OILY WATER TREATMENTS FOR SOUTHERN IRAQI OIL FIELDS

A Thesis Submitted to the College of Engineering of Nahrain University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering

by

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ABSTRACT

The oil drilling operations create large quantities of contaminated water known as “Produced Water” (PW), or water that is produced from the well. An experimental investigation was conducted using 1litter stainless steel autoclave to treat the oily water produced from North Rumaila and Zubair oil fields. The first approach was a pretreatment to remove solid particles using sedimentation with and without flocculation. The second approach included studied the effect of pH, pressure, temperature, salinity, operation time, outlet time and RPM. The third approach was investigate the effect of the surfactants (detergents and alcohol) to reduce surface tension, finally, was addition of some sorbents like polypropylene, polyethylene, used plastic and sawdust.

The ranges of salinity, pH, pressure and temperature were selected according to the PW conditions which out from dehydrator and desalter (80000 ppm, 6, 3bar and 60°C respectively), the RPM of mixer was selected to satisfy laminar flow, while the time of operation and outlet product represented the minimum residence time in batch reactor and its discharge to choose the minimum design cost. The results showed that the best conditions were:-

Pressure =1 bar, temperature =45°C, mixer speed =300 RPM, treating time =15 min and skim time starting =5 minutes. Best additives to reduce surface tension: ethanol volume = 0.05vol %, powder detergent = 400 mg/litter and liquid detergent volume = 0.03vol%.

Best sorbents: Sawdust amount addition = 2.5 gm, polypropylene = 4 gm, polyethylene = 3 gm and used plastic = 2.5 gm.

The results showed that using polymers made a great change in the oil recovery percent (all the oil was recovered).

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List of Symbols (Nomenclature and Abbreviation)

Symbols	Notations
AP	Alkyl phenols
APTS	Amino propyl triethoxy silane
CCl_4	Carbon tetrachloride
$C_2F_3Cl_3$	Freon
C_2Cl_4	Tetra chloro ethylene
C_D	Drag coefficient
CES	2carboxymethylthio ethyl tri methyl silane
CFV	Cross flow velocity
Cl^-	Chlorine ions
DAF	Dissolved –Air Floatation
DBPs. NOM	Complex mixture compounds such as fulvic and humic acid
G	Gas
G_v	Velocity gradient
GAC	Granular Activated Carbon
g	Gravitational constant of acceleration
H^+	Acidic indicate
IGF	Induced gas flotation
IOGCC	Interstate Oil and Gas Compact Commission
K_B	Boltzmann’s constant
L/H	Lipophilic to Hydrophilic ratio
MBF	Micro-Bubble Flotation
MHF	Membrane Hydrophobic filtration
MF	Micro filtration

NF	Nano filtration
NOM	Natural organic matter
NORM	Naturally occurring radioactive materials
O	Oil
OSPAR	Oil Spill Prevention, Administration and Response Fund
O/W	Oil - in - water emulsion
O/W/O	Oil-in-Water-in Oil
P	Pressure, bar
PAN	Polyacrylonitrile
PD & RC	Petroleum Development and Research Center Min. of oil, Iraq
PECT	Performance Enhanced Coalescence Technology
PECT-F	Performance Enhanced Coalescence Technology Fiber based
PPM	Part Per Million = mg/lit.
PVDF	Polyvinylidene
PW	Produced Water
PWT	Produced Water Treatment
PS	Poly Sulfone
Re	Reynolds number
RPM	Revolution Per Minutes
RO	Reverse Osmosis
S	Solid
SAR	Sodium Adsorption Ratio
SDI	Silt density index
S.O. C.	South Oil Company, Basra, Iraq

t	Time, min.
T	Temperature, °C
TDS	Total dissolved solid
TSS	Total suspended solid
UF	Ultra Filtration
UV	Ultraviolet
V_t	Terminal settling velocity
W	Water
W/O	Water- in – oil emulsion
W/O/W	Water-in-oil-in-water emulsion
W/O/W/O	Water-in-Oil-in- Water-in-Oil
Φ	Particle Volumetric Concentration

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ACKNOWLEDGMENTS

First of all, praise is to God, Who stood beside me to pass all difficulties

I would like to dedicate this work to the memory of MARTYR Ismael (1967–1994), a brother and a sincere friend (whom left us early), and all MARTYRS who sacrificed for us to be live

I greatly appreciate the insights gained from my supervisor Asst. Prof. Dr. Khalid M. Mousa through his explanation and stimulating discussion of some controversial and sometimes confusing and His many comments and suggestions had been very helpful issues.

Such appreciation is extended to Professor Dr. Mohammed Baqer Al shadeedi and Asst. Prof. Dr.Naseer Abbood Al-Haboubi Head of Chemical Engineering Department at Al Nahrain University and all stuff of department

My biggest thanks must go to my wife for her patience, understanding, and support, very grateful for having sacrificed so much of her leisure to give us happy life

I owe much to my tiny sons Muslim and Jaffar for the time I should have shared with them as their father.

I am also thankful to my greater family for their continuing support.

Finally, I am indebted to all the staff of south oil co. and Petroleum Development & Research Center who had given me the permission and information to continue my study

APPENDIX A

Produced Water Amount and Appearance

Table A-1 Production rate of produced water at 2003 for
Al- Basra oil fields /main pay [3]

Field	Station	Water m^3/d	Water bbl/d
ZUBAIR	Zubair	120	756
=	Zubair-Mushrif	73	460
=	Hammar	84	529
=	Hammar-Mushrif	80	504
=	Rafedia	278	1751
=	Qubat_Safwan	40	252
SOUTH RUMAILA	Marqazia	2889	18200
=	Janobia	2064	13003
=	Shamia	2286	14401
=	Qorainat	1500	9450
=	Ratka	109	687
=	Mushrif-Shamia	-----	-----
=	Mushrif-Qorainat	-----	-----
NORTH RUMAILA	Ds1	480	3024
	Ds2	2280	14364
	Ds3	840	5292
	Ds4	1850	11655
	Ds5	1630	10269
	Luhais	480	3024

Total =107621bbl /d

Table A-2 Production rate expected of produced water from 2010 - 2025for South Rumaila /main pay [4].

year	**Production rate 1000bbl /d**		
	Oil	**Water**	**Total**
2010	500	220	720
2011	500	290	790
2012	600	360	960
2013	600	435	1035
2014	600	510	1110
2015	600	585	1185
2016	600	660	1260
2017	500	730	1230
2018	500	800	1300
2019	500	800	1300
2020	400	800	1200
2021	400	800	1200
2022	400	800	1100
2023	300	800	1100
2024	300	800	1100
2025	300	800	1100

Table A-3 Production rate expected of produced water from 2010 -2025 for North Rumaila / main pay [4].

year	Production rate 1000bbl/d		
	Oil	Water	Total
2010	200	65	265
2011	200	90	290
2012	175	130	305
2013	175	170	345
2014	150	210	360
2015	150	245	395
2016	150	290	440
2017	150	330	480
2018	125	375	500
2019	125	415	540
2020	125	460	585
2021	100	500	600
2022	100	500	600
2023	100	500	600
2024	100	500	600
2025	100	500	600

Table A- 4 PW appearance according tests results for North Rumaila field in the South Oil Company [4].

variables	**Time every 1 hour started with 11 am date :20 April 2012**				
	11am	12am	1pm	2pm	3pm
pH	5.84	6.27	6.2	6.33	6.7
%oil ppm	60.11	270	273	140	250
TSSmg/lit.	53	44.2	96.5	53	68
Turbidity	135	136	209	105.2	157
Fe ppm	36.5	36.5	47.4	41.8	33.5
TDS ppm	85860	86580	83706	87390	84600

APPENDIX B

Sediment and Parameters with %Oil Removed Data

Table B-1 %TSS removed using settling with and without addition different doses (100 -500) of flocculent polyacrylamide (PAA) vs time

Time (min)	% sediment removed without PAA	% sediment removed at 100ppm PAA	% sediment removed at 200ppm PAA	% sediment removed at 300ppm PAA	% sediment removed at 400ppm PAA	% sediment removed at 500ppm PAA
0	0	0	0	0	0	0
15	20	25	30	36	40	50
30	38	43	49	55	65	80
45	55	59	65	74	85	100
60	68	75	80	88	100	
75	79	85	93	100		
90	88	94	100			
105	95	100				
120	100					

Table B-2 %Oil removal vs operation time (5-30) min, fixed outlet time=10 min, pressure =3bar, salinity= 80gm/lit., temperature =60°C and pH=6 without additives or mixing

Operation time	%Oil removed without flocculation	%Oil removed with flocculation
5	75.79	80.28
10	81.28	82.65
15	83.16	85.70
20	82.28	83.88
25	82.10	83.67
30	79.41	82.80

Table B-3 %Oil removal vs outlet time, fixed operation time=15 min, pressure =3bar, salinity= 80gm/lit., temperature =60°C and pH=6 without additives or mixing

Outlet time	%Oil removed without flocculation	%Oil removed with flocculation
2	82.75	83.75
4	84.14	86.50
6	85.00	87.15
8	83.74	85.97
10	83.10	85.65

Table B-4%Oil removal vs salinity (20-100) gm, fixed operation time=15min, outlet time=5 pressure=3bar, temperature=60°C, min and pH=6 without additives or mixing

Salinity(ppm)	%Oil removed without flocculation	%Oil removed with flocculation
20000	78.15	82.19
40000	83.60	86.28
60000	85.80	87.18
80000	87.82	89.64
100000	89.12	90.56

Table B-5 %Oil removal vs mixing (0, 300, 1100) RPM, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., pressure=3bar, temperature=60°C and pH=6 without additives

RPM	%Oil removed without flocculation	%Oil removed with flocculation
0	83.55	87.96
300	84.83	89.17
500	79.51	82.26
700	77.35	78.96
900	74.41	77.70
1100	71.42	76.29

Table B-6 %Oil removal vs temperature 20-60°C, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300RPM, pressure=3bar, and pH=6 without additives

Temperature	%Oil removed without flocculation	%Oil removed with flocculation
20	78.58	83.11
30	82.99	85.15
40	87.57	89.60
50	87.67	89.89
60	80.71	84.05

Table B-7 %Oil removal vs pressure (0, 1, 5) bar, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300RPM, temperature=45°C and pH=6 without additives

Pressure (bar)	%Oil removed without flocculation	%Oil removed with flocculation
0	88.06	88.64
1	88.21	89.59
2	88.31	89.86
3	83.32	84.52
4	80.06	83.25
5	75.14	79.17

Table B-8 %Oil removal vs pH (2-8), fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300RPM, temperature=45°C and pressure=1bar without additives

pH	%Oil removed without flocculation	%Oil removed with flocculation
2	٨١.٦٧	85.73
3	85.62	87.49
4	87.65	88.62
5	88.94	90.32
6	89.91	91.88
7	91.06	93.09
8	92.2	93.11

Table B-9 %Oil removal vs vol. % ethanol (0.01-0.06) vol. %, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

Ethanol (vol%)	%Oil removed without flocculation	%Oil removed with flocculation
0.01	83.47	84.17
0.02	85.65	88.23
0.03	87.28	90.44
0.04	89.69	91.42
0.05	91.33	93.21
0.06	93.17	94.22

Table B- 10 %Oil removal vs vol. % liquid detergent (0.01-0.06) vol. %, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

Liquid detergent (vol%)	%Oil removed without flocculation	%Oil removed with flocculation
0.01	80.57	82.36
0.02	84.29	86.57
0.03	86.38	87.85
0.04	88.61	89.78
0.05	89.84	91.85
0.06	91.72	92.84

Table B-11 %Oil removal vs powder detergent (100-600) ppm, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

Powder detergent(ppm)	%Oil removed without flocculation	%Oil removed with flocculation
100	87.85	89.75
200	89.73	90.37
300	91.27	92.07
400	92.57	93.51
500	93.31	94.35
600	94.08	94.76

TableB-12 %Oil removal vs sawdust (0.5-3) gm, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

Sawdust(gm)	%Oil removed without flocculation	%Oil removed with flocculation
0.5	90.53	92.87
1	94.11	95.31
1.5	96.10	96.81
2.0	96.99	97.08
2.5	97.63	98.91
3.0	98.34	99.25

Table B-13 %Oil removal vs polypropylene (1-6) gm, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

Polypropylene(gm)	%Oil removed without flocculation	%Oil removed with flocculation
1	91.32	95.40
2	94.33	97.86
3	96.27	99.10
4	97.87	99.76
5	98.35	99.84
6	99.03	99.88

Table B-14 %Oil removal vs polyethylene (1-6) gm, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

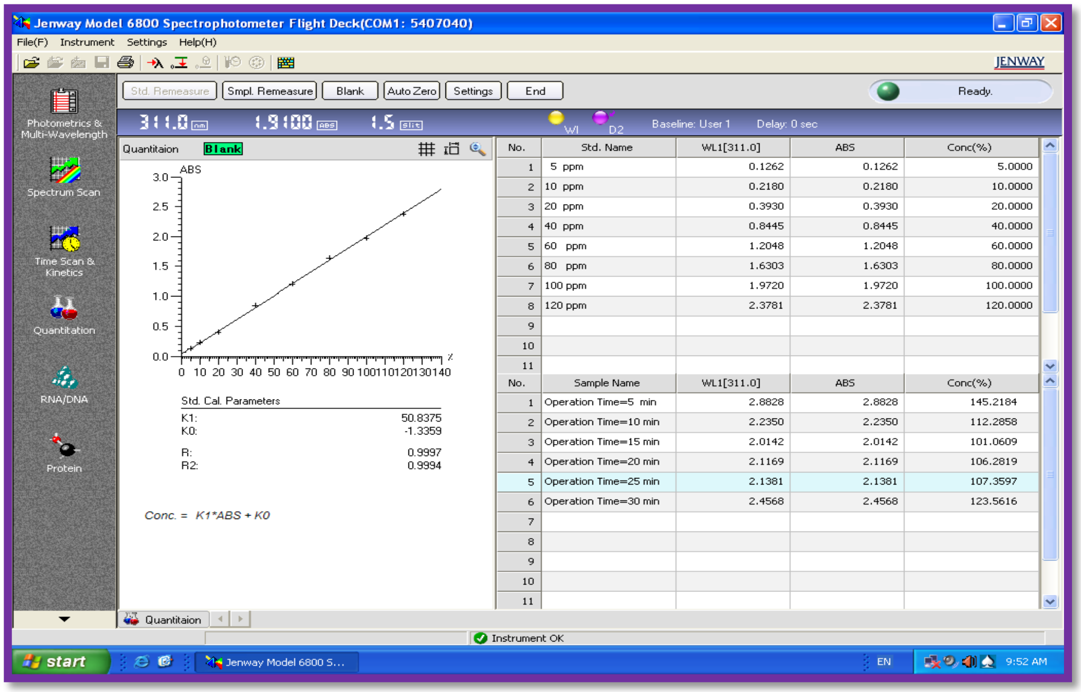
Polyethylene(gm)	%Oil removed without flocculation	%Oil removed with flocculation
1	93.03	97.85
2	95.63	99.06
3	97.28	99.89
4	98.31	99.98
5	98.99	99.99
6	99.98	100.00

Table B-15 %Oil removal vs used plastic (0.5-3) gm, fixed operation time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

Used Plastic(gm)	%Oil removed without flocculation	%Oil removed with flocculation
0.5	92.96	96.82
1.0	96.05	98.44
1.5	97.98	99.80
2.0	99.50	99.95
2.5	99.80	99.98
3.0	99.99	100

APPENDIX C

Photo Pictures of UV Measurement



Std. Cal. Parameters
K1: 50.8375
K0: -1.3359
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Operation Time=5 min	2.8828	2.8828	145.2184
2	Operation Time=10 min	2.2350	2.2350	112.2858
3	Operation Time=15 min	2.0142	2.0142	101.0609
4	Operation Time=20 min	2.1169	2.1169	106.2819
5	Operation Time=25 min	2.1381	2.1381	107.3597
6	Operation Time=30 min	2.4568	2.4568	123.5616
7				
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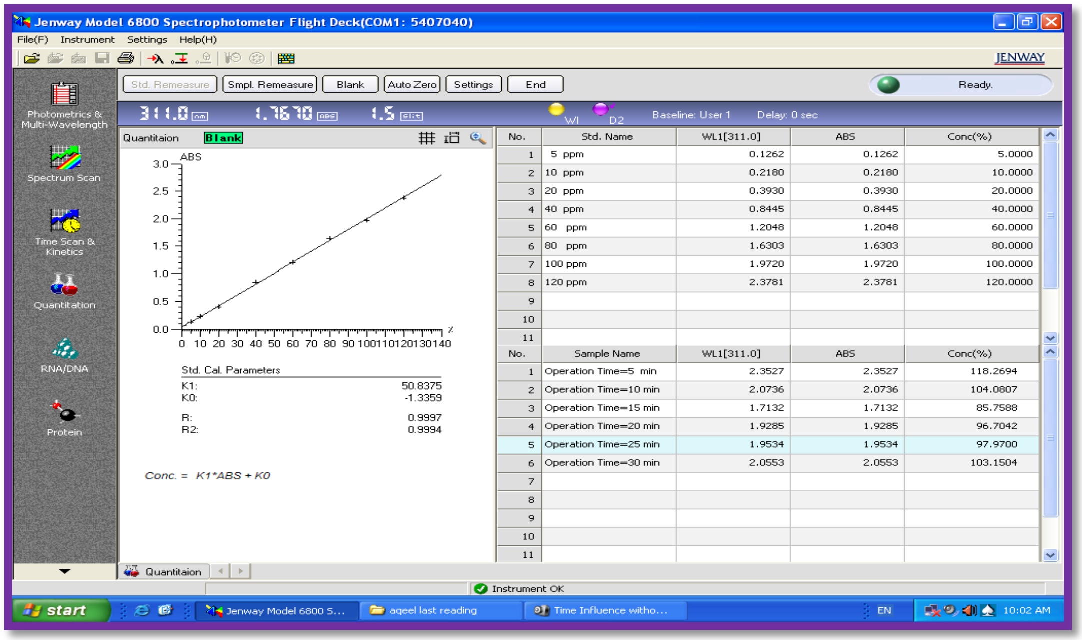
10				
11				

Figure C-1 Operation time influence without flocculation



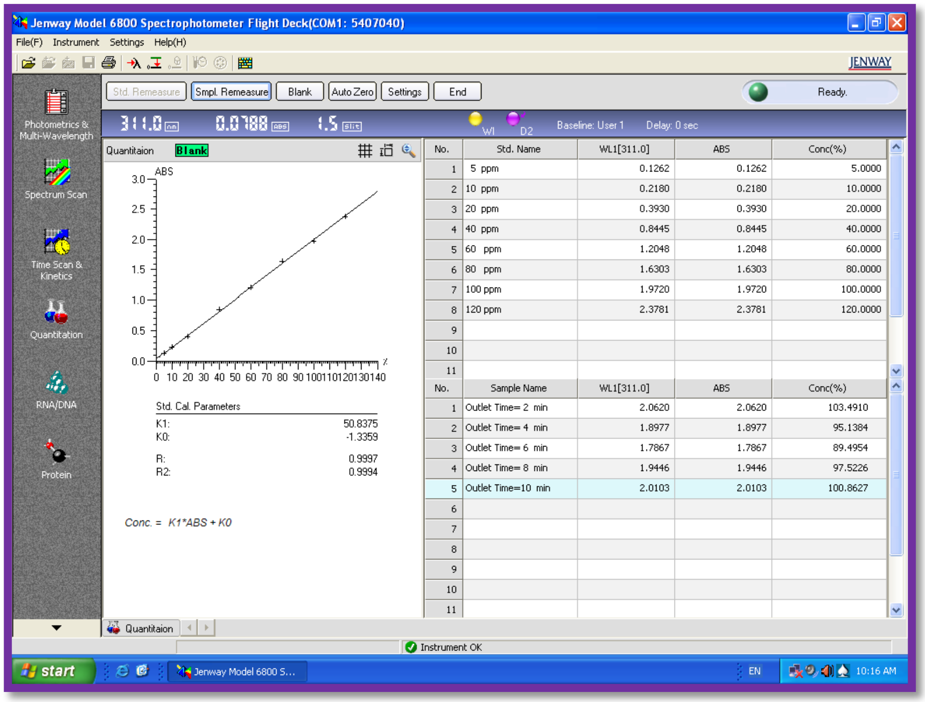
Std. Cal. Parameters
K1: 50.8375
K0: -1.3359
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Operation Time=5 min	2.3527	2.3527	118.2694
2	Operation Time=10 min	2.0736	2.0736	104.0807
3	Operation Time=15 min	1.7132	1.7132	85.7588
4	Operation Time=20 min	1.9285	1.9285	96.7042
5	Operation Time=25 min	1.9534	1.9534	97.9700
6	Operation Time=30 min	2.0553	2.0553	103.1504
7				
8				
9				
10				
11				

Figure C-2 Operation time influence with flocculation



Std. Cal. Parameters

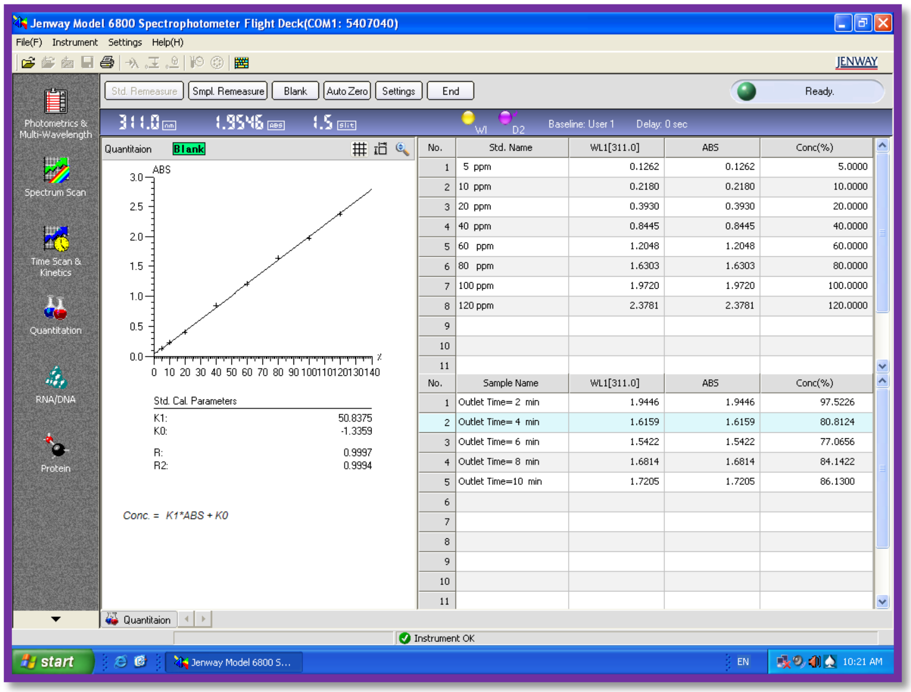
K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Outlet Time= 2 min	2.0620	2.0620	103.4910
2	Outlet Time= 4 min	1.8977	1.8977	95.1384
3	Outlet Time= 6 min	1.7867	1.7867	89.4954
4	Outlet Time= 8 min	1.9446	1.9446	97.5226
5	Outlet Time=10 min	2.0103	2.0103	100.8627
6				
7				
8				
9				
10				
11				

Figure C -3 Outlet time influence without flocculation



Std. Cal. Parameters

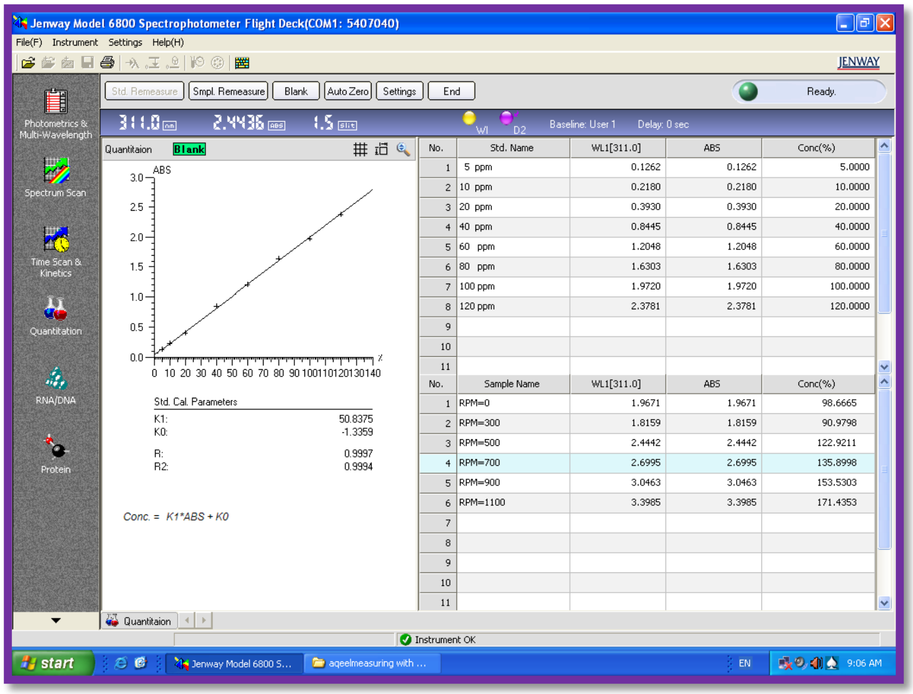
K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Outlet Time= 2 min	1.9446	1.9446	97.5226
2	Outlet Time= 4 min	1.6159	1.6159	80.8124
3	Outlet Time= 6 min	1.5422	1.5422	77.0656
4	Outlet Time= 8 min	1.6814	1.6814	84.1422
5	Outlet Time=10 min	1.7205	1.7205	86.1300
6				
7				
8				
9				
10				
11				

Figure C - 4 Outlet time influence with flocculation



Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

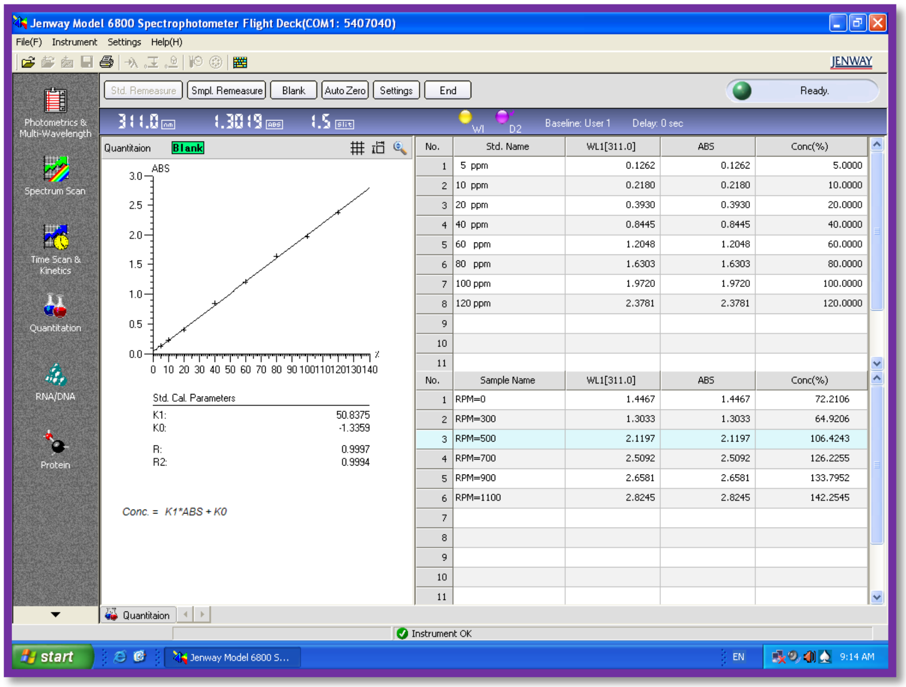
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	RPM=0	1.9671	1.9671	98.6665
2	RPM=300	1.8159	1.8159	90.9798
3	RPM=500	2.4442	2.4442	122.9211
4	RPM=700	2.6995	2.6995	135.8998
5	RPM=900	3.0463	3.0463	153.5303
6	RPM=1100	3.3985	3.3985	171.4353
7				
8				
9				
10				
11				

Figure C -5 Mixing effect without flocculation



Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

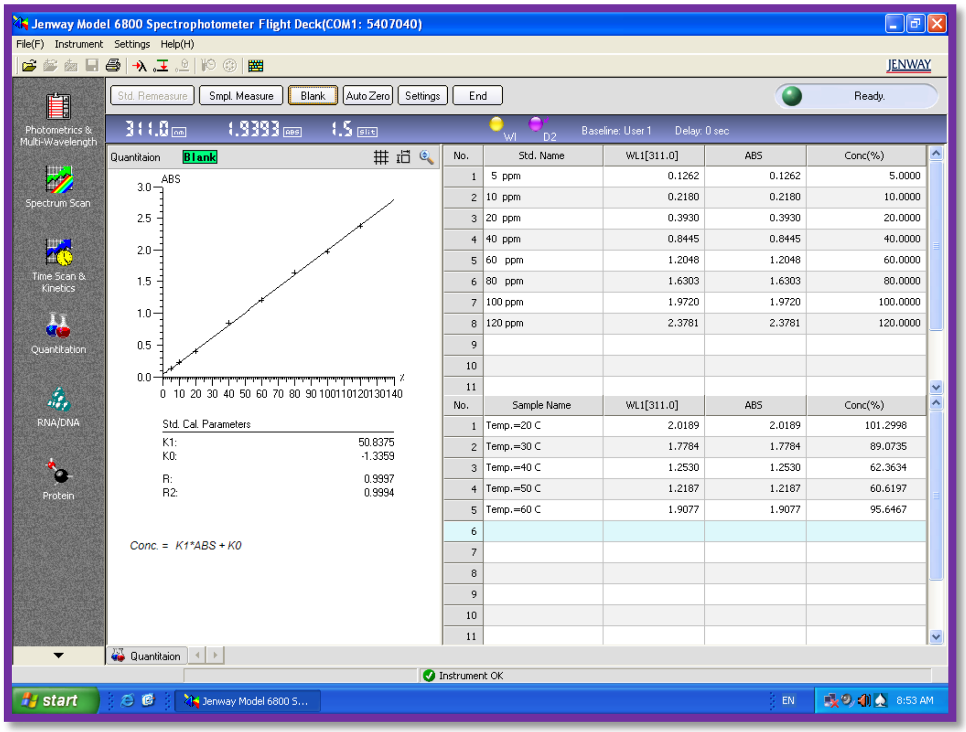
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	RPM=0	1.4467	1.4467	72.2106
2	RPM=300	1.3033	1.3033	64.9206
3	RPM=500	2.1197	2.1197	106.4243
4	RPM=700	2.5092	2.5092	126.2255
5	RPM=900	2.6581	2.6581	133.7952
6	RPM=1100	2.8245	2.8245	142.2545
7				
8				
9				
10				
11				

Figure C- 6 Mixing effect with flocculation



Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

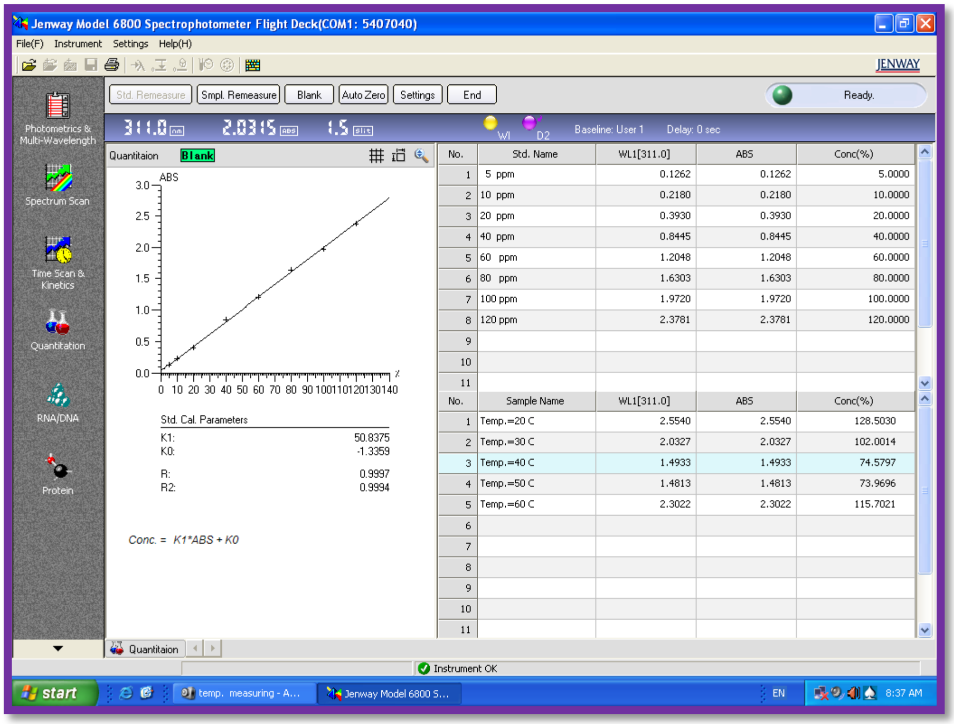
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Temp.=20 C	2.0189	2.0189	101.2998
2	Temp.=30 C	1.7784	1.7784	89.0735
3	Temp.=40 C	1.2530	1.2530	62.3634
4	Temp.=50 C	1.2187	1.2187	60.6197
5	Temp.=60 C	1.9077	1.9077	95.6467
6				
7				
8				
9				
10				
11				

Figure C -7 Temperature influence without flocculation



Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

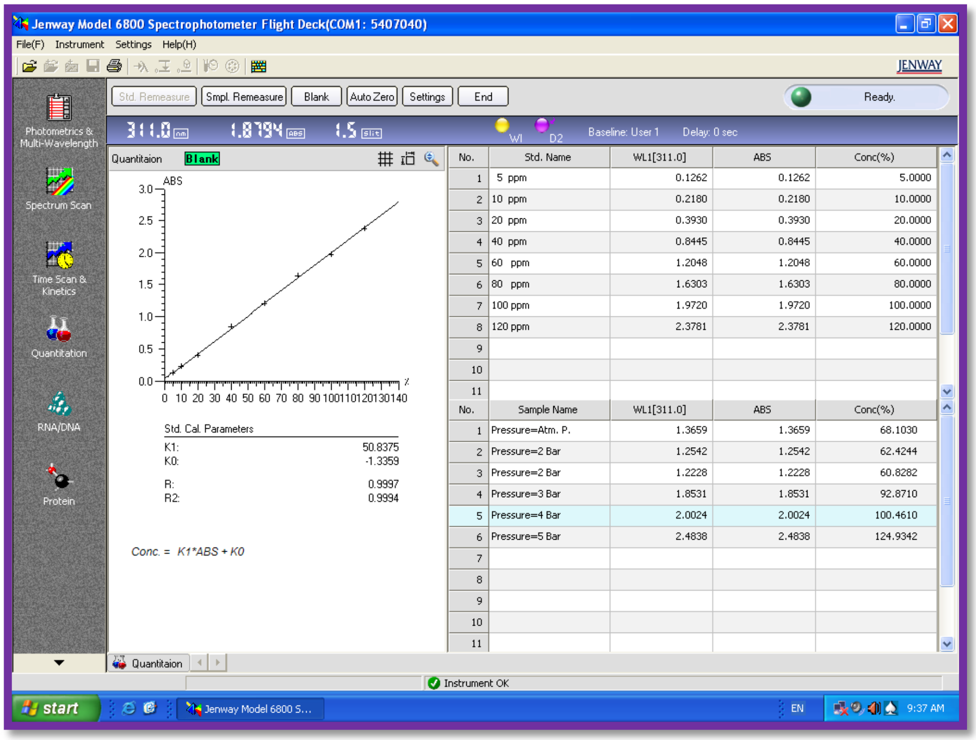
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Temp.=20 C	2.5540	2.5540	128.5030
2	Temp.=30 C	2.0327	2.0327	102.0014
3	Temp.=40 C	1.4933	1.4933	74.5797
4	Temp.=50 C	1.4813	1.4813	73.9696
5	Temp.=60 C	2.3022	2.3022	115.7021
6				
7				
8				
9				
10				
11				

Figure C -8 Temperature influence with flocculation



Std. Cal. Parameters

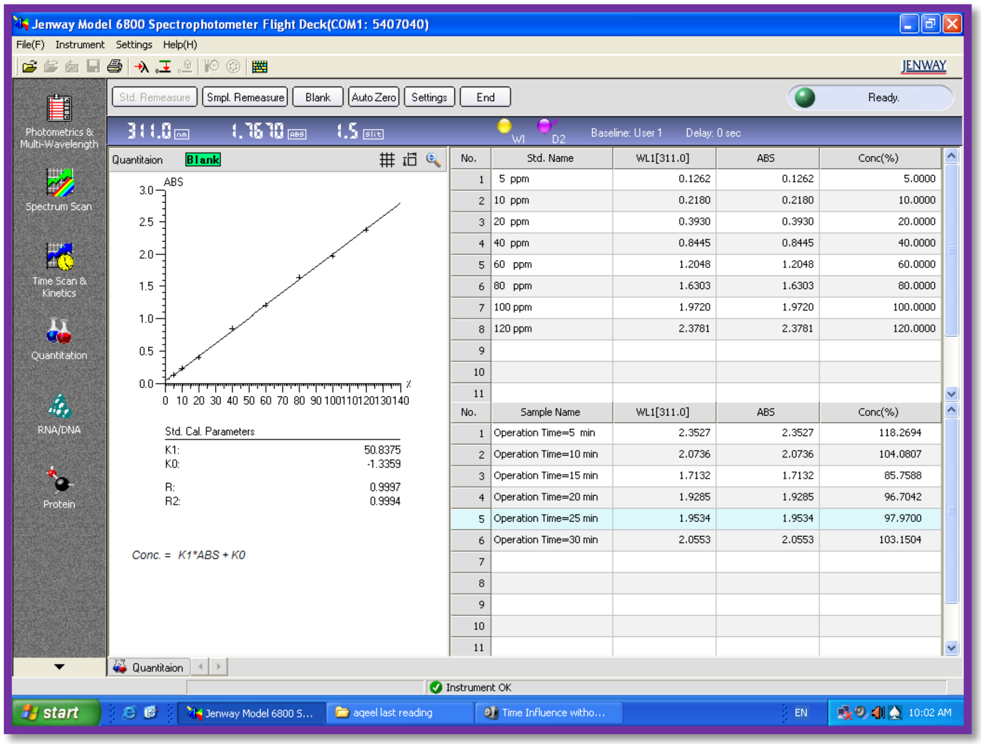
K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Pressure=Atm. P.	1.3659	1.3659	68.1030
2	Pressure=2 Bar	1.2542	1.2542	62.4244
3	Pressure=2 Bar	1.2228	1.2228	60.8282
4	Pressure=3 Bar	1.8531	1.8531	92.8710
5	Pressure=4 Bar	2.0024	2.0024	100.4610
6	Pressure=5 Bar	2.4838	2.4838	124.9342
7				
8				
9				
10				
11				

Figure C- 9 Pressure influence without flocculation



Std. Cal. Parameters

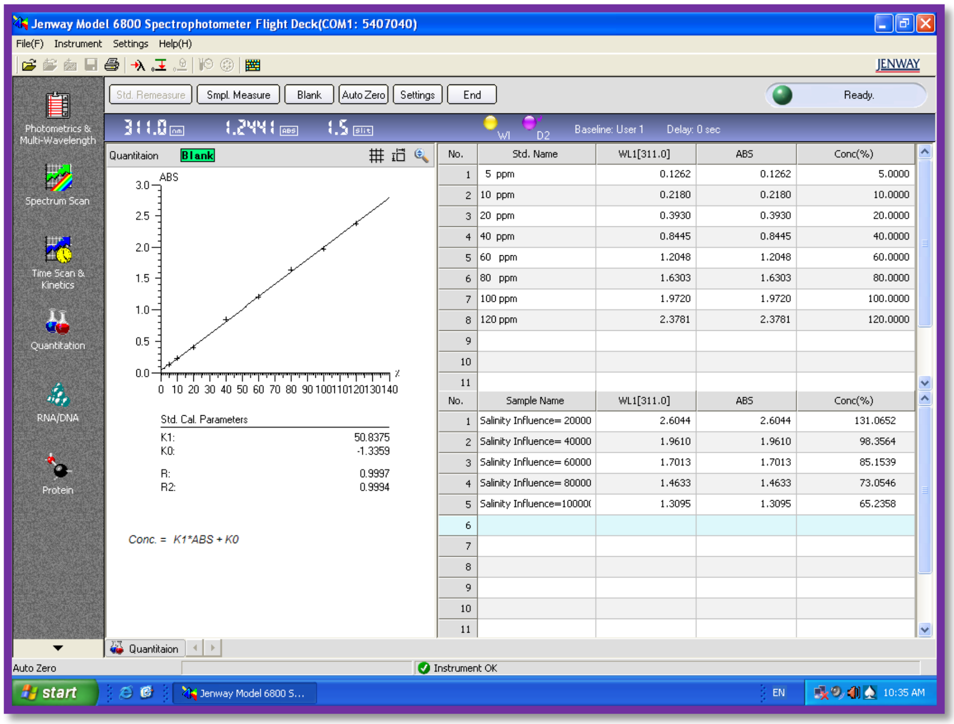
K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Operation Time=5 min	2.3527	2.3527	118.2694
2	Operation Time=10 min	2.0736	2.0736	104.0807
3	Operation Time=15 min	1.7132	1.7132	85.7588
4	Operation Time=20 min	1.9285	1.9285	96.7042
5	Operation Time=25 min	1.9534	1.9534	97.9700
6	Operation Time=30 min	2.0553	2.0553	103.1504
7				
8				
9				
10				
11				

Figure C -10 Pressure influence with flocculation



Std. Cal. Parameters

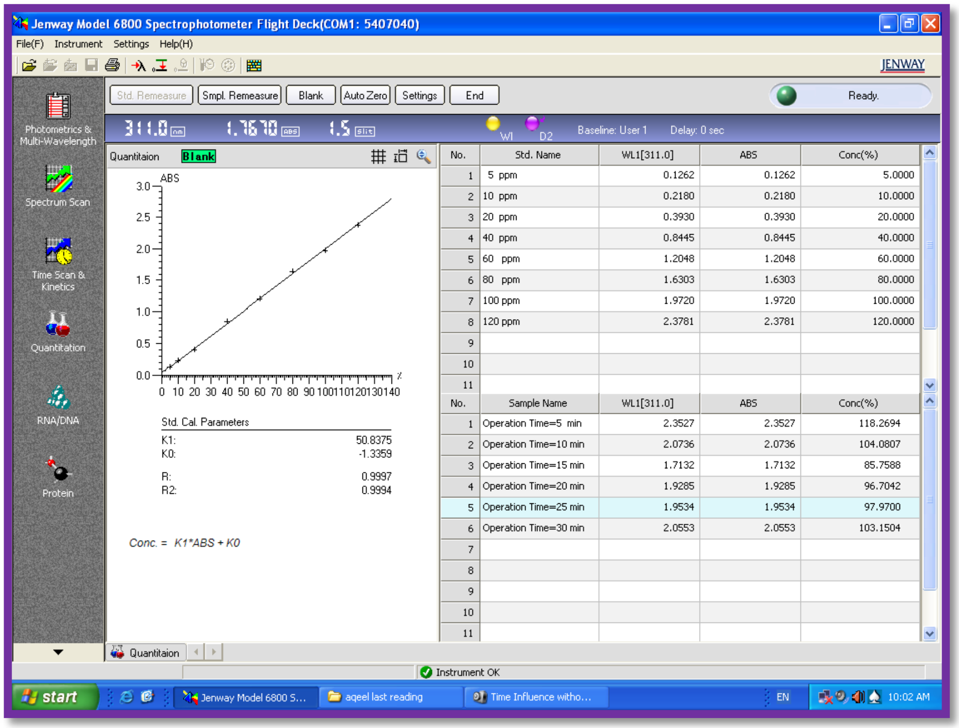
K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Salinity Influence= 20000	2.6044	2.6044	131.0652
2	Salinity Influence= 40000	1.9610	1.9610	98.3564
3	Salinity Influence= 60000	1.7013	1.7013	85.1539
4	Salinity Influence= 80000	1.4633	1.4633	73.0546
5	Salinity Influence=10000(	1.3095	1.3095	65.2358
6				
7				
8				
9				
10				
11				

FigureC – 11 Salinity effect without flocculation



Std. Cal. Parameters

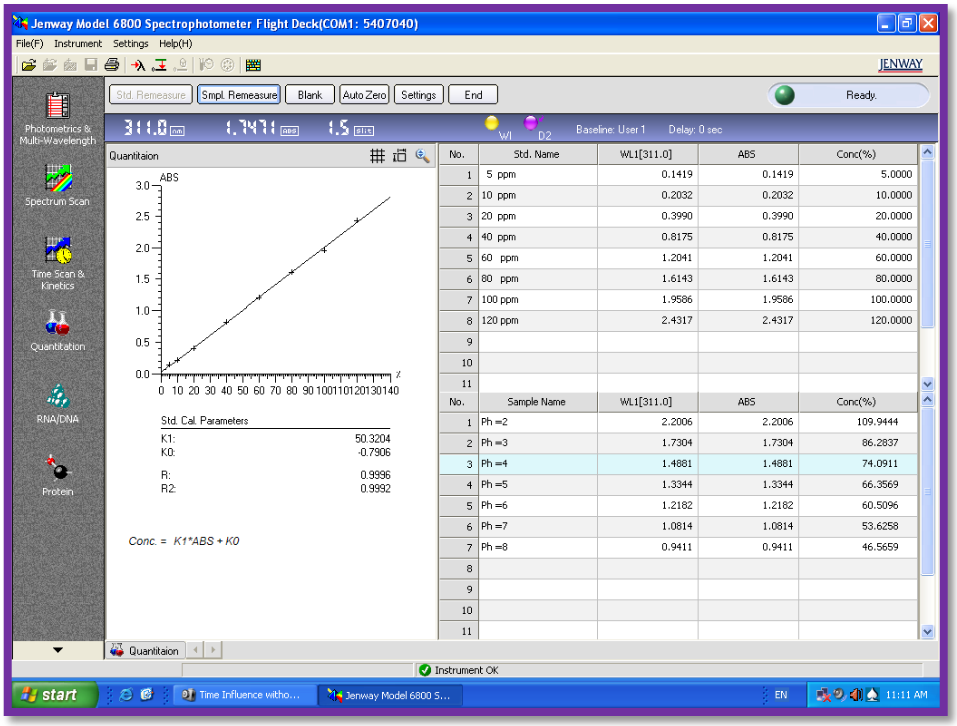
K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Operation Time=5 min	2.3527	2.3527	118.2694
2	Operation Time=10 min	2.0736	2.0736	104.0807
3	Operation Time=15 min	1.7132	1.7132	85.7588
4	Operation Time=20 min	1.9285	1.9285	96.7042
5	Operation Time=25 min	1.9534	1.9534	97.9700
6	Operation Time=30 min	2.0553	2.0553	103.1504
7				
8				
9				
10				
11				

FigureC – 12 Salinity effect with flocculation



Std. Cal. Parameters

K1: 50.3204
K0: -0.7906

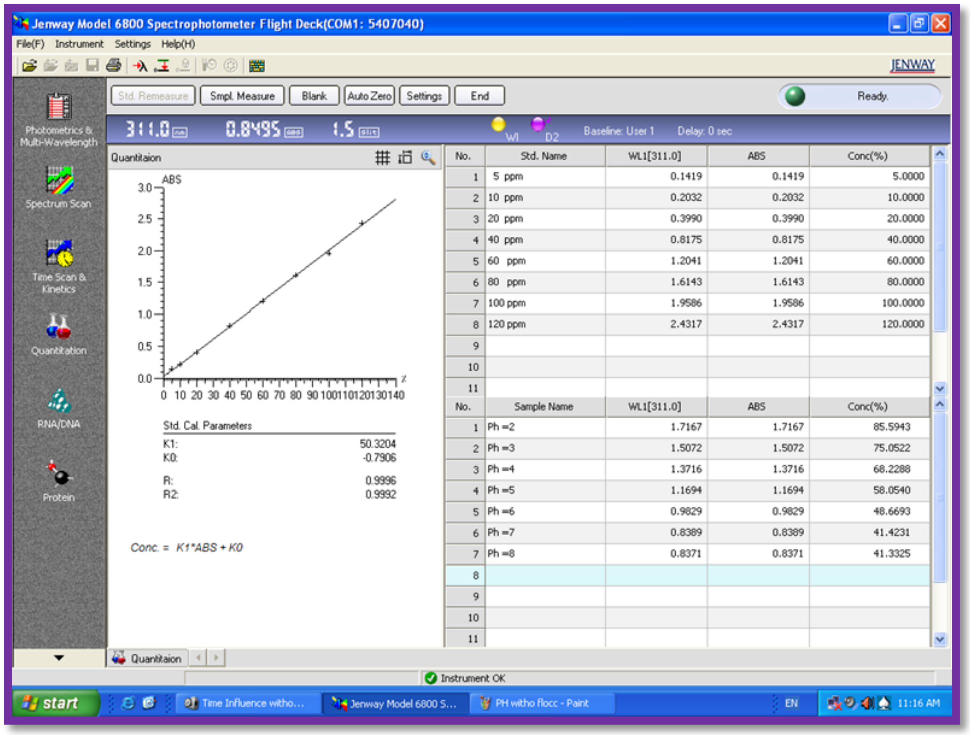
R: 0.9996
R2: 0.9992

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1419	0.1419	5.0000
2	10 ppm	0.2032	0.2032	10.0000
3	20 ppm	0.3990	0.3990	20.0000
4	40 ppm	0.8175	0.8175	40.0000
5	60 ppm	1.2041	1.2041	60.0000
6	80 ppm	1.6143	1.6143	80.0000
7	100 ppm	1.9586	1.9586	100.0000
8	120 ppm	2.4317	2.4317	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Ph =2	2.2006	2.2006	109.9444
2	Ph =3	1.7304	1.7304	86.2837
3	Ph =4	1.4881	1.4881	74.0911
4	Ph =5	1.3344	1.3344	66.3569
5	Ph =6	1.2182	1.2182	60.5096
6	Ph =7	1.0814	1.0814	53.6258
7	Ph =8	0.9411	0.9411	46.5659
8				
9				
10				
11				

Figure C -13 pH effect without flocculation



Std. Cal. Parameters

K1: 50.3204
K0: -0.7906

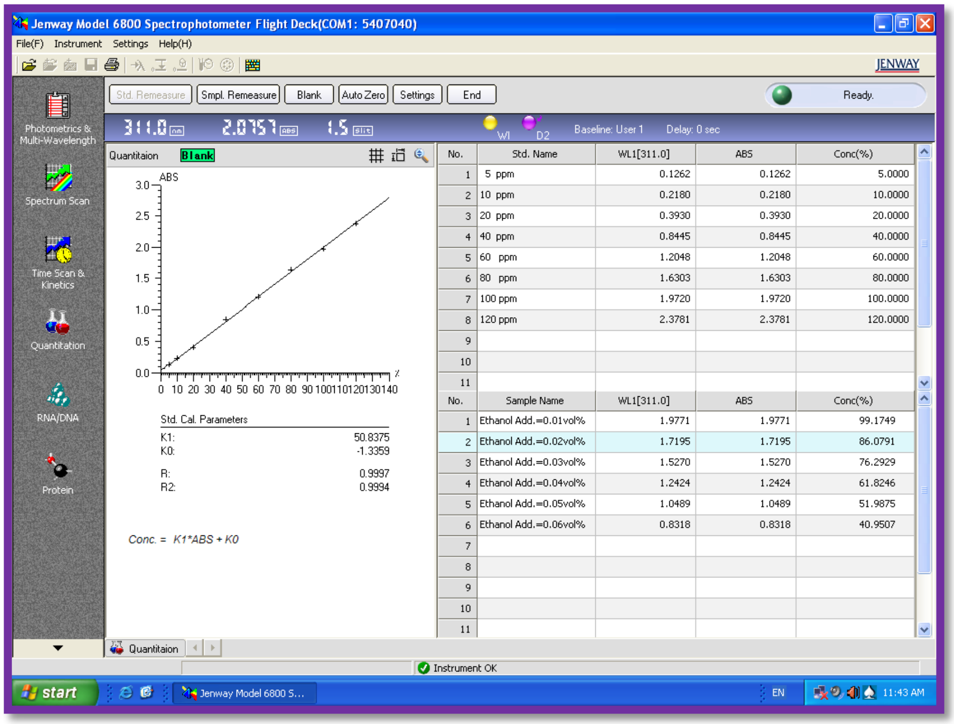
R: 0.9996
R2: 0.9992

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1419	0.1419	5.0000
2	10 ppm	0.2032	0.2032	10.0000
3	20 ppm	0.3990	0.3990	20.0000
4	40 ppm	0.8175	0.8175	40.0000
5	60 ppm	1.2041	1.2041	60.0000
6	80 ppm	1.6143	1.6143	80.0000
7	100 ppm	1.9586	1.9586	100.0000
8	120 ppm	2.4317	2.4317	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Ph =2	1.7167	1.7167	85.5943
2	Ph =3	1.5072	1.5072	75.0522
3	Ph =4	1.3716	1.3716	68.2288
4	Ph =5	1.1694	1.1694	58.0540
5	Ph =6	0.9829	0.9829	48.6693
6	Ph =7	0.8389	0.8389	41.4231
7	Ph =8	0.8371	0.8371	41.3325
8				
9				
10				
11				

Figure C- 14 pH effect with flocculation



Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

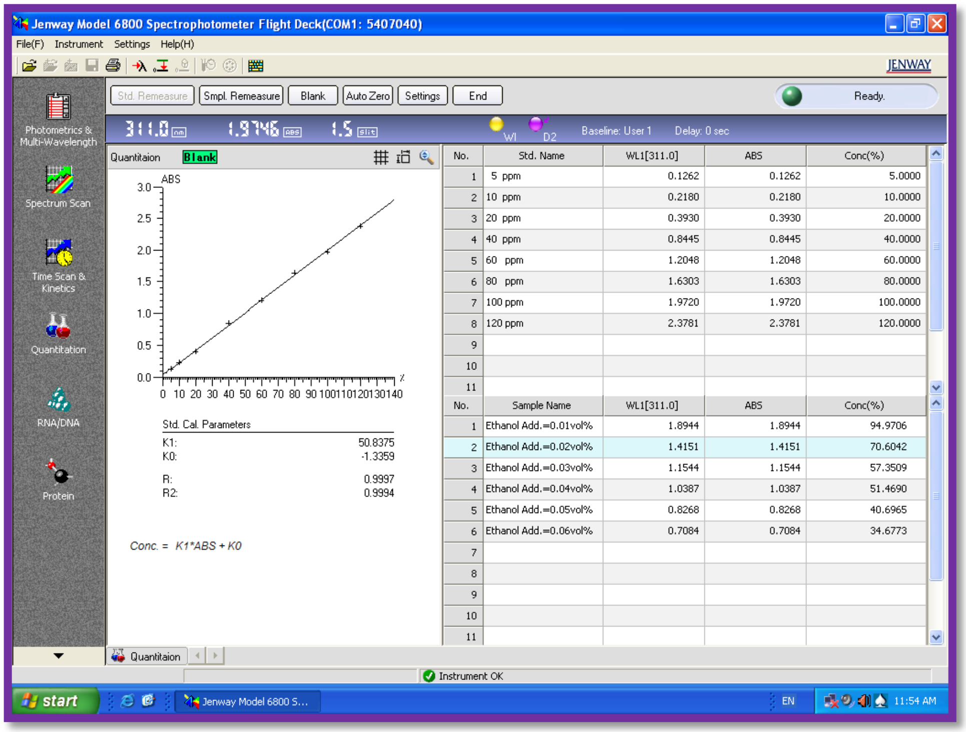
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Ethanol Add.=0.01vol%	1.9771	1.9771	99.1749
2	Ethanol Add.=0.02vol%	1.7195	1.7195	86.0791
3	Ethanol Add.=0.03vol%	1.5270	1.5270	76.2929
4	Ethanol Add.=0.04vol%	1.2424	1.2424	61.8246
5	Ethanol Add.=0.05vol%	1.0489	1.0489	51.9875
6	Ethanol Add.=0.06vol%	0.8318	0.8318	40.9507
7				
8				
9				
10				
11				

Figure C - 15 Ethanol addition effect without flocculation



Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

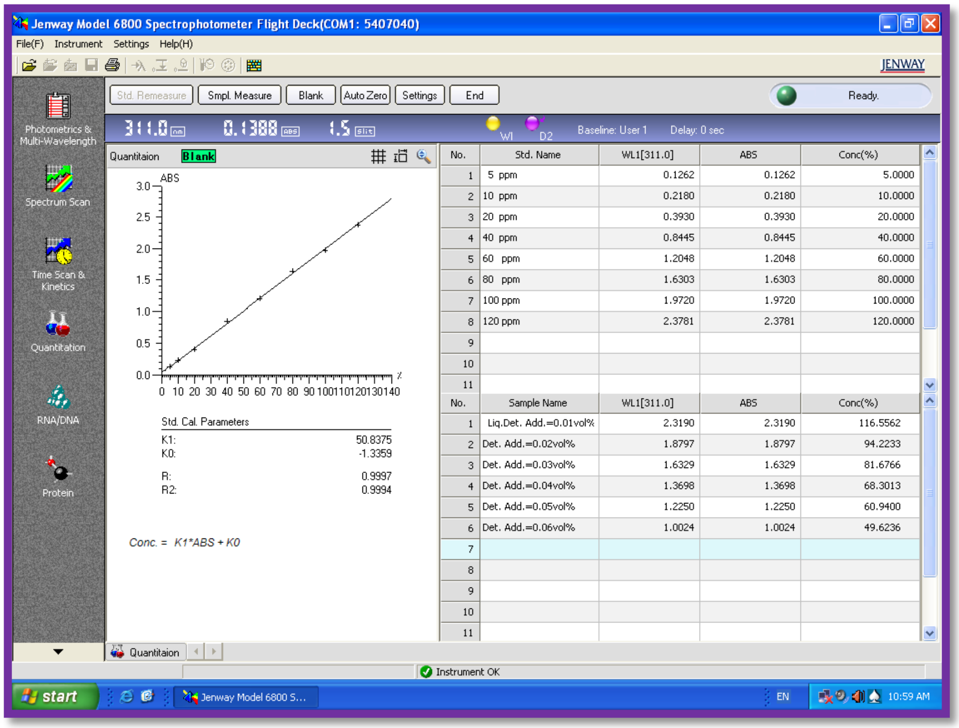
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Ethanol Add.=0.01vol%	1.8944	1.8944	94.9706
2	Ethanol Add.=0.02vol%	1.4151	1.4151	70.6042
3	Ethanol Add.=0.03vol%	1.1544	1.1544	57.3509
4	Ethanol Add.=0.04vol%	1.0387	1.0387	51.4690
5	Ethanol Add.=0.05vol%	0.8268	0.8268	40.6965
6	Ethanol Add.=0.06vol%	0.7084	0.7084	34.6773
7				
8				
9				
10				
11				

Figure C -16 Ethanol addition effect with flocculation



No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

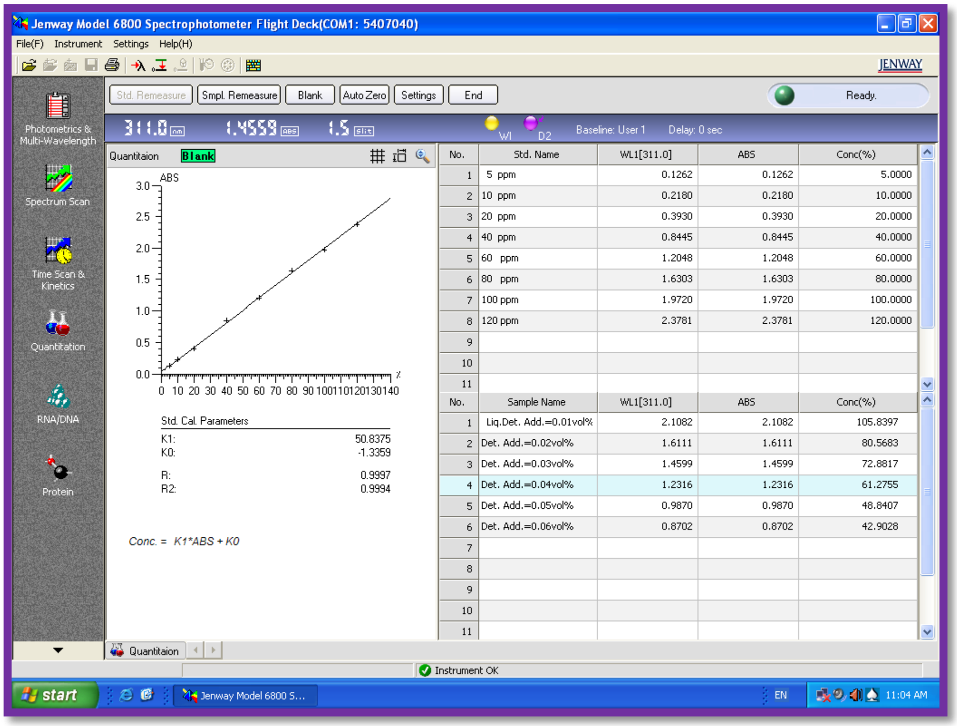
No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Liq.Det. Add.=0.01vol%	2.3190	2.3190	116.5562
2	Det. Add.=0.02vol%	1.8797	1.8797	94.2233
3	Det. Add.=0.03vol%	1.6329	1.6329	81.6766
4	Det. Add.=0.04vol%	1.3698	1.3698	68.3013
5	Det. Add.=0.05vol%	1.2250	1.2250	60.9400
6	Det. Add.=0.06vol%	1.0024	1.0024	49.6236
7				
8				
9				
10				
11				

Std. Cal. Parameters

K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

Figure C -17 Liquid detergent additions without flocculation



No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Liq.Det. Add.=0.01vol%	2.1082	2.1082	105.8397
2	Det. Add.=0.02vol%	1.6111	1.6111	80.5683
3	Det. Add.=0.03vol%	1.4599	1.4599	72.8817
4	Det. Add.=0.04vol%	1.2316	1.2316	61.2755
5	Det. Add.=0.05vol%	0.9870	0.9870	48.8407
6	Det. Add.=0.06vol%	0.8702	0.8702	42.9028
7				
8				
9				
10				
11				

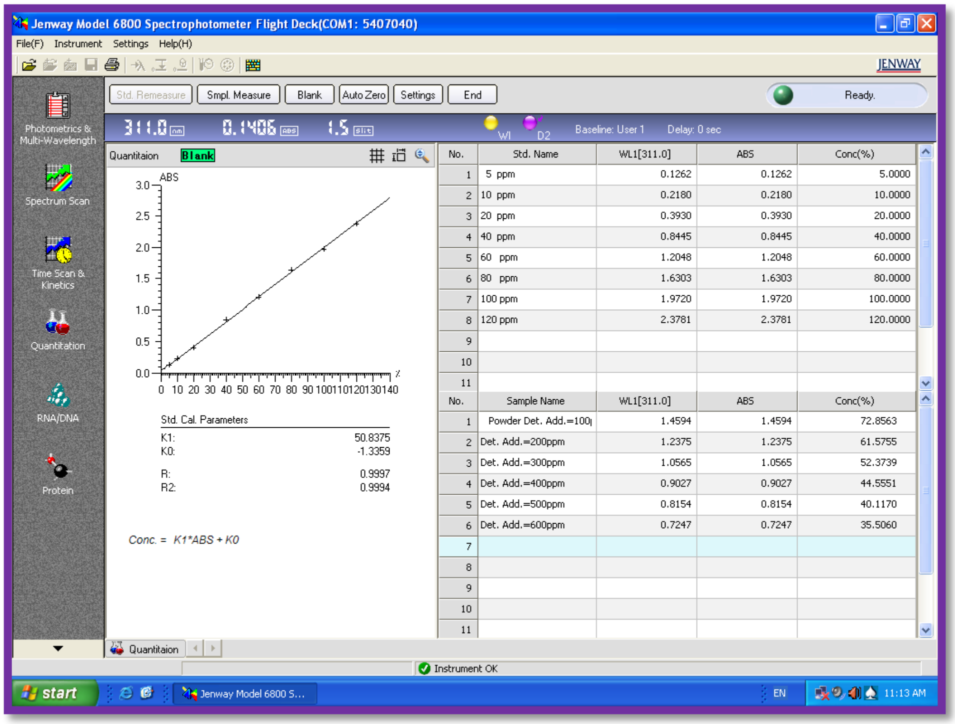
Std. Cal. Parameters

K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

c

Figure C -18 Liquid detergent additions with flocculation



Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

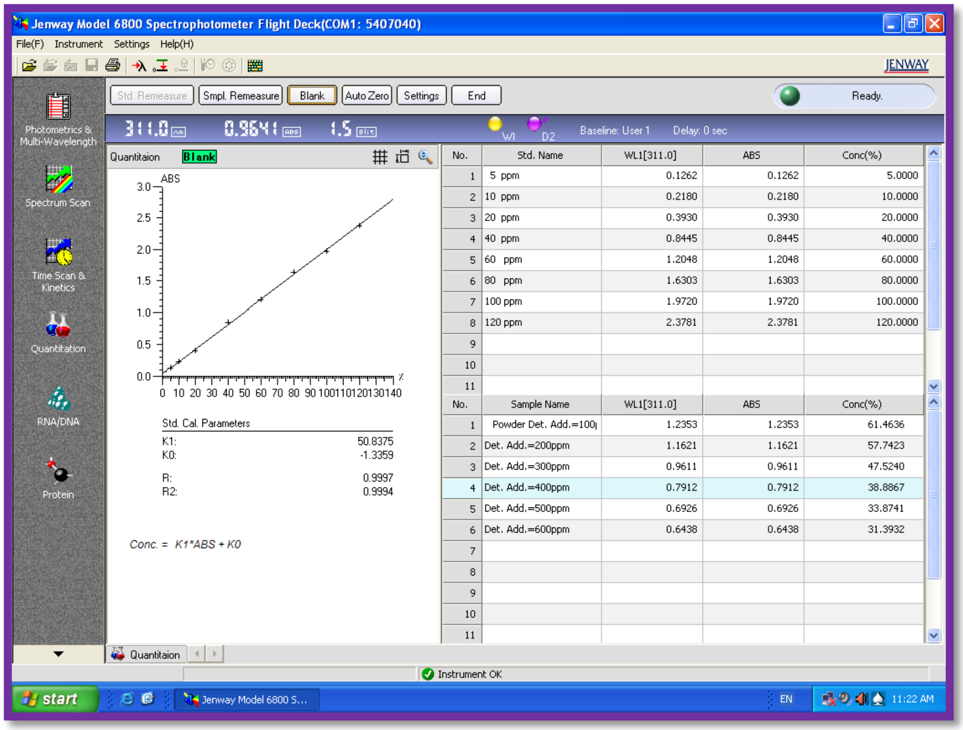
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Powder Det. Add.=100	1.4594	1.4594	72.8563
2	Det. Add.=200ppm	1.2375	1.2375	61.5755
3	Det. Add.=300ppm	1.0565	1.0565	52.3739
4	Det. Add.=400ppm	0.9027	0.9027	44.5551
5	Det. Add.=500ppm	0.8154	0.8154	40.1170
6	Det. Add.=600ppm	0.7247	0.7247	35.5060
7				
8				
9				
10				
11				

Figure C -19 powder detergent addition without flocculation



Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

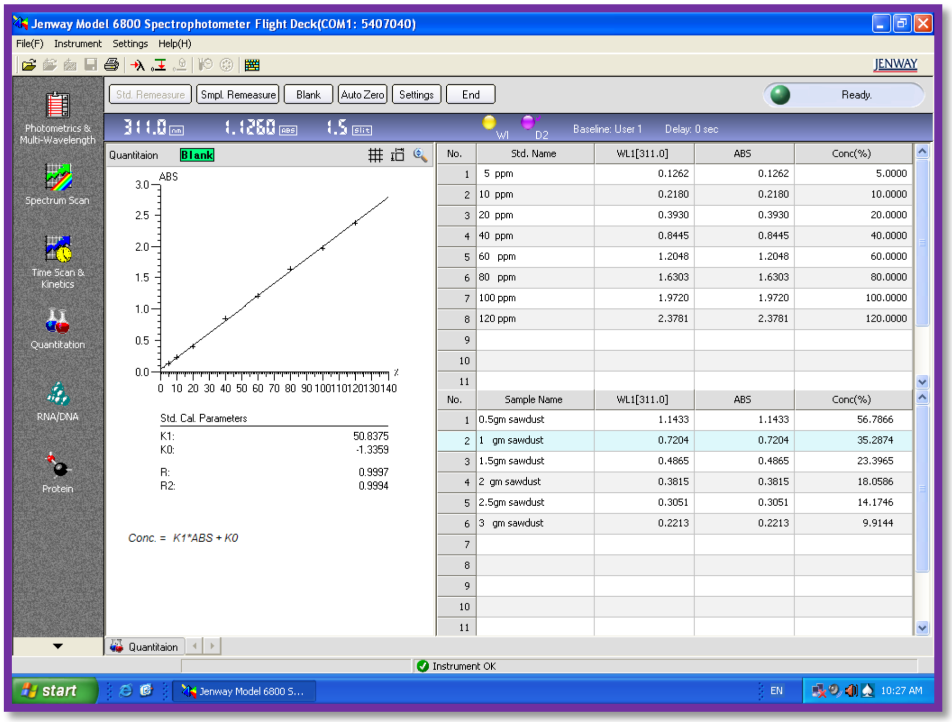
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Powder Det. Add.=100	1.2353	1.2353	61.4636
2	Det. Add.=200ppm	1.1621	1.1621	57.7423
3	Det. Add.=300ppm	0.9611	0.9611	47.5240
4	Det. Add.=400ppm	0.7912	0.7912	38.8867
5	Det. Add.=500ppm	0.6926	0.6926	33.8741
6	Det. Add.=600ppm	0.6438	0.6438	31.3932
7				
8				
9				
10				
11				

Figure C - 20 powder detergent addition with flocculation



Baseline: User 1 Delay: 0 sec

Std. Cal. Parameters

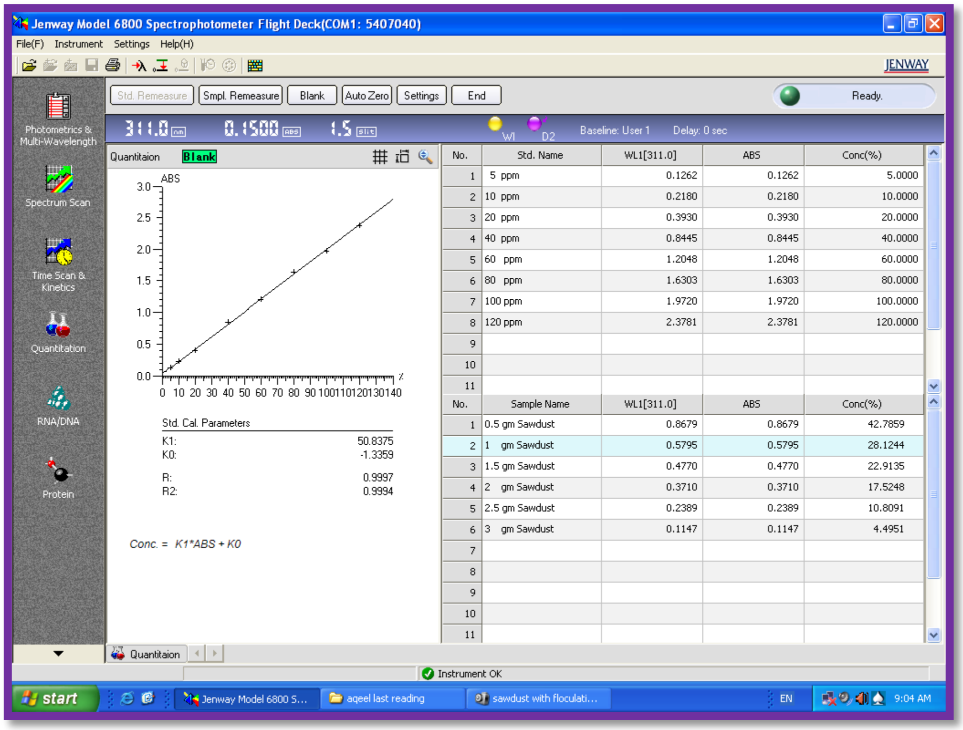
K1: 50.8375
K0: -1.3359
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	0.5gm sawdust	1.1433	1.1433	56.7866
2	1 gm sawdust	0.7204	0.7204	35.2874
3	1.5gm sawdust	0.4865	0.4865	23.3965
4	2 gm sawdust	0.3815	0.3815	18.0586
5	2.5gm sawdust	0.3051	0.3051	14.1746
6	3 gm sawdust	0.2213	0.2213	9.9144
7				
8				
9				
10				
11				

Figure C -21 Sawdust effect without flocculation



Baseline: User 1 Delay: 0 sec

Std. Cal. Parameters

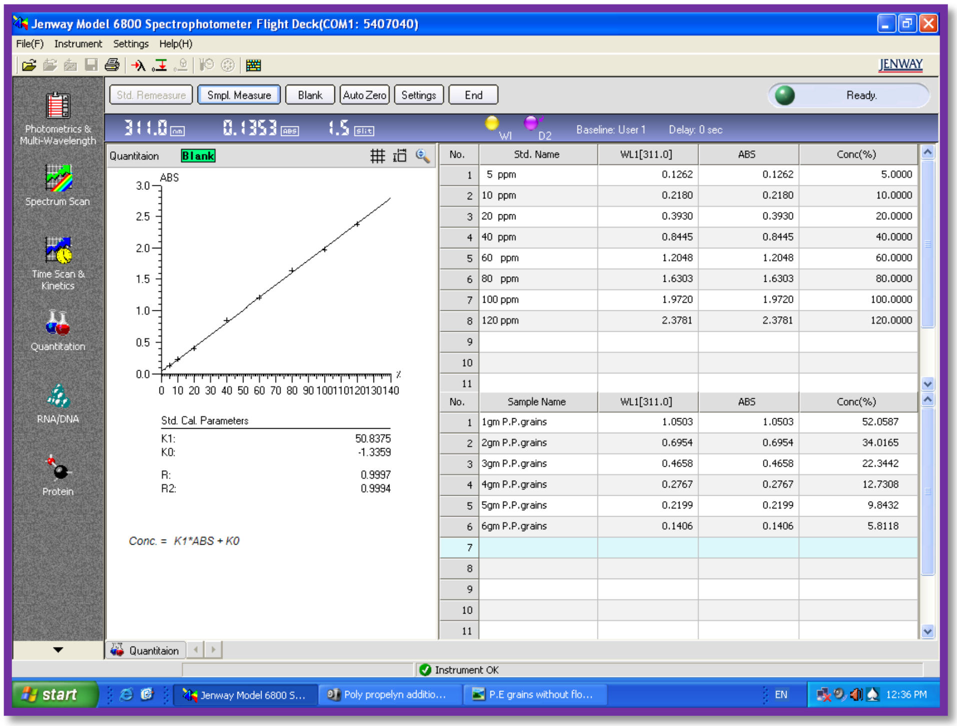
K1: 50.8375
K0: -1.3359
R: 0.9997
R2: 0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	0.5 gm Sawdust	0.8679	0.8679	42.7859
2	1 gm Sawdust	0.5795	0.5795	28.1244
3	1.5 gm Sawdust	0.4770	0.4770	22.9135
4	2 gm Sawdust	0.3710	0.3710	17.5248
5	2.5 gm Sawdust	0.2389	0.2389	10.8091
6	3 gm Sawdust	0.1147	0.1147	4.4951
7				
8				
9				
10				
11				

Figure C- 22 Sawdust effect with flocculation



Baseline: User 1 Delay: 0 sec

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	1gm P.P.grains	1.0503	1.0503	52.0587
2	2gm P.P.grains	0.6954	0.6954	34.0165
3	3gm P.P.grains	0.4658	0.4658	22.3442
4	4gm P.P.grains	0.2767	0.2767	12.7308
5	5gm P.P.grains	0.2199	0.2199	9.8432
6	6gm P.P.grains	0.1406	0.1406	5.8118
7				
8				
9				
10				
11				

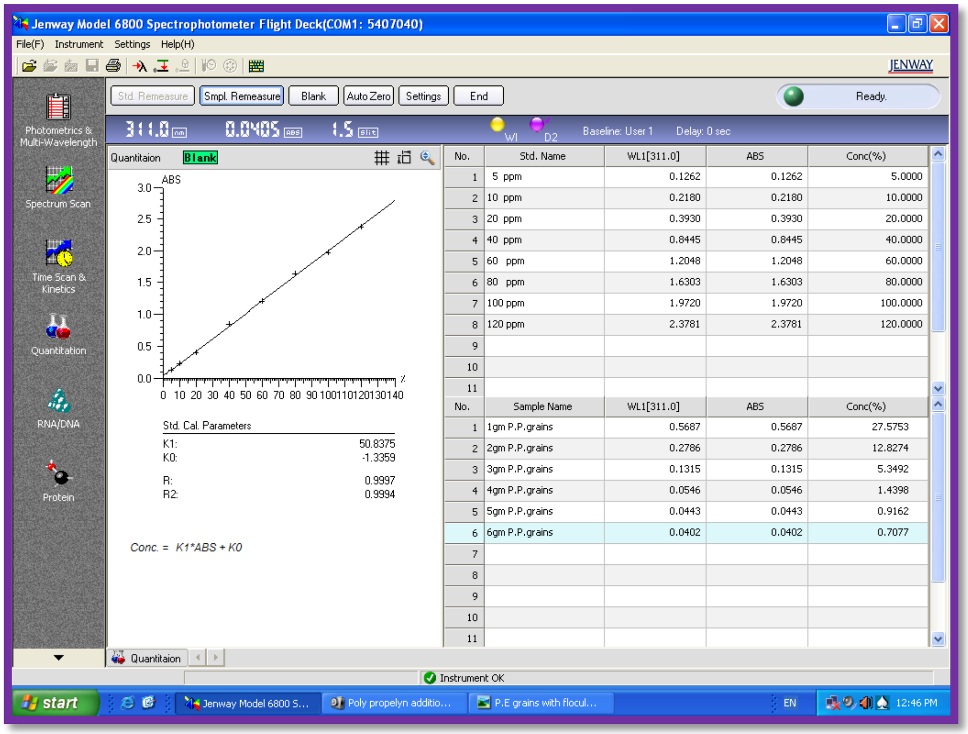
Std. Cal. Parameters

K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

Instrument OK

Figure C - 23 Polypropylene grains effect without flocculation



Baseline: User 1 Delay: 0 sec

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	1gm P.P.grains	0.5687	0.5687	27.5753
2	2gm P.P.grains	0.2786	0.2786	12.8274
3	3gm P.P.grains	0.1315	0.1315	5.3492
4	4gm P.P.grains	0.0546	0.0546	1.4398
5	5gm P.P.grains	0.0443	0.0443	0.9162
6	6gm P.P.grains	0.0402	0.0402	0.7077
7				
8				
9				
10				
11				

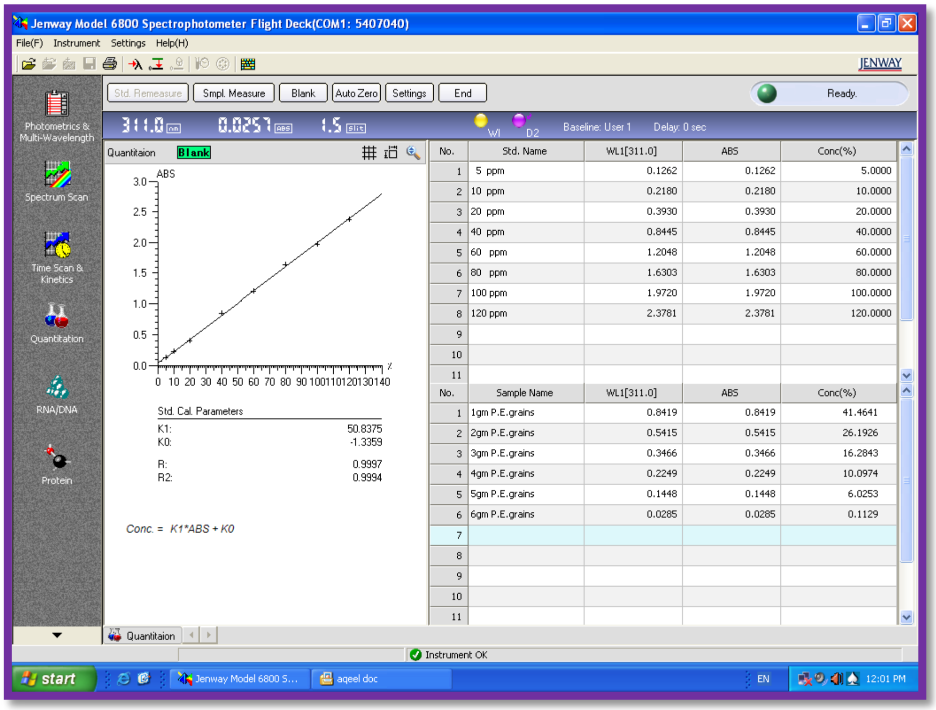
Std. Cal. Parameters

K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

Instrument OK

Figure C -24 Polypropylene grains effect with flocculation



Baseline: User 1 Delay: 0 sec

Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

R: 0.9997
R2: 0.9994

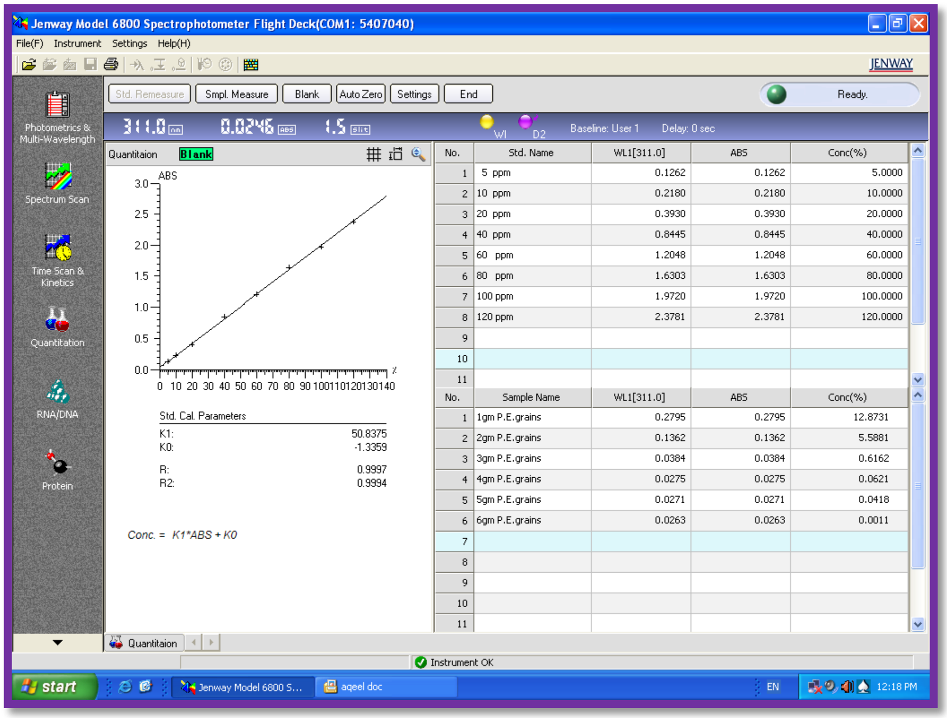
Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	1gm P.E.grains	0.8419	0.8419	41.4641
2	2gm P.E.grains	0.5415	0.5415	26.1926
3	3gm P.E.grains	0.3466	0.3466	16.2843
4	4gm P.E.grains	0.2249	0.2249	10.0974
5	5gm P.E.grains	0.1448	0.1448	6.0253
6	6gm P.E.grains	0.0285	0.0285	0.1129
7				
8				
9				
10				
11				

Instrument OK

Figure C - 25 Polyethylene grains effect without flocculation



Baseline: User 1 Delay: 0 sec

Std. Cal. Parameters

K1: 50.8375
K0: -1.3359

R: 0.9997
R2: 0.9994

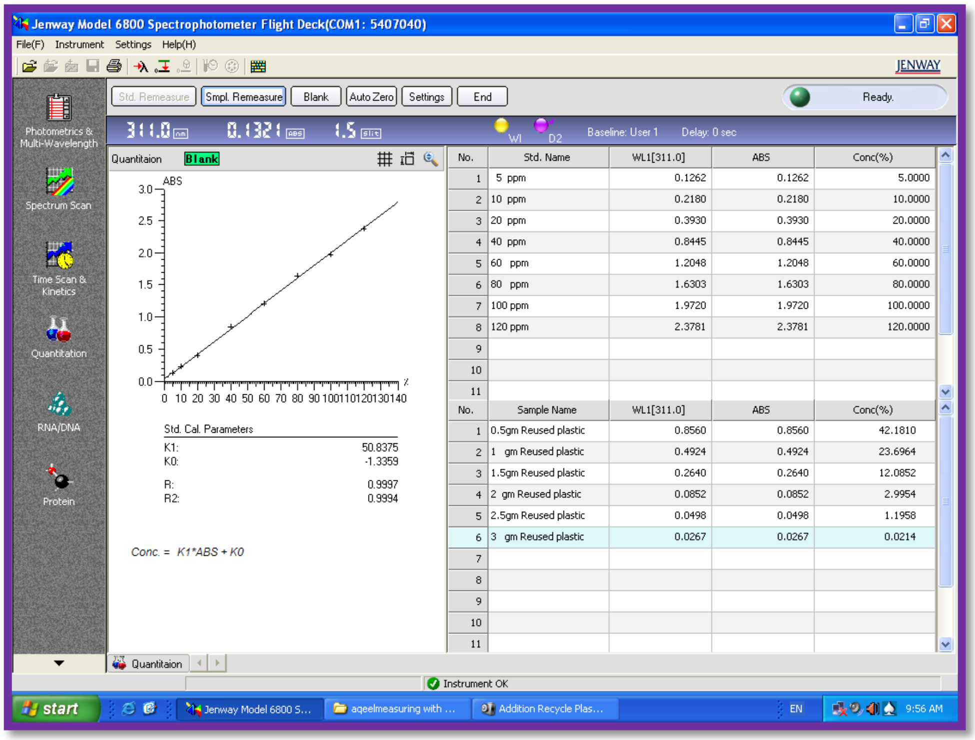
Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	1gm P.E.grains	0.2795	0.2795	12.8731
2	2gm P.E.grains	0.1362	0.1362	5.5881
3	3gm P.E.grains	0.0384	0.0384	0.6162
4	4gm P.E.grains	0.0275	0.0275	0.0621
5	5gm P.E.grains	0.0271	0.0271	0.0418
6	6gm P.E.grains	0.0263	0.0263	0.0011
7				
8				
9				
10				
11				

Instrument OK

Figure C - 26 Polyethylene grains effect with flocculation



Std. Cal. Parameters

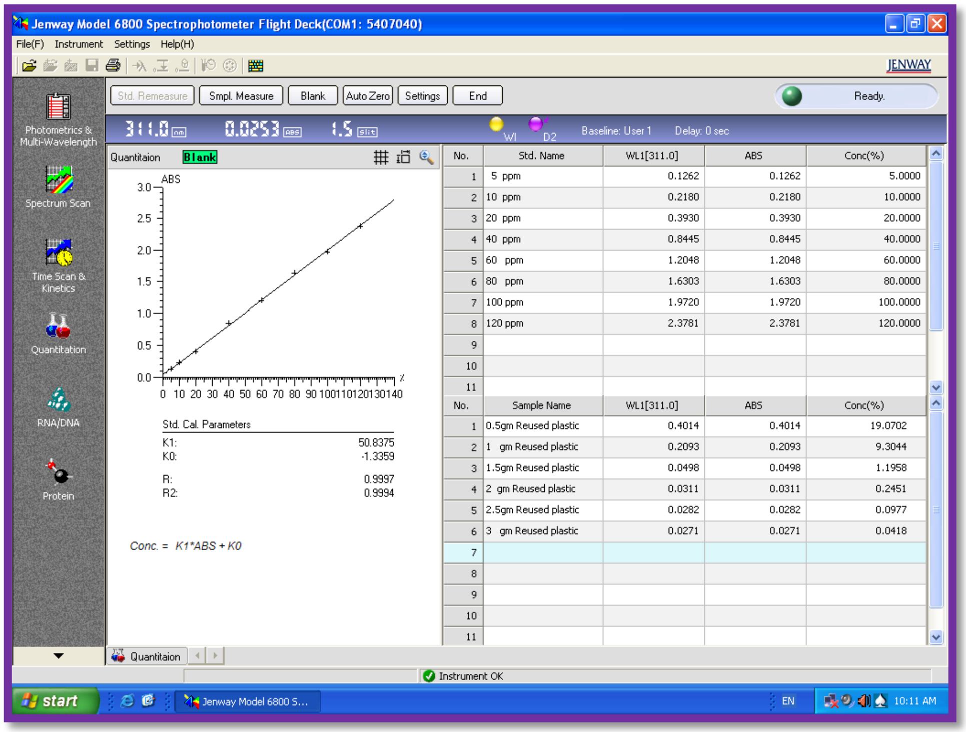
K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	0.5gm Reused plastic	0.8560	0.8560	42.1810
2	1 gm Reused plastic	0.4924	0.4924	23.6964
3	1.5gm Reused plastic	0.2640	0.2640	12.0852
4	2 gm Reused plastic	0.0852	0.0852	2.9954
5	2.5gm Reused plastic	0.0498	0.0498	1.1958
6	3 gm Reused plastic	0.0267	0.0267	0.0214
7				
8				
9				
10				
11				

Figure C -27 Reused plastic effect without flocculation



Std. Cal. Parameters

K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	0.5gm Reused plastic	0.4014	0.4014	19.0702
2	1 gm Reused plastic	0.2093	0.2093	9.3044
3	1.5gm Reused plastic	0.0498	0.0498	1.1958
4	2 gm Reused plastic	0.0311	0.0311	0.2451
5	2.5gm Reused plastic	0.0282	0.0282	0.0977
6	3 gm Reused plastic	0.0271	0.0271	0.0418
7				
8				
9				
10				
11				

Figure C – 28 Reused plastic effect with flocculation

APPENDIX D

Surface area and isotherm plot

Sample1: wood aqeel(Sawdust) Operator: sattar Submitter: aqeel nahrain university File: C:\2020\DATA\2362.SMP

Started: 2/13/2014 10:09:52AM Analysis Adsorptive: N2
Completed: 2/13/2014 1:01:29PM
Analysis Bath Temp.: 77.410
Report Time: 2/18/2014 2:04:20PM Thermal Correction: No
Sample Mass: 0.2842 g
Warm Free Space: 28.3323 cm³ Measured
Cold Free Space: 85.7377 cm³ Equilibration Interval: 10 s
Low Pressure Dose: None Automatic Degas: No

Summary Report

Surface Area Single point surface area at p/p° = 0.068961113:0.0083 m²/g
BET Surface Area: 0.0068 m²/g
Langmuir Surface Area: 0.0072m²/g

Sample2: recycl plastic (used plastic) Operator: khalifa Submitter: aqeel nahrain university File: C:\2020\DATA\2364.SMP
Started: 2/17/2014 8:05:15AM Analysis Adsorptive: N2 Completed: 2/17/2014 9:59:32AM
Analysis Bath Temp.: 77.390 K
Report Time: 2/18/2014 2:05:33PM Thermal Correction: No
Sample Mass: 0.3098 g
Warm Free Space: 28.5179 cm³ Measured
Cold Free Space: 83.9067 cm³ Equilibration Interval: 10 s
Low Pressure Dose: None Automatic Degas: No

Summary Report

Surface Area Single point surface area at p/p° = 0.114881419:0.0153 m²/g
BET Surface Area: 0.0163m²/g
Langmuir Surface Area: 0.0180m²/g

Sample3: POLY ETHYLENE Operator: khalifa Submitter: akeel nahrain university File: C:\2020\DATA\2363.SMP

Started: 2/16/2014 8:08:26AM Analysis Adsorptive: N2
Completed: 2/16/2014 10:01:41AM Analysis Bath Temp.: 77.347K
Report Time: 2/16/2014 10:17:45AM Thermal Correction: No
Sample Mass: 0.3024 g Warm Free Space: 28.0798 cm³ Measured
Cold Free Space: 82.2617 cm³ Equilibration Interval: 10 s
Low Pressure Dose: None Automatic Degas: No

Summary Report

Surface Area Single point surface area at p/p° = 0.099773964:0.2773 m²/g
BET Surface Area: 0.3811 m²/g
Langmuir Surface Area: 0.4668 m²/g

Sample4: p. propylene Operator: khalifa Submitter: Aqeel nahrain University file: C:\2020\DATA\2365.SMP
Started: 2/17/2014 11:24:52AM
Analysis Adsorptive: N2
Completed: 2/17/2014 1:23:38PM
Analysis Bath Temp.: 77.393 K
Report Time: 2/18/2014 2:06:24PM Thermal Correction: No
Sample Mass: 0.3013 g
Warm Free Space: 27.9466 cm³ Measured
Cold Free Space: 81.9669 c Equilibration Interval: 10 s
Low Pressure Dose: None Automatic Degas: No

Summary Report

Surface Area Single point surface area at p/p° = 0.114815835:0.0318 m²/g
BET Surface Area: -0.0033 m²/g
Langmuir Surface Area: -0.0031 m²/g

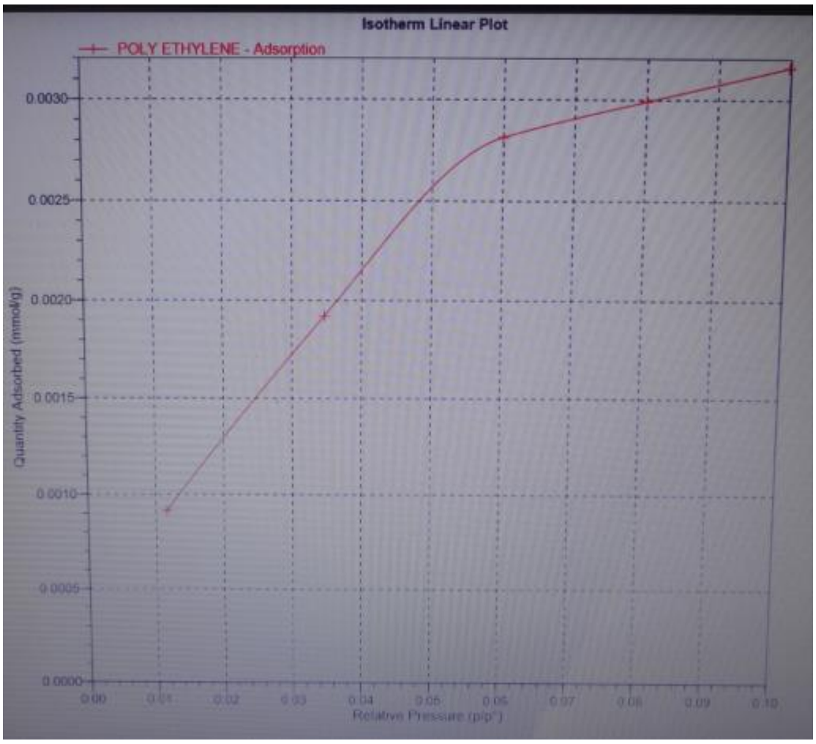


Figure D-1 Polyethylene adsorption isotherm linear plot

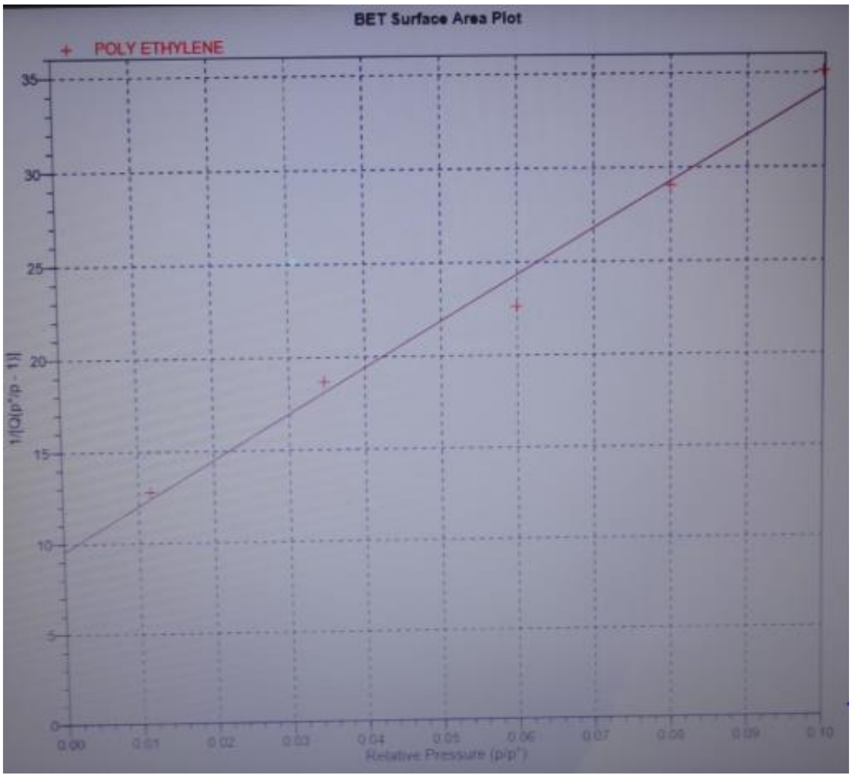


Figure D-2 Polyethylene adsorption isotherm Bet surface area plot

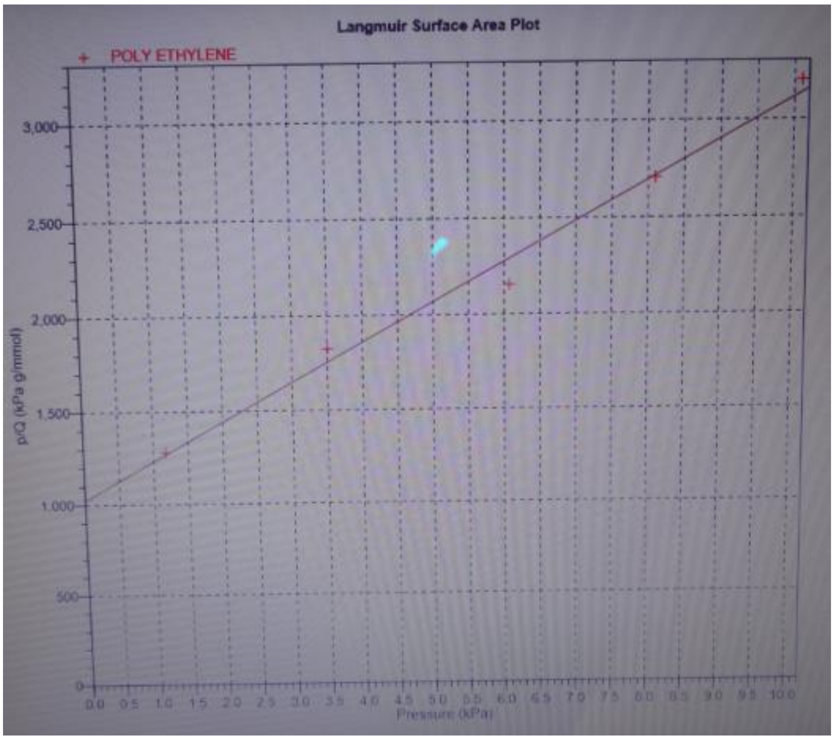


Figure D-3 Polyethylene adsorption isotherm Langmuir surface area plot

Figure D-4 Reused plastic adsorption isotherm linear plot

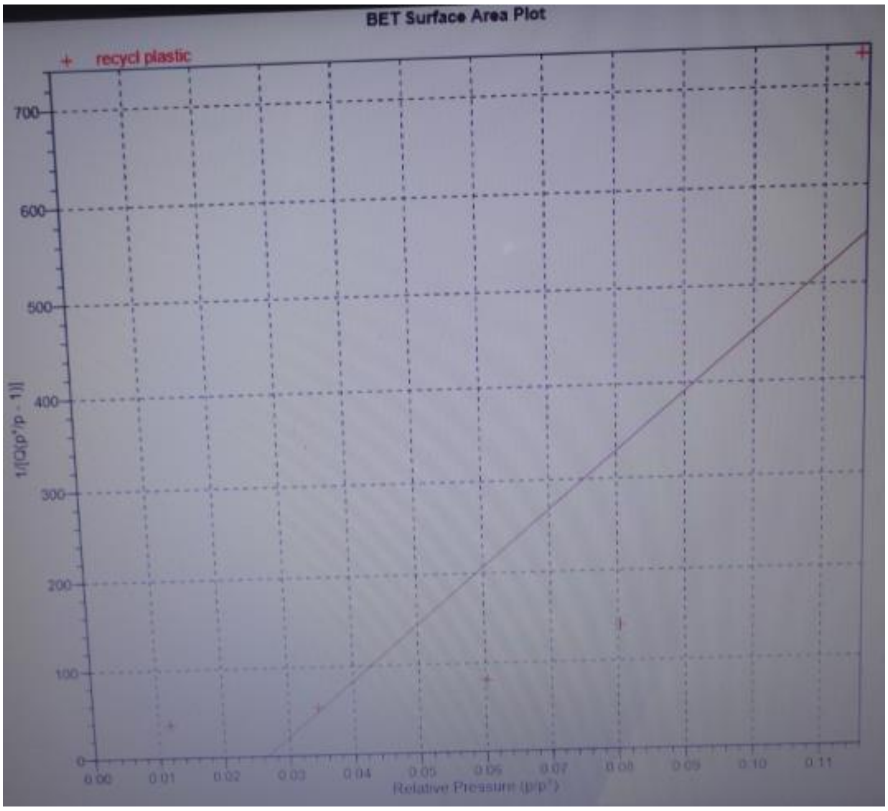


Figure D-5 Reused plastic adsorption isotherm Bet surface area plot

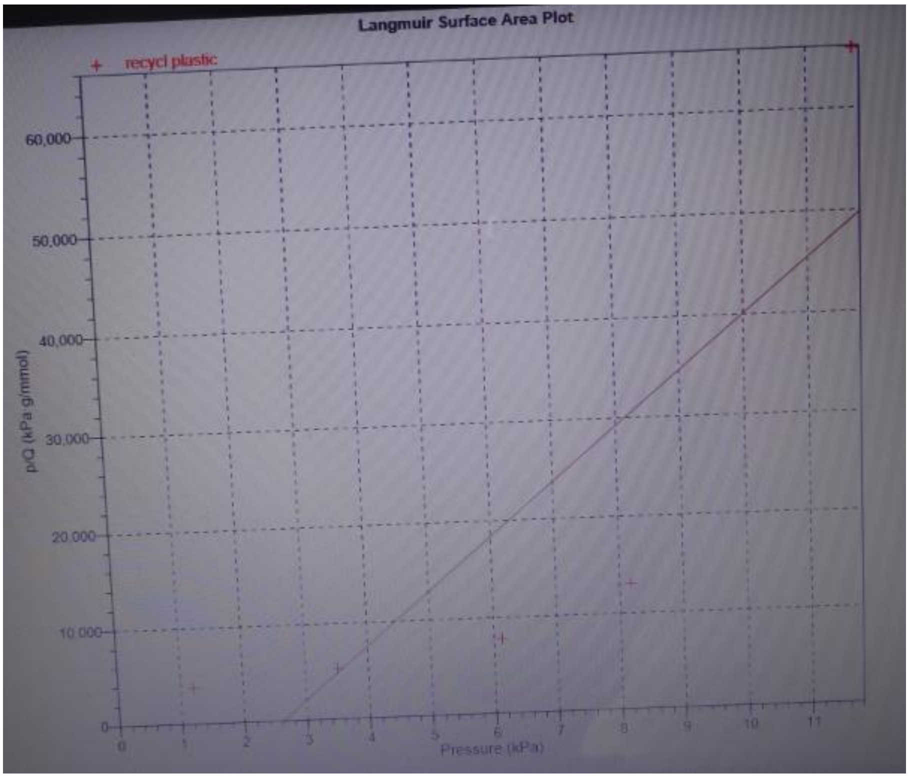


Figure D-6 Reused plastic adsorption isotherm Langmuir surface area plot

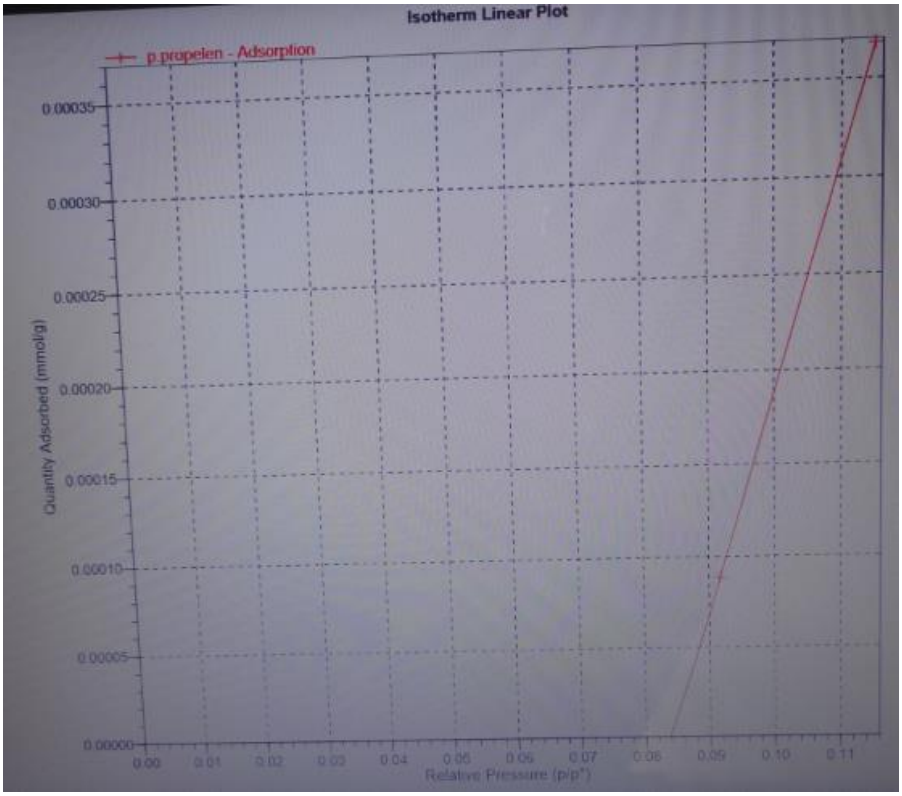


Figure D-7 Polypropylene adsorption isotherm linear plot

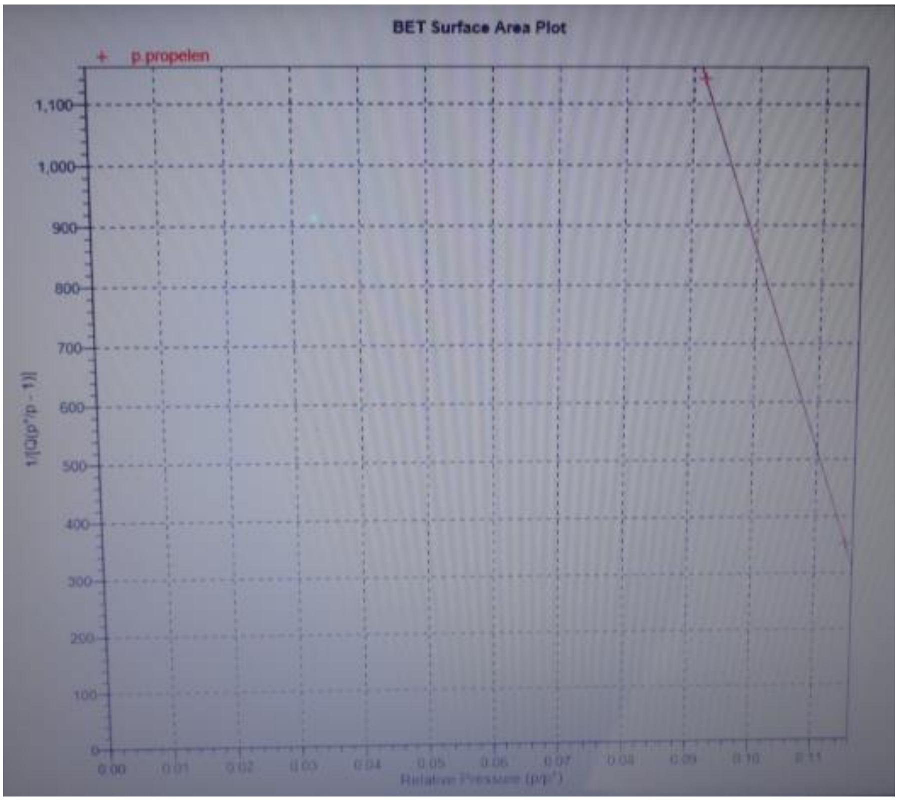


Figure D-8 Polypropylene adsorption isotherm Bet surface area plot

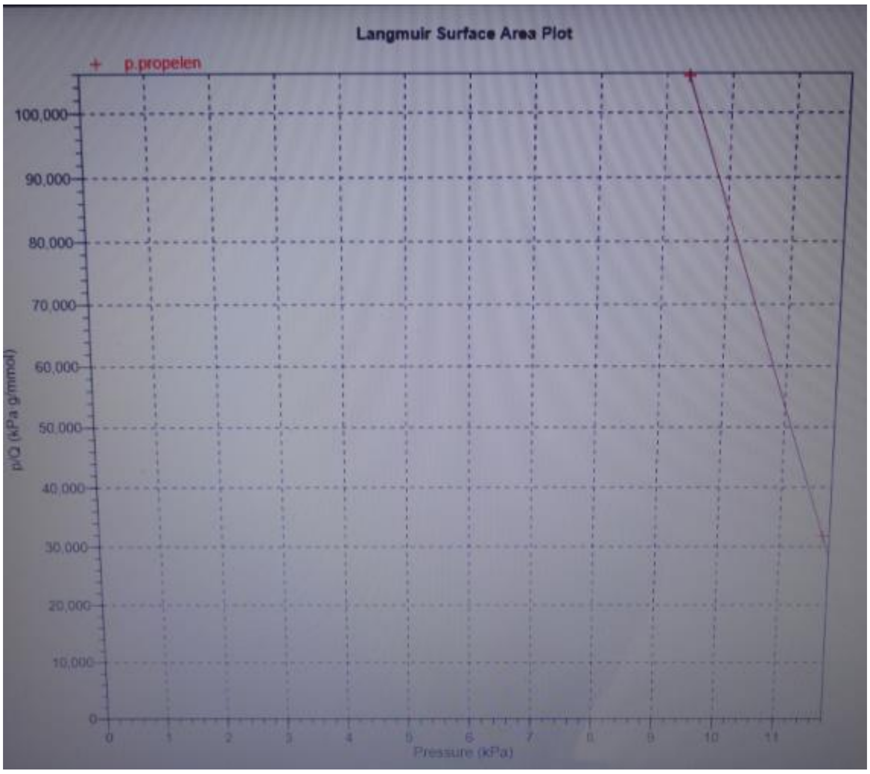


Figure D-9 Polypropylene adsorption isotherm Langmuir surface area plot

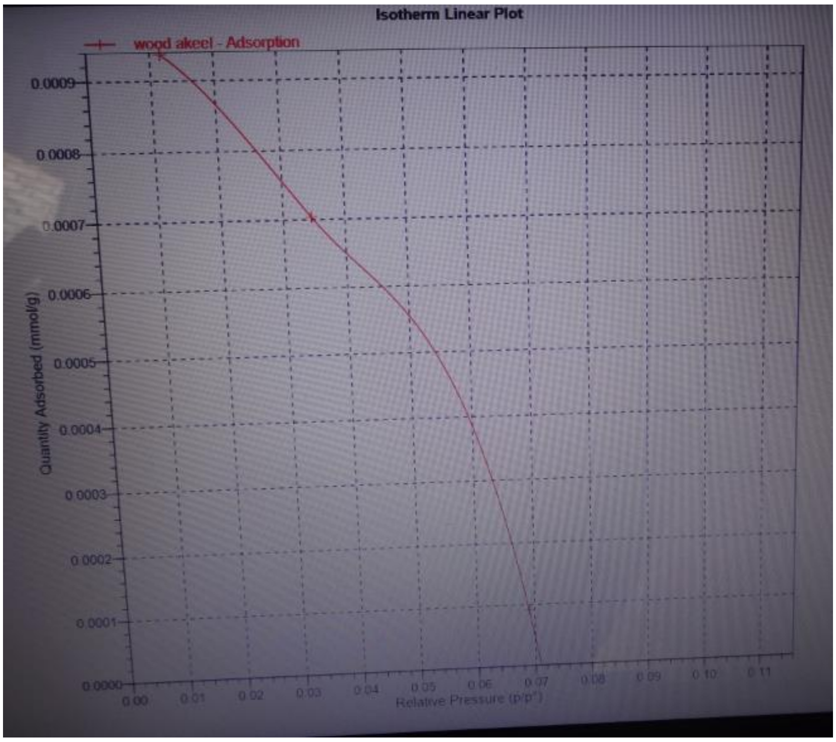


Figure D-10 sawdust adsorption isotherm linear plot

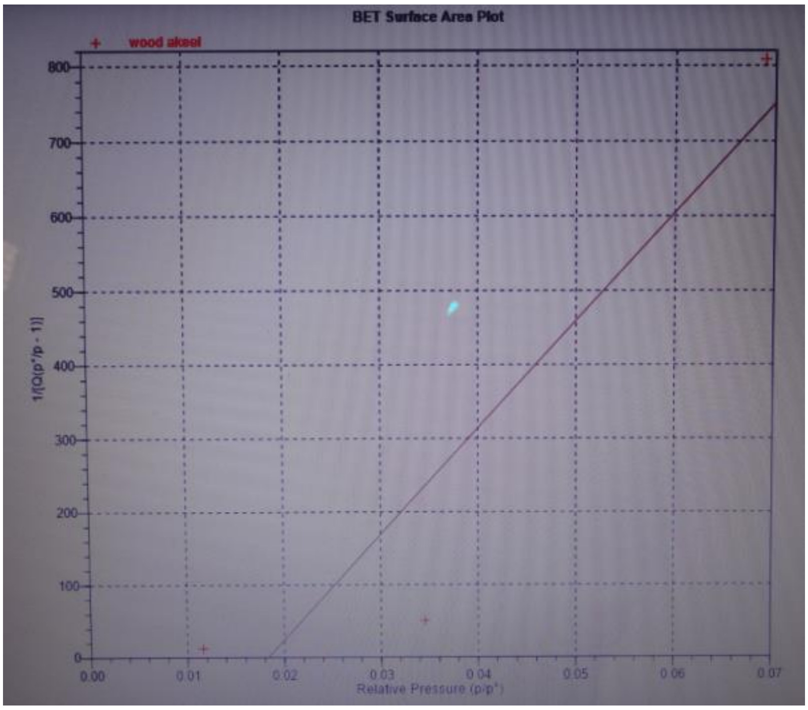


Figure D-11 sawdust adsorption isotherm Bet surface area plot

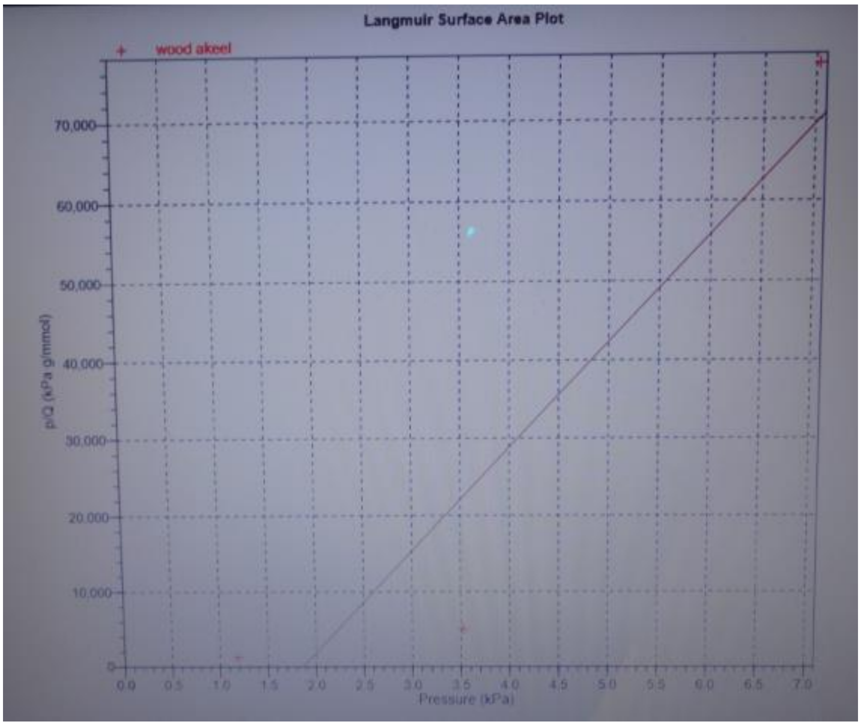


Figure D-12 sawdust adsorption isotherm Langmuir surface area plot

Certification

I certify that this thesis entitled **“Oily Water Treatments for Southern Iraqi Oil Fields**” was prepared by **Aqeel Sheikha Arafat** under my supervision at Nahrain University / College of Engineering in partial fulfillment of the requirement for the degree of Master of Science in Chemical Engineering.

Signature:
Name: **Asst. Prof. Dr. Khalid M. Mousa**
Date: /   /

Signature:
Name: **Asst. Prof. Dr.Naseer Abbood**
Al-Haboubi
(Head of Department)
Date: /   /

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. The time for Settling without flocculation as pretreatment to remove solid particles calculated was 2hours while time reduced to 45minutes with flocculent polyacrylamide in flocculation.
2. The best operating time was found is 15 minutes whereas the outlet time of stability to skim starting was obtained 5 minutes which was average of (4-6) minutes.
3. The oil removal percent increased with increased salinity concentration, the highest range (100 gm/lit.) gave highest removed efficiency.
4. Operation needed a slow mixing to have high contacts between surfactant and sorbents with oil droplets, 300 RPM was best speed.
5. pH influence significant increasing of percentage oil removal, best value of pH was 7.
6. The optimum value of temperature was (40 - 50) °C. 45 °C as an average value was taken.
7. The optimum value of pressure was 1 bar.
8. The % oil removal increase with the dose of surfactant addition like ethanol, liquid and powder detergent by reduced surface tension of solution, oil recovery was over 94%. Ethanol is the best among others.
9. At 2.5gm sawdust gave 99 percent of oil recovery. A disadvantages of sawdust was ability to absorb water, rested in bottom, hard to separate, its cause lose in oil recovery and a pollutant accumulation problem

10. Hydrophobic sorbents had given high percentage removed reached 100% used plastic base polyethylene had highest recovery with lowest amount

11. Best features of polymer grains and used plastic that the efficiency of removal didn’t change when reused many times after cleaning by steam or sprayed hot water from oil droplets.

5.2 Recommendations

1. Using non uniform surface of polyethylene and polypropylene grains which contact to the shell because the rough surface can capture droplets more than smooth.

2. Choose horizontal reactor to increase the surface oil skimmed and compare effect of liquid column height effect.

3. Using packed bed column to treat oily water rather than batch and compare results with batch.

4. Using PVC reactor because it has hydrophobic criteria addition to resistance salts effect

5. Apply the autoclave to treatment oily water which produced from the refinery process.

CHAPTER THREE

EXPERIMENTAL WORK

To explain steps of experimental work we need to know more information about feed, types of O/W emulsions and the methods of founding concentration of oil in water.

3.1 Study Approaches

1-The first approach using pretreatment to remove solid particles using sedimentation with and without flocculation

2-The second approach included studied the effects of pH, pressure, temperature, salinity, operation time, outlet time and RPM. The ranges as in table 3.1

3-The third approach was investigate the effect of the surfactants (detergents and alcohol) to reduce surface tension, see table 3.2

4-The fourth approach was addition of some sorbents like polypropylene, polyethylene, used plastic and sawdust.

The ranges of salinity, pH, pressure and temperature were selected according to the PW conditions which out from dehydrator and desalter 80000 ppm, 6, 3bar and 60°C respectively [3], [4], the RPM of mixer was selected to satisfy laminar flow as in figure 2.4 while the time of operation and outlet product represented the minimum residence time in batch reactor and its discharge to choose the minimum design cost

Table 3.1 Range of conditions and variables used in the present work

Step	**Variable**	**Range**
1	Pressure, (bar)	0 - 5
2	pH effect	2 - 8
3	Temperature, (°C)	30 - 70
4	Salinity, (mg/lit.)	20,000 - 100,000
5	Mixer (RPM)	0 -1100
6	Operation time (min)	5 -30
7	Outlet time (min)	2 - 10

Table 3.2 Amount range of surfactants addition to the present work

Step	Surfactant	Amount Range
1	Powder (solid)detergent gm	0.5 - 3
2	Ethanol volume%	0.1 -0.6
3	Liquid detergent volume%	0.1 -0.6

Table 3.3 Amount range of sorbent additions to the present work

Step	Additive	Amount Range
1	Polyethylene grains gm	1 - 6
2	Polypropylene grains gm	1 - 6
3	Recycle Plastic/ gm	0.5 - 3
4	Sawdust / gm	0.5 - 3

3.2 Materials

The materials which were used in the experiment of the present work as sorbents materials used with high efficiency of oil concentration removal are shown in figure3.1 .The other materials listed in Tables 3.4, 3.5 and 3.6

Figure 3.1 sorbent materials which used as adsorbents

Figure 3.2 Flocculent polyacrylamide (PAA)

Table 3.4 Materials and Their specifications [4].

Material	**Specifications**
Produced Water	were brought from North Rumaila and Zubbair oil fields
Crude oil	Samples were brought from Rumaila and Zubbair oil field with API of 27
Air	Atmospheric compressed air
Sodium chloride	Commercial sodium chloride
Carbon tetra chloride(CCl_4)	MWt =153.82, density=1.59kg/L, Germany Merck, extra purity> 99%
HCl	0.01 molarity
NaOH aqueous	0.01 molarity
Polyacrylamide(C_3H_5NO)	Polymer base flocculent, China
Ethanol(C_2H_5OH)	Fluka purity 96%
Powder (solid)detergent	High solubility in water
Liquid detergent	anionic surfactant KSA
Polyethylene grains	Low density, real density 0.8885gm/cm^3 KSA
Polypropylene grains	Low density, real density 0.916 gm/cm^3 KSA
Recycle plastic	Polyethylene residuals, real density0.9gm/cm^3 Basra Iraq
Sawdust	Carpentry ash, real density 1.2819gm/cm^3

Tables 3.5 and 3.6 show the physical properties of polyethylene and polypropylene respectively

Table 3.5 Important properties of polyethylene [28].

Polyethylene type	**range point Melting °C**	**Density g/cm^3**	**Degree of Crystallinity**	**Stiffness modules psi ×10^3**
Medium density	107–121	0.92	60–65	25–30
Linear,–High density	—	0.935	75	60–65
Ziegler 125	—	0.95	85	90–110
Phillips type	132	0.96	91	130–150

Table3.6 Important properties of polypropylene [28]

Polypropylene’s properties	**Value range**
Density, g/cm^3	0.90–0.91
Fill temperature, max. °C 130	**130**
Tensile strength, psi	3,200–5,000
Water absorption, 24 hr.,	% 0.01
Elongation,	% 3–700
Melting point, Tm °C	176
Thermal expansion,	10–5 in./in for each 5.8–10°C
Specific volume, cm^2/lb	30.4–30.8

3.3 Equipment:

1. Autoclave: Main process equipment, consist of 1 litter(operating volume) pressurized reactor, isolated well to keep heat, working under control with different temperatures ranges, connect with control panel as shown in figure 3.3, the numbers were selected according table 3.7

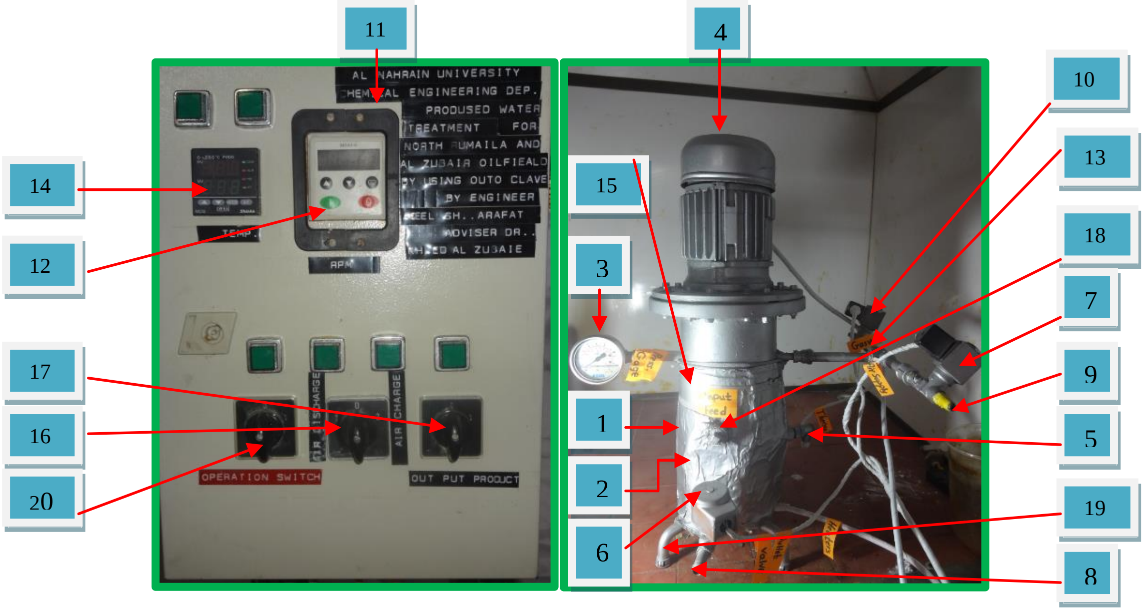


Figure 3.3 Photo pictures of laboratory Autoclave reactor system and its control panel

A schematic diagram of experimental system used to carry out the laboratory experimental work as shown in Figure. 3.4

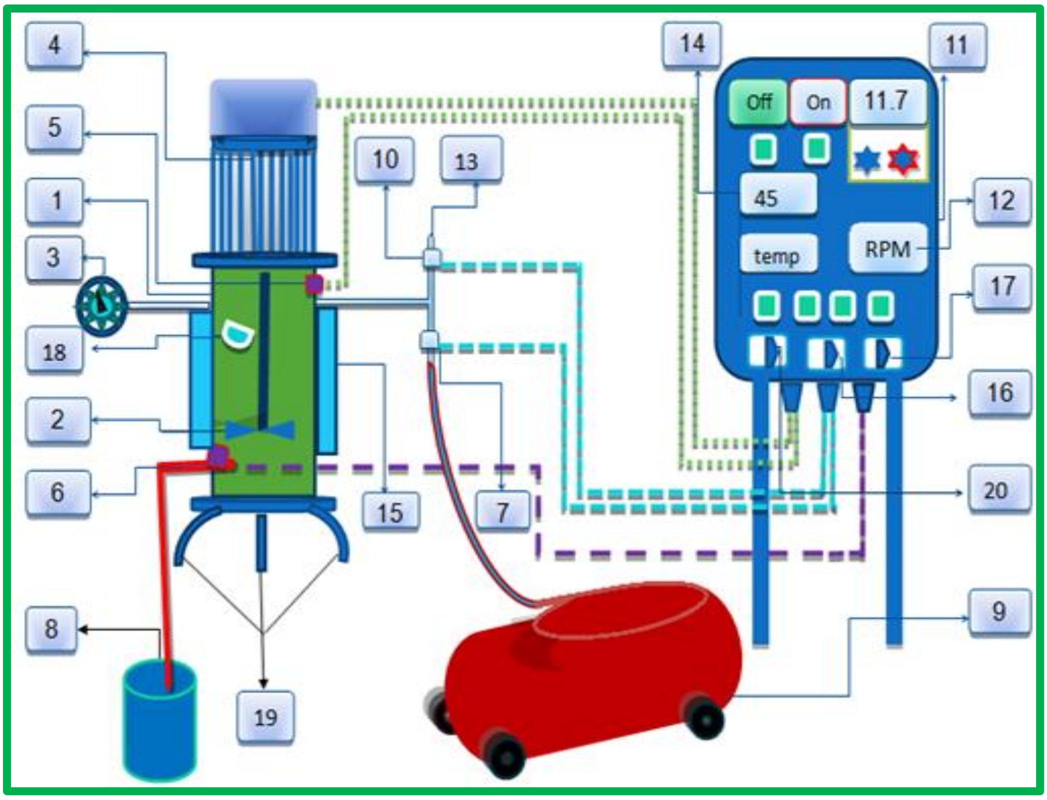


Figure 3.4 Schematic diagram of laboratory autoclave reactor System

Table 3.7 Schematic an autoclave parts

1	An autoclave reactor	2	impeller fan
3	Pressure gage(10 bar)	4	Electrical motor
5	Pt 100 thermocouple	6	Outlet product Solenoid valve (1/2 inch)
7	Inlet air solenoid valve1/4inch	8	PW output
9	air compressor	10	Outlet air solenoid valve
11	Autoclave board	12	digital regulator of the mixer
13	Vent gas	14	Temperature controller s
15	Asbestos isolator layer	16	Power switch of the inlet and outlet air valve
17	Power switch of the product.	18	Input feed
19	Reactor foundations	20	Power switch

2. Magnetic stirrer: Used instead of autoclave when the experiments have low pH due to corrosion, supplied by Daihan lab. as in figure 3.5

3. TDS detector: Conductivity meter: Auto- ranging microprocessor type HI2300 Manufactured by Hanna instruments. As shown in figure 3.6

Figure 3.5 Magnetic stirrer **Figure 3.6** TDS detector

4. pH detector: Read pH of solution Hanna inst. shown in the figure 3.7

5. Digital Balance: Electronic high accuracy 4 decimal places of gram digital balance type Sartorius with maximum weight of 210 gm. which have accuracy of 0.1 mg as shown in Figure 3.8

Figure3.7 pH meter **Figure 3.8** Electric Digital balance

6. **UV 6800Jenway**, Germany, to determine oil, as shown in figure 3.9

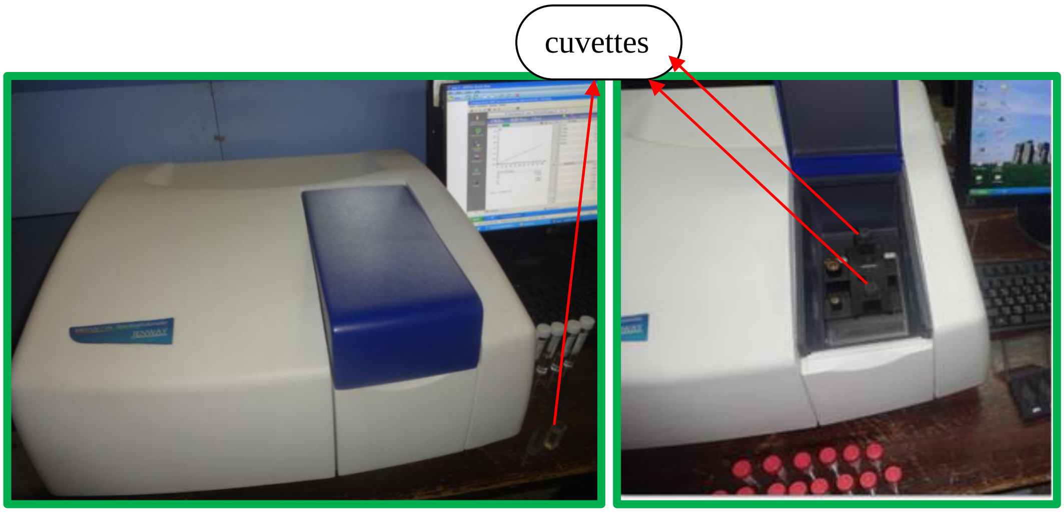


Figure 3.9 The UV6800 photo picture

3.4 Describe Laboratory Experimental Unit:

The experiments were carried out in actual operating reactor volume (1 liter). Autoclave stainless steel reactor have dimensions 11.5cm, 10 mm, 30cm (inner diameter, thickness of the shell wall and the height) respectively. To raise the temperature, the reactor supplied by heaters. The reactor was connected to the controller to a chief a desired temperature. Stainless steel mixer shaft, screwed with impeller was used to mix the solution in order to achieve a maximum contact of solution.

The diameter of impeller was 3 cm. made of stainless steel to resistance corrosion.

The stirrer rotated by an electrical 3 phase motor (N_{max}= 1300 rpm). The speed of agitation was controlled by the digital regulator (50 digits) in the board. Three solenoid operated valves were out from the wall of the reactor, two operated valves (1/4 inch) in the upper side for charging and discharging of air and the bottom Solenoid operated valve (1/2 inch) in for discharge the product.

The process designed well under control with control board and safety conditions to work for different temperature and pressure. For more safety the autoclave parts put inside laboratory hood containing vent.

3.5 Experiments Steps and Procedures

1- Sedimentation: Removing the sediment without flocculation and checked the time of removed undesired colors for iron oxides then added flocculent (polyacrylamide) with different doses (100-500) ppm and calculated the time of sedimentation.

The flocculent halved the time of sedimentation, on the other hand oil droplets will aggregation and floating to the surface that will make mission of oil separation easiest.

2- Fixing the Conditions: By series of experiments and check optimum effective value of conditions like pressure, temperature and pH

3- Study Variables Effects: Choose best fit value of some variables like operation and residence of stable time to skim oil, mixer rapid and salinity.

4- Surfactants Influents: Addition the surfactants (alcohol, powder detergent and liquid detergent) will reduce surface tension which will cause oil floating**.**

5- Sorbents Addition: Features of polymers and sawdust as hydrophobic materials which have attractive to adhere with oil droplets according to polarity and Van Der Waals forces, on the other hand its work as adsorbents and sorbents. Unlike sorbent sawdust, the other additives (polyethylene, polypropylene and used plastic) have ability to reuse.

3.5.1 Procedure of Sedimentation Step.

Starting with first step, filling one litter of PW which prepared with 600ppm of emulsion oil to dispose of sediments without any flocculent addition, then observe the changing of color with time and test by filtration with filtration paper every 15 minutes then calculate the percentage of sediment removing the accumulation of particles decrease linearly with time see Appendix B. The brown color of PW convert to colorless.

The same procedure was repeated using the flocculent polyacrylamide and checked percentage of sediment removing, the observes indicated that the solution reached stability after 45 minutes, this led to be formed gel layer of oil droplets on surface which helped oil removal operation.

3.5.2 Procedure of Experimental Work of Fixing Variables Operating Time, Outlet Time and Mixing.

To estimate the optimum conditions for operation with ranges in table 3.2, the operation time (5 – 30) min was the first variable checked with fixing other original conditions of PW according table A-4 of PW appearances. To reach best suitable time for process design, the pressure fixed at 3bar, the temperature fixed at 60°C (PW temperature out at 63°C), salinity of PW 80000 ppm without mixing or any additives.

After 10 minutes of experiments samples were took and estimated the oil recovery according to UV standard curve depending on changing absorbance measurement then, the oil concentration calculate from the equation below:

% oil removed = [(input –remainder conc.)/input] ×100----Eq3.1

For outlet time repeated the same condition with ranges 2 to10 min and fixed operation time on 15 min then applied the equation 3.1 for each experiment.

Salinity ranges started from (20000-100000) ppm with same conditions (operating time =15 min, outlet time=6 min, P=3bar and T=60°C), also without mixing or additions, the 100000 ppm had best %oil removed.

The RPM of mixer ranged (300 -1100), the 300RPM gave laminar mixing that's led to fix it to estimate other conditions like pH, temperature and pressure .Which found the high recovery oil in values (7, 40-50°C, 1-2bar) respectively, pH value was adjusted by adding HCl and NaOH.

3.5.3 Procedure of Experimental Work for Surfactants Addition.

Repeat steps of experiments with addition alcohol, liquid detergent with ranges (0.01 – 0.06) vol. % and powder detergent from100 to 600 ppm with fixing other conditions and variables on the operating time =15 min, outlet time=5 min, 100000 ppm of salinity, 300RPM T=45°C and P=1bar.

3.5.4 Procedure of Experimental Work for Sorbents Additions.

A repeated steps of experiments with sorbents polyethylene and polypropylene with 1 to 6gm were used, while the used plastic and sawdust with 0.5 to 3 gm at the same conditions were used.

3.6 Determination of Oil Concentration

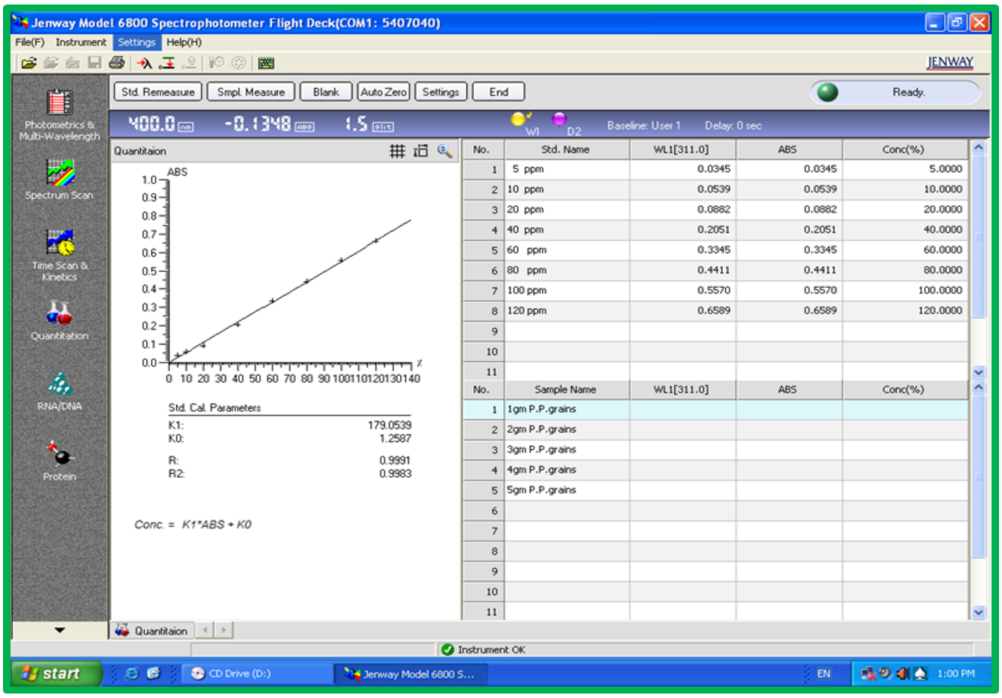
Hydrocarbons which absorb infrared at certain wavelengths, aromatic hydrocarbons absorb ultraviolet (UV) light are measuring the UV absorbance of a sample extract in a similar fashion to the reference infrared method, but using UV spectroscopy [25].

The UV6800 in the figure 3.9 was used in this work to determine the oil concentration.

3.6.1 Standard Curve of UV Analysis

First prepare known samples with ranges (5, 10, 20, 40, 60, 80, 100, 120 and 140 ppm, respectively).

Oil was extracted from the water by carbon tetrachloride CCl_4. The standard calibration curve is shown in Figure 3.10. Absorbance represent the Y axis and concentration the X axis.



Jenway Model 6800 Spectrophotometer Flight Deck(COM1: 5407040)

Baseline: User 1   Delay: 0 sec

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.0345	0.0345	5.0000
2	10 ppm	0.0539	0.0539	10.0000
3	20 ppm	0.0882	0.0882	20.0000
4	40 ppm	0.2051	0.2051	40.0000
5	60 ppm	0.3345	0.3345	60.0000
6	80 ppm	0.4411	0.4411	80.0000
7	100 ppm	0.5570	0.5570	100.0000
8	120 ppm	0.6589	0.6589	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	1gm P.P.grains			
2	2gm P.P.grains			
3	3gm P.P.grains			
4	4gm P.P.grains			
5	5gm P.P.grains			
6				
7				
8				
9				
10				
11				

Std. Cal. Parameters

K1: 179.0539
K0: 1.2587

R: 0.9991
R2: 0.9983

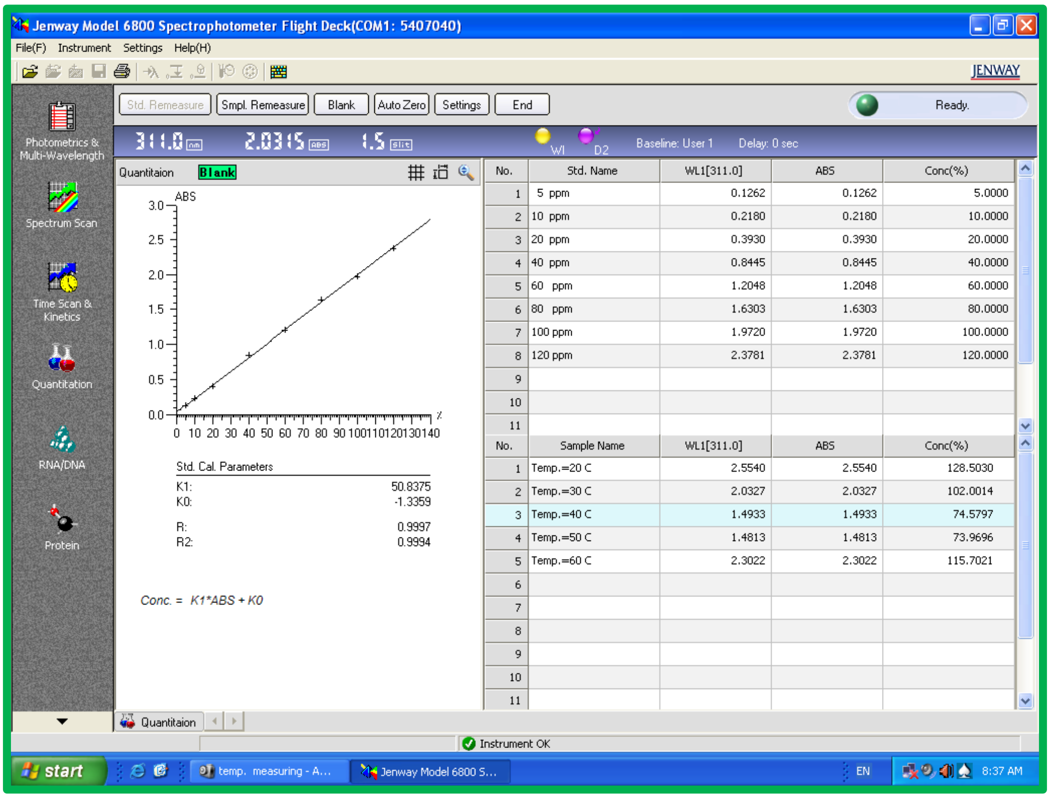
Conc. = K1*ABS + K0

Figure 3.10 Standard curve according UV digital determination

3.6.2 Procedure of Samples Determine

20 ml of the solvent carbon tetrachloride (solvent has been known to be a good extractnt for oil in water) [29], was added to 200 ml of produce water sample which was taken from outlet product to extract oil from water and put in a separating funnel. 1 gm of NaCl was added in order to break the emulsion of oil and followed by vigorous shaking for one min. After 15 min., the lower layer of higher density of CCl_4 rest taken for the absorbance measurement [18], then put the reference blank (CCl_4) inside both cuvettes see figure 3.9, then fill the nearest one with sample, click sample measuring, the result was processing directly according the standard curve and calculated by equation 3.2 as shown in figure 3.11

$$\textbf{Conc.} = \textbf{K}_1 * \textbf{ABS.} + \textbf{K}_0 \ \ldots\ldots\ldots.3.2$$



Std. Cal. Parameters

K1:	50.8375
K0:	-1.3359
R:	0.9997
R2:	0.9994

Conc. = K1*ABS + K0

No.	Std. Name	WL1[311.0]	ABS	Conc(%)
1	5 ppm	0.1262	0.1262	5.0000
2	10 ppm	0.2180	0.2180	10.0000
3	20 ppm	0.3930	0.3930	20.0000
4	40 ppm	0.8445	0.8445	40.0000
5	60 ppm	1.2048	1.2048	60.0000
6	80 ppm	1.6303	1.6303	80.0000
7	100 ppm	1.9720	1.9720	100.0000
8	120 ppm	2.3781	2.3781	120.0000
9				
10				
11				

No.	Sample Name	WL1[311.0]	ABS	Conc(%)
1	Temp.=20 C	2.5540	2.5540	128.5030
2	Temp.=30 C	2.0327	2.0327	102.0014
3	Temp.=40 C	1.4933	1.4933	74.5797
4	Temp.=50 C	1.4813	1.4813	73.9696
5	Temp.=60 C	2.3022	2.3022	115.7021
6				
7				
8				
9				
10				
11				

Figure 3.11 UV photo picture for digital page, samples measurements

From Equation 3.2 the UV processing the results auto and find sample concentration remainder, directly.

To find % oil recovery substitute the sample remainder value which estimated by UV, into equation 3.1, detailed of all analysis of samples are shown in Appendix C.

Figure 3.12 show a photo of all samples

Figure 3.12 Samples of experiments

CHAPTER ONE

1.1 Introduction

The oil drilling operations create large quantities of contaminated water known as Produced Water (PW), or water that is produced from the well. Most underground oil reservoirs have a natural water layer called formation water, which lies underneath the hydrocarbons .The basis definition of produced water is salty water that is trapped inside of rock. It’s brought to the surface when gas and oil is extracted from the earth and normally exists under high temperatures and pressures. An oil well will likely produce much more oil than water however at some point an oil well begins to produce much more water than oil [١].Oil and gas reservoirs have a natural water layer (formation water) that lies under the hydrocarbons. Oil reservoirs frequently contain large volumes of water, while gas reservoirs tend to have smaller quantities .To achieve maximum oil recovery additional water is often injected into the reservoirs to help force the oil to the surface. Both the formation water and the injected water are eventually produced along with the oil, therefore; the field becomes depleted the produced water content of the oil increases [٢].

As long as the oil production nonstop for next years the produced water continual .The terrible huge quantities of produced water take off the consideration .Thus the most petroleum researchers focus to solve this problem of this pollute water. Whatever the case, an appropriate solution must be developed. Therefore; it would be normally to see thousands studied in this field and most companies race to find root solutions as much as possible, very significant to reflect on the humanity side appropriate aim. Experimentally, the conventional methods of PWT would be shock when applied in fait accompli, also proved inability to find permanent solution right now, just imagine how much if the studies referred that the PW amount will double in future. According subsequent data in South Iraq oilfields supplied by petroleum development & research center (P.D.&R.C.) and South Oil Company (S.O.C.)Production rate of produced water at 2003 for Basra oil fields /main pay was found 107,621bbl/d detailed in a table A-1 [٣].While the Production rate of produced water at 2014 for North Rumaila /main pay only, equal to 210,000bbl/d and Production rate expected of produced water at 2025 for North Rumaila /Main Pay reach to 500,000bbl/d, also the Production rate of produced water at 2014 for South Rumaila/ main pay only, equal to 510,000bbl/d and Production rate expected of produced water at 2025 for South Rumaila/ main pay reach to 800,000bbl/d, A detailed in tables A-2 and A- 3 [٤] .

Although estimates of produced water volumes vary, the quantity will continue to increase globally. As an oil field matures, oil production decreases while water production increases [5]. Produced water associated with oil and gas production, it may include water from the reservoir, water injected into the formation and any chemicals added during the production adding the wash water during oil separation which used to wash salts in de-salter unit separation step before supplied to out stream of PW. A multidisciplinary approach, integrating subsurface performance, facilities design and environmental discharge, is required to minimize its impacts [5]. In Iraq for each 5bbl of oil produced, an average of 1bbl of water is produced. The current water/oil ratio is estimated at 1:5[3], while in USA the current water/oil ratio is 10:1, for an annual total of about 3 billion tons, this is by some estimates the largest single waste stream in the USA[6].Reinjection (for enhanced recovery or disposal) accounts for as much as 95% of this water[7]. The remaining fraction is still considerable. Reinjection is not always feasible because of geographic and cost considerations[8].

1.1.1 Produced Water Treatment (PWT)

A treatment process is needed when gas and oil are extracted from fields then produced water arises out of the ground. It must be treated through produced water treatment and properly disposed of because the process is crucial for successful oil production to avoid environmental & health concerns [1]. Its treatment and management are growing challenges in all producing regions [5].

There are many conventional treatment methods for produce water, the methods and their disadvantages summarized in table 1.1

Table 1.1 Conventional methods and their disadvantages [16], [15], [4] and [13].

Treatment	**Disadvantage**
Hydro cyclone	Energy requirement to pressurize inlet, no solid separation, fouling and higher maintenance cost
Corrugated Plate Interceptor	Inefficient for fine oil particles ,retention time and maintenance
Dissolved –Air Floatation	Generation large amount air, retention time for separation and skim volume
Flotation	If high temperatures are present, a high press and requires to dissolve the gas in the water
Membrane (hydrophilic) Filtration (MF)	Fouling from colloidal scale formation, Elaborate pretreatment requiring a long train of multi-stage treatment Large foot print area and complex treatment system design, High energy usage as in horsepower per square foot of membrane and Anti-scalants and other pretreatment chemicals require handling and storage
Mf (Micro Filtration)	High energy required, less efficiency for divalent, monovalent salts, viruses, Iron fouling can be a problem.
UF (Ultra Filtration)	High energy, Iron fouling can be a problem, membrane fouling, low MW organics, salts ,reject may contain radioactive material
NF(Nano filtration)	High energy required, less efficient for monovalent salts and lower MW organics, membrane fouling ,reject may contain radioactive material

Due to a disadvantage of conventional methods is proposed a physical method with high quantity product to avoid the amount of doubled PW in future. Simply, our method is invers the production of crude oil production by depending on vary conditions like operation and outlet time, temperature, pressure, pH, mixing, salinity and using some additives to achieve maximum oil removing like surfactants, sorbent and adsorbents

1.1.2 The Aim of This Work is:

1- Pretreatment study to remove solid particles using sedimentation with and without flocculation

2- Study the effect of pH, pressure, temperature, salinity, operation time and outlet time and RPM on the recovery of oil percent to find the optimum conditions.

3- Investigate the effect of the surfactants (detergents and alcohol) to reduce surface tension.

4- Study the effect of addition of some adsorbents and sorbent materials like polypropylene, polyethylene, used plastic and sawdust.

CHAPTER TWO

LITERATURE SURVEY

2.1 Introduction

Interest in oil-water separation techniques is motivated in part by a need for treating oil polluted waste waters. Addition to PW, oil water emulsions are found in waste water effluent streams from many sources, including the discharge of petroleum refineries, rolling mills, chemical processing and manufacturing plants. Although there are many commercial devices being marketed for the removal of emulsified oil from water, a single, economical, and efficient method is still lacking techniques for separating emulsified oil from water includes chemical, physicochemical, mechanical, electrical, magnetic, biological, and thermal treatments [11].

The main objective in the mechanical method of water cleaning is to remove insoluble or solid contaminants from waste water by settling and filtration. Mechanical solid contaminants are separated by grids or fine filters depending on the size of the contaminant particles. Liquid contamination from crude oil or its products must be separated from the water in special reservoirs by settling. The mechanical cleaning allows the separation from industrial waste water up to 95% of contaminants. The principle in mechanical water cleaning by settling is separation with regard to density differences of the mixture constituents .The lightest constituents such as crude oil are collected at the top of the separating container and the heaviest at the bottom of the separator. The main idea in the chemical method of water cleaning is the addition of special chemicals that react with the contaminants to form insoluble heavy residues .These residues can be easily separated from the waste water by settling using the principles discussed for mechanical cleaning. Fine colloidal or soluble inorganic contaminants are removed from water by physical-chemical methods of waste water cleaning [11].

2.2 Interaction of Oil in PW (Emulsion).

Underground pressure and high temperature create complex emulsion between fluids droplets and interaction between phases that’s lead to describe some of emulsion kinds

2.2.1 Emulsions

Emulsions are colloidal dispersions in which a liquid is dispersed in a continuous liquid phase of different composition. The dispersed phase is sometimes referred to as the internal (disperse) phase and the continuous phase as the external phase. Practical emulsions may well contain droplets that exceed the classical size range limits, sometimes ranging upwards to tens or hundreds of micro-metres. In most emulsions, one of the liquids is aqueous while the other is hydro- carbon and referred to as oil. Two types of emulsion are readily distinguished in principle, depending upon which kind of liquid forms the continuous phase Figure 2.1 [9].

- Oil - in - water (O/W) for oil droplets dispersed in water.
- Water- in - oil (W/O) for water droplets dispersed in oil.

Practical situations are not always so simple and one may encounter double emulsions, that is, emulsions that are oil-in-water-in oil (O/W/O) and water-in-oil-in-water (W/O/W). For example, O/W/O denotes a double emulsion, containing oil droplets dispersed in aqueous droplets that are in turn dispersed in a continuous oil phase. The double emulsion droplets can be quite large (tens of mm) and can contain many tens of droplets of the ultimate internal phase. There can even be more complex emulsion types. Figures 2.1 to2.3 shows an example of crude oil W/O/W/O emulsion. The type of emulsion that is formed depends upon a number of factors. If the ratio of phase volumes is very large or very small then the phase having the smaller volume is frequently the dispersed phase, [9].

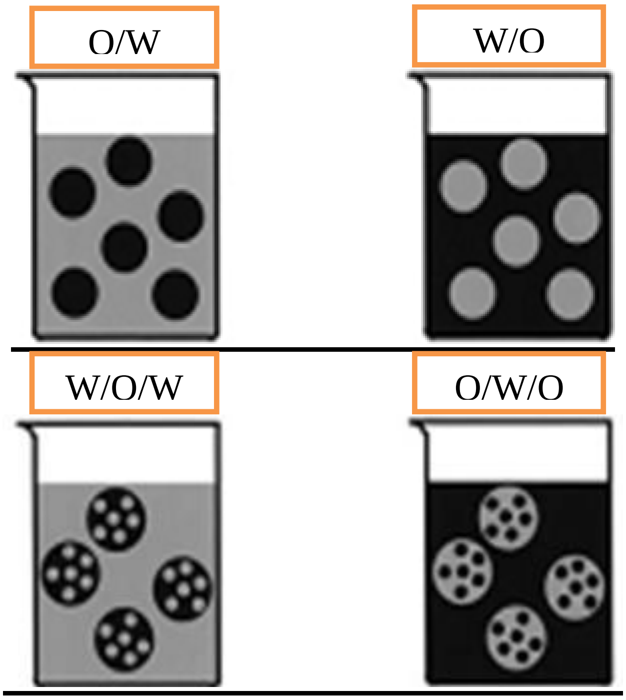


Figure2.1 Upper, emulsions, O/W and W/O .Lower, complex emulsion, W/O/W and O/W/O [9]

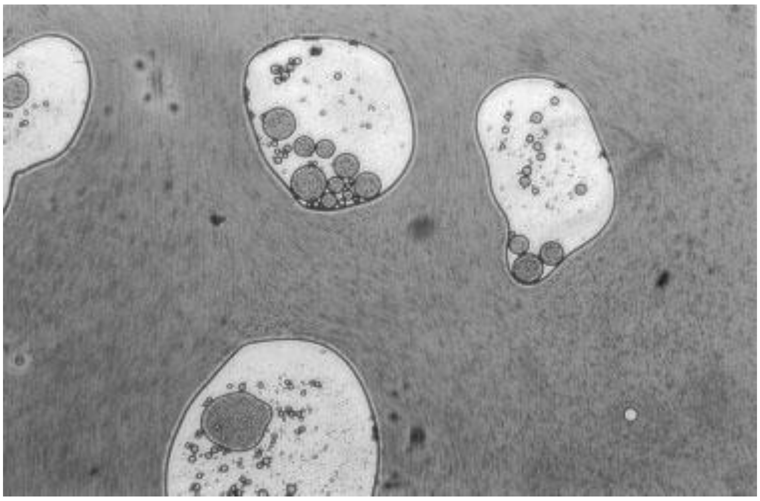


Figure 2.2 Photomicrograph of an emulsified droplet of a crude oil [9].

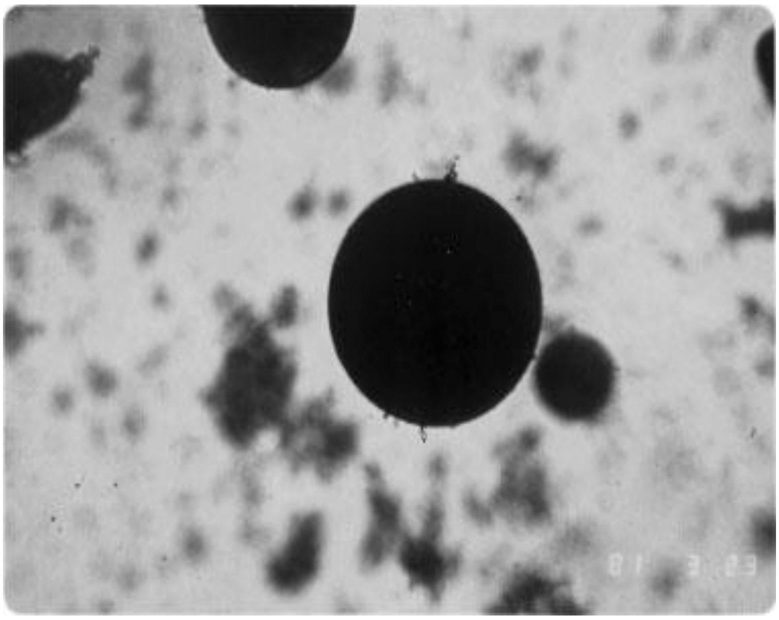


Figure 2.3 Water-in-oil-in- water-in-oil (W/O/W/O) emulsion [9].

Undesirable emulsions happen by product as in table 2.1 has list of some kinds which need suitable treatment for each type while in table 2.2 industrial create this kinds of emulsions to complete reaction or mixing [9].

Tables 2.1and 2.2 show some emulsions, foams, and suspensions in the petroleum industry (Undesirable and desirable emulsion kinds).include water (W), oil (O), gas (G), and solids (S) [9].

Table 2.1 Undesirable emulsion kinds [9].

Producing (well-head) emulsions	W/O	Fuel oil and jet fuel tank (truck) foams	G/O
Producing oil-well and well-head foams	G/O	Migrating fines in a reservoir	S/W
Fuel-oil emulsions	W/O	Dispersions of asphaltenes in crude oils	S/O
Oil-flotation process froth emulsions	W/O, O/W	Migrating fines during secondary and enhanced oil recovery	S/W
Oil-flotation process diluted froth emulsions	O/W/O	Producing (well-head) solids in conventional oil recovery	S/W, S/O
Oil-spill mousse emulsions	W/O	Oil-sands tailings ponds	S/W
Tanker bilge emulsions	O/W	Oil-field surface facility sludges	S/W, S/O
Distillation and fractionation tower foams	G/O	Produce water	O/W

Table 2.2 Desirable emulsion kinds [9].

Desirable Foam drilling fluid	G/W	Heavy-oil pipeline emulsions	O/W	Blocking and diverting foams	G/W
Foam fracturing and stimulation fluids	G/W	Well-stimulation emulsions	O/W, W/O	Gas-mobility control foams	G/W
Foam acidizing fluid	G/W	Oil and oil-sand flotation-process emulsions	O/W	Drilling fluid (mud) suspensions	S/W
Producing (well-bore) foams in cold, heavy-oil recovery	G/O	Emulsion drilling fluid: oil-emulsion mud	O/W	Well stimulation and hydraulic fracturing suspensions	S/W
Oil-flotation process froths	G/O	oil-based mud	W/O	Well cementing slurries	S/W
(70% heavy oil)	O/W	Asphalt emulsion	O/W	Oil-sand slurries in bitumen recovery	S/W
Transportation fuel emulsion (70% heavy oil)	O/W	Enhanced oil recovery in situ emulsions	O/W	Producing (well-head) solids in primary heavy oil recovery	S/W
Fire-fighting foam	G/W	Emulsion fuel emulsion Sludges	O/W, W/O		

2.2.2 Appearance and Emulsion Types

Not all emulsions exhibit the classical “milky” opaqueness with which they are usually associated. A tremendous range of appearances is possible, depending upon the droplet sizes and the difference in refractive indices between the phases. An emulsion can be transparent if either the refractive index of each phase is the same, or alternatively, if the dispersed phase is made up of droplets that are sufficiently small compared with the wavelength of the illuminating light. Thus an O/W micro- emulsion of even a crude oil in water may be transparent. If the droplets are of the order of 1 mm diameter a dilute O/W emulsion will take on a somewhat milky-blue cast; if the droplets are very much larger, the oil phase will become quite distinguishable and apparent. Physically the nature of the simple emulsion types can be determined by methods such as: [9].

2.2.2.1 Texture

The texture of an emulsion frequently reflects that of the external phase. Thus O/W emulsions usually feel “watery or creamy” while W/O emulsions feel “oily or greasy”. This distinction becomes less evident as the emulsion viscosity increases, so that a very viscous O/W emulsion may feel oily.

2.2.2.2 Mixing

An emulsion readily mixes with a liquid that is miscible with the continuous phase. Thus, milk (O/W) can be diluted with water while mayonnaise (W/O) can be diluted with oil. Usually, an emulsion that retains a uniform and milky appearance when greatly diluted is more stable than one that aggregates upon dilution

2.2.2.3 Dyeing

Emulsions are most readily and consistently colored by dyes soluble in the continuous phase e.g., methylene blue for water or fuschin for oil

2.2.2.4 Conductance

O/W emulsions usually have a very high specific conductance, like that of the aqueous phase itself, while W/O emulsions have a very low specific conductance.

2.2.2.5 Inversion

If an emulsion is very concentrated, it will probably invert when diluted with additional internal phase.

2.2.2.6 Fluorescence

If the oil phase fluoresces then fluorescence microscopy can be used to determine the emulsion type as long as the drop sizes are larger than the microscope’s limit of resolution (> 0.5 mm).

2.3 Pretreatments Steps for PW

There are many chemical and physical processes carry out on PW to prepare it for main conventional treatments methods as bellow:

2.3.1 Flocculation.

Flocculation is a process of aggregation and attrition. Aggregation can occur by Brownian diffusion, differential settling, and velocity gradients caused by fluid shear, namely flocculation. Attrition is caused mainly by excessive velocity gradients. The theory of flocculation detailed in recognizes the role of velocity gradient (G_v) and time (t) as well as particle volumetric concentration Φ. For dilute suspension, shape factor value is difficult to determine for flocculate particles because their size and shape are interlinked with the mechanics of their formation and disruption in any set of flow conditions .When particles flocculate, a loose and irregular structure is formed, which is likely to have a relatively large value shape factor, Additionally while the effective particle size increases in flocculation [12], [38].

2.3.2 Coagulation

It is a process for increasing the tendency of small particles in an aqueous suspension to attach to one another and to attach to surfaces such as the grains in a filter bed .It is also used to effect the removal of certain soluble materials by adsorption or precipitation .The coagulation process typically includes promoting the interaction of particles to form larger aggregates [38].

2.3.3 Settling

Removed particles from liquids by gravity called settling, there are many types of settling:

2.3.3.1 Types of Settling

Type 1 .Settling of discrete particles in low concentration, with flocculation and other inter particle effects being negligible.

Type 2 Settling of particles in low concentration but with coalescence or flocculation .As coalescence occurs, particle masses increase and particles settle more rapidly.

Type 3 Hindered, or zone, settling in which particle concentration causes inter- particle effects, which might include flocculation, to the extent that the rate of settling is a function of solids concentration.

Type 4 Compression settling or subsidence develops under the layers of zone settling. The rate of compression is dependent on time and the force caused by the weight of solids above [38].

2.3.3.2 Terminal Settling Velocity

When the concentration of particles is small, each particle settles discretely, as if it were alone, unhindered by the presence of other particles. Starting from rest, the velocity of a single particle settling under gravity in a liquid will increase, where the density of the particle is greater than the density of the liquid. Acceleration continues until the resistance to flow through the liquid, or drag, equals the effective weight of the particle. Thereafter, the settling velocity remains essentially constant. This velocity is called the terminal settling velocity (V_t). The terminal settling velocity depends on various factors relating to the particle and the liquid. For most theoretical and practical computations of settling velocities, the shape of particles is assumed to be spherical .The size of particles that are not spherical can be expressed in terms of a sphere of equivalent volume [38].

Region (a) Figure 2.4: 10−4 < Re < 0.2. In this region of small Re value, the laminar flow region, the equation of the relationship approximates to

Stokes' equation for laminar flow:

$$V_t = \left[g\,(\rho_p - \rho)\, d^2 / \; 18\, \mu \right]$$

Region (b) Figure2.4: 0.2 < Re < 500 to 1000. This transition zone is the most difficult to represent.

Region (c) Figure2.4: 500 to 1000 <Re <2 ×105. In this region of turbulent flow, the value of C_D is almost constant at 0.44.

Region (d) Figure 2.4: Re > 2 × 105. The drag force decreases considerably with the development of turbulent flow at the surface of the particle called boundary-layer turbulence, such that the value of C_D becomes equal to 0.1. This region is unlikely to be encountered in sedimentation in water treatment [38].

Figure 2.4 shows the regions of settling

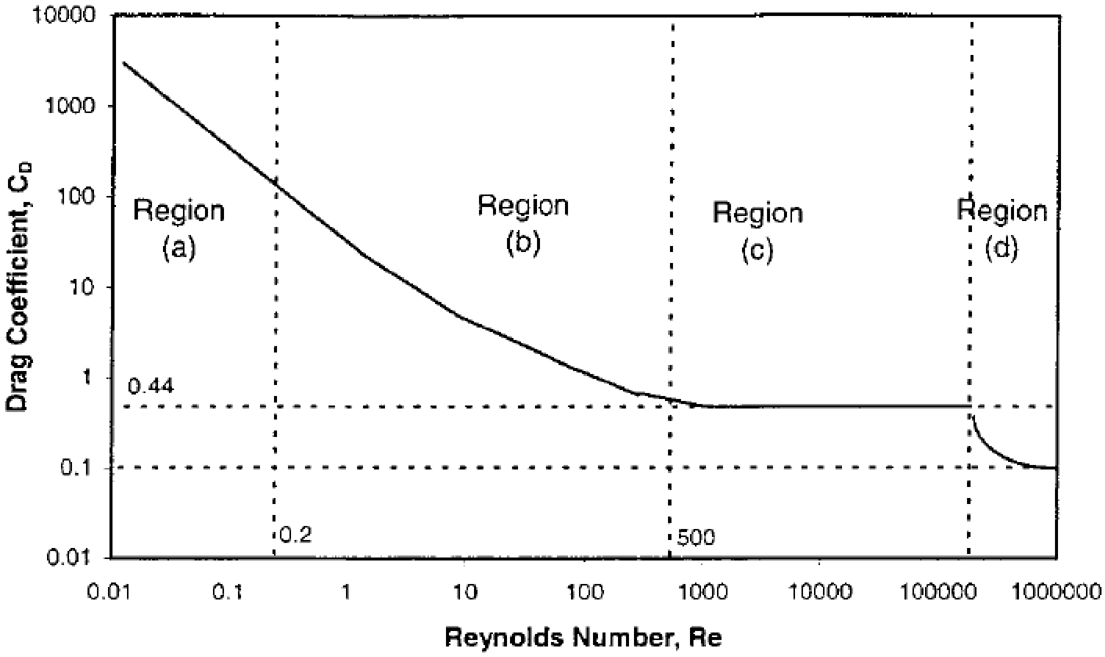


Figure 2.4 Variation of drag coefficient C_D with Reynolds number, Re, for single particle sedimentation [38].

2.3.3.3 Mechanism of Settling with and without Flocculation

The purpose of the flocculation process is to promote the interaction of particles and form aggregates that can be efficiently removed in subsequent separation processes such as sedimentation, flotation, and coarse bed filtration. For efficient flocculation to occur, the suspension must be destabilized. This is usually accomplished by the addition of a coagulant. transport mechanisms .A number of mechanisms can cause relative motion and collisions between particles in a destabilized suspension, including Brownian motion, velocity gradients in laminar flow, unequal settling velocities, and turbulent diffusion figure 2.4 [12], [38].

Small particles suspended in a fluid move about in a random way due to continuous bombardment by the surrounding water molecules. The intensity of this motion is a function of the thermal energy of the fluid, k_BT, where k_B is Boltzmann’s constant and T is the absolute temperature. The process is called Brownian diffusion, and the particle interaction it causes is Brownian, or Perikinetic, flocculation [38], [12].

Particle of TSS sedimentation with and without flocculent explain by figure 2.5.

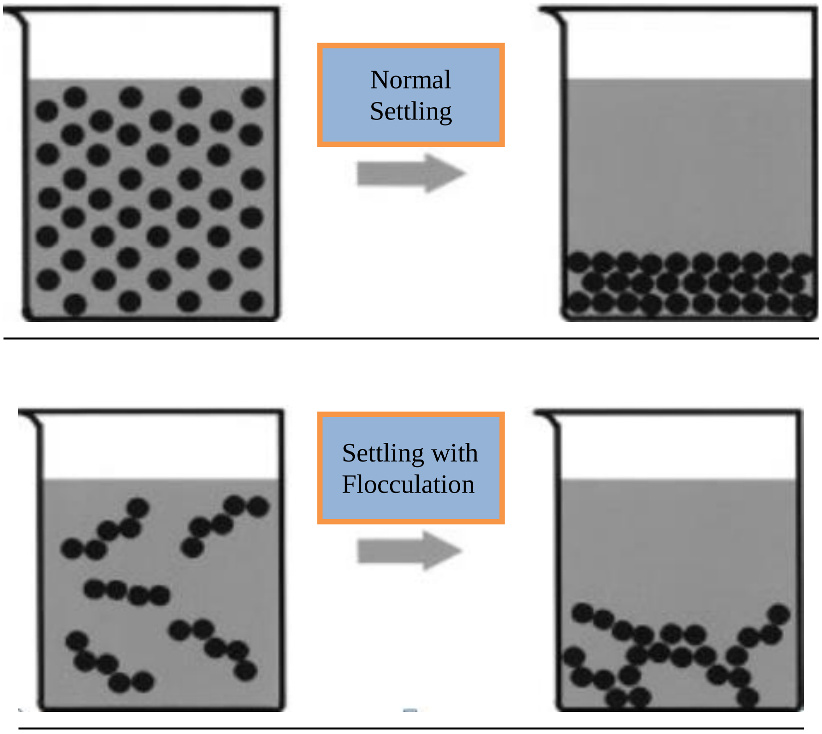


Figure 2.5 Mechanism of particle settling with and without flocculation [9].

2.4 Additives:

To improve oil treatments there are some additives to increase separation some kinds are added as solid sorbents materials, other additives are liquids such as surfactants.

2.4.1 Sorbents Additives

To increase separation efficiency, some companies added sorbents materials depending on its appearance as hydrophobic high intensity to attraction the oil and high wettability to the water, there are many types of sorbents depending on its base as bellow:

1. Organic Sorbent Materials: Bark, beat, paper, sawdust, pulp, chicken feathers, cork, wool ,straw ,human hair, woven or non-woven cotton, wool, kenaf, activated carbon, reed canary ,grass, flax, hemp fibre, salvinia, wood chip, rice husk, coconut husk and bagasse.

2. Inorganic Sorbent Materials: Vermiculite and pumice

3. Synthetic Sorbent Materials: Primarily, polyethylene, polypropylene, nomex, polyethylene terephthalate, teflon and poly (vinyl chloride), various rubbers including natural rubber, poly isoprene, and polymers derived from butadiene, polyurethanes, polyamide (nylon) and polycarbonates. Silicone polymers surrounded by minerals such as zinc oxide, for example zinc oxide nano-rods that are super hydrophobic and the like coated by thereon such as various silanes , 3aminopropyltriethoxysilane (APTS), 2carboxymethylthio, ethyl tri methyl silane, heptadecafluoro-1,1,2,3-tetrahydrodecyl and trichlorosilane. Glirman[42], [44], [39].

2.4.1.1 Wettability of Solid Additives

Wettability defined as ability of any solid surface to be wetted when in contact with a liquid; that is, the surface tension of the liquid is reduced so that the liquid spreads over the surface [31].

The wettability of an immiscible liquid e.g. emulsion such as water in a continuous phase liquid such as oil utilizing a filter that has significant influence on the water removal efficiency .Wettability is an important parameter in designing such filter media. The wettability of the filter media is mainly governed by surface properties of fiber material and porosity of filter. The surface properties of filter can be expressed in terms of hydrophilic or hydrophobic nature of the filter. The wettability of the filter can be characterized using the concept of lipophilic to hydrophilic ratio (L/H) by using a modified Washburn equation that is based on capillary rise phenomena. Oil and water are used as reference liquids in the wettability characterization. In liquid-liquid coalescence filtration, separation efficiency depends on various factors including face velocity, fiber structures, fiber geometry, fiber orientations, also wettability of filter especially when interfacial tension between liquid phases is low. The hydrophilic and hydrophobic fibers used in the filter capture the immiscible liquid and form drops on the hydrophilic material that stay on the fiber surface for extended periods of time. Fibers having varying hydrophilic and hydrophobic properties can be mixed into filter media, so that the hydrophobic fibers will aid in drop migration towards the hydrophilic fibers and the formation of large drops on the hydrophilic surface. Large drops are desired for coalescence and drainage [50], [41].

2.4.2 Surfactants

Surfactants have amphiphilic structures consisting of a hydrophilic and a hydrophobic part. These special structures cause their surface-active properties like concentration at surfaces, reduction of the surface tension, and formation of micelles in bulk solution. Therefore, they are widely used in formulations for washing, wetting, emulsifying, and dispersing .Laundry detergents, cleaning agents, and personal care products are by far the largest class of surfactant-containing products for domestic use. After use they are mainly discharged into municipal wastewaters, which enter sewage treatment plants [48].The surfactants types as below:

2.4.2.1 Anionic Surfactants.

Anionic Surfactant A surfactant molecule that can dissociate to yield a surfactant ion whose polar group is negatively charged foaming agent (surfactant), Laurier L, 2005[9]. The hydrophilic groups of anionic surfactants consist in most cases of sulfonate , sulfate, or carboxyl groups. Amongst them, LAS (linear alkylbenzene sulfonates) are produced in the largest quantities worldwide. They are mainly used in powdery and liquid laundry detergents and household cleaners [48].

2.4.2.2 Non-ionic Surfactants.

The hydrophilic behavior of nonionic surfactants is caused either by polymerized glycol ether or glucose units. They are almost exclusively synthesized by the addition of ethylene oxide or propylene oxide to alkyl phenols (AP), fatty alcohols, fatty acids, or fatty acid amides. Major applications of nonionic surfactants are found in the following: detergents, emulsifiers, wetting agents, and dispersing agents. They are used in many sectors, including household, industrial and institutional cleaning products, textile processing, pulp and paper processing, emulsion polymerization, paints, coatings, and agrochemicals [48].

2.4.2.3 Cationic Surfactants.

Cationic surfactants contain quaternary ammonium ions as their hydrophilic parts. This class of surfactants has gained importance because of its bacteriostatic properties [48].

2.5 Adsorption.

Adsorption processes use a solid material (adsorbent) possessing a large surface area and the ability to selectively adsorb a gas or a liquid on its surface. Adsorption processes are also used to separate liquid mixtures [28]. Also adsorption of a substance involves its accumulation at the interface between two phases, such as a liquid and a solid or a gas and a solid. The molecule that accumulates, or adsorbs, at the interface is called an adsorbate, and the solid on which adsorption occurs is the adsorbent. Adsorbents of interest in water treatment include activated carbon; ion exchange resins; adsorbent resins; metal oxides, hydroxides, and carbonates; activated alumina; clays; and other solids that are suspended in or in contact with water. Adsorption plays an important role in the improvement of water quality. Activated carbon, for example, can be used to adsorb specific organic molecules that cause taste and odor, mutagenicity, and toxicity, as well as natural organic matter (NOM) that causes color and that can react with chlorine to form disinfection by-products (DBPs). NOM is a complex mixture of compounds such as fulvic and humic acids, hydrophilic acids and carbohydrates .The aluminum hydroxide and ferric hydroxide solids that form during coagulation will also adsorb NOM. Adsorption of NOM on anion exchange resins may reduce their capacity for anions, but ion exchange resins and adsorbent resins are available that can be used for efficient removal of selected organic compounds. Calcium carbonate and magnesium hydroxide solids formed in the lime softening process have some adsorption capacity, and pesticides adsorbed on clay particles can be removed by coagulation [38]. Surface interaction of adsorption at a surface is the result of binding forces between the individual atoms, ions, or molecules of an adsorbate and the surface. These forces originated from electromagnetic interactions. Ion exchanges, physical, chemical and specific are the four major types of adsorption. Ion exchange adsorption is electrostatic attachment of ionic species to sites of opposite charge at the surface of an adsorbent. Physical adsorption results from the action of Van Der Waals force. Chemical adsorption involves a reaction between an adsorbate and an adsorbent resulting in a change in the chemical form of the adsorbate. The chemiosorptive bond is usually stronger than that derived from the physical Van Der Waals forces. When attachment of adsorbate molecules at functional groups adsorbent surfaces result from specific interactions which do not result in adsorbate transformation is designated as specific adsorption. Adsorption from emulsion onto a solid can take place as a result of one or both of two characteristic properties for a given solvent adsorbate-adsorbent system. Solvophobic or lyphobic character or a particular affinity of the adsorbate for the surface of the adsorbent of the adsorbate is the primary driving force. Adsorbate and adsorbent properties have a great impact on the adsorption process [33], [30].

2.6 Coalesce

Coalesce is a process of collect small droplets size to beggar then the removal would be easiest.

Several new technologies that are available and emerging into the mainstream PWT industry called pre-coalesce. These are often included in pipe or treatment processes upstream of gravity type or centrifugal separation technologies and operate by increasing the overall oil droplet size. Increase sizing makes it easier to remove oil in a subsequent downstream process. These devices are usually composed of numerous fine polyethylene strands packed in close proximity to each other. The strands provide high surface area contact within the flowing PW and attract small oil particles and aid in their coalescence until they are too large to be held by the media. The Performance Enhanced Coalescence Technology (PECT) is one of these application method .The first commercialized technology is the (PECT-F) denoting a Fiber based coalesce concept. PECT-F developed to achieve a significant improvement in separation efficiency of PW. The PECT-F is a media based coalesce which is installed as a cartridge assembly into either the inlet chamber of the vessel or into a bespoke vessel located upstream of the PWT system, the vessel has residence time constructively to achieve partial oil droplet coalescence to capture and grow droplets from size that would not be separated to the size can be separated [19].

2.7 Produced Water Management.

Decision making of managing purpose should take before treating to choose one of these PW management requests [15].

- Avoid production of water onto the surface: Using polymer gels that block water contributing fissures or fractures or downhole water

Separators which separate water from oil or gas streams downhole and re-inject it into suitable formations. This option eliminates waste water and is one of the more elegant solutions, but is not always possible.

- Inject produced water: Inject the produced water into the same formation or another suitable formation; involves transportation of produced water from the producing to the injection site. Treatment of the injectate to reduce fouling and scaling agents and bacteria might be necessary. While waste water is generated in this option, the waste is emplaced back underground.
- Discharge produced water: Treat the produced water to meet onshore or offshore discharge regulations. In some cases the treatment of produced water might not be necessary.
- Reuse in oil and gas operations: Treat the produced water to meet the quality required to use it for drilling, stimulation, and workover operations.
- Consume in beneficial use: In some cases, significant treatment of produced water is required to meet the quality required for beneficial uses such as irrigation, rangeland restoration, cattle and animal consumption, and drinking water for private use or in public water systems.

PW must be cleaned before discharge to sea. Often this water contains sand particles bound to the oil/water emulsion. The environmental regulations in most countries are quite strict, as an example, in the North-East Atlantic the OSPAR **(**Oil Spill Prevention, Administration and Response Fund) convention limits oil in water discharged to sea to 40 mg/liter (ppm). It also places limits other forms of contaminants. This still means up to one barrel of oil per day for the above production, but in this form, the microscopic oil drops are broken down fast by natural bacteria. Finally the water is collected in the water de-gassing drum. Dispersed gas will slowly rise to the surface and pull remaining oil droplets to the surface by flotation. The surface oil film is drained, and the produced water can be discharged to sea. Recovered oil in the water treatment system is typically recycled to the third stage separator [24].

2.8 The General Objectives for Operators When Plan Produced Water Treatment: [15].

1. De-oiling: Removal of free and dispersed oil and grease present in produced water.

2. Soluble organics removal: Removal of dissolved organics.

3. Disinfection: Removal of bacteria, microorganisms, algae, etc.

4. Suspended solids removal: Removal of suspended particles, sand, turbidity, etc.

5. Dissolved gas removal: Removal of light hydrocarbon gases, carbon dioxide, hydrogen sulfide, etc.

6. Desalination or demineralization: Removal of dissolved salts, sulfates, nitrates, contaminants, scaling agents, etc.

7. Softening – Removal of excess water hardness.

8. Sodium Adsorption Ratio (SAR) adjustment: Addition of calcium or magnesium ions into the produced water to adjust sodicity levels prior to irrigation.

9. Miscellaneous: Naturally occurring radioactive materials (NORM) removal

2.9 Conventional Methods of Produced Water Treatment:

For more than 50 years ago, the oil companies searching solutions to solve the PW pollutions and convert it to benefit product, until now couldn’t reach the perfect method because of complex component in PW and huge amount, there important conventional treatments for PW as bellow:

2.9.1 Flotation

Flotation is a process used to separate solid or liquid particles from a liquid phase by gravity, perhaps aided by coagulation, flocculation or dissolved air. A dissolved soluble or emulsified chemical or a fat, oil, or grease that is of lower specific gravity than water must be chemically converted to a filterable chemical, or it must have its emulsion broken before flotation [12]. Flotation is a process in which fine gas bubbles are used to separate small, suspended particles that are difficult to separate by settling or sedimentation .Gas is injected into the water to be treated and particulates and oil droplets suspended in the water are attached to the air bubbles and they both rise to the surface. As a result, foam develops on the surface, which is commonly removed by skimming [16].The types of floatation systems; dissolved air floatation and induced gas floatation, Micro-Bubble Flotation and Adsorption flotation.

2.9.1.1 Dissolved –Air Floatation.

Gas floatation units use air/gas to float out oil more rapidly from the produced water. The density of oil particles reduce as they attach to gas bubbles. Reduced density improves the speed of oil floatation to the surface. The oil lumps on the surface are skimmed off.

There are two dissolved air floatation are use an air compressor to inject and dissolve air into the produced water steam [18].

2.9.1.2 Induced Gas Floatation.

Creates fine gas bubbles through mechanical, hydraulic or sparging systems .The induced gas bubbles adhere to the oil droplets as they move upward to the surface. It provides high oil removal efficiency at larger throughput or lesser retention time for a given rate. Efficient performance is limited to oil droplet size of greater than 25 microns .To achieve higher efficiency if smaller droplets are present, flocculants and coagulants are added to improve the performance [20].

2.9.1.3 Micro-Bubble Flotation.

MBF is a proven technology that is used to create micron sized gas bubbles in liquids for various purposes. The application of MBF in the oil patch is very similar to the application of induced gas flotation (IGF), systems also in the oil patch. The principles of this application involve tiny gas bubbles that adhere to oil droplets and solids in produced water and help float them to the surface. A major difference between induced gas flotation and micro bubble flotation exists in the size of the gas bubbles in the liquid. MBF uses bubbles that are 5-50 microns (10 micron nominal) in diameter. These smaller bubbles, approximately one trillion per cubic foot, allow for a greater total number of bubbles and this creates a higher probability for oil droplets to contact the more buoyant gas bubbles. The smaller bubbles also provide a larger total surface area for attachment and surface tension of the bubble and oil droplet; thereby, attaching to more droplets of oil for a longer period of time as the bubbles are rising and coalescing within the water column. Another significant difference between MBF and IGF is that the MBF technology does not require new vessels or piping arrangements. Instead the MBF technology can be applied directly to the skim tank allowing flotation to be enhanced at the point that was already engineered for water de-oiling and oil skimming [35], [20], [39].

2.9.1.4 Adsorption Flotation.

This process involves the addition of powder activated carbon to the flotation unit where the added powdered carbon adsorbs the oily and dissolved pollutants in waste water. The spent carbon, as well as other suspended pollutants in the flotation unit, become attached to rising bubbles, and eventually are removed from the overhead of the flotation unit [22]. Adsorption can be accomplished using a variety of materials, including zeolites, organoclays, activated alumina, and activated carbon. Chemicals are not required for normal operation of adsorptive processes. Chemicals may be used to regenerate media when all active sites are occupied [10].

2.9.2 Corrugated Plate Interceptor.

Corrugated plates are packed to enhance the performance of gravity separation tanks. The oil droplets coalesce and form larger oil droplets as the corrugated plates provide a longer path for the oil droplets to travel to the top of the tank. It is a simple operation that allows the compact design of the API separation tank; however the efficient oil removal limits the oil droplet size of 40 microns and larger. Removal of smaller oil droplets is difficult with corrugated plate separator [20].

2.9.3 Hydro-cyclone.

Hydro-cyclone is use to separate solids from liquids based on the density of the materials to be separated. Normally have a cylindrical section at the top where the liquid is fed tangentially and a conical base. The angle of the conical section determines the performance and separating capability of the hydro-cyclone. It can be made from metal, plastic or ceramic and have no moving parts. It has two exits, one at the bottom, called the underflow or reject for the more dense fraction and one, called the overflow or product at the top for the less dense fraction of the original stream P.J.R. K. Wagner,1986[34]. It can also provide significant saving in weight, space, and power usage and particularly effective where system operating pressure is high. If system pressure is low, booster pumps are required to increase the operating pressure for the hydro-cyclone. This however induces a shearing action on the oil droplets and will reduce overall system efficiency and requires relatively high and constant flow rates. If flow rate is low or variable, a recycle flow stream throw a surge tank can be added [19].

2.9.4 Membrane Hydrophilic Filtration (MHF)

Ceramic membranes are capable of removing particulates, organic matter, oil and grease, and metal oxides. Ceramic membranes alone cannot remove dissolved ions and dissolved organics. Pre-coagulation, injection of a chemical coagulant upstream from the membrane, improves removal efficiencies of dissolved organic carbon and smaller particulates. As with conventional ultrafiltration and microfiltration, a strainer or cartridge filter is necessary as pretreatment for ceramic membranes Polymeric MF/UF membranes are made from materials like polyacrylonitrile (PAN) and polyvinylidene (PVDF). Because there is a large market for polymeric ultrafiltration membranes, there are many vendors and suppliers for these membranes. They are also relatively inexpensive. Typically, package systems are purchased and installed by the vendor. An important consideration for polymeric MF/UF membranes is integrity testing to ensure that the membrane is not damaged and is operating properly. Typically, the filtrate turbidity is monitored to give a rough indication of membrane integrity. Membrane integrity can be tested through a pressure decay test. In this test, pressurized air is applied to the membranes at a pressure less than would cause the air to flow through the membrane, and the pressure decay is measured. Membrane filtration can be used in a variety of applications for the treatment of wastewater. Membrane filtration represents a treatment technology that is capable of separation not possible in classic wastewater treatment. This use of membrane filtration technology is especially common in areas where clean water is scarce, such as in dry, arid climates, especially for removing salt from seawater. In biological treatment processes, membrane filtration can be used as a tertiary filtration process following secondary clarification. It can also be used in a variety of physical/chemical treatment systems such as oil removal, organics removal, heavy metals removal, and process water reuse [12], [43]

2.9.4.1 Reverse Osmosis.

Reverse osmosis is a membrane separation process, which, through the application of pressure, reverses the natural phenomenon of osmosis. Osmosis is the flow of water from an area of low ionic concentration to an area of high ionic concentration. Under an applied pressure, water is forced through a semi-permeable membrane from an area of high concentration to that of low concentration. The semi-permeable membrane rejects the solutes and suspended matter in the water while allowing the clean water to pass through. The effective pore sizes of reverse osmosis membranes are typically on the order of 2 to 5 angstroms. This pore size allows the passage of only molecular water. System should have an SDI (silt density index) of less than 3.5 to protect the membrane from fouling [12].

2.9.4 2 Nano-filtration (NF).

NF uses membranes that have a larger effective pore size than reverse osmosis membranes. This results in lower dissolved solids rejection rates or if the pores are large enough, a complete passage of dissolved ions through the membrane. The osmotic pressure difference across the membrane will be lower or may be zero [12].

2.9.4 .3 Ultrafiltration.

Ultrafiltration (UF) uses membranes that have effective pore sizes several orders of magnitude larger than reverse osmosis. UF units are capable of separating large molecular weight organics from wastewater. UF units can also be used as a pretreatment option for nano-filtration or reverse osmosis. In the case of food processing, UF units can be used to separate proteins and carbohydrates from the wastewater. The proteins and carbohydrates may then be reused in the process or sold as a by-product. Another use of UF units is the separation of emulsified fats, oils, and grease from wastewater [12].

2.9.4 .4 Microfiltration. (MF)

Uses micro-porous membrane that have effective pore sizes much larger than UF membrane. Flow through a micro-porous membrane can occur without the application of pressure on the feed side of the membrane, but in most wastewater applications, a small pressure difference across the membrane produces significant increases in flow. Microfiltration is most often used to separate suspended and colloidal solids from wastewater [12].

The choose of process according the ranges of membranes as shown in table 2.3

Table 2.3 Membrane pore sizes [12]

Membrane type	Minimum pore size (nm)	Maximum pore size (nm)
Microfiltration	200	10000
Ultrafiltration	1	20
Nano filtration	0.5	2
Reverse Osmosis	0.1	1

2.10 Polymer Filters

George et al, 2010 [50]carry out chain experiments in his claim on filter contain hydrophobic utilized fibers, inert, such as [polyethylene, polypropylene, nomex, polyester such as polyethylene terephthalate, halogen-containing polymers such as Teflon and poly (vinyl chloride), various rubbers including natural rubber, poly isoprene, and polymers derived from butadiene, polyurethanes, polycarbonates, silicone polymers surrounded by minerals such as zinc oxide, for example zinc oxide nano-rods that are super hydrophobic, and the like coated by thereon such as various silanes such as (3-aminopropyltriethoxysilane) APTS, (2carboxymethylthio) ethyl tri methyl silane) CES, and (heptadecafluoro-1,1,2,3-tetrahydrodecyl), trichlorosilane. Fibers having hydrophilic and hydrophobic properties are mixed, layered, etc., and formed into a filter. The separation mechanism involves capture of small droplets of the immiscible phase, coalescence of the small droplets into larger droplets as the immiscible liquid flows through the fiber filter, and release of the large immiscible droplets from the filter. With respect to separation of a hydrophilic immiscible fluid such as water in a lipophilic continuous fluid such as oil, the hydrophobic fibers will cause small water droplets to migrate towards the hydrophilic fibers whereby large droplets are formed on hydrophilic surface. The large droplets stay on hydrophilic fiber surface for extended periods of time and continue to coalescence until they are so large that they can no longer be maintained by the hydrophilic fibers and are released and drained off of the filter. In designing such filter, wettability of the filter media is an important parameter. The filter media can be designed by mixing hydrophilic and hydrophobic fibers in various proportions to achieve an optimum wettability range for separation of the immiscible liquid

Scott, 2006[47] studied three commercial membranes, JW, 5k and BN, for the pretreatment of produced water. The study conducted showed that PVDF ultrafiltration membranes could provide treatment to less than 5 NTU for subsequent desalination for an onsite produced water treatment system. The results showed that the turbidity removal ranges for JW, 5k, and BN ultrafiltration membranes were 99.27% to 99.87%, 95.75% to 99.82%, and 99.71% to 99.82%, respectively. The study showed that the oil removal ranged for JW, 5k, and BN ultrafiltration membranes were 59.52% to 90.43%, 47.32% to 87.27%, and 78.20% to 94.31%, respectively

J. Fraser, 1996[37] compared filter Twenty-five polymeric (organic) and eight inorganic membranes, the tested referred that after six hours the polymeric membranes had been lesser extent with decreasing pore size, while Inorganic membrane an opposite effect in that large pore size had tendency for increasing flux rates .It was noted a pH adjustment pretreatment evaluated for control of membranes fouling. The results demonstrated that increased flux rates were realized at pH=5 and pH=11 for all organic membranes.

2.11 Studies Effects of Variables and Conditions the %Oil Recovery.

2.11.1 Effect of Pressure

Scott, 2006[47]suggested to help achieve the goal is to design the treatment system in stages with increasing water quality or separation requirements as you progress through the treatment train. Two of the major contaminants that need to be removed from oilfield brine to meet water quality standards are suspended and dissolved oil and grease and suspended solids. Removal of dissolved solids has been commercially available for seawater and utilize well characterized technologies like reverse osmosis and multistage flash evaporation .An operational pressure of about 30 psi or 207 kilopascals (kPa) .This pressure indicated three factor levels of 20, 30, and 40 psi (corresponding to 138, 207, and 276kPa) for the factorial design The results showed that increasing pressure yielded higher fluxes than doubling the flow rate provided.

2.11.2 Effect of Salinity

Huishu Li, 2013[49]connected the relation between pH and TDS with ground layer depth .The plot refers that both pH and TDS decrease with depth increasing which will change characteristic of produce water appearances and referred that Constituents of produced water vary a lot depending on a number of factors, including geographic locations, characteristics of formations (i.e. the depth of formation, porosity and permeability of formation rocks/sands, water content) and injected fracturing fluid The main objective which was study to statistically evaluate the produced water quality and to provide an assessment on the spatial distribution of specific groundwater quality parameters.

Abouther, 2003[18] investigated the effect of salinity on percent oil removal. The results explained that the removal percent increases with increase in the salinity

2.11.3 Effect of Temperature

Abouther, 2003[18] tested the net effect of temperature on the removal percent the results showed that improvement in oil recovery with increasing temperature

J. Fraser, 1996, [37] checked influence of high temperatures ranges65to 80°C on both types of inorganic and polymeric membranes the tests didn’t mention to significant temperature influence, so the effect was neglected.

2.11.4 Effect of pH

The pH of a wastewater is very important in selecting membrane material. Certain membrane material is not resistant to wide pH ranges, therefore; a misapplication of membrane material may cause corrosion resulting in failure of the membrane unit. Another reason for the importance of knowing the pH of a wastewater prior to system design is that several chemical reactions that form precipitates are pH dependent. If precipitates are formed in the membrane unit, scaling will form and reduce the life of the membrane [12].

Scott, 2006[47] thought that the pH of the produced water feed was monitored throughout the duration of the experiment for any major change.

Rafique et al, 2013[23].claim in his invent that raise of pH in produce water treatment will increase silica solubility in PW and breaks emulsions of oil in water.

Others, like Mareth, 2006[45].agreed with Rafique, that pH adjustment may be the simplest option for plants with high silica or $Ca(CO)_3$ scaling potential, the Reducing pH decreases silica solubility, but increases $Ca\ (CO)_3$ solubility.

2.12 Studies Enhancement Treatments by Chemicals Additions.

Jixiang et al, 2013[46]was added four kinds of agents (SL-2, 1227, PAC and HEDP),the investigation results showed that increasing of SL2 and 1227 decreased interfacial tension of oil-water emulsion means they were higher interfacial activity then others

Abdolhamid et al, 2009[17] applied ultrafiltration (UF) on produced water treatment with two filters types a poly sulfone (PS) and a poly acrylonitrile (PAN) effects of. The optimum operating conditions of the UF process were found as following trans membrane pressure (TMP), (3 bar), cross flow velocity CFV (1 m/s), operating temperature (40°C) and pH=9. The PAN membrane showed higher rejection.

Sonia, 2006[32]studied the efficacy of using organoclay to remove oil by measuring its adsorption capacity to remove the oil and to investigate how closely the experimentally obtained data matches the kinetic model, also suggested, that conventional adsorbent such as GAC (Granular Activated Carbon), be investigated to determine if there is any further improvement in the adsorption capacity.

Jing Zhong et al, 2003[21] treated the PW using Micro-filtration method with flocculation used polymer flocculent polyacrylamide, Poly1, 3530S which is derivative of polyacrylamide, Al_2 (SO_4).18H_2O, $FeSO_4$. 7H_2O and FeC_{12}.H_2O) as pretreatment, laboratory tests explained that the removed oil concentration increased with flocculation more than without flocculation’s pretreatment, 3530S gave highest removing among other flocculants.

Abouther, 2003[18]compared among three types of straight chain alcohols; ethanol, propanol and hexanol with different concentrations 0.025-0.5 vol. % The addition of alcohols to the oil-water emulsion causes a reduction in surface tension of the solution. Results showed that the removal percent increased with the increase in alcohols concentrations; on the other hand, the removal percent increased with the increase their chain length.

Shah, 1982[26] mentioned that the reduction in surface tension reduce the energy required to form the bubble.

E. Dahlqvist et al, 1990[40]investigate the influence of surfactant on coalescence filtration, the study showed that the efficiency of filter are affected by different filter structure surface coating, additions surfactants and mention that considering complete filter performance film are the elasticity and viscosity are of major importance, compared to other properties.

Table2.4 Some researchers, years and methods, which studied in this thesis

step	Researcher name	Treatment method	year	Native	Type of research
1	Huishu Li	PW appearances	2013	USA	thesis
2	Jixiang et al,	Flocculation/ adsorption	2013	China	report
3	Rafique et al,	hydrocyclone	2013	USA	patent
4	George et al,	UF	2010	USA	patent
5	Abdolhamid et al,2009	Coalescence Filtration	2009	Iran	report
6	Sonia	Adsorption GAC	2006	USA	thesis
7	Mareth	RO	2006	USA	thesis
8	Douglas W.Lee	MBF	2004	USA	Technical Paper
9	Jing Zh. et al,	Flocculation	2003	China	report
10	Abouther	DAF	2003	Iraq	thesis
11	J. Fraser	MF	1996	USA	report
12	E.Dahlqvist et al,	Coalescence Filtration	1990	Sweden	report

Certificate

We certify, as an examining committee, that we have read this thesis entitled **"Oily Water Treatments for Southern Iraqi Oil Fields"**, examined the student **Aqeel Sheikha Arafat** in its content and found it meets the standard of thesis for the degree of Master of Science in Chemical Engineering.

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CHAPTER FOUR

RESULTS & DISCUSSION

4.1 Study the Settling With and Without Flocculation.

The effect of sedimentation time on the percent of sediment removed is shown in figure 4.1, its clear from this figure that after an hour a 65% of solid particle was removed. A Physical separation by absorbed water layers predominate over the natural aggregating forces (Van Der Waals) and the natural mechanism (Brownian movement) tends to cause particle contact which is lead to increased the settling rate . During the first hour, the heavy particles settle to the bottom after that the settling rate was practically a straight line [27].

The plot started to inclined because rate of sedimentation slightly decrease as aresult of heavy particles sit in the bottom and light particles take time to fill down depending on gravity force .

To increase the settling velocity, flocculants was added to increase the size of particles in order to enhance particle aggregation which lead to faster or more effective settling [27]. Also figure 4.1 shows the effects of fluc douseg on the percent of sediment removed. Refer to this figure one cas see that the rate of settling increase with increase the dose of flocculant, the 400 ppm of PAA reduce the settling time to half while 500 ppm give 100% of settling in 45 minute because the flocculation results have close relation with flocculation conditions, such as, dosage of flocculant, stirring time, holding time after stirring, flocculation temperature, on the other hand the better performance of polymer flocculants is due to its long chain bridged between and/or absorbed the particles and emulsified oil in wastewater, then increase their sedimentation rate [21].

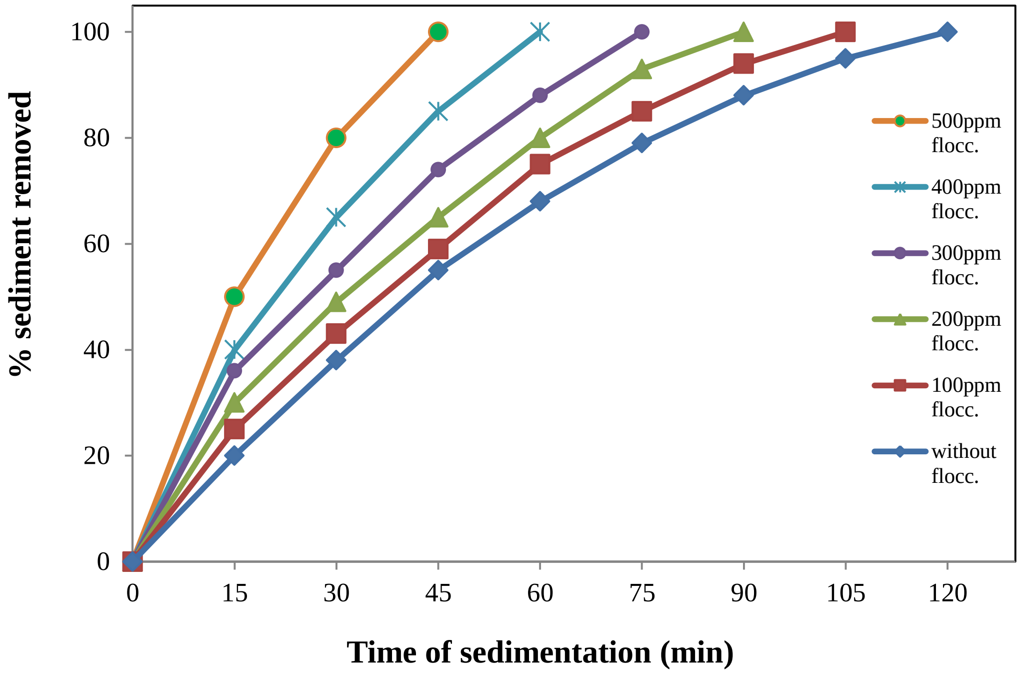

Figure 4.1 %TSS removed using settling with addition different doses(100 -500) of flocculent (polyacrylamide) and without flocculation

4.2 Study Impact of Time on % Oil Removed.

According to the figures 4.2 and 4.3 the percentage oil removed increase during the first (5 – 10) min, the maximum oil recovery occur at 15 min with and without flocculent, then the behavior was declined, the reason is the oil droplets until 15 minute were coalesce, when residence time increase the dispersed started again because droplets were lose attractive between each other, that’s led to decreased the oil recovery. Same mechanisim effected on operation time of separation occur with outlet time, this appear clearly at the 4 to 6 minute then the efficiancy of oil recovery decreased for this results.

The outlet waiting time was fixed at fifth minute for next experiments.

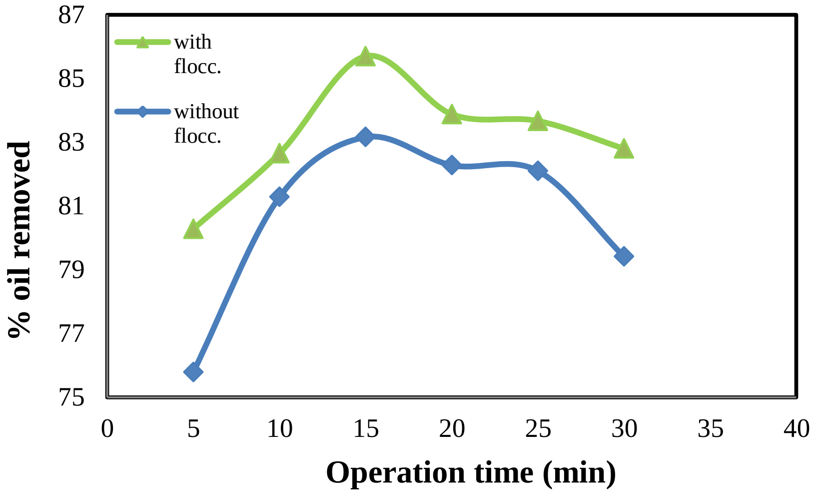

Figure 4.2 Effect of operating time on %oil recovery, fixed outlet time=10 min, pressure =3bar, salinity= 80gm/lit., temp. =60°C and pH=6

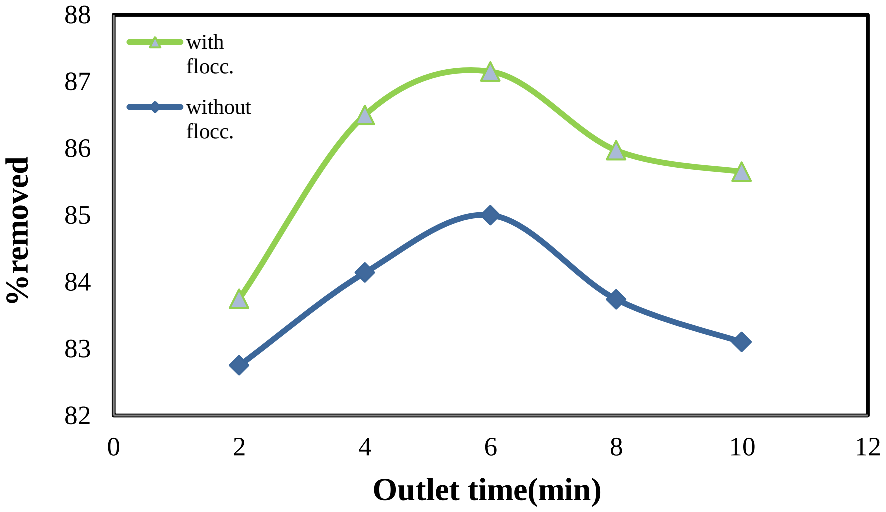

Figure 4.3 Effect of outlet time on %oil recovery, fixed operation time =15 min, pressure =3bar, salinity= 80gm/lit., temperature =60°C and PH=6

4.3 Effect of Salinity on Percentage Oil Removal.

Figure 4.4 shows the effect of salinity on oil removal percentag, its clearly that the removal percent increases with increasing in the salinity, this con be attrebuted to the reduction in surface tension of the solution. The second effect cations will increase the electrical Cl^- in solution changes the electrical and surface properties of the system.

The polarity plays importance factor in increase adherence between oil droplets themselves depending on attractive force and cohesion property which refers to the attraction of a material to itself thereby opposing spreading on a surface [39] then increase separation efficiency.

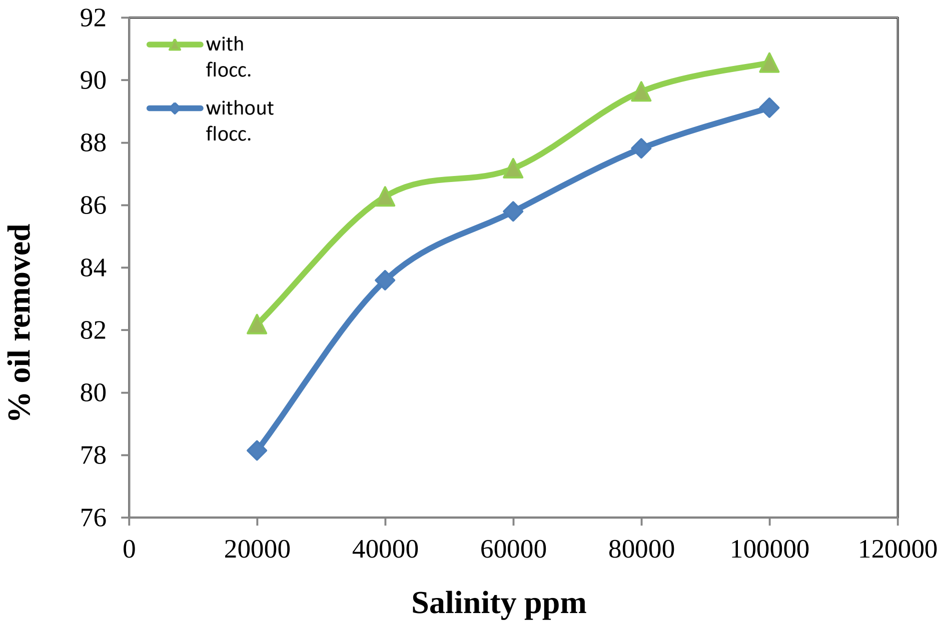

Figure 4.4 Effect of salinity on %oil recovery, fixed operating time=15, outlet time=5 min and pH=6 without additives or mixing, pressure=3bar, temperature=60°C

4.4 Effect of Mixing on Percentage Oil Removal.

The effects of mixing on the removed oil persent was presented in figure 4.5. A declined in the resulte was conducted after 300 RPM. The slightly mixing will enhance flocculation, then flooting the oil droplets. The torbin impler in the mixing system producd a centrifuge force pushs oil up. The slight mixing (mixing at laminar zone) give two benefits, firstly create homogenious aggregation among droplets itself, secondly reach maximum contact among oil droplets and sorbents additives which leades to important results. Its warthly to indicate that a high mixing produced emulsion which is greatly deacrising the separation efficiency .

The oil removal percent fill down when the RPM was during the range of 300 to 1100 .

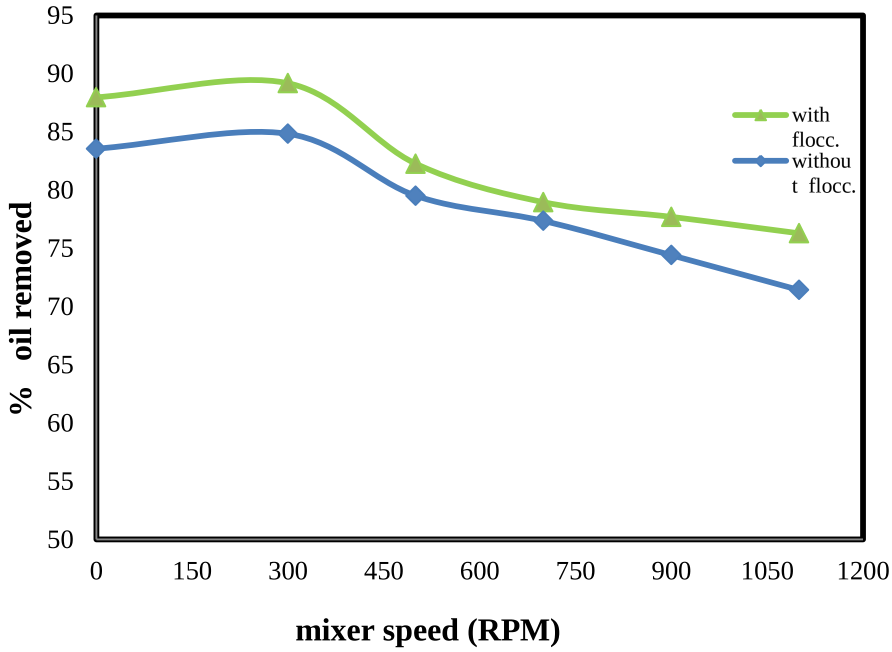

Figure 4.5 Effect of mixing on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100 gm/lit., pressure=3bar, temperature=60°C and pH=6 without additives

4.5 Temperature Effect.

Figure 4.6 investigate the effect of temperature on the oil recoverd percentag. The increase of temperatere will decrease the viscosity in liquids which lead to increase velocity of separation according to stakes' equation. Examining figure 4.6, indicate that after 50°C the oil removal percent decreased sharply, the reason is increasing collosion between particles in high temperatures due to free bonds then emulsion will reform and dispresed between oil and water occur again as aresult, the droplets are moving faster and so collide more frequently which cause an increasing of the collision frequency of the molecules which will lead to speed up oil droplets movement, this confirm that the hypothesis of an increasing of mass transfer coefficients according to an increasing of temperature, which is leading to an increasing of the rate of mass transfer, all of these events are leading to an increasing oil recovery percent.

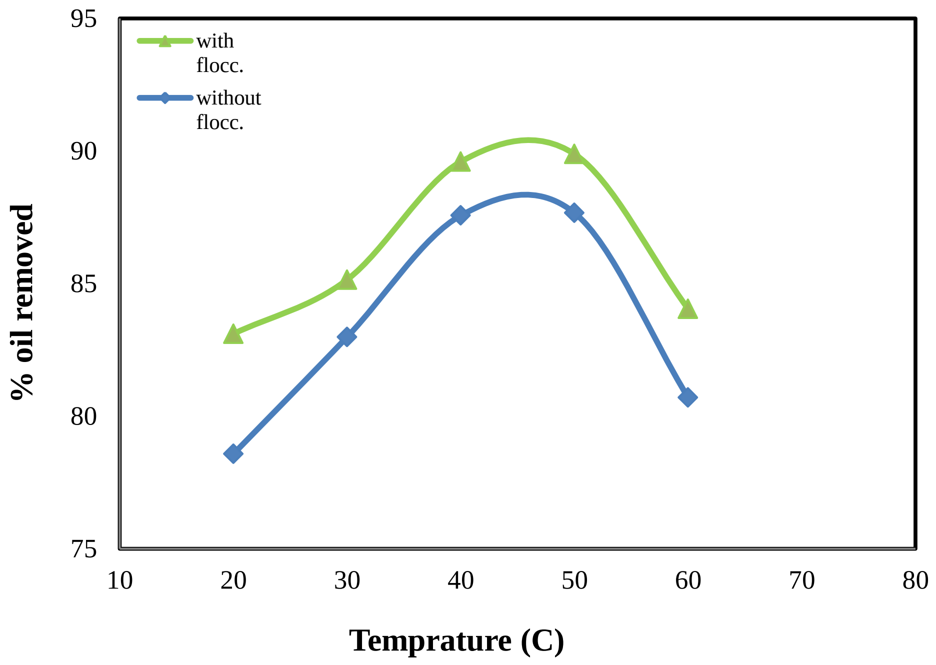

Figure 4.6 Effect of temperature on %oil recovery, fixed operating time=15min, mixing=300RPM, outlet time=5 min, salinity=100gm/lit., pressure=3bar and pH=6 without additives

4.6 Pressure Effect.

Figure 4.7 shows that the oil recovery percent is strongly influenced by change in pressure. For example, examining figure 4.7 it can be seen that the percentage of oil recovery was increased from 88% to 90% according to pressure increase from 0 to 2 bar which increases to the highest limits when the other variables were fixed at the upper limits. As the same enforced the percentage of recovery was decreased from about 90% to 79% according the pressure values from 2 to 5 bars, in the case of other variables were fixed at the minimum limits, the reason is emulsion between oil and water occurred as the same areason of emulsion in wells.

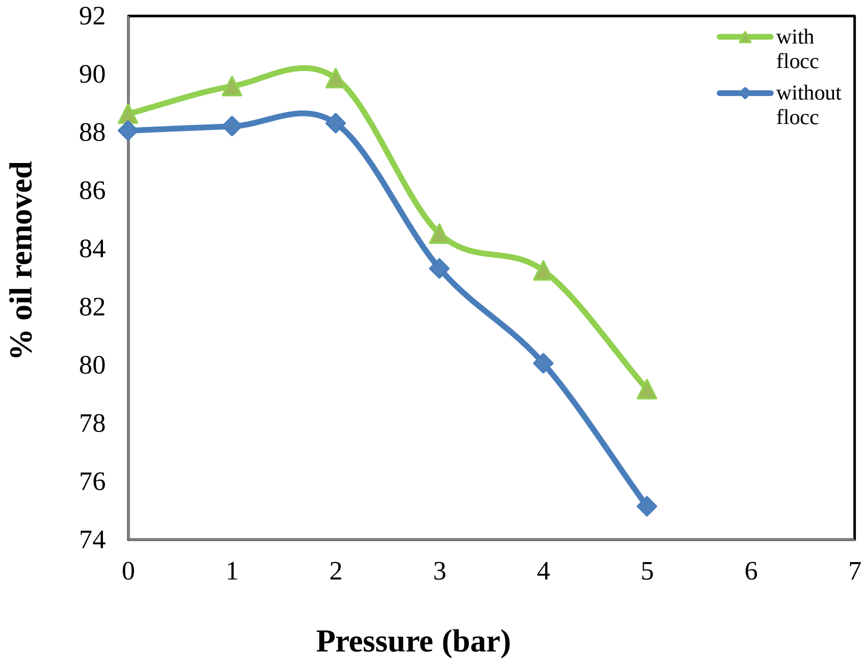

Figure 4.7 Effect of pressure on %oil recovery, fixed operating time=15min, outlet time=5min, mixing=300 RPM salinity=100g/lit., temperature=45°C and pH=6 without additives

4.7 Enhance Oil Recovery % With Raise pH

Figure 4.8 investigate the effect of pH on the oil recovery. The investigation was conducted in the range of 2to 8, it can be seen clearly from figure 4.8 that the oil removal percent increased with pH increasing. The maximum separation was observed within the pH range 7 to 8, that's enhance the separation in acidic solutions less then base solutions.

The percentage oil removal increases with increase in pH. The minimum separation was observed at low pH. This behavior may be due to the fact that the presence of higher concentration and higher mobility of H^+. This idea was highlighted that the strong influence of pH in most of reasons aforesaid.

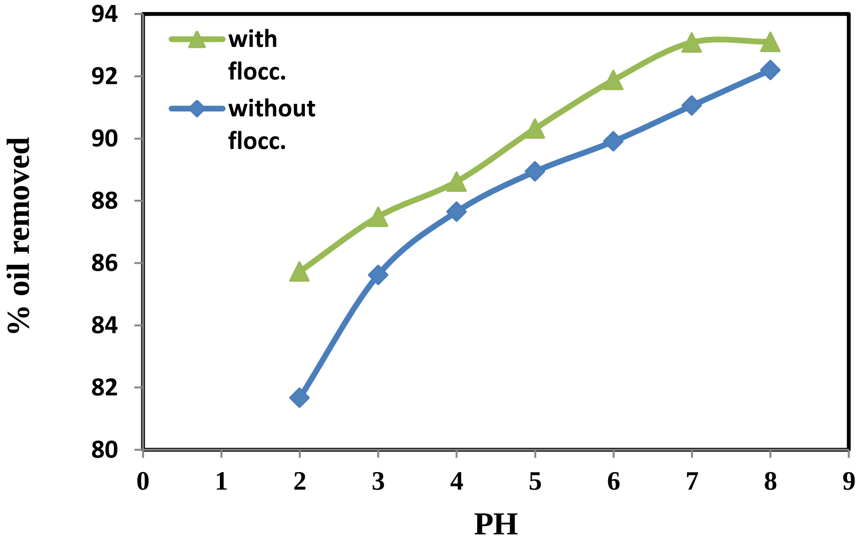

Figure 4.8 Effect of pH on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300RPM, temperature=45°C and pressure=1bar without additives

4.8 Surfactant Influence on Oil Droplets Removing.

Figures 4.9, 4.10 and 4.11 show the effect of surfactant on oil removed. It can be concluded that changing the dos of ethanol surfactant from 0.01 to 0.04 lead to change in removal percent from 84 to 92 percent and more sluggish results was obtained (0.04 to 0.06) and that a gree with [41], he state that the addition of excess production chemicals (such as serfuctants) can reduce the interfacial tension so that coalescence and separationof small droplets become extreamly diffecult. According to the stoke’s equation the size of the oil droplet is principle parameter of concern in this separation and the velocity of the oil droplet rises through the water and varies directly with the square of the droplet diameter. Also according the stakes’ equation velocity effect directly with the viscosity, so the surfactant reduces the viscosity of oil droplets then increase the separation, also the effective salinity decreases with the temperature for anionic surfactants but increases with the temperature for nonionic surfactants, the reason is turbidity effect decrease with high temperature, then action ionic effective will decrease. Whatever the case, these figures were deduced that the recovery efficiency was increased with increase surfactants. Thus these reasons are illustrating the impact of surfactants at different doses with the same method to install the other variables.

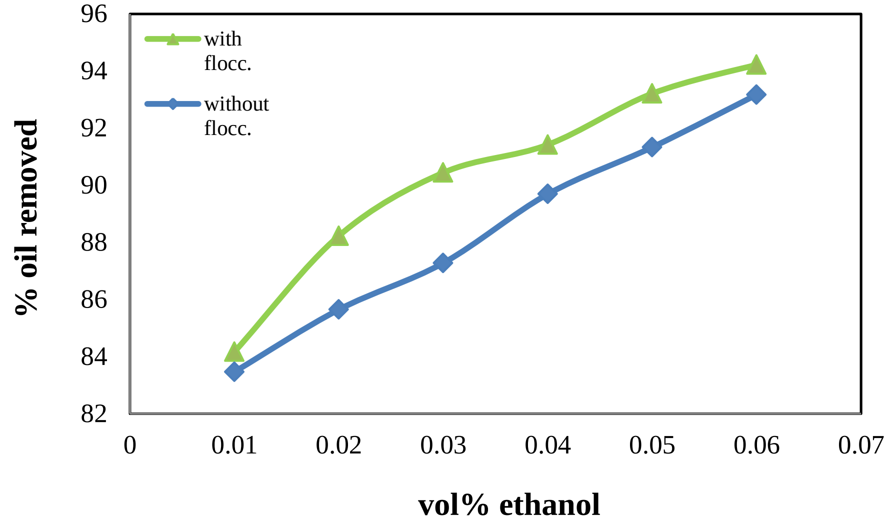

Figure 4.9 Effect of ethanol on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

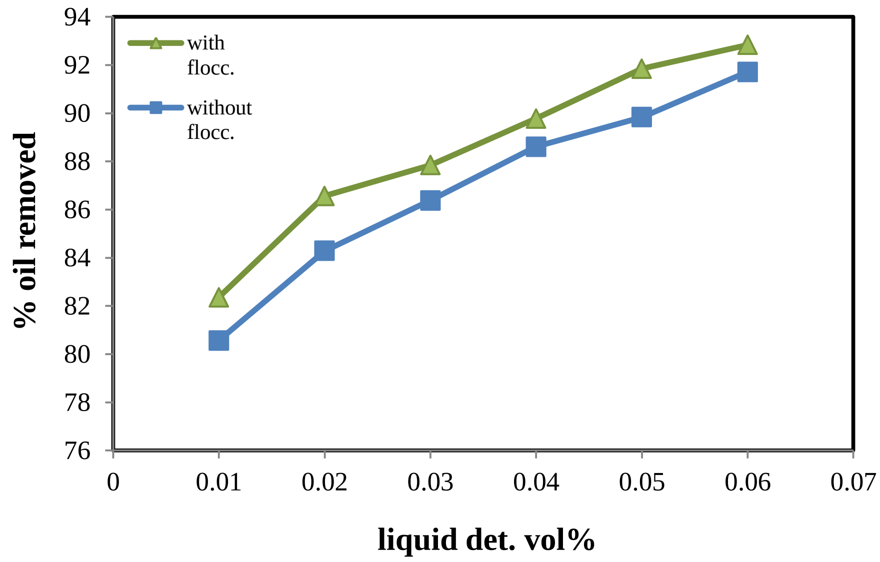

Figure 4.10 Effect of liquid detergent on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/l, mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

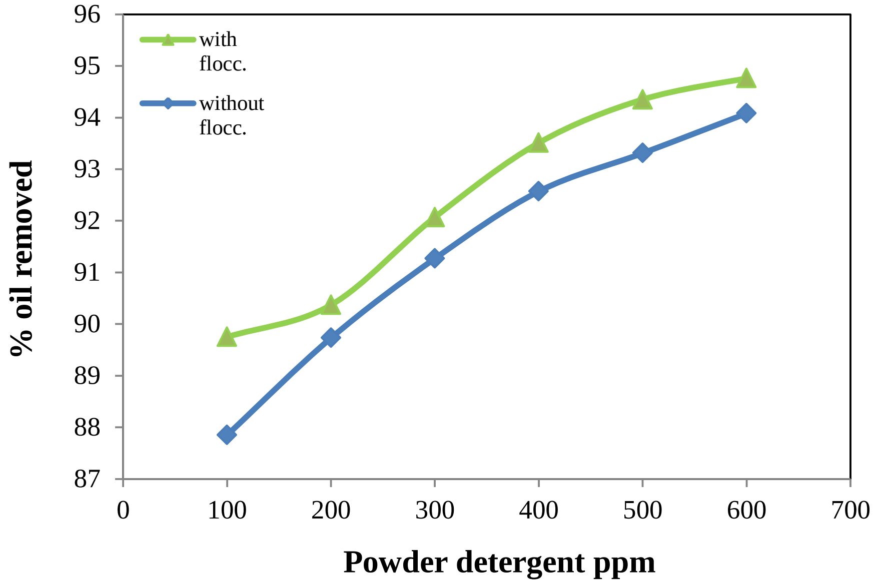

Figure 4.11 Effect of powder detergent on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

4.9 Effect of Sorbents (Sawdust)Addition on Oil Recovery.

Figure 4.12 shows the effect of sawdust on oil removal percent, examining this figure indicate that 99 percent of oil recovery was reached. A disadvantages of sawdust addition was noted, firstly it has ability to absorb water, secondly when saturated with oil its rested in bottom with different layers in reactor, then would be hard to separate, thirdly, its cause lose in oil recovery, finally a pollutant problem was arise from using a sawdust. The reason behind the separation efficiency is that the sorbents had hydrophobic properties separated oil droplets greater with the milling edges leaving conservative of its un uniform shape like used plastic and bacillary shape like sawdust with smaller amount than the spherical shape of polyethylene and polypropylene grains because it weren’t milled which have less contact.

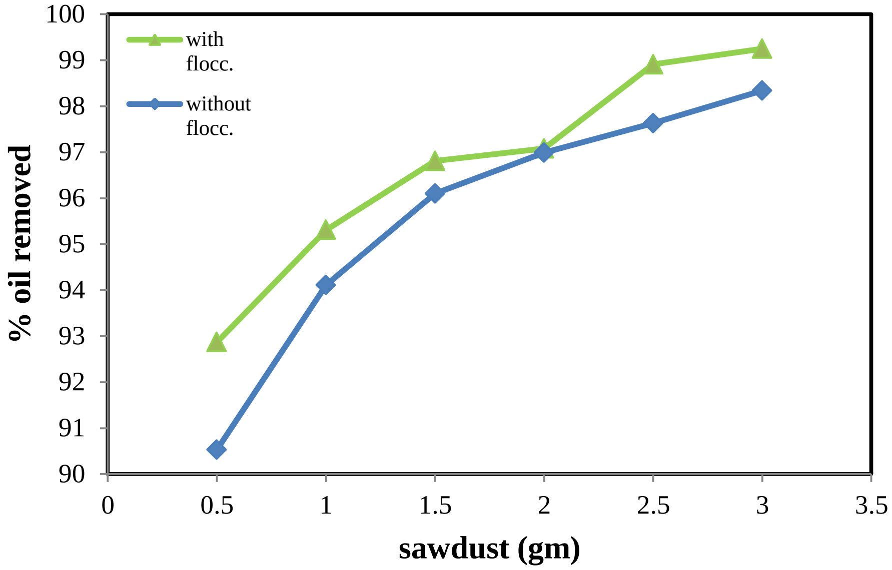

Figure 4.12 Effect of sawdust on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

4.10 Improving Performance Used Polymer Sorbents.

Figures 4.13, 4.14 and 4.15 show the effect of polymer sorbents addition on the performans of separation system. Investigat thes figure indicated excellent separation results, the main reason was return to the adhesion property of some polymers which refer to the attraction of one material to another sorbent rely be attractive as they are often either abundant in a nature or are the waste by product of an industrial process and can be purchased readily at low cost or are freely available [39]. So the polyethylene, polypropylene and used plastic, which made of polyethylene, are adhesion components with high wettability [51], as long as they were classified as hydrophobic materials possessive high attractive to the oil. The best benefit of polymer grains and used plastic, are keep their efficiency after reused in experiments because it didn’t change with process conditions and easy to recover oil by washing with sprayed warm water or steam.

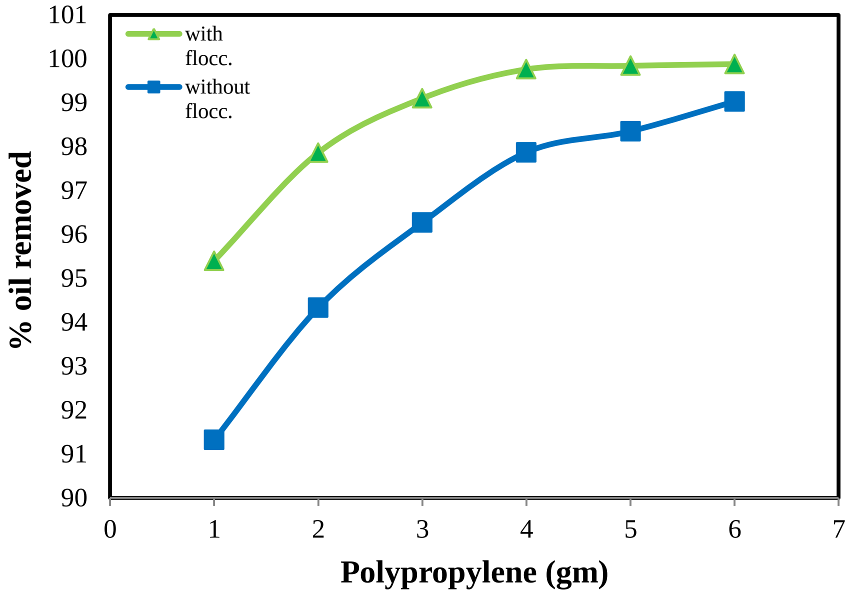

Figure 4.13 Effect of polypropylene on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

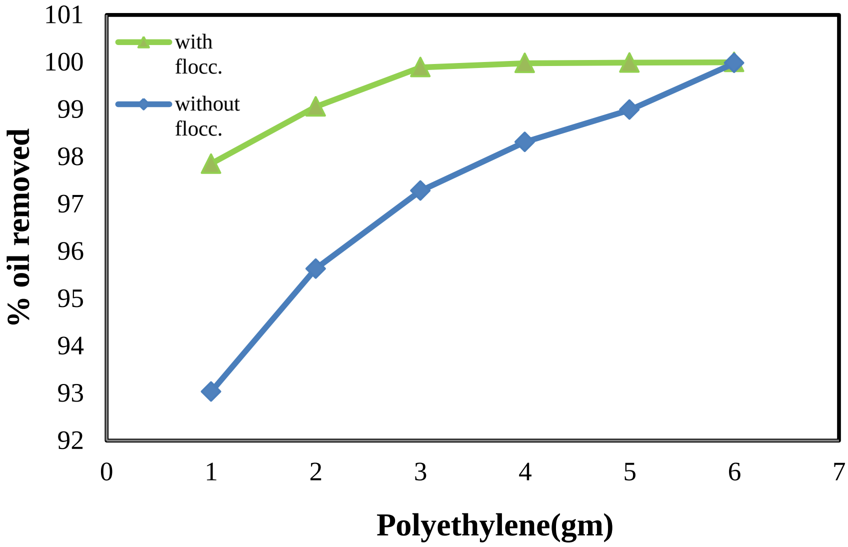

Figure 4.14 Effect of polyethylene on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

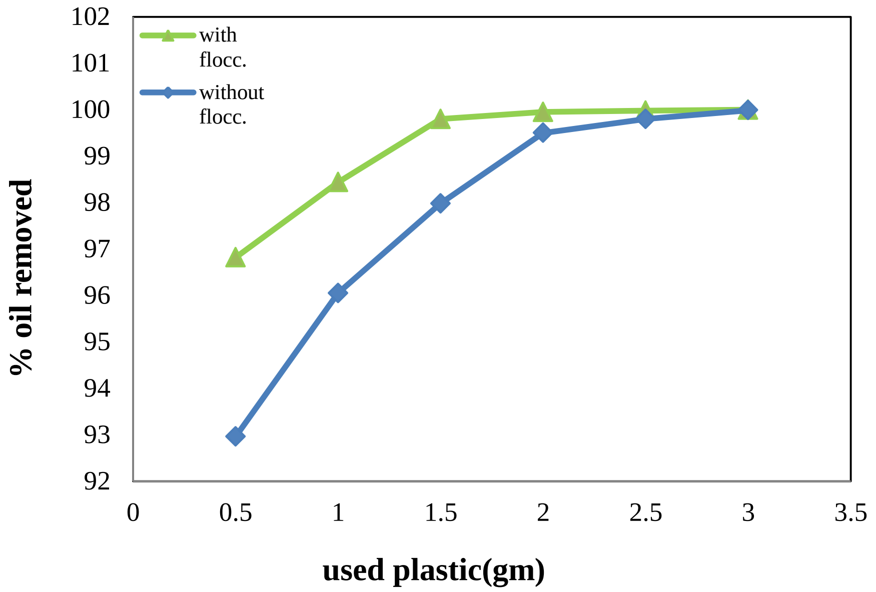

Figure 4.15 Effect of used plastic on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45°C, pressure=1bar and pH=7

4.11 Compares between Ethanol and Liquid Detergent Separation Efficiency.

Figures 4.16 and 4.17 show compares between ethanol and Liquid detergent on separation efficiency without and with flocculation respectively. It clear from these figures a preferable of ethanol for both cases (with and without flocculation), this can be attributed that the ethanol improve the hydrocarbons appearance because it dilute it, additionally the detergents have sulfonic cycle which add problem to mercaptan components which is a group of organo sulfur compounds that are derivatives of hydrogen sulfide in the same way that alcohols are derivatives of water [31].

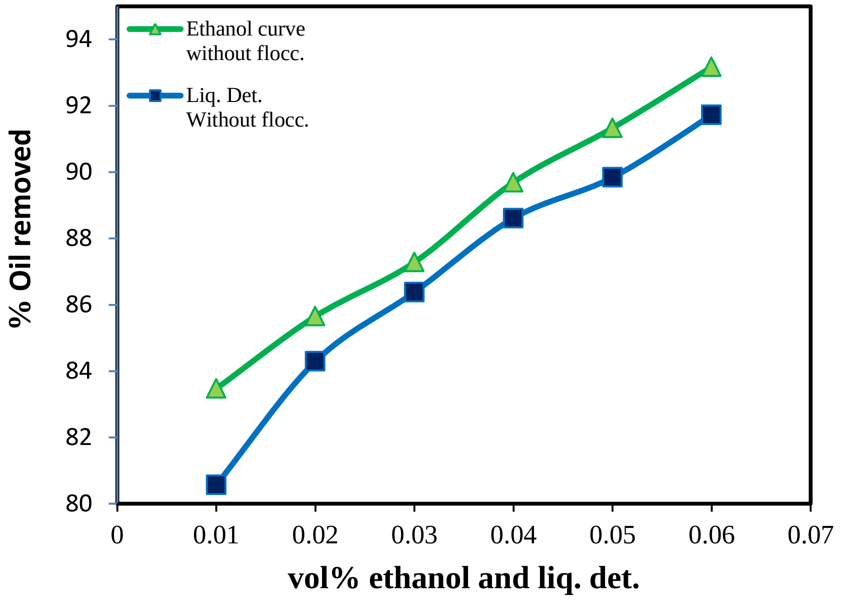

Figure 4.16 Compare between ethanol and liquid detergent with % oil recovery, without flocculation

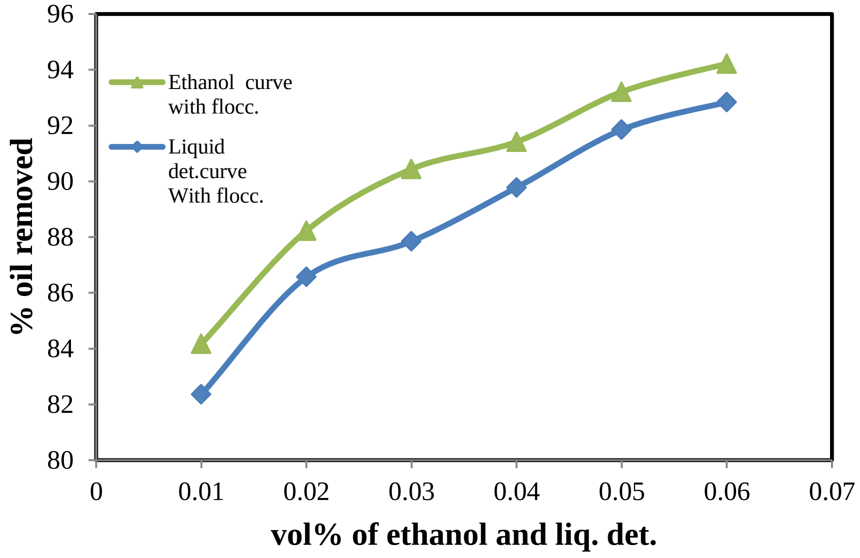

Figure 4.17 Compare between ethanol and liquid detergent with % oil recovery, with flocculation

4.12 Compares between Sorbents Separation Efficiency

As discussed previously in section 4.10 (figures 4.13, 4.14 and 4.15), the results showed a high separation efficiency.

To compare between sorbents, it has to be noted that as a result of the use of modern technologies for sorbents, the figures (4.18, 4.19, 4.20, 4.21, 4.22 and 4.23, respectively) were showed high % oil recovery achieved full recovery with low cost

Figure 4.18 showed that the used plastic over sawdust with the same amount additional, the disadvantage of sawdust compared with used plastic, the separation efficiency didn't change when its reuse again also polymers has same features of oil, the explanation of these phenomena is lie in at immersed particles of sawdust whereas the used plastic particles weren't immersed in solution.

Figure 4.19 showed concave when it reach 2gm of sawdust curve while a sharp plot of used plastic until 1.5 gm to reach maximum.

Figures 4.20 and 4.21 are referring to the superiority, of polyethylene plot due to the high density of polyethylene compare polypropylene in cm^3 [2].

The same reasons gave the high peak of used plastic plot in figures 4.22 and 4.23 this attributed to high real density of used plastic which give much contact particles surface with oil.

The used plastic was working with high efficiency with or without flocculation, while efficiency of polyethylene improved with flocculation that's lead to more advantages to used plastic.

This phenomena incidence was reoccurred to an increasing of separation according to an increase of this addition.

It is clear from these figures that the best amount which lead to maximum recovery of oil located in the region of sorbents between 1 to 2 gm. Finally the study of isotherm was conducted and awkward result due to obtained low surface area. Appendix D showed surface area measurements

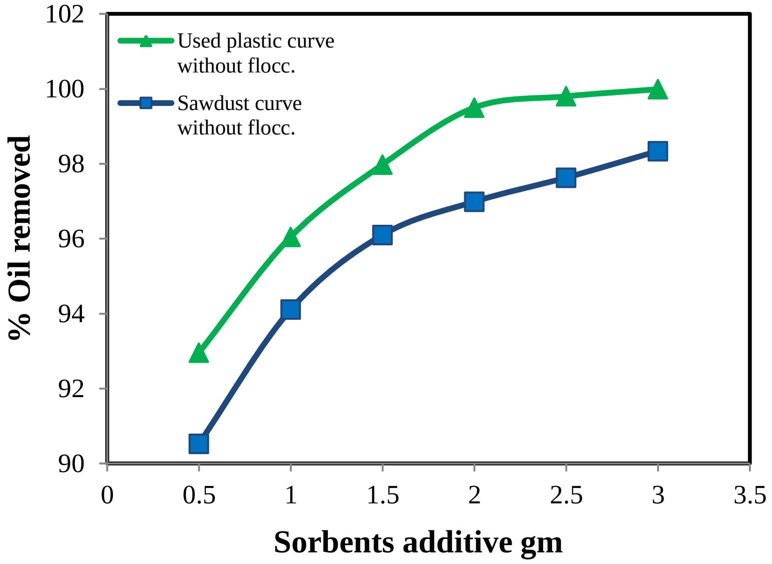

Figure 4.18 Compare between Used plastic and Sawdust with %oil recovery without flocculation.

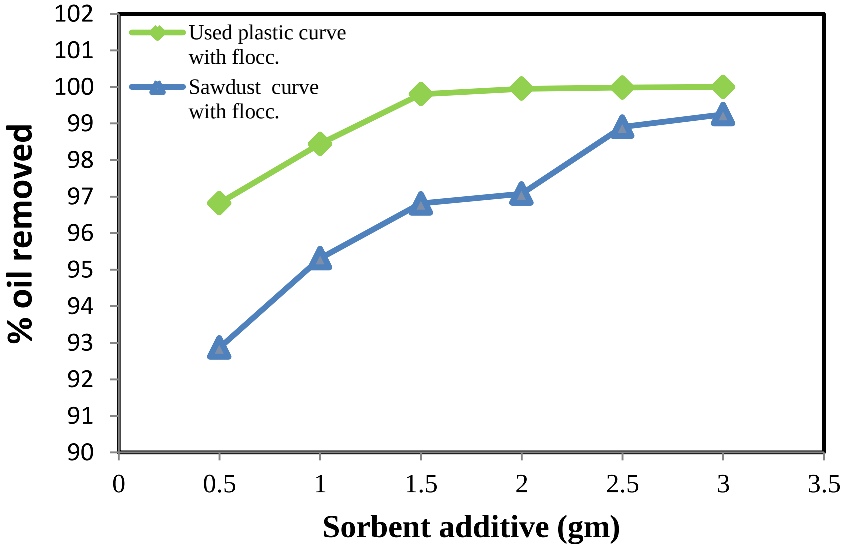

Figure 4.19 Compare between Used plastic and Sawdust with % oil recovery with flocculation.

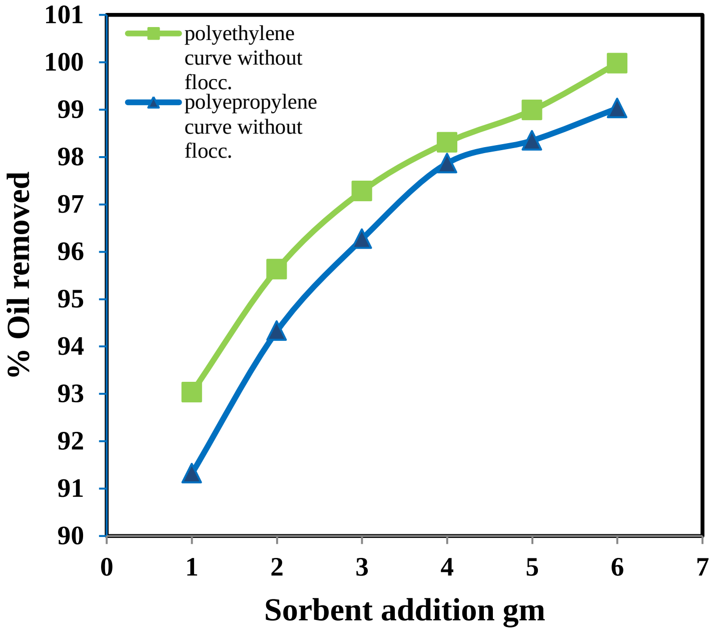

Figure 4.20 Compare between polypropylene and polyethylene with % oil recovery without flocculation.

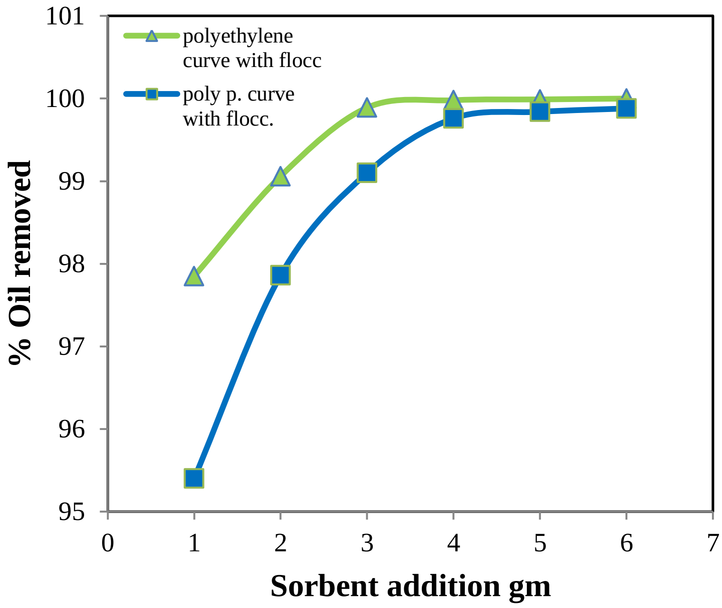

Figure 4.21 Compare between polypropylene and polyethylene % oil removal with flocculation

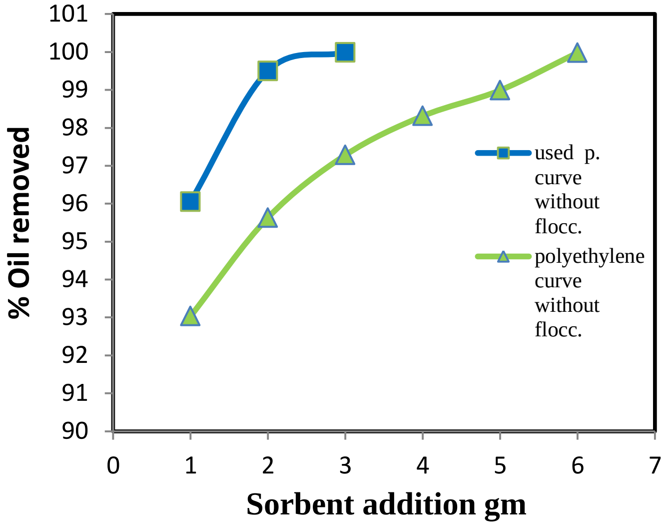

Figure 4.22 Compare between Used plastic and polyethylene with %oil recovery without flocculation.

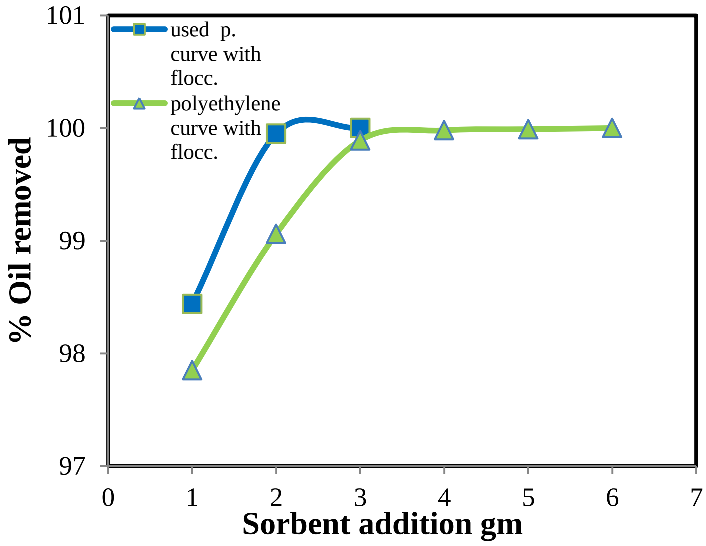

Figure 4.23 Compare between Used plastic and polyethylene with %oil recovery with flocculation.

بسم الله الرحمن الرحيم

والله خلق كل دابة من ماء

صدق الله العظيم

النور ٤٤

الخلاصة

عمليات الحفر تنتج كميات كبيرة من الماء الملوث يعرف بالماء المنتج او الماء المنتج من البئر. مختبريا تم التحقق باستخدام Autoclave بحجم لتر واحد مصنوع من مادة الصلب stainless steel لمعالجة الماء المنتج من حقول الرميلة الشمالية والزبير الخطوة الاولى استخدمت معالجة اولية لازالة العولق الصلبة بالترسيب مع التلبيد وبدونه ودراسة الفرق.المسار الثاني يتضمن دراسة تاثيرالدالة الحامضية والضغط والحرارة والملوحة وزمن التشغيل وزمن بدء القشط والخلط . الخطوة الثالثة هي فحص تاثير اضافة بعض المواد التي تقلل الشد السطحي مثل الكحول والمنظفات.اخيرا اضيفت مواد ماصة ومازة لازالة النفط مثل حبيبات بولي اثيلين وبولي بروبيلين والبلاستك المستخدم ونشارة الخشب.

اختيرت معدلات الظروف المستخدمة في التجارب حسب ظروف الماء المنتج الخارج من ال dehydratorوdesalter كالاتي الملوحةppm 80000 ال pH=7 الضغط = 3بار وحرارة = 60 درجة مئوية اما الخلط فاختير ضمن الجريان الخطي وزمن الفصل والقشط مثل اقل زمن بقاء لتقليل الكلفة في التصميم . افضل النتائج والظروف كما يلي:

أفضل ظروف تشغيل: ضغط = 1بار, وحرارة = 45 درجة سيليزية , سرعة ألخلاط = 300 دورة بالدقيقة, زمن عملية ألمعالجة = 15 دقيقة وزمن بدء القشط = 5 دقائق.

أفضل أضافات لتقليل الشد السطحي :

ايثانول = 0.05 % حجمية, منظف بودر = 400ملغ\لتر و منظف سائل = 0.03 % حجمية

أفضل كمية نشارة خشب مضافة = 2.5 غرام

أفضل عامل مساعد لمواد البلاستك هي : بولي بروبيلين =4غم , بولي اثيلين = 3 غم وبلاستك معاد = 2.5 غم.

النتائج بينت بان النفط تمت ازالته بالكامل باستخدام البلاستك المعاد.

شكر وتقدير

قبل كل شئ أشكر ألله واحمده أذ وقف بجانبي لأعبر كل ألصعوبات

أحب أن أهدي هذا العمل الى ذكرى ألشهيد اسماعيل أخي وصديقي ألمخلص ألذي ذهب عنا مبكرا وكل ألشهداء أللذين ضحوا من أجلنا لنعيش

أحيي وأقدر زيادة ألبصيرة من قبل ألدكتور خالد مخلف موسى ألذي أشرف على هذه ألاطروحة بتوضيحاته وحثه ومناقشته وأقتراحاته ألتي ساعدتني لتقديم هذا ألعمل

كل ألتقدير للدكتور محمد باقر ألشديدي وألدكتور نصير عبود الحبوبي رئيس قسم ألهندسة ألكيمياوية في جامعة ألنهرين وكل أساتذة ألقسم

شكري ألكبير لزوجتي على صبرها وتفهمها ووقوفها معي لأسعادنا

أعتذاري لولدي الصغيرين مسلم وجعفر على أخذ ألوقت ألذي كان يجب أن أشاركهم فيه كأب

كذلك شكري ألكبير لعائلتي ألتي ساندتني بأستمرار

أخيرا أنا ممتن لكل كادر نفط ألجنوب ومركز ألبحث وألتدريب ألنفطي على ألمعلومات وألتسهيلات لاكمال دراستي

معالجة الماء الحاوي على النفط في حقول نفط العراق الجنوبية

رسالة

مقدمة الى كلية الهندسة في جامعة النهرين

وهي جزء من متطلبات نيل درجة ماجستير علوم

في الهندسة الكيمياوية

من قبل

عقيل شيخه عرفات

بكولوريوس علوم في الهندسة الكيمياوية1999

شعبان 1435

حزيران 2014