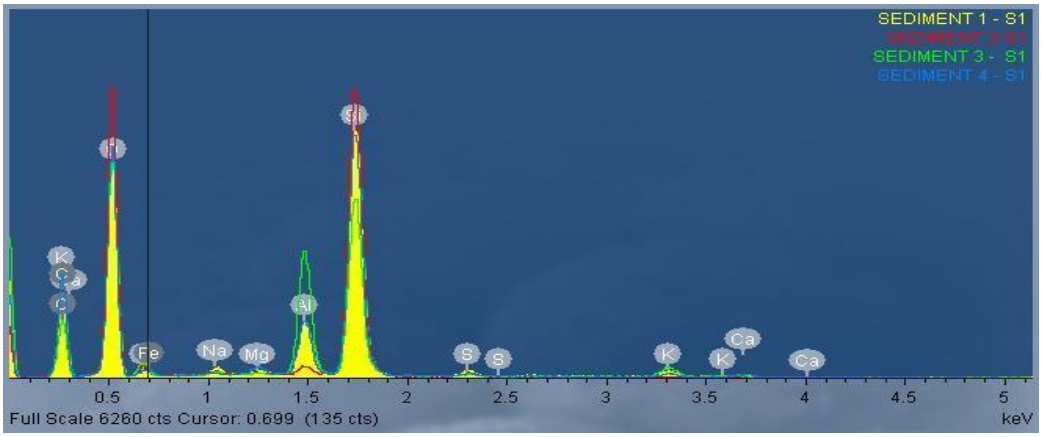
(d) **(e)** **(f)**



(g) **(h)** **(i)**



(i) **(j)** **(k)**



(l)

Figure 7 (a) Reference Sediment after 4th round of LP coating (b) scattering of F element on the membrane surface (c) element C (d) element O (e) element F (f) element Na (g) element Al (h) element Si (i) element K (k) Fe and (l) energy dispersion X-ray spectroscopy

In Figure 7 and table 5, the SEM and EDS results of the membrane surface layer formed on glass after 4th LP hydrophobic nanoparticle coating are presented and table of descriptive analysis results. All SEM photos show different spread of surface density of F, O, Al, Si, S, Mg, Ca, Na, Fe and K on the sediment membrane surface. Additionally, les clusters are observed on the reference image and mix F element when compared with and 2rd LP coating. On the coated hydrophobic nanoparticle mixed surface, the inter-separation distances are very small when compared with 2nd and 3rd LP coating. The surface coated with hydrophobic nanoparticle have high O, F, Si, Al, and K which can be correlated with the EDS and statistical analysis results as for 4th LP coating. Membrane clusters have significantly decreased with more F replacing the cluster with better orientation of F, morphology and spatial distribution of F. The decrease in cluster increases surface smoothness which enhances wettability. It was necessary to performed HP coating and tests their impact on wettability.

SOB - Series 2 Project:

SOB - Series 2

Owner: INCA Operator Site: Site of Interest 1

Sample: SEDIMENT HP 2

Type: Default

ID: SEDIMENT HP 2

Processing option: All elements analysed (Normalized)

Table 6. Descriptive statistics of the amount of elements in the surface layer formed in sediment 2rd round of HP coating

ESD setting

SOB 2Project	Project	Owner	Site:	Sample	ID
1					
	SOB 2Project 1	INCA Operator	Site of Interest 1	Sediment HP 2nd	Sediment HP 2nd

Descriptive statistics

Spectrum	In stats.	O	F	Na	Mg	Al	Si	S	K	Ca	Fe	Total
SEDIMENT H 2- S1	Yes	44.61	9.42	0.32	0.29	4.32	36.97	0.77	0.89	0.85	1.57	100.00
SEDIMENT H 2- S2	Yes	52.88	6.68		0.21	0.52	39.40	0.32				100.00
SEDIMENT H 2- S3	Yes	54.16	4.33			1.31	39.89	0.31				100.00
SEDIMENT H 2- S4		54.21	6.70	0.39		4.14	32.24	0.55	1.77			100.00
Max.		54.21	9.42	0.39	0.29	4.32	39.89	0.77	1.77	0.85	1.57	
Min.		44.61	4.33	0.32	0.21	0.52	32.24	0.31	0.89	0.85	1.57	

All results in weight%

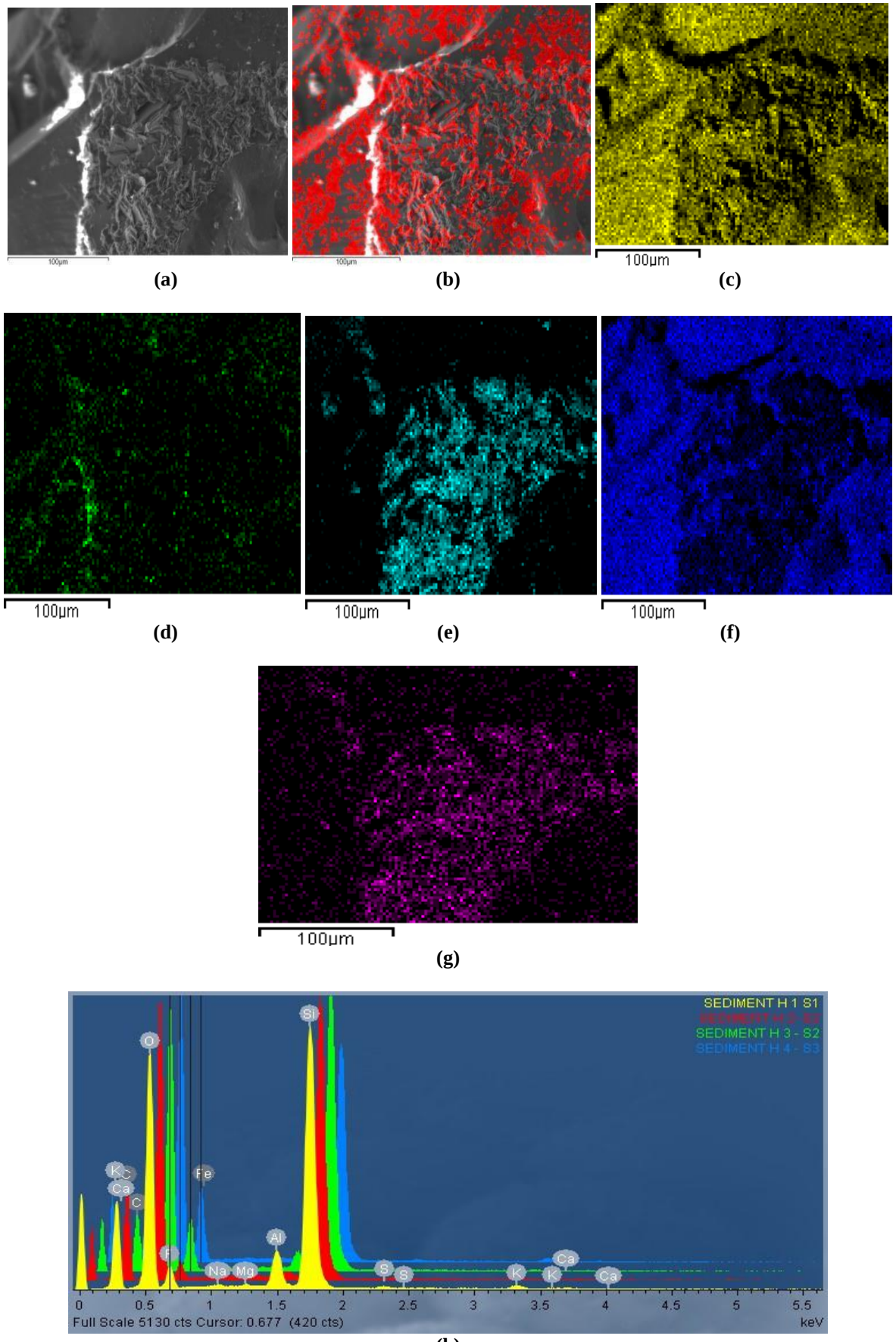


Figure 8 (a) Reference Sediment after 2rdround of HP coating (b) mix showing F element on the membrane surface (c) element O (d) element F (e) element Al (f) element Si (g) element K and (h) energy dispersion X-ray spectroscopy.

In Figure 7 and table 6, the SEM and EDS results of the membrane surface layer formed on sediment after 2nd HP hydrophobic nanoparticle coating are presented table of descriptive analysis results. All SEM photos show different spread of surface density of K, Ca, C, F, Fe, Na, Mg, Al, Si, and S on the sediment membrane surface. Additionally, more clusters are observed on the reference image and mix F element. Fig. 8 (a) revealed the sediment surface coated by nanoparticles and Fig. 8 (b) revealed sediment surface with uneven distribution of F on the membrane surface. Membrane clusters are observed in concentrated position in Fig.8 (a-b) having bigger spread. Poor orientation, size, shape and morphology and scattering of fluorine are revealed in Fig. 8 (a-b) after 2nd round of HP coating. The orientation, size, shape and morphology of F appear very poor around the clusters region as shown in Fig. 8 (a-b). The formation of membrane clusters during coating seems to have swept away F element during coating. There seem to be more even distribution of F element with uneven orientation, size, shape and morphology during 2nd round of coating as shown in Fig. 8 (b). For efficient and stable wettability process, there should be more even distribution of F on the membrane surface with proper F orientation, and proper size, shape and morphological distribution of F that enhances the contact angles of water on the membrane surface. The lotus effects revealed that smooth membrane lower membrane surface energy which enhances membrane wettability. The lotus effects clearly revealed that to enhance membrane wettability the coated membrane surface must be very smooth. Figure 8 (c-g) revealed different distributions of O, F, Al, Si and K after nanoparticle coating. Silicon (Si) and O are reported to have the highest quantity on the surface of the sediment, followed by Ca, F, Al, Fe, K, Ca, S, Na and Mg. The EDS results shown in Fig. 8 (h) are used for validation of the different intensity of existing element coating. The EDS results and statistical analysis revealed data that shows close correlation between the SEM images when comparing the different intensity of the elements. It was necessary to analysed glass 3rd HP coating.

SOB - Series 2 Project:

SOB - Series 2

Owner: INCA Operator Site: Site of Interest 1

Sample: SEDIMENT HP 3

Type: Default

ID: SEDIMENT HP 3

Processing option: All elements analysed (Normalized)

Table 7. Descriptive statistics of the amount of elements in the surface layer formed in sediment 3rd round of HP coating

ESD setting

SOB 2Project 1	Project	Owner	Site:	Sample	ID
	SOB 2Project 1	INCA Operator	Site of Interest 1	Sediment HP 3rd	Sediment HP 3rd

Descriptive statistics

Spectrum	In stats.	O	F	Na	Al	Si	S	K	Ca	Fe	Total
SEDIMENT H 3- S1	Yes	47.54	8.94	5.70	8.79	25.53	0.36	0.68	0.76	1.71	100.00
SEDIMENT H 3- S2	Yes	45.22	16.83		1.64	36.31					100.00
SEDIMENT H 3- S3	Yes	46.74	5.58	0.30	9.30	32.99		5.09			100.00
Max.		47.54	16.83	5.70	9.30	36.31	0.36	5.09	0.76	1.71	
Min.		45.22	5.58	0.30	1.64	25.53	0.36	0.68	0.76	1.71	

All results in weight%

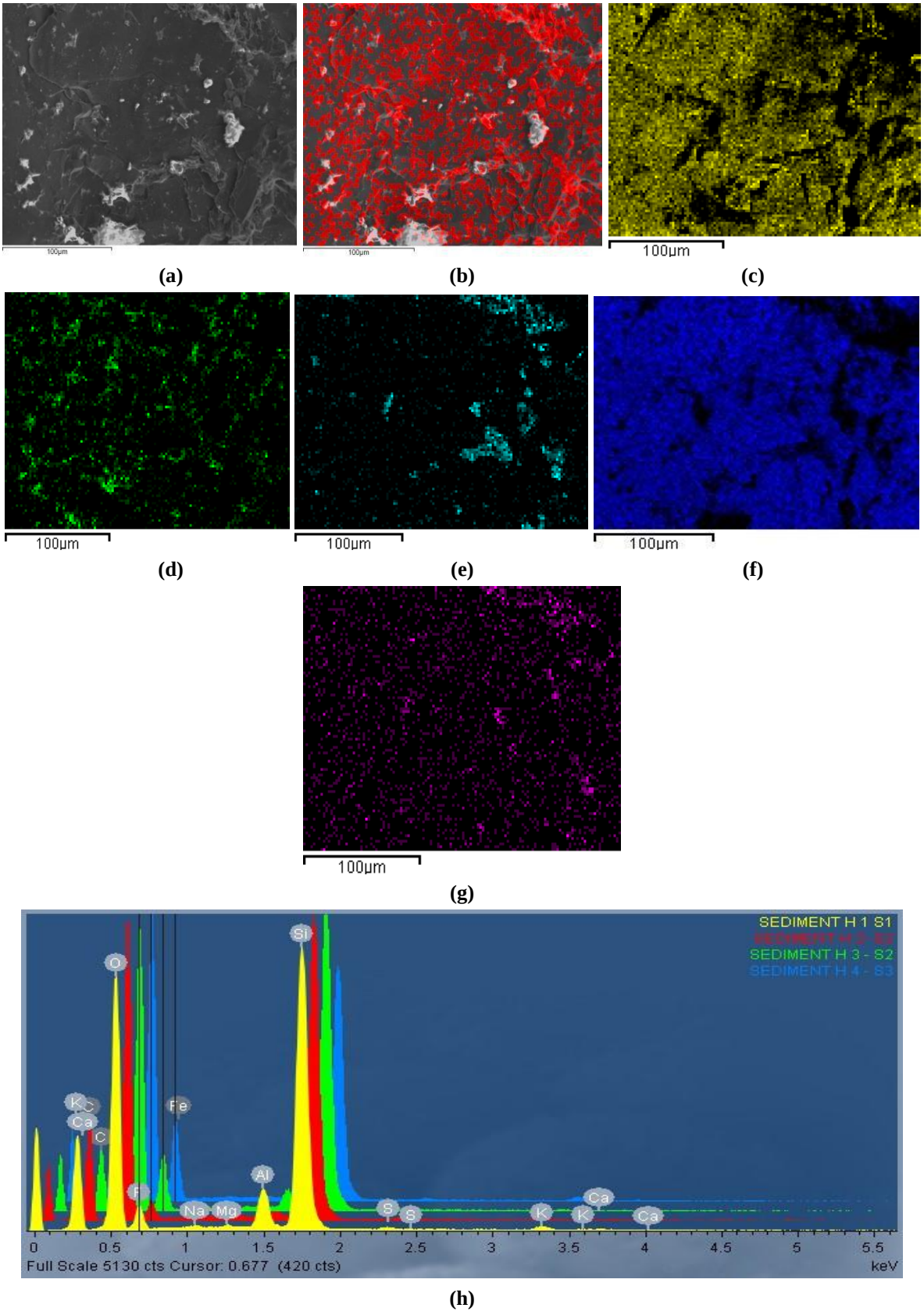


Figure 9 (a) Sediment 3rdround of HP coating without microscopy indication of the other element (b) scattering of F element during 3rdround of coating (c) the presence of element O during coating (c) the presence of element F during coating (d) the presence of Al during coating (e) the presence of Si element during coating (g) the presence of K element during coating and (h) Energy dispersive X-ray spectroscopy showing the intensity of F and other element after 3rdround of HP coating.

In Figure 9 and table 7, the SEM and EDS results of the membrane surface layer formed on sediment after 3rd HP hydrophobic nanoparticle coating are presented table of descriptive analysis results. All SEM photos show different spread of surface density of K, Ca, C, F, Fe, Na, Mg, Al, Si, and S on the sediment membrane surface. Additionally the membrane surface appears with few membrane clusters when compared with 2rd of HP coating. Membrane clusters are significantly decreased with F replacing the cluster with better orientation, size and morphology. This increases the contact angles of water on the membrane surface and lowers the surface energy of water resulting to a membrane surface with proper wettability. Figure 9 (b) revealed significant increase in F when compared 2rd round of coating. The increase in F decreases membrane clusters that were generated during 2rd round of coating. The decrease in cluster increases surface smoothness which enhances wettability. The produced membrane revealed smoother membrane surface with higher surface density of F which enhances wettability. The other elements in the membrane surface such as O, Si, and F increases more than K, and Al and this is validated by the EDS results as shown in Fig. 9 (h). Good correlation can be seen between the results of EDS and statistical analysis. Si and O were observed to have the highest peak intensity.

SOB 2Project 1

Project: SOB 2Project 1 Owner: INCA Operator Site: Site of Interest 1

Sample: SEDIMENT H 4

Type: Default

ID: SEDIMENT H 4

Processing option: All elements analysed (Normalized)

Table 8. Descriptive statistics of the amount of elements in the surface layer formed in sediment 4th round of HP coating

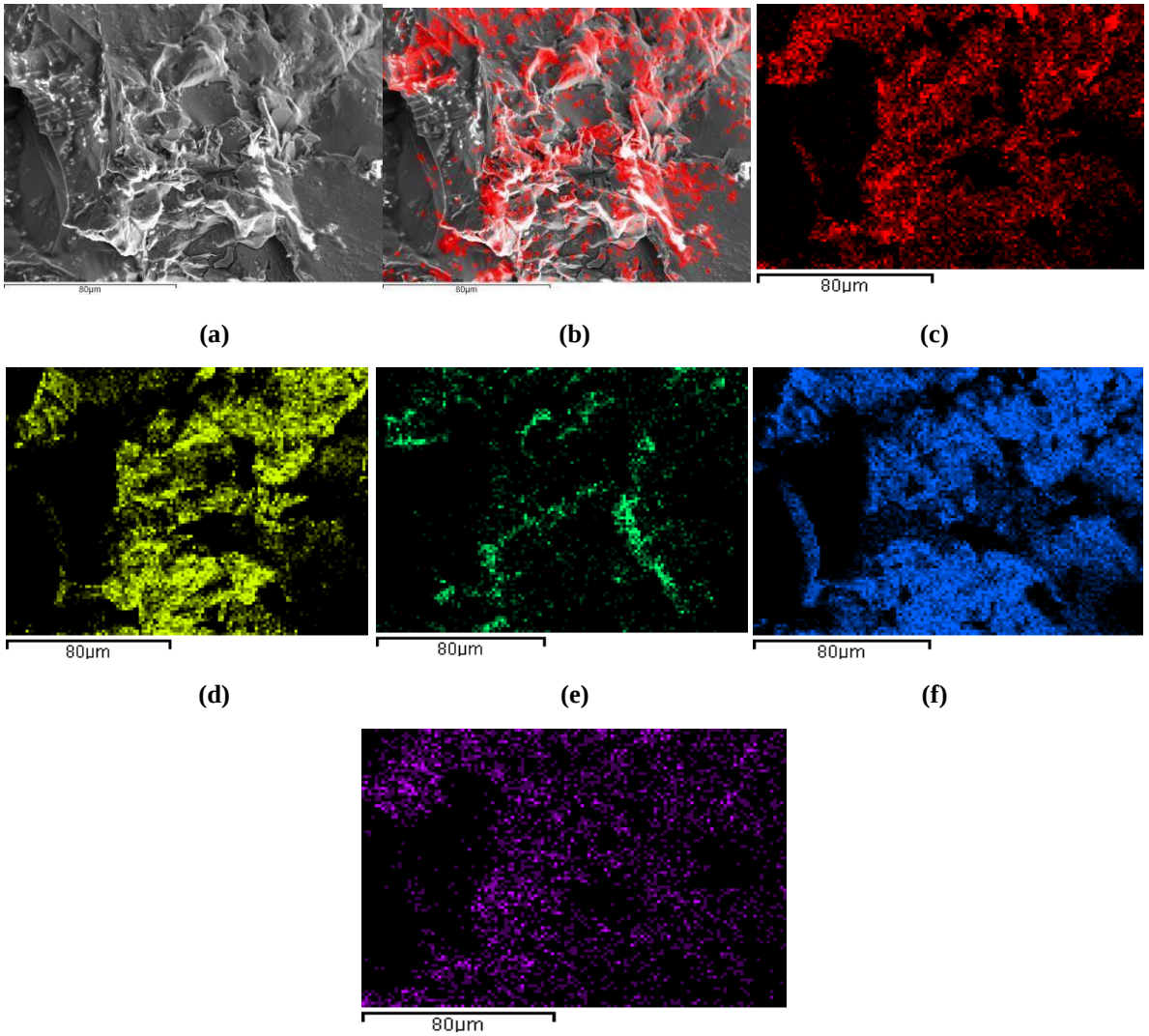
ESD setting

SOB 2Project 1	Project	Owner	Site:	Sample	ID
	SOB 2Project 1	INCA Operator	Site of Interest 1	Sediment HP 4th	Sediment HP 4th

Descriptive statistics

Spectrum	In stats.	O	F	Na	Al	Si	S	K	Ca	Fe	Total
SEDIMENT H 4- S1	Yes	51.08	9.10	0.51	6.76	22.99	0.51	0.95	0.45	6.85	100.00
SEDIMENT H 4- S2	Yes	49.27	6.47	0.29	6.82	17.44	0.73	0.90	8.19	6.56	100.00
SEDIMENT H 4- S3	Yes	43.08	23.33	0.16	3.57	28.14	0.32	1.05	0.22	0.00	100.00
SH4-SAMEAS-S1- 20KV		49.02	15.94	0.43	5.23	25.42	0.44	0.44	0.27	2.21	100.00
Mean		48.11	13.71	0.35	5.60	23.50	0.50	0.83	2.28	3.90	100.00
Std. deviation		3.48	7.55	0.16	1.54	4.55	0.17	0.27	3.94	3.36	
Max.		51.08	23.33	0.51	6.82	28.14	0.73	1.05	8.19	6.85	
Min.		43.08	6.47	0.16	3.57	17.44	0.32	0.44	0.22	0.00	

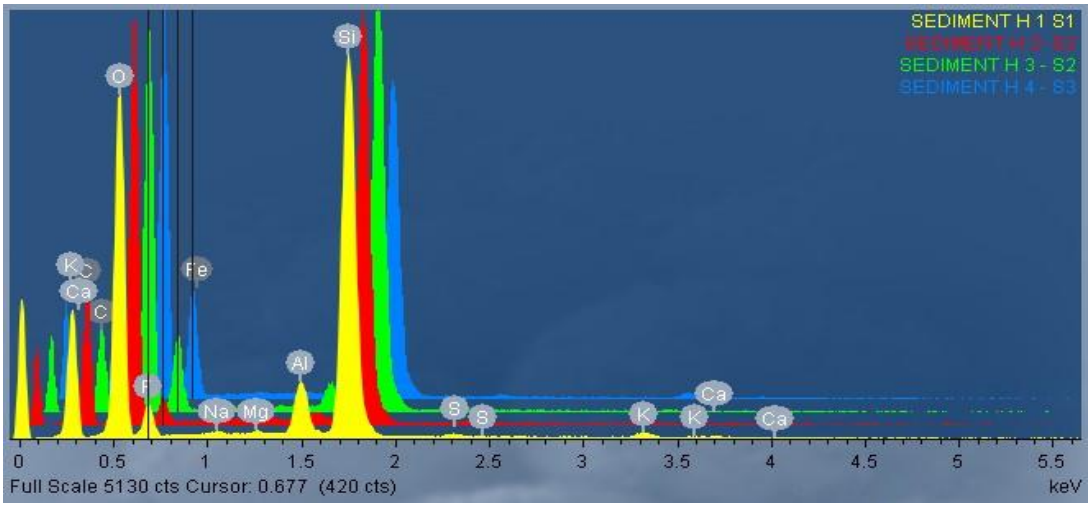
All results in weight%



(a) **(b)** **(c)**

(d) **(e)** **(f)**

(g)

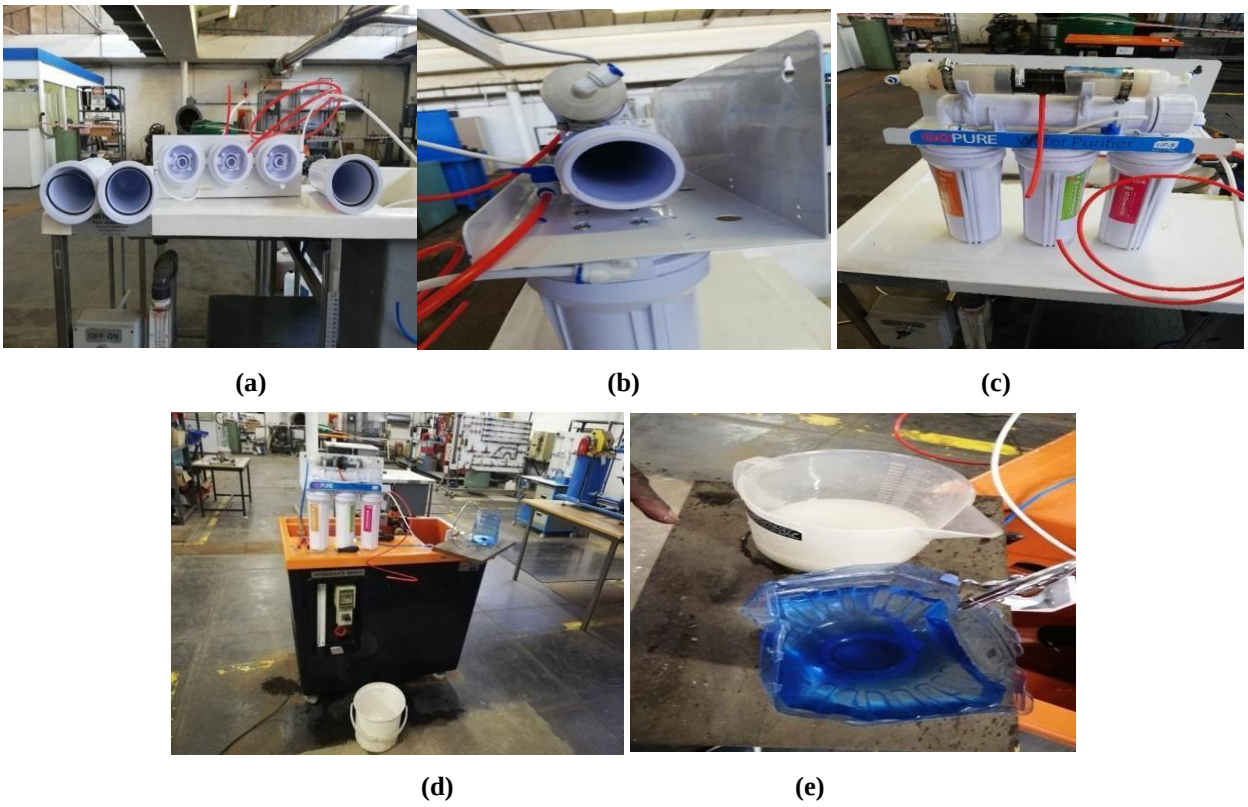


(h)

Figure 10 (a) Reference Sediment after 4th round of HP coating (b) mix showing F element on the membrane surface (c) element C (d) element O (e) element F (f) element Si (g) element S and (h) energy dispersion X-ray spectroscopy

In Figure 10 and table 8, the SEM and EDS results of the membrane surface layer formed on sediment after 4th HP hydrophobic nanoparticle coating are presented table of descriptive analysis results. All SEM photos show different spread of surface density of K, Ca, C, F, Fe, Na, Mg, Al, Si, and S on the sediment membrane surface. Additionally the result in Fig.10 revealed membrane surface after 4th round of HP coating with poor distributed F when compared to 3rd round of HP coating. The coated membrane surface appears with membrane clusters which were observed during 3rd round HP coating. There is generally poor morphology, size and spatial distribution of coated F on the membrane surface which will hinder membrane wettability. Interestingly it is revealed that Si have the highest intensity followed by O, C, K, Ca, and F as shown in Fig.10 (f, d and c) which can be validated by the EDS results in Fig.10 (h). It was shown that O, Al, Si, S and K decrease while F, Na, Mg, and Ca increase during 4th HP coating. There was a proper correlation between the SEM images and EDS results when comparing both results. There was a need to perform the wettability test of sediment LP and HP coated membrane for validation purpose in the current study.

2.3 Experimental setup of the new membrane technology used in oil/water separation



(a) **(b)** **(c)**

(d) **(e)**

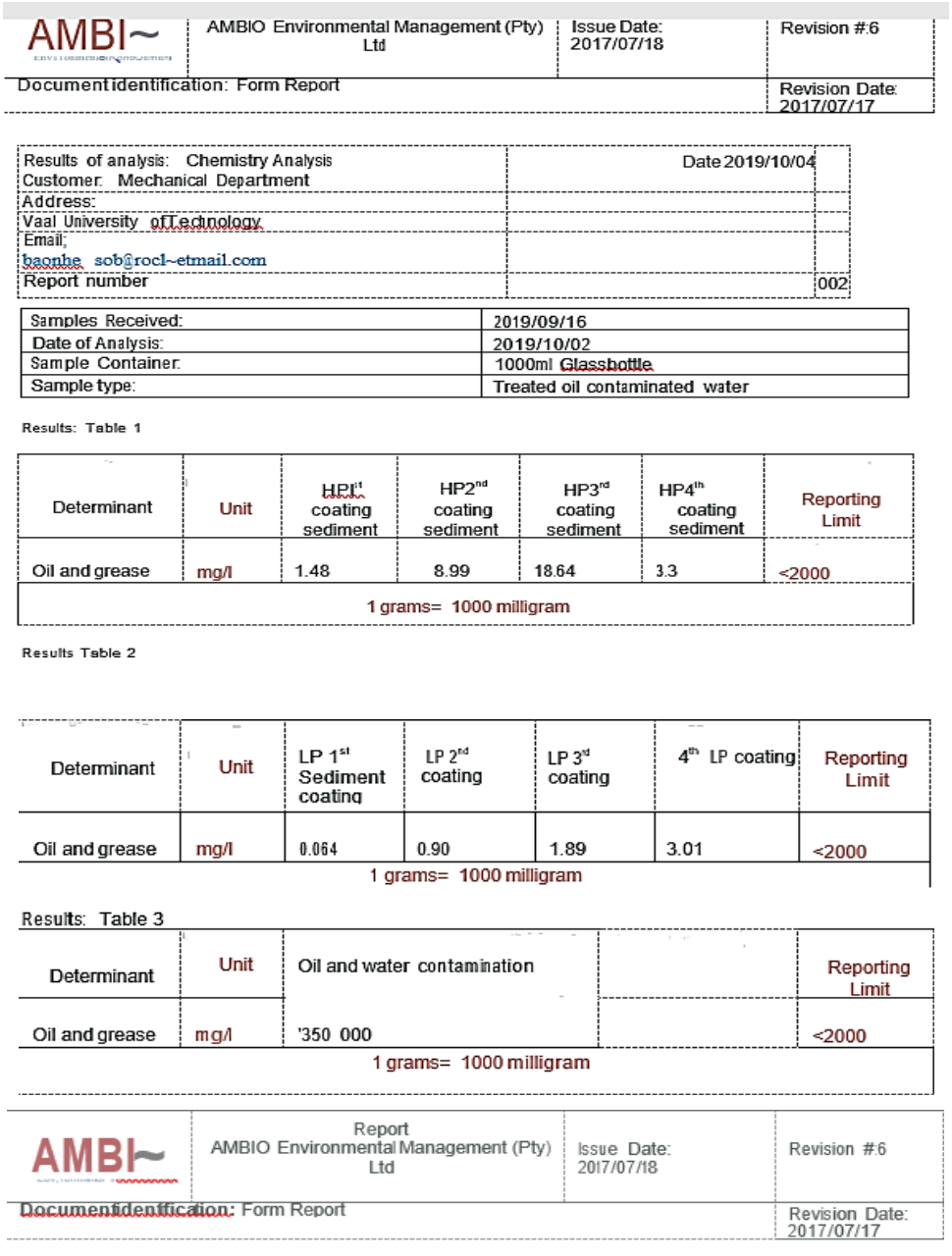
Figure 11 (a-b) membrane installations in progress (c) installation of proposed nanostructured membrane, (d) experimental setup of Nanostructure Membrane technology used in oil/water separation (e) separated water from contaminated oil/water after experimentation

2.4 Experimentation of oil/water separation to validate the newly design nanostructured membrane A centrifugal pump was used to pump oil/water mixture from the storage tank through the nanostructured membrane to the final point were only pure water was collected as shown in Fig. 10 (e). The gauge pressure was at 180 kPa during oil/water separation and the rate of flow of water during pump operation was 10 litres/s. The experiment was performed at room temperature and at a steady pressure supply by the centrifugal pump. Sediment 2nd LP, 3rd LP, 4th, 2nd, 3rd HP and 4th HP were tested for validation of wettability surface. The different obtained results were sent for analysis chemical analysis at AMBIO laboratory to detect the level the impurities of oil that was not filtered by the membrane technology. This was also done to adhere to National Engineering practice and regulation given by the South Africa Engineering Council for pollution control and environmental safety.

2.5 Oil and Grease Analysis Using US EPA Method 1664B with the SPE-DEX 1000 Oil and Grease System

The extraction of oil (Petrol) from the purify water after experiments was done using US EPA method 1664B with the SPE-DEX 1000 oil system using the four main step (1) Pre-wet/Conditioning solvent: when the disc is Pre-wet with a solvent to make it ready for the sample. Step 2 Processing of sample: when the sample from its original sample bottle is process through the SPE-Disk. Step 3 Solvent rinse of sample

bottle: a solvent is used to rinsing the bottle and to ensure the entire sample is extracted. Step 4: Extraction of the SPE Disk: the disk is extracted and analysed in a small volume of solvent rather than in a large volume of water were they started. The pan is removed from the heat source (compressor). Any oil or grease will be evidence by a white spot on the pan when pure water must have been evaporated during the heating process. Then the pan was weigh, the pan and subtract the initial anti pan value from the full pan value to get your gravimetric value. The following obtained results for glass LP and HP rounds of coating were obtained as shown in Fig.11.



AMBIO Environmental Management (Pty) Ltd	Issue Date: 2017/07/18	Revision #:6
Document identification: Form Report		Revision Date: 2017/07/17

Results of analysis: Chemistry Analysis Customer: Mechanical Department	Date 2019/10/04	
Address: Vaal University ofTechnology		
Email; baonhe sob@rocl~etmail.com		
Report number		002

Samples Received:	2019/09/16
Date of Analysis:	2019/10/02
Sample Container:	1000ml Glassbottle
Sample type:	Treated oil contaminated water

Results: Table 1

Determinant	Unit	HP1st coating sediment	HP2nd coating sediment	HP3rd coating sediment	HP4th coating sediment	Reporting Limit
Oil and grease	mg/l	1.48	8.99	18.64	3.3	<2000
1 grams= 1000 milligram						

Results Table 2

Determinant	Unit	LP 1st Sediment coating	LP 2nd coating	LP 3rd coating	4th LP coating	Reporting Limit
Oil and grease	mg/l	0.064	0.90	1.89	3.01	<2000
1 grams= 1000 milligram						

Results: Table 3

Determinant	Unit	Oil and water contamination		Reporting Limit
Oil and grease	mg/l	'350 000		<2000
1 grams= 1000 milligram				

Report AMBIO Environmental Management (Pty) Ltd	Issue Date: 2017/07/18	Revision #:6
Document identification: Form Report		Revision Date: 2017/07/17

<1 indicates that the determinant was not detected

- AMBIO will perform correct analyses, AMBIO shall not be liable for damages arising from loss or injury caused directly or indirectly by or contributed by or arising from any inaccuracy of the analysis or the interpretation thereof.
- Results relate only to items tested by the laboratory.
- The Laboratory does not give any opinions and interpretations as that falls outside the scope of

Figure 12 Wettability test for oil/water separation on glass LP and HP rounds

Table 1 and table 2 of Fig. 11 revealed the final laboratory results after oil and grease Analysis were performed. The determinant was oil in the contaminated water and oil that were filtered through the designed nanostructured membrane. The wettability of eight sediments after HP and LP tested were validated. The obtained values greater 1 revealed that oil was not detected in the filtered water. The obtained values less than 1 indicated that oil was detected in the filtered water after wettability test. Therefore these obtained results can be correlated with the different results of HP and LP coating rounds.

It is observed during the wettability test that sediment HP 3 show more efficient wettability when compared with all the sediment coating rounds. It was important to compare the SEM images for validation of their surface properties. It was observed that 3rd HP coating rounds have little or no clusters on its surface when compared with the other wetting rounds. Therefore it is clear that the presence of clutters is an indication of poor wettability. Sediment 1st and 2nd round LP coating revealed the membrane surface with poor wettability since few oil molecules were observed in the separated water. The reason for poor oil/water separation process as shown in 1st and 2nd LP are due to high surface roughness and more clusters being observed.

CONCLUSION

The current study was aimed at designing a membrane surface with stable and efficient wettability process. To achieve this objective sediment membrane surface was coated and their surface properties were analysed and characterised in relation to the lotus effect of wettability surfaces. SEM, EDS, statistica analyses and contact angles of water was measured for validation purpose after relating the membrane surface to lotus effect. The following facts were revealed and validated experimentally. Different orientations of nanoparticles were also observed to impact membrane wettability due to membrane clusters. Clusters were also observed on the membrane and more clusters were observed in LP coating when compared with HP coating and these clusters impacts wettability. The membrane surface after 2nd and 3rd HP revealed more enhanced wettability. Good correlation can be seen between the results of EDS and statistical analysis and SEM images. Different nanoparticle orientation and inter- separation distances impacted membrane wettability as shown in the current findings. It shown that was 3rd HP coating rounds have little or no clusters on its surface when compared with the other wetting rounds. Therefore it is clear that the presence of clutters is an indication of poor wettability. The results of Sediment 1st and 2nd round LP coating revealed the membrane surface with poor wettability since few oil molecules were observed in the separated water. The reason for poor oil/water separation process as shown in 1st and 2nd LP are due to high surface roughness and more clusters being observed.

Conflicts of Interest

The authors declare that they have no conflicts of interest in the manuscripts between authors and involved institutions.

Acknowledgement

The research is supported by the Vaal University of Technology South Africa and the National Research Foundation (NRF). The relevant experiments and simulations were performed using Engineering Equation Solver (EES) and experimental data were captured at the microscopy unit in SEFAKO MENDUNSA HEALTH SCIENCE UNIVERSITY PRETORIA SOUTH AFRICA.

Data availability

The authors have given simulated data and data obtained during TEM, SEM and energy dispersion spectroscopy as requested by the editor. Other data could not be disclosed for confidentiality. See the appendix section of this paper.

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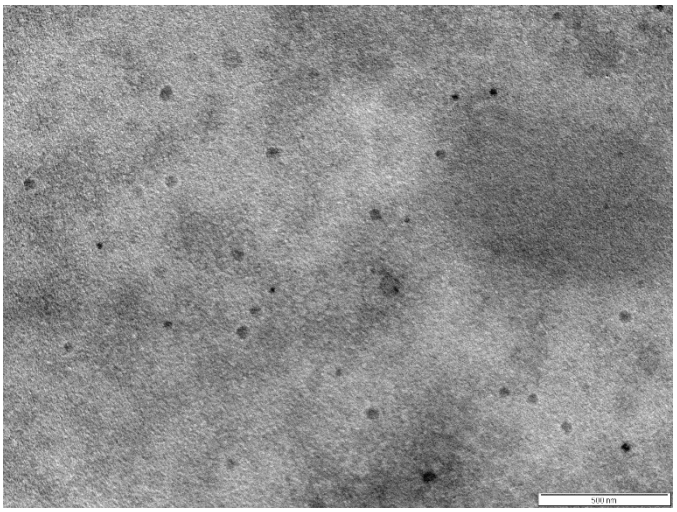
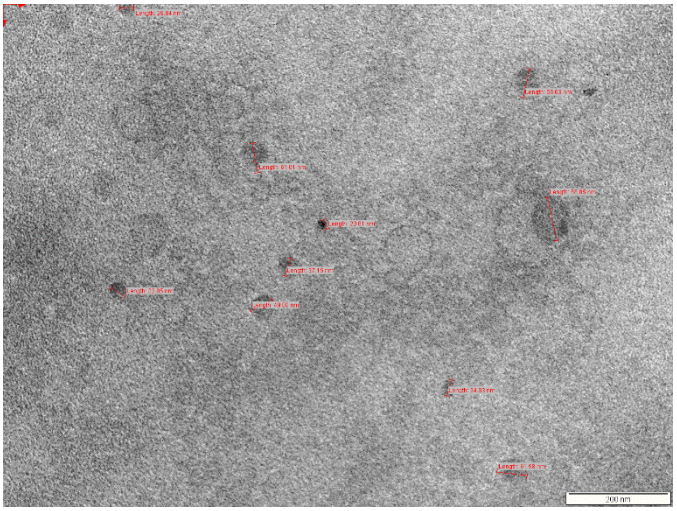
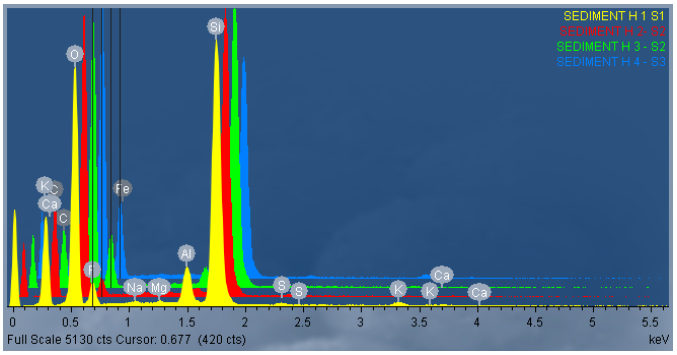
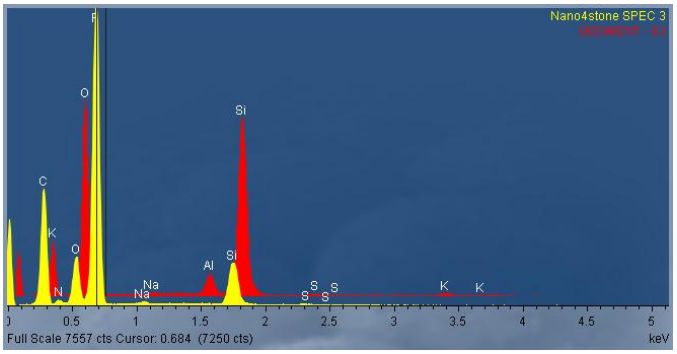
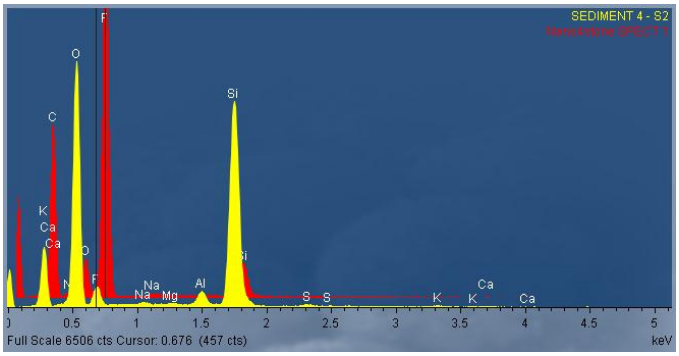
APPENDIX










SEDIMENT 4 - S2
O
Si
C
K
Ca
Ca
Na
Na
Mg
Al
S
S
K
K
Ca
Ca
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Full Scale 6506 cts Cursor: 0.676 (457 cts)
keV