DISSERTATION

MITIGATING SILICATE SCALING USING GREEN INHIBITOR

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ABSTRACT

Silicate scaling has becomes the major problem in oil and gas industry nowadays. The production of oil and gas is affected because of this silicate scaling as the production is stop to remove the scale from the equipments, which need a lot of money and time consuming. Usually, the silicate scale is removed by using the mechanical work that is physically removing the scale from the equipments. Thus, an inhibitor is created to prevent or slowdown the formation the silicate scaling by using chemical. The use of chemical as the inhibitor created new problem to environment, so study on green inhibitor is done to reduce the use of chemical in silicate scaling inhibitor. The reactions of minerals after the flooding of alkaline surfactant polymer (ASP) cause silica deposition. The factors such as concentration of magnesium ions and calcium ions, temperature and pH value associate the formation of scale. Five of types of plants have been identified to be test as the green inhibitor to prevent or slow down the scaling. The plants are 1) *Psidium Guajava* (Jambu Batu) 2*) Centella Asiatica* 3) *Persicaria odorata* (Kesum) and 4) *Orthosiphon Stamineus* (Misai Kucing). These plants have a good potential as the green inhibitors as they have a lot of benefits in medical practice and abundant in Malaysia. Suitable experiments are conducted to determine the efficiency of this green inhibitor in mitigating silicate scale. Three sets of test have been carried out to determine the potential green inhibitor to mitigate the silicate scale. The tests are 1) Test at different pH values to investigate the tendency of silicate scale to form. 2) Test at different concentrations of inhibitor to determine how the concentration effect the performance of inhibitor. 3) Performance test of Orthosiphon Stamineus and Centella Asiatica as inhibitor to mitigate silicate scale. The green inhibitors show a good potential to become alternative inhibitor for silicate scale, but further studies should be done to explore more their potential as green inhibitor.

ACKNOWLEDGEMENT

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CHAPTER 1

Introduction

1. 1 Background of Study

Enhanced Oil Recovery (EOR) is done in order to get back the oil production after the failure of natural drive and water or gas injection. This secondary recovery is done using chemical injection, Water Alternating Gas (WAG) and others. One of the methods in chemical injection is by using Alkaline Surfactant Polymer (ASP) flooding. The interfacial tension (IFT) between residual oil and injected fluids will be lower using the surfactant, while the reaction of alkali with acidic components of the oil will further lower the IFT, thus form additional surfactants within formation. The viscosity of the fluids is increase by using the polymer in ASP flooding. The uses of these three fluid injection additives offer great synergistic effects in term of oil recovery and sweep efficiency (Arensdorf et al.2010).

High pH value in ASP flooding fluids eventually associate the silicate scaling as the quartz silica is dissolve from the sandstone formation. The alkaline ASP then meet the neutral pH connate water, thus the decrease of mixed waters will polymerize the dissolve silica and forms colloidal silica. The presence of magnesium or calcium in connate water will form the magnesium silicate or calcium silicate scale. The factors that determined the types and amount of silicate depend upon the pH value, magnesium concentration and the ratio of calcium to magnesium. The presence of silicate scaling will cause the deferment to the production as it stuck to the production tubing, pumps and pipes, thus work over is needed to continue the production. Work over job to remove the scale form the equipments is very time consuming and not economical.

In order to save the money and time spend for the work over, an inhibitor is needed to prevent or slow down the silicate scaling. The inhibitors can be divided into two types; i.e. threshold inhibitor and non-threshold inhibitor (Arensdorf et al. 2011). The threshold inhibitor will totally prevent the formation of silicate scaling, while non-threshold inhibitor will slow down the formation of scaling. Threshold inhibitor obviously better from non-threshold as it stops the scale from producing, but non-threshold is good enough as it delays the formation and gives enough time to drive the oil to the surface. Commonly, chemical is used as the scaling inhibitor to mitigate the silicate scaling. Chemical is injected together with ASP fluids during the flooding and this chemical will react with the mixed water, thus inhibit the formation of silicate scale.

The use of chemical to prevent or slow down the scaling is contains with toxic and contaminants, thus will indirectly affected the environment. So, the green inhibitor will be produce as the alternative to mitigate the silicate scaling. Natural product is used as the main component as the inhibitor to inhibit the scaling. Several plants was identified to be extracted as the inhibitor such as *persicaria odorata* (kesum), *ficus deltoidea* (mas cotek), *aloe vera* (lidah buaya), *Orthosiphon stamineus,Benth* (misai kucing) and *psidium guajava linn* (jambu batu). The toxicity level in the environment will decrease by using the green product as the inhibitor.

1.2 Problem Statement

Silicate scaling is form after the use of ASP flooding as the secondary recovery because of its high pH value. The scale form from the reaction of ASP fluids and connate water will accumulate and block the equipments such as pipes, pumps and production tubing that directly effects the production of oil. In order to continue the production, work over has to be done to remove and clean all the scale at the equipments which is time consuming and uneconomical.

Usually, the inhibitor use to mitigate the silicate scaling is produce from chemical. Chemical is injected together with ASP fluids during the flooding to stop or slow the formation of scale. The chemical is containing with toxic and contaminants that will give negative impact to the environment.

1.3 Objectives and Scope of Study

The objectives of this project are as follow:

- To investigate the performance of inhibitor at different concentrations.
- To study the potential of Centella Asiatica and Orthosiphon stamineus as green inhibitor to mitigate silicates scale.
- To compare the performance between green inhibitor and commercialized green inhibitor.

The scopes of study are:

- Conducting research on the theory and definition of terms related to the study.
- Conducting experiment to investigate the performance of inhibitor and also its potential to become alternative inhibitor to mitigate silicate scale.

CHAPTER 2

Literature Review

2.0 Literature Review

This study is focusing on the use of green inhibitors as the medium to mitigate the silicate scaling during ASP flooding. This literature review will further explain about the theory and concept of ASP flooding, silicate scaling and green inhibitors.

2.1 Alkaline Surfactant Polymer (ASP) Flooding

Enhanced oil recovery (EOR) is any method that can be used to extract hydrocarbons from the reservoir after the production is depleted by the mean of primary recovery. EOR is defined as the process of producing hydrocarbons other than conventional method such as the mean of reservoir own energy or the reservoir re-pressuring schemes either with gas, water or chemical. One of the methods used in EOR is Alkaline Surfactant Polymer (ASP) flooding. ASP flooding is the tertiary EOR method designed to lower interfacial tension (IFT), water wet the formation and decrease water mobility to produce residual oil (Wyatt et al. 2002). This method is drive by the mixture of alkali, surfactant and polymer and is injected thorough injector wells. In ASP flood, the purpose of the surfactant is to lower the IFT between residual oil and injected fluids. The alkali exists to further lower the IFT by reacting with acidic components of the oil to form additional surfactant within the formation. The use of alkali is much less costly than equivalent levels of surfactant, allowing for a more cost efficient flood (Demin et al. 1997). The polymer used in ASP flood is designed for better swap of the reservoir due to its ability to increase the viscosity of the fluids. This allows for better mobility control. The use of these three fluid injection additives offers great synergistic effects in term of oil recovery and sweep efficiency (Huang and Dong 2004).

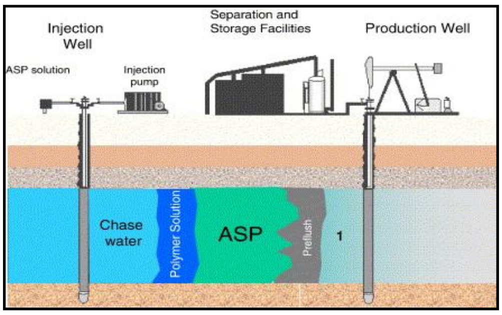


Figure 1 ASP Flooding

Five ASP flooding pilot tests have been carried out in different regions of Daqing oil field since 1994 and oil recoveries have been enhanced by 20% as compared to water flooding [4-5]. Three factors have been found out to be catalysts in ASP flooding field test: 1) Good performance of oil displacement agents. 2) Good profile control and oil displacement ability. 3) Reasonable well pattern and well spacing (Zhu et al. 2012)

Table 1 ASP Flooding pilot tests in PetroChina

Field and Projects		Well Number and Pattern	Well Spacing (m)	Effective Thickness (m)	Effective Permeability (μm^2)	Improved Recovery (OOIP%)
Pilot test in Daqing	West part of middle zones	4 injectors/9 producers Five spots	106	8.6	0.809	21.4
	Middle part of Xing-5 zone	1 injector/ 4 producers Five spots	141	6.8	0.789	25.0
	North-middle zone short well space	3 injectors/4 producers Four spots	75	10.7	0.767	23.24
	West part of Xing-2 zone	4 injectors/9 producers Five spots	200	5.8	0.858	19.3
	West part of North-1 zone	6 injectors/ 12 producers Five spots	250	9.76	0.812	20.63

Youyi Zhu et al. 2012 stated that ASP flooding gives side effects in field tests. The problem encounters are as follow: 1) scaling and corrosion damages the lifting system and shorten the average pump-checking cycle accordingly. 2) Strong emulsification resulted in many liquid treatment problems such as the excess solid particle content over the standard of water circulation and high cost of water treatment. 3) The liquid production decreased greatly.

2.2 Silicate Scaling

Quartz silica is dissolved when the high pH ASP flood moves through the sandstone formation (Arensdorf et al.2010), then after the alkaline ASP water meets the lower pH formation water, the decreased pH of the mixed waters dramatically lowers the solubility of monomeric silica and colloidal silica will form as the silica begins to polymerize at pH levels below 10.5.The following mechanism explains the polymerization of silica in the present of hydroxide ions (Amjad and Zuhl 2008):

$$SiOH_4 + OH^- \rightarrow (OH)_3SiO^- + H_20$$

$$(OH)_3SiO^- + Si(OH)_4 \rightarrow (OH)_3Si - O - Si(OH)_3 + OH^-$$

Arensdorf et al. (2010) stated that silicate scale formation is a complex and poorly understood process. It first started with silica dissolution when the alkaline flood sweeps the reservoir. The high pH water dissolves quartz in the formation, which results in dissolves monomeric silica flowing with the water flood. Then, as the ASP water flows to the production well, it encounters neutral pH connate water near the wellbore. As the high pH ASP water is partially neutralized by the connate water, dissolve silica begins to polymerize and forms colloidal silica nanoparticles. Colloidal silica forms when solubility level of monomeric silica is exceeded. In the present of magnesium, it can bridge the colloidal silicate particles and form an amorphous magnesium silicate scale. Magnesium silicate scale typically has non-stoichiometric ratios of magnesium to silicate. Similar interactions are possible with other polyvalent metal ions (iron, aluminium and calcium), but magnesium silicate has higher scaling index than other metal silicates. In absence of divalent cations, the polymerized silicate may continue to grow and form an amorphous silica scale. In oil field, different ratios of the two scales are likely forming in various well as pH and cation concentration differ.

Several studies have been done to determine influencing factors of silicate scale formation. Study by Jinling et al. (2009) has been done by considering the field conditions; Na_2SiO_3 solution and mineralized water were made up to different simulating produced water. The temperature, correlative ion concentration and pH value were the manipulative variables and the influence of these factors to scale formation was the responding variable. The first is silica-only solution. The second is Si, Ca^{2+} and Mg^{2+} solution. The thirds is Si, Ca^{2+}, Mg^{2+} and Al solution. The fourth is Si,Ca^{2+},Mg^{2+}, Al and PAM solution. The fifth is Si, Ca^{2+}, Mg^{2+}, Al , PAM and surfactant solution.

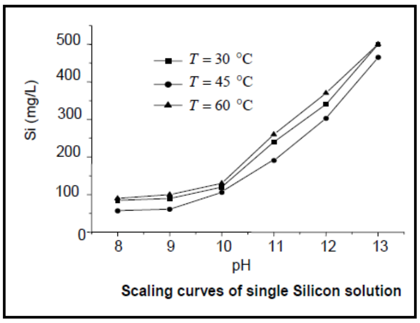


Figure 2: Scaling Curves of Single Silicon Solution

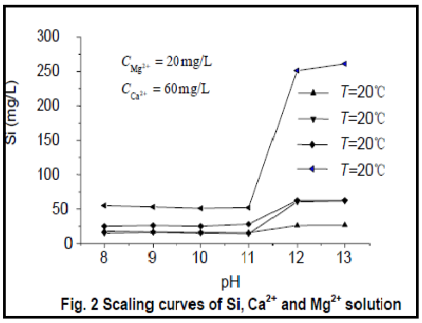


Figure 3: Scaling Curves of Si, Ca^{2+} and Mg^{2+}

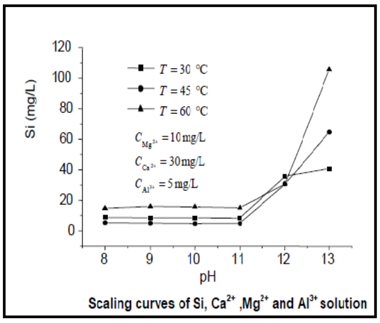


Figure 4: Scaling curves of Si, Ca^{2+}, Mg^{2+} and Al^{2+}

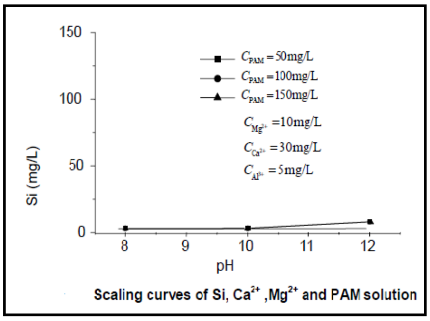


Figure 5: Scaling Curves of Si, Ca^{2+}, Mg^{2+} and PAM

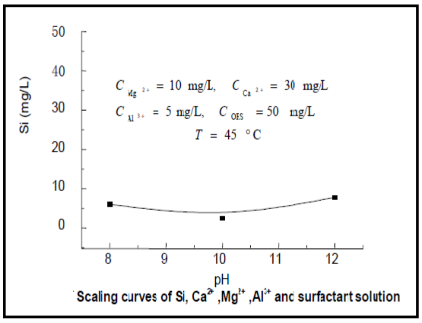
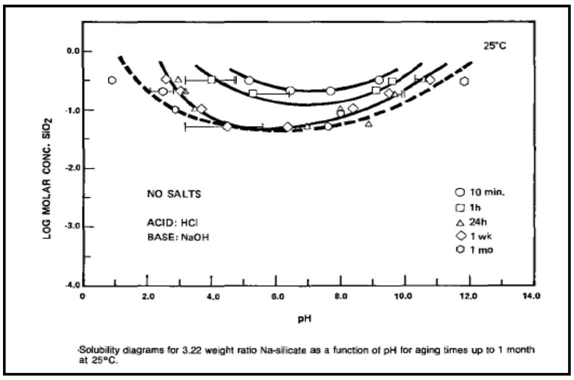


Figure 6: Scaling Curve of Si, Ca^{2+}, $Mg2^{+}$, $Al2^{+}$ and Surfactant

Figure 2 shows that there is scaling in single silicon solution. Concentration of soluble silicon ion increase with pH value increase, but the temperature's influences are not obvious. Figure 3 and Figure 4 shows that Ca^{2+}, Mg$^{2+,}$ Al decrease the concentration of soluble ion sharply. Scaling rules are approximately same when temperature is between 20^0 C ~ 45^{0}C and pH <11. Figure 5 and Figure 6 show that HPAM and surfactant decrease the concentration of soluble silicon ion sharply and scaling becomes more easily. This study shows that the Ca^{2+}, Mg^{2+}, Al, HPAM and surfactant increase the silicate scale forming tendency and speed.

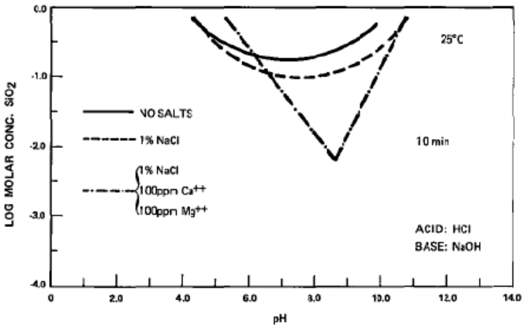
Study in 1983 by Katsanis et al. also discussed about causes of silicate scaling formation. The test was done by preparing samples that containing different amounts of base and salts by mixing the contents of two sets of test tube. A known volume of silicate was placed in first set of tubes and the other set was filled with acid, base or salts and a suitable volume of water. The tubes were gently inverted several times before measurements were taken to determine turbidity of systems containing settled precipitate. In all cases, hydrochloric acid and sodium hydroxide were used to adjust pH values. The following figures describe the results of the experiment.



Solubility diagrams for 3.22 weight ratio Na-silicate as a function of pH for aging times up to 1 month at 25°C.

Figure 7: Na-Silicate as function of pH

Figure above shows the boundaries in the absence of salts. For a given pH value, it is also clear that after one month precipitate forms in the presence of dilute silicate solutions which were stable at least up to 1 hour of aging. The rate at which the position of the boundaries change decrease after 24 hours of aging.



-Solubility diagrams for 3.22 weight ratio Na-silicate alone or in combination with 1% NaCl or 1% NaCl and 100 ppm each of Ca and Mg ions as a function of pH after 10 minutes of aging at 25°C

Figure 8: Na-Silicate mixed with Ca and Mg ions

The effects of 1% NaCl alone and combination with 100 ppm each of Ca and Mg ions on the precipitation boundaries is shown in figure 7. In the presence of Ca and Mg ions the parabolic shape of the precipitation boundary changes to two intersecting lines whose minimum in SiO_2 concentration.

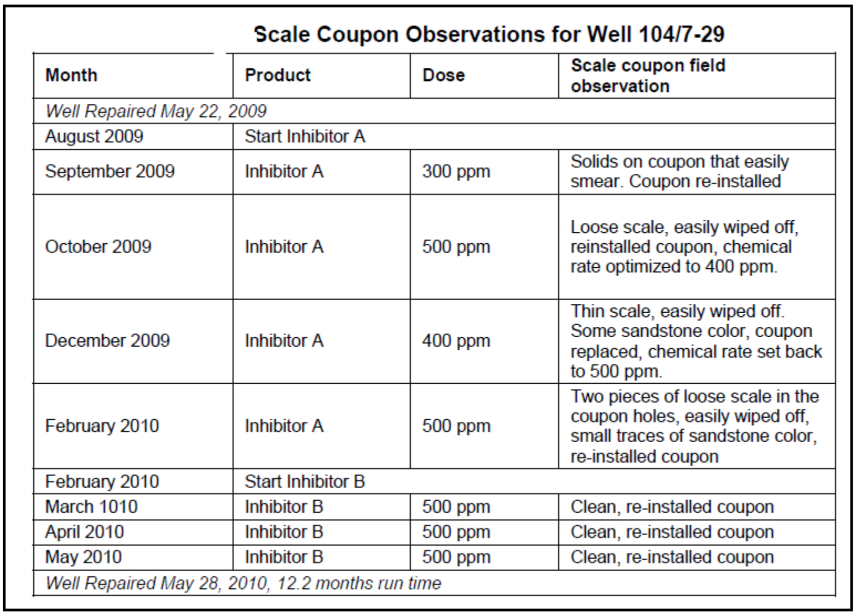
The results obtained explain that the formation of silicate scale is likely to occur both under alkaline and acidic conditions. The main factors of scaling are due to aging, temperature and hardness ions present and a lesser degree to NaCl.

From the studies done by the authors, it shows that the pH value, temperature, concentration of hydrogen ions are the main factors of silicate scaling during the ASP flooding.

2.3 Inhibitor

An inhibitor is produce in order to continue the production of oil. The inhibitor will remove the scaling from the equipments. The study on this subject has been done by Arensdorf et al. (2011) by developed two new silicate scale inhibitors namely as Inhibitor A and Inhibitor B and applied down hole to production wells via continuous injection. The data that was collected during the test consisted of 1) time between well workovers, 2) scale upon observations and 3) torque on progressing cavity pumps (PCPs). Downhole scale was observed during routine workover after 40 months of operation in Well 104/7-29 after the ASP flood was started. Two months after the third work over, continuous application of Inhibitor A was started at 500 ppm continuous application in a slipstream at the wellhead. After 6 months, Inhibitor B was switched into well. The well then operated for 12.2 continuous months before silicate scale accumulated to a level that impacted operation.

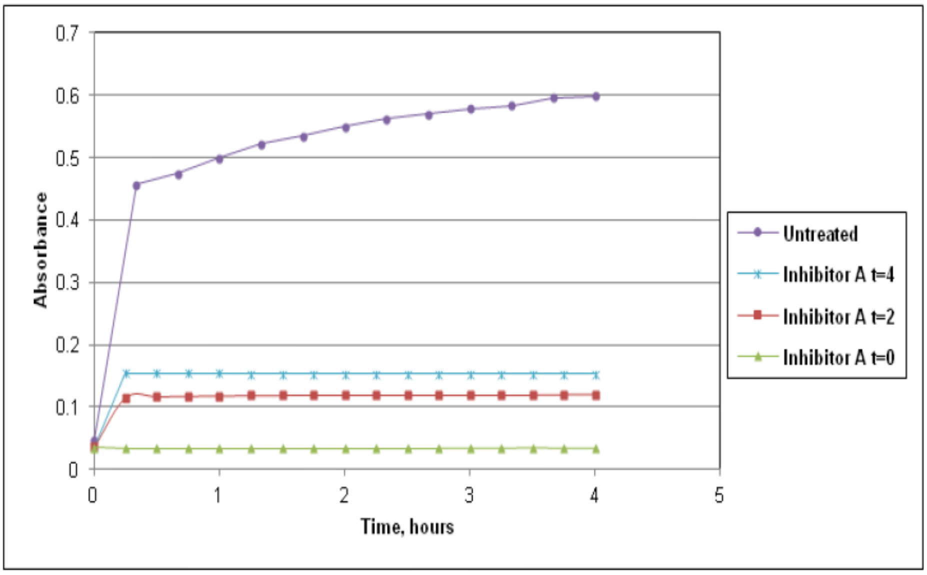
Table 2: Scale Coupon Obervation for Well 104/7-29



Scale Coupon Observations for Well 104/7-29

Month	**Product**	**Dose**	**Scale coupon field observation**
Well Repaired May 22, 2009			
August 2009	Start Inhibitor A		
September 2009	Inhibitor A	300 ppm	Solids on coupon that easily smear. Coupon re-installed
October 2009	Inhibitor A	500 ppm	Loose scale, easily wiped off, reinstalled coupon, chemical rate optimized to 400 ppm.
December 2009	Inhibitor A	400 ppm	Thin scale, easily wiped off. Some sandstone color, coupon replaced, chemical rate set back to 500 ppm.
February 2010	Inhibitor A	500 ppm	Two pieces of loose scale in the coupon holes, easily wiped off, small traces of sandstone color, re-installed coupon
February 2010	Start Inhibitor B		
March 1010	Inhibitor B	500 ppm	Clean, re-installed coupon
April 2010	Inhibitor B	500 ppm	Clean, re-installed coupon
May 2010	Inhibitor B	500 ppm	Clean, re-installed coupon
Well Repaired May 28, 2010, 12.2 months run time			

Sonne et al. (2012) did the initial testing of Baker Hughes's available inhibitors and possible new chemistries by applying scanning bottle test. A litre of synthetic brine was allowed to scale over 24 hours to confirm the presence of silicate scale in this test. X-ray fluorescence (XRF) and x-ray diffraction (XRD) were used to determine elemental composition and crystal structural of precipitated solids. Significant level of elements found in calcium carbonate and metal silicates by using XRF. XRD testing confirms the presence of calcium carbonate in the form of aragonite and magnesium silicate. The test is done by running 'delay' reaction when anion water, ASP water and cation water were mixed without inhibitor. The initial Turbiscan run was completed on the mixed water. Approximately 500 ppm of inhibitor was added after 2 hour and 4 hour and the Turbiscan run was carried out as before.



Scanning bottle test of varied product injection delay times

Figure 9: Scanning Bottle Test of Varied Product Injection Delay Times

From the test, it explained that the ‘delay’ reactions show the best application of silicate scale control products may be to squeeze inhibitor into the formation. The interaction with the dissolved ions is sooner when using the squeezing technique compared to continuous injection. Besides, this will also lead to lower dosage rates.

The case study by Wang et al. (2004) explained on the application and effect of scale removal and inhibition at Daqing field. The scale formation was prevented by using chemical and physical method. Using chemical approach, the well was clean using scale removal agent and pump check recycle was prolonged from 30 days to 109 days. Compared with liquid removal, solid scale removal agent is easy to deliver, easy to add on site with a low cost. The physical measure was applied in serious scale places by using three layer metal-coated pipes, porcelain coating method to prevent scale. Nickel-phosphorus, three layers coated pipes and ordinary pipes on top, middle and bottom positions of the well were applied in central well. After 101 days of operation, the pumps was checked and founded that on top and middle positions, the three –layer compound coated pipe did not scale neither on the inner wall nor the surface. The nickel-phosphorus coated pipe and ordinary pipe scaled for 3mm of thickness, with high density and difficult to remove. On bottom of the well, three layers compound coated pipes scale with thickness about 1mm and easily to remove by nail, but nickel-phosphorus coated pipe and ordinary pipe scaled and difficult to remove.

Chemical scale removal methods applied in producing wells cam prolong the effectiveness of equipments, but the long operating period and the big amount of chemical adding made a high cost. Physical scale prevention method showed a good effect, it could prevent 90% of the scale from forming.

2.4 Green Inhibitor

Green inhibitor or called as green chemistry, or pollution prevention at the molecular level is chemistry designed to reduce or eliminate the use or generation of chemicals that are hazardous to human health and environment (Darling and Rakshpal, 1998). Five types of local plants has been identified as a potential green inhibitor. The plants are *psidium guajava* (jambu batu), aloe Vera, *Ficus deltoidea* (mas cotek), *Persicaria odorata* (daun kesum) and *Orthosiphon Stamineus* (misai kucing).

2.4.1 Psidium Guajava (Guava).

Psidium Guajava is called guayaba in Spanish speaking countries and goiaba in Brazil. Guava is a common shade tree or shrub in door-yard gardens in the tropics. It belongs to family Myrtaceae, genus of Psidium and species of guajava. Plants parts which are used are fruits leave and bark (Vyas et al. 2010). In medical application, P. guajava leaves showed significant inhibitory activities against the growths of two isolates bacteria, *Salmonella* and *Shigella*. Guava sprout extracts by 50% diluted ethanol showed the most effective inhibiton of E.coli, while those 50% acetone were less effective. It is concluded that guava sprout extracts constitute a feasible treatment option for diarrhea caused by E. coli or by S. aureus produced toxins, due to their quick therapeutic action, easy availability in tropical countries and low cost (Viera et al. 2003). Zheng wt al proposed that quercetin present in guava inhibit the intestinal movement and reduce capillary permeability in the abdominal cavity and this may explain the antidiarrhoeal mechanism of Psidium guajava extract. The methanol extract of guava was found out to inhibit paw oedema induced by carrageenan in rats, and pain induced by acetic acid in mice, and it exhibit antipyretic effect in mice (Olajide et al). In addition, the leaves also used for inflammation of kidney and kidney problems.

The leaves contain fixed oil 6% and volatile oil 0.365 %, 3.15% resin, 8.5% tannin and a number of other fixed substances. In addition, the leaves contain an essential oil rich in cineol and four triterpenic acids as well as three flavonoids;

quercdetin, avicularin and its 3-L-4 –pyranoside with strong antibacterial action (Oliver- Bever). The essential oil from the leaves has been shown to contain nerolidiol, β-sitosterol, ursolic, crategolic and guayavoli acids have also been identified (Iwu).

Figure 10 Psidium Guajava (Guava).

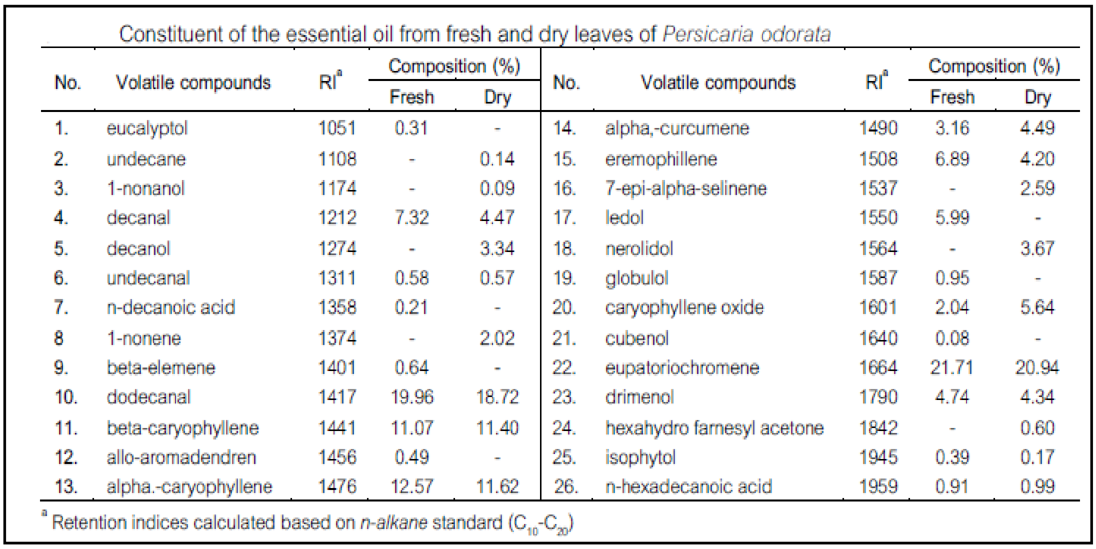
2.4.2 *Persicaria odorata* (Kesum)

Persicaria Odorata, the Vietnamese coriander is an herb whose leaves are used in Southeast Asian cooking. Other English names for the herb include Vietnamese mint, Vietnamese cilantro, Cambodian mint and hot mint. In Malaysia and Singapore it is called daun kesom or laksa leaf. This plant is a perennial herb 30-35 cm height with pointed leaves 6-15 cm with distinctive dark purple marking in the center of the leaves (Starkenmann et al., 2006).

Figure 11: Persicaria Odorata (Kesum)

Volatile compound from essential oil of Persicaria odorata contains aldehyde such as decanal (28%) and dodecanol (44%), as well as decanol (11%). Although volatile compound from essential oil of the plant has been determined, the plant which extracted by different condition and extraction methods gave different organoleptic profile. The difference in the composition of volatile compound obtained by solvent extraction as opposed to distillation and this may also influence on chemical and volatile properties (Hashemi et al., 2008).

Table 3: Constituents of the essential oil from fresh and dry leaves of Persicaria odorata (Sasongko. P et al.2011)



Constituent of the essential oil from fresh and dry leaves of *Persicaria odorata*

No.	Volatile compounds	RI^a	Composition (%)		No.	Volatile compounds	RI^a	Composition (%)	
			Fresh	Dry				Fresh	Dry
1.	eucalyptol	1051	0.31	-	14.	alpha,-curcumene	1490	3.16	4.49
2.	undecane	1108	-	0.14	15.	eremophillene	1508	6.89	4.20
3.	1-nonanol	1174	-	0.09	16.	7-epi-alpha-selinene	1537	-	2.59
4.	decanal	1212	7.32	4.47	17.	ledol	1550	5.99	-
5.	decanol	1274	-	3.34	18.	nerolidol	1564	-	3.67
6.	undecanal	1311	0.58	0.57	19.	globulol	1587	0.95	-
7.	n-decanoic acid	1358	0.21	-	20.	caryophyllene oxide	1601	2.04	5.64
8	1-nonene	1374	-	2.02	21.	cubenol	1640	0.08	-
9.	beta-elemene	1401	0.64	-	22.	eupatoriochromene	1664	21.71	20.94
10.	dodecanal	1417	19.96	18.72	23.	drimenol	1790	4.74	4.34
11.	beta-caryophyllene	1441	11.07	11.40	24.	hexahydro farnesyl acetone	1842	-	0.60
12.	allo-aromadendren	1456	0.49	-	25.	isophytol	1945	0.39	0.17
13.	alpha.-caryophyllene	1476	12.57	11.62	26.	n-hexadecanoic acid	1959	0.91	0.99

^{a} Retention indices calculated based on *n-alkane* standard (C_{10}-C_{20})

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2.4.3*Orthosiphon Stamineus* (misai kucing).

Orthosiphon Stamineus Benth or locally known as “cat whisker”, is a medicinal herb which have ethnomedicinal applications in South East Asia, particularly Malaysia and Indonesia (Mat-Salleh , K, 2002). Historically, this herb were used as a traditionally folk medicine for the treatment of diabetes, edema, epilepsy, eruptive fever, gallstones, hepatitis, hypertension, renal stones as well as rheumatism (Awale, S. 2003). Study by Guerin et al. 1989 has led to isolation of the two novel highly oxygenated pimarane diterpenes, orthisiphols A. Olah et al. revealed the presence of caffeic acid, cichoric acid, rosmarinic acid, sinesetine and patorine. Four novel highly oxygenated ispimarene-type diterpenes, namely, siphonoles A-D and a novel biogenetically interesting norisopimarane-type diterpine named siphonol E.

Figure 12: Orthisiphols A and *Orthosiphon Stamineus* (misai kucing).

2.4.5 *Centella Asiatica* (Pegaga)

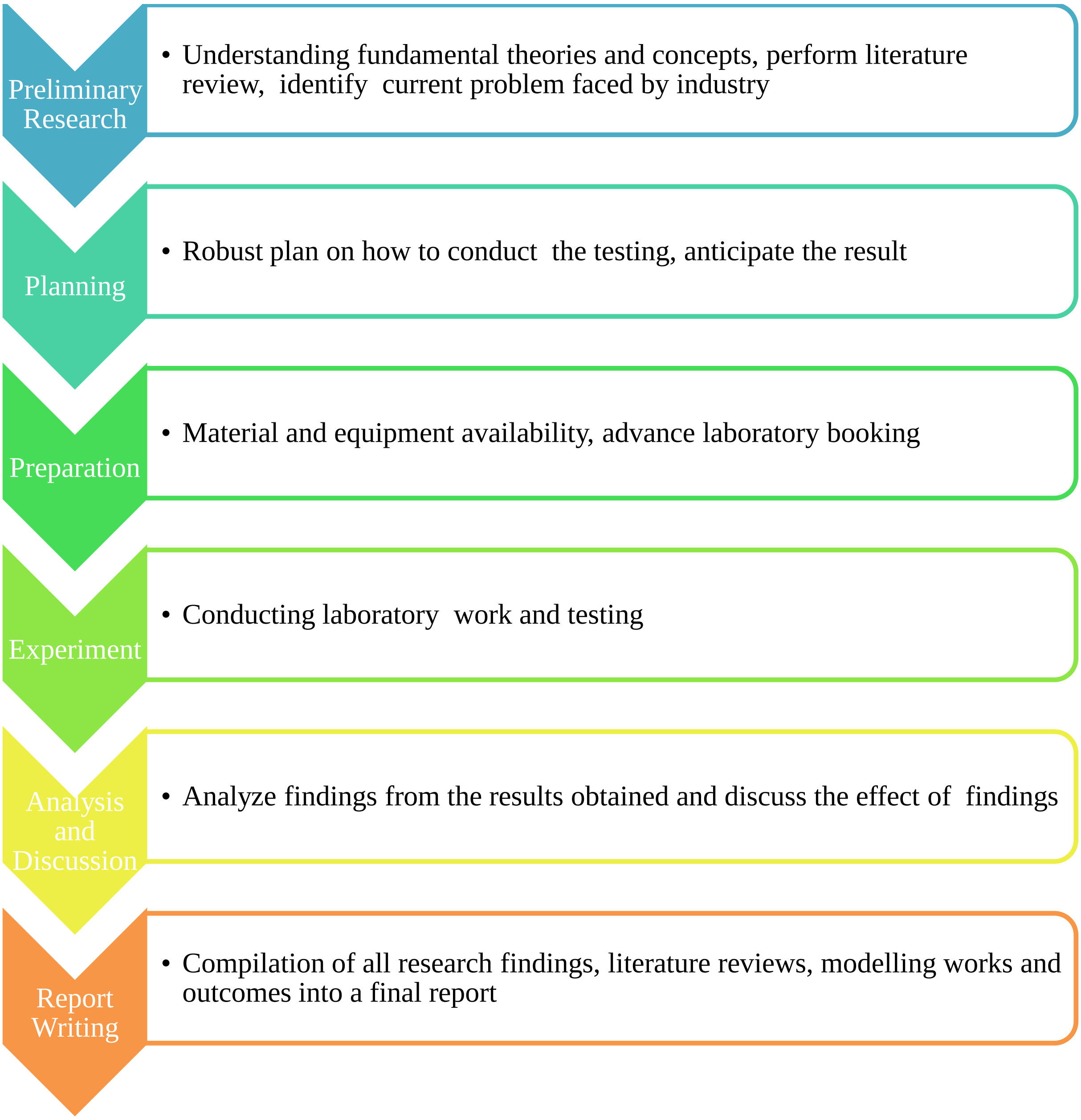
Centella asiatica (CA), a clonal, perennial herbaceous creeper belonging to the family*Umbellifere* (*Apiceae*) is found throughout India growing in moist places up to an altitude of 1800 m (Gohil et al, 2010). The primary active constituents of CA are saponins (also called triterpenoids), which include asiaticosides, in which a trisaccharide moiety is linked to the aglycone asiatic acid, madecassoside and madasiatic acid (Singh B, Rastogi RP, 1969). In addition, the total extract contains plant sterols, flavonoids, and other components with no known pharmacological activity, namely, abundant tannins (20-25%), essential acid (0.1% with beta-chariophylen, trans-beta-pharnesen and germachrene D), phytosterols (campesterol, sitosterol, stigmasterol), mucilages, resins, free aminoacids (alanine, serine, aminobutyrate, aspartate, glutamate, lysine and treonine), flavonoids (derivates of chercetin and kempferol), an alkaloid (hydrochotine), a bitter component (vallerine), fatty acids (linoleic acids, linolnelic, oleic, palmitic and stearic acids) (Srivastava R, Shukla YN, Kumar S., 1997).

Figure 13: Centella Asiatica

CHAPTER 3

Methodology

3.1 Project Methodology



- Understanding fundamental theories and concepts, perform literature review, identify current problem faced by industry
- Robust plan on how to conduct the testing, anticipate the result
- Material and equipment availability, advance laboratory booking
- Conducting laboratory work and testing
- Analyze findings from the results obtained and discuss the effect of findings
- Compilation of all research findings, literature reviews, modelling works and outcomes into a final report

3.2 Key Milestones

Week	Objectives
	FYP I
5	Completion of preliminary research work
6	Submission of extended proposal
9	Completion of proposal defence
12	Confirmation on lab material and equipment for conducting experiment
13	Submission of Interim draft report
14	Submission of Interim report
	FYP II
5	Finalized the experiment procedure
6	Conducting experiment
7	Result analysis and discussion
8	Submission of progress report
9	Preparation for Pre-SEDEX
11	Pre-SEDEX
12	Submission of draft report
13	Submission of technical paper and dissertation
14	Oral presentation
15	Submission of project dissertation

3.3 Experiment Methodology

3.3.1 Samples Preparation

The following green plant samples will be extracted:

a. Centella Asiatica (Pegaga)
b. Orthosipon Staminus (Misai Kucing)
c. Psidium Guajava (Jambu Batu)
d. Polygonum Minus (Kesum)

A. Samples Drying and Grinding

Samples were all obtained from a wet market in Batu Gajah, Perak, Malaysia. The plants were thoroughly washed under a running tap water. The plant samples were dried under shade and were milled using mortar grinder machine. The powdered was sieved and stored in plastic bottle at room temperature.

Figure 14: Drying of Sample

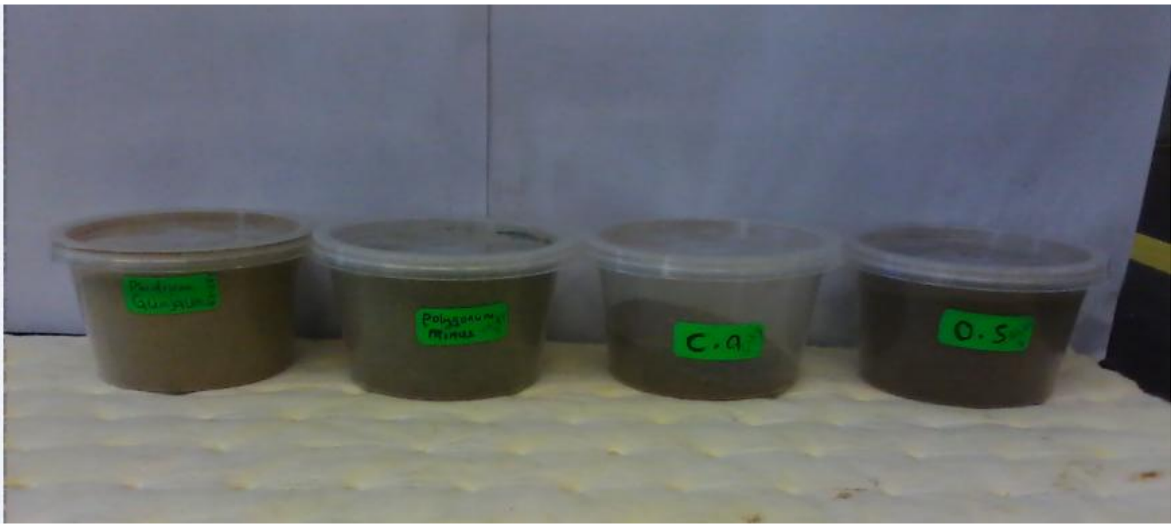


Figure 15: Samples Powder

B. The samples then were extracted using Soxhlet Extractor.

Soxhlet Extraction Procedure:

1. The sample is placed in a porous cellulose thimble.
2. The thimble is placed in an extraction chamber, which is suspended above a flask containing the solvent and below a condenser.
3. The flask is heated and the solvent evaporated and moves up into the condenser where it is converted into a liquid that trickles into extraction chamber containing the samples.
4. The extraction chamber is designed in such way that when the solvent surrounding the sample exceeds a certain level, it overflows and trickles back down into boiling flask.
5. At the end of extraction process, which last for few hours depending on the volume of extract required, the flask containing the solvent and sample is removed.

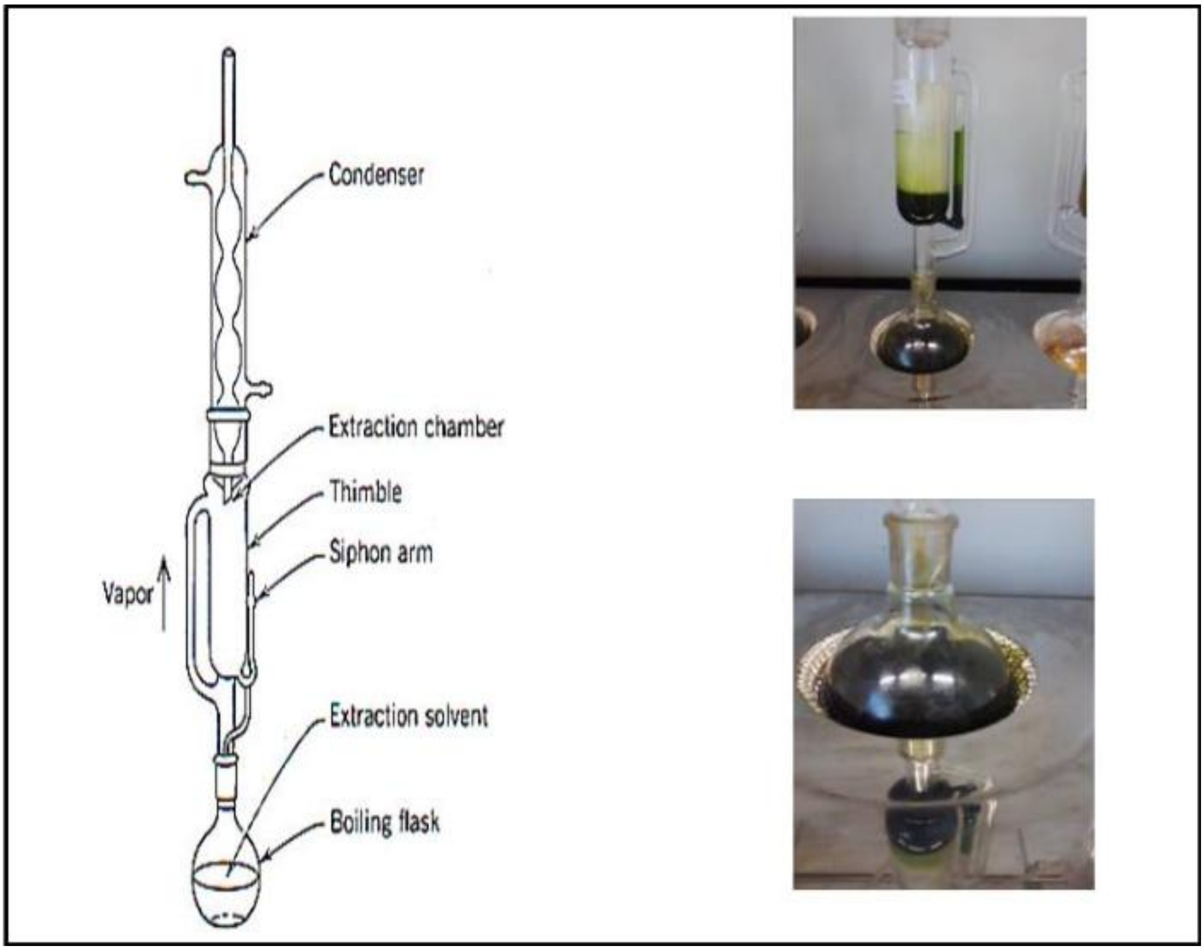


Figure 16: Soxhlet Extractor

C. Samples Purification

Rotary evaporator is used to separate the methanol from the extracted samples.

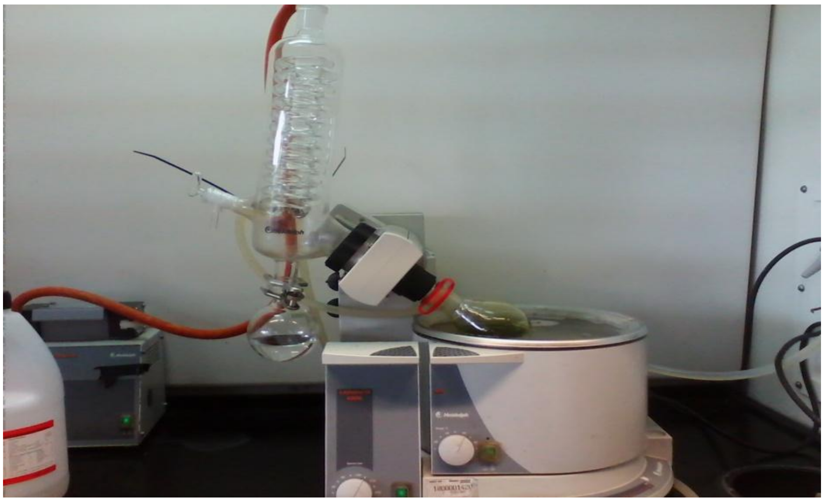


Figure 17: Rotary Evaporator

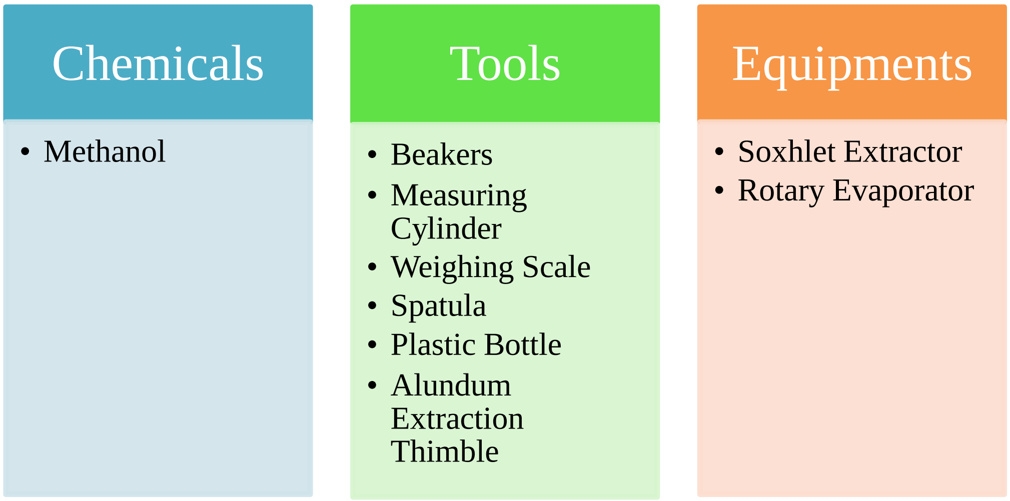


Figure 18 : Materials and Tools for Samples Preparation

3.3.2 Static Test

1. ASP, Connate Anion and Connate Cation water were prepared and pH of ASP adjusted to 10.7, while connate anion 7.0.

Table 4: Composition of Salts to Create Silicate Scale [3]

Salts	ASP Water (g/l)	Connate Anion Water (g/l)	Connate Cation Water (g/l)
NaCl	2.5	2.4	3.5
KCl	0.08		0.16
$NaHCO_3$	2.8	5.6	
Na_2SO_4	0.3	0.6	
$NaSiO_{3-}\ 5H_2O$	14.2		4.0
$CaCl_2$- $5H_2O$			1.8
$BaCl_{2-}\ 5H_2O$			0.06
pH	10.7	7.0	

2. 25 ml of connate anion water was added into plastic bottle of 150 ml.

3. Then, add 25 ml of connate cation water and mix.

4. Immediately add 50 ml ASP water while still mixing.

5. Monitor turbidity of mix water over time.

6. Record the turbidity using Turbidimeter.

Notes:

The parameters of solution such as pH and temperature can be adjusted, if desired to test the effect of other parameters to the turbidity of solution.

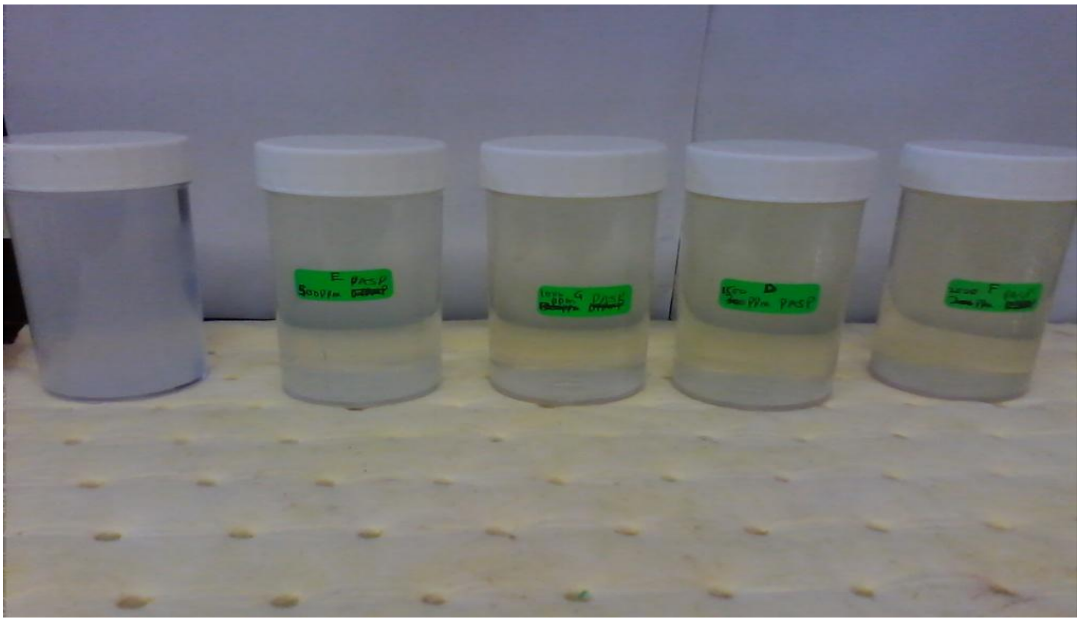
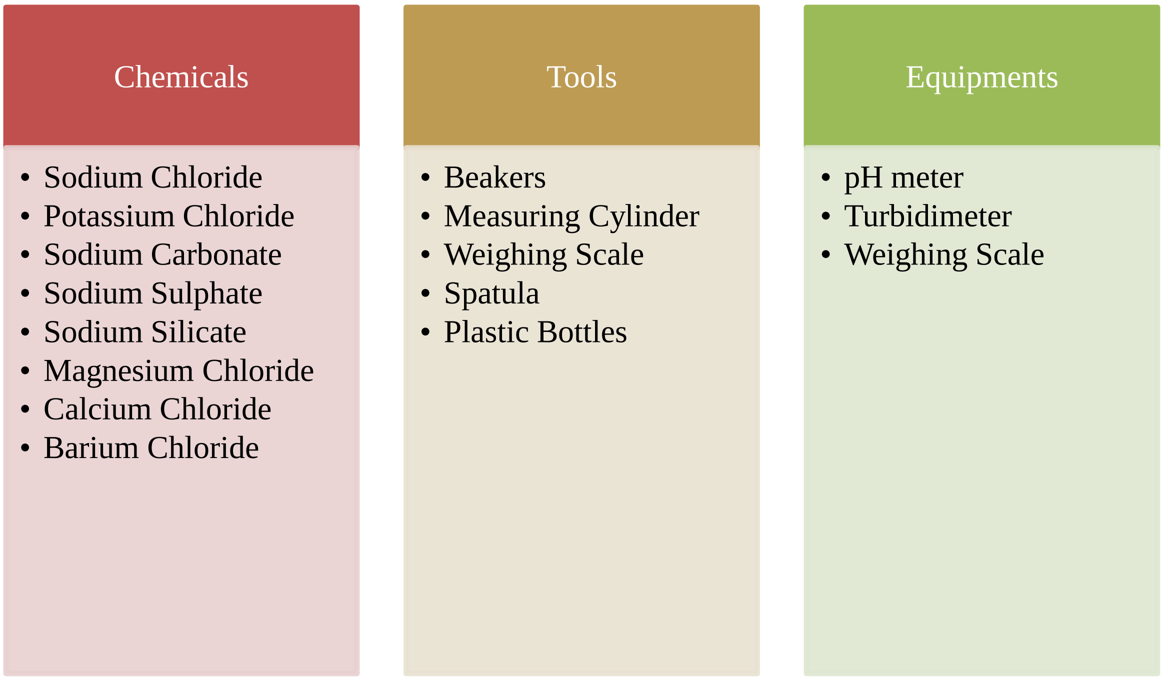


Figure 19 : Mixture Solution and Turbidimeter

3.3.1.2 Materials and Tools for Static Test



Chemicals

- Sodium Chloride
- Potassium Chloride
- Sodium Carbonate
- Sodium Sulphate
- Sodium Silicate
- Magnesium Chloride
- Calcium Chloride
- Barium Chloride

Tools

- Beakers
- Measuring Cylinder
- Weighing Scale
- Spatula
- Plastic Bottles

Equipments

- pH meter
- Turbidimeter
- Weighing Scale

Figure 20: Materials and Tools for Static Test

3.4 Gantt Chart

TOPIC	PROJECT ACTIVITIES	WEEKS																											
		Final Year Project 1														Final Year Project 2													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Project Scope Validation	🟥																											
	Project Introduction		🟥	🟥	🟥	🟥	🟥																						
	Submission of Extended Proposal						🟨																						
	Identify material and equipment						🟥	🟥																					
	Training on how to conduct experiment							🟥	🟥	🟥																			
	Proposal Defence									🟨																			
	Detail Study									🟥	🟥	🟥	🟥	🟥	🟥														
	Submission of Interim Draft Report														🟨														
	Finalized Procedure														🟥	🟥	🟥												
	Conducting Experiment															🟥	🟥	🟥	🟥	🟥									
	Result analysis and discussion																		🟥	🟥	🟥	🟥							
	Submission of progress report																						🟨						
	Preparation for Pre-SEDEX																						🟥	🟥	🟥	🟥			
	Pre-SEDEX																									🟨			
	Submission of draft report																									🟥	🟥		
	Submission of technical paper and dissertation																										🟨		
	Oral presentation																											🟨	
	Submission of project dissertation																												🟨

CHAPTER 4

Result and Discussion

This chapter will discuss about the results of static test that have been experimented..

4. 1 Effect of pH to Silicate Scale

A. Result

Table 5: Effect of pH to Silicate Scale Formation

	pH		
Time (Hour)	pH 7.5	pH 8.5	pH 10.7
0.00	18.80	21.90	67.70
1.00	22.00	24.40	84.10
2.00	23.40	25.80	91.80
3.00	24.30	26.20	99.20
4.00	25.40	27.60	103.80
5.00	27.10	29.60	105.60

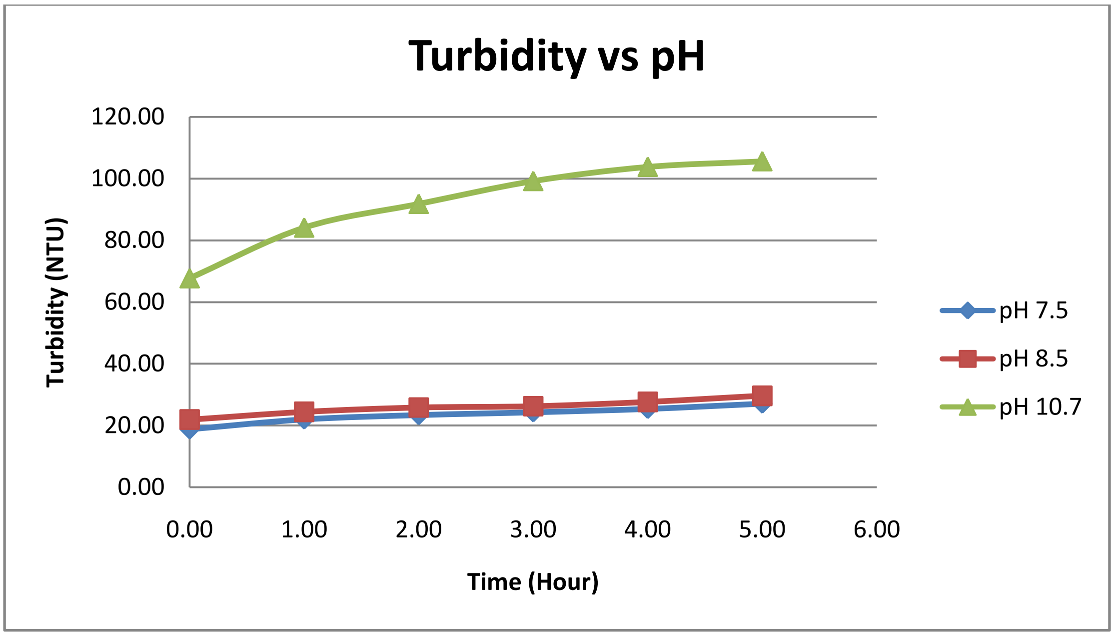


Figure 21: Formation of Silicate Scale with Different pH Values

Figure 22 shows the graph of turbidity versus pH at different time where blank bottle is used with pH of 7.5, 8.5 and 10.7. At pH 10.7, the turbidity is 67.70 NTU at 0 hour, 99.20 NTU at 3 hours and 105.60 NTU at 5 hours. The turbidity at 0 hour for pH 7.5 is 18.80 NTU, 24.30 NTU at 3 hours and 27.10 NTU at 5 hours. It clearly shows that when the pH is high, then silicate scale formation is high.

B. Discussion

Quartz silica is dissolved when the high pH ASP flood moves through the sandstone formation (Arensdorf et al.2010), then after the alkaline ASP water meets the lower pH formation water, the decreased pH of the mixed waters dramatically lowers the solubility of monomeric silica and colloidal silica will form as the silica begins to polymerize at pH levels below 10.5.The following mechanism explains the polymerization of silica in the present of hydroxide ions (Amjad and Zuhl 2008):

$$SiOH_4 + OH^- \rightarrow (OH)_3SiO^- + H_20$$

The speed of reactions largely depends on the present of H^+ ion and OH^- ion during the reaction. If the reaction involves H^+, then more acidic solution will have a faster rate. So, if H^+ is a reactant, then a low pH will have a higher concentration of that reactant, making a faster reaction. Similarly, if OH^- is a reactant, then a high pH will make the reaction go faster because at high pH, the concentration of OH^- is large. [18]

The present of OH^- ions during the polymerization of silica increase the volume of reactant in formation, then when using high pH ASP water, the reaction is faster because high concentration of OH^- at high Ph.

The formation of silicate scale is fast when pH 10.7 is because alkaline solution increases the concentration of OH^- ion that increases the reaction. However, when using pH 7.5, the formation of silicate scale is slow because of slow reaction between solutions as the ion's concentration is low.

The high concentration of OH^- ion speeds up the reaction although inhibitor is introduced to the formation. The lower pH of inhibitor does not give effect to the reaction as compared to high pH of ASP water. When using 300 ppm of inhibitor to the pH 10.7 of ASP water, the turbidity value kept increasing, thus explain pH give significant effect to reaction than the concentration of inhibitor.

4.2. The Effect of Concentration of Inhibitor to Silicate Scale

A. Result

Table 6: Effect of Concentration of Inhibitor to Silicate Scale

		Time (Hour)				
		0.00	1.00	2.00	3.00	4.00
Turbidity (NTU)	Blank Bottle	67.70	84.10	91.80	98.90	102.40
	100ppm	46.20	56.80	65.40	71.80	82.40
	200ppm	32.20	34.30	41.30	49.70	50.20
	300ppm	27.20	33.50	39.00	42.90	45.30
	400ppm	23.90	30.50	34.10	37.40	39.80
	500ppm	23.90	37.40	39.40	40.10	42.50
	1000ppm	6.91	10.10	11.10	12.90	13.20
	1500ppm	2.77	3.91	4.31	5.42	6.78
	2000ppm	2.63	2.84	3.49	4.11	5.23

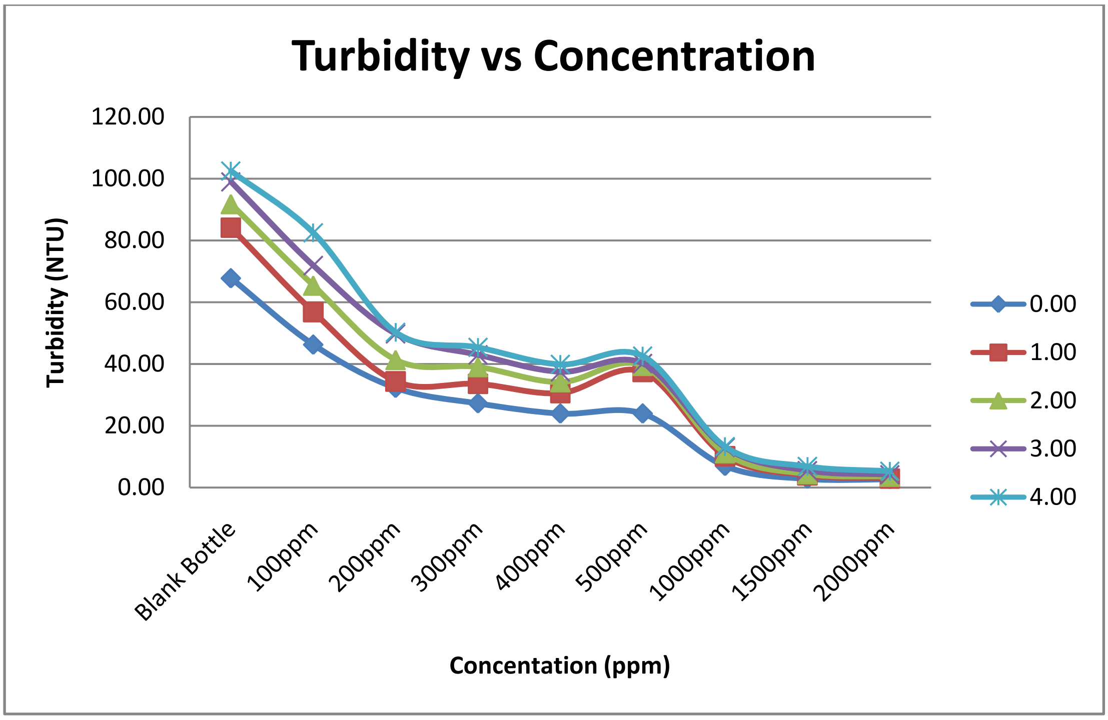


Figure 22: Performance of Inhibitor with Different Concentrations

Figure 24 above shows the turbidity versus concentration of inhibitor with different time. It shows that the inhibitor's concentration give effect to the silicate scale. It can be clearly observed from the figure that the turbidity is decreasing with increasing of inhibitor's concentration. At 0 hour, turbidity for blank bottle is 67.70 NTU, the highest and keeps increasing until 102.4 NTU at 4 hours. 2000ppm of PASP inhibitor gives 2.63 NTU, the lowest turbidity at 0 hour and gradually increasing until 5.23 NTU at 4 hours. The moderate value is shown by 500ppm of PASP inhibitor which gives 23.90 NTU of turbidity at 0 hour and 42.50 NTU at 4 hours. The turbidity values of all samples are decreasing when the concentration of inhibitor is increasing, but the value is increasing within time.

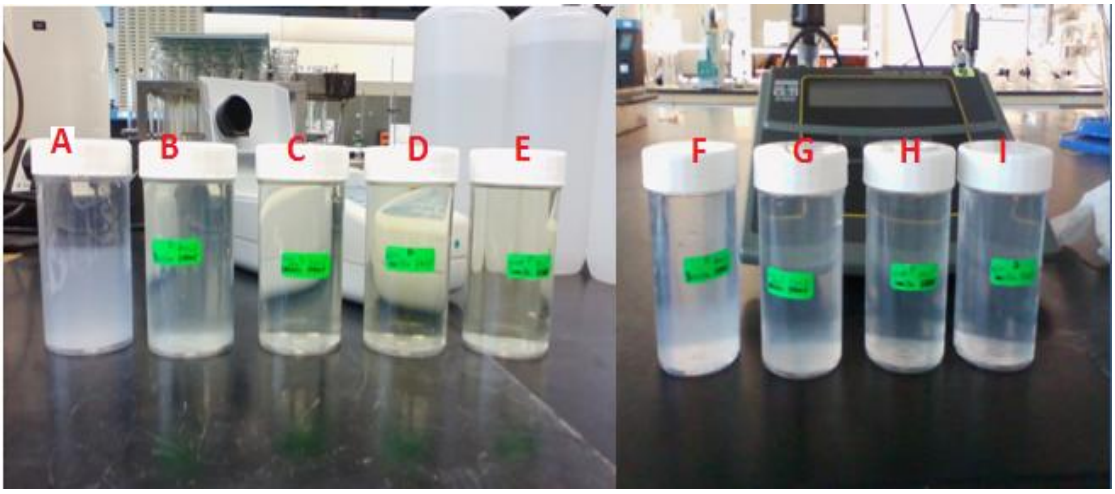


Figure 23: Samples at 0 hour

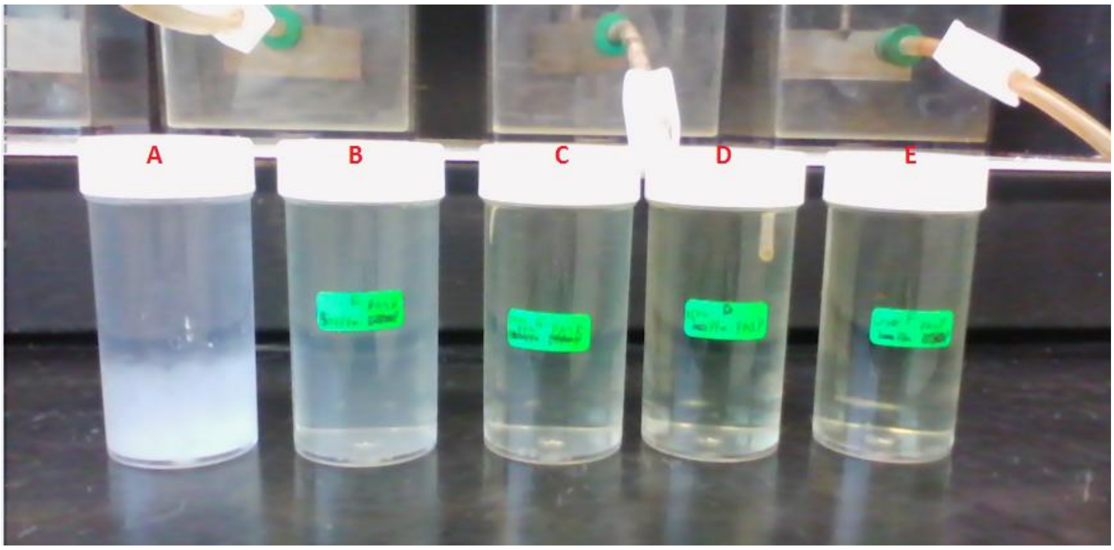


Figure 24: Samples at 4 hours

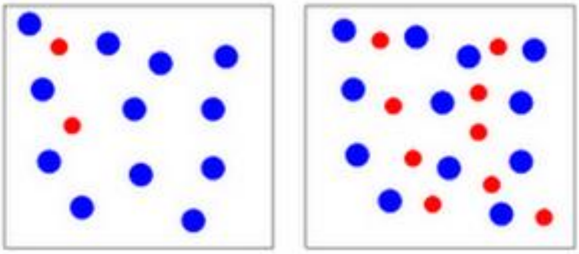
From figure 25 and figure 26, the raw observation of samples can be compared. At 0 hour, all the samples are clear in colour, except the blank bottle (cloudy). Meanwhile, at 4 hours, all the samples become cloudy, showing there is formation of scale in the samples.

Table 7: Samples Description

Sample	Description
A	Blank Sample
B	500 ppm PASP
C	1500 ppm PASP
D	1500 ppm PASP
E	2000 ppm PASP
F	100 ppm PASP
G	200 ppm PASP
H	300 ppm PASP
I	400 ppm PASP

B. Discussion

The function of inhibitor is to slow down or stop the formation of silicate scale. If there is less substances of matter the reaction rate would go at a slower speed and fewer collisions. If there is more substance of matter the reaction rate would speed up because the molecules would come together. As shown in figure below, when the number of red balls per unit volume is increase, then probability for blue balls and red balls to collide is higher. [5]



Formation of silicate scale is slow down by inhibitor if the concentration is high because collisions between particles are high and speed up the reaction. So, when using 2000 ppm of inhibitor, the reaction is fast because of high collision between particles and slow down the formation of silicate scale. Reverse reaction happen when using 100 ppm of inhibitor.

Thus, to slow down formation of silicate scale during ASP flooding, high concentration of inhibitor should be use to slow down the scaling as the inhibitor

4.3 Performance of Green Inhibitor (Orthosipon Staminus and Centella Asiatica) and PASP

A. Result

Table 8 : Turbidity Values of Orthosipon Staminus

	Turbidity				
Time (Hour)	100ppm	200ppm	300ppm	400ppm	500ppm
0.0	29.8	59.3	81.0	75.9	93.0
1.0	62.3	66.5	86.9	72.1	52.1
2.0	81.1	82.9	97.3	94.2	121.0
3.0	79.8	76.0	98.7	94.3	123.0
4.0	88.1	82.7	103.0	109.0	117.0

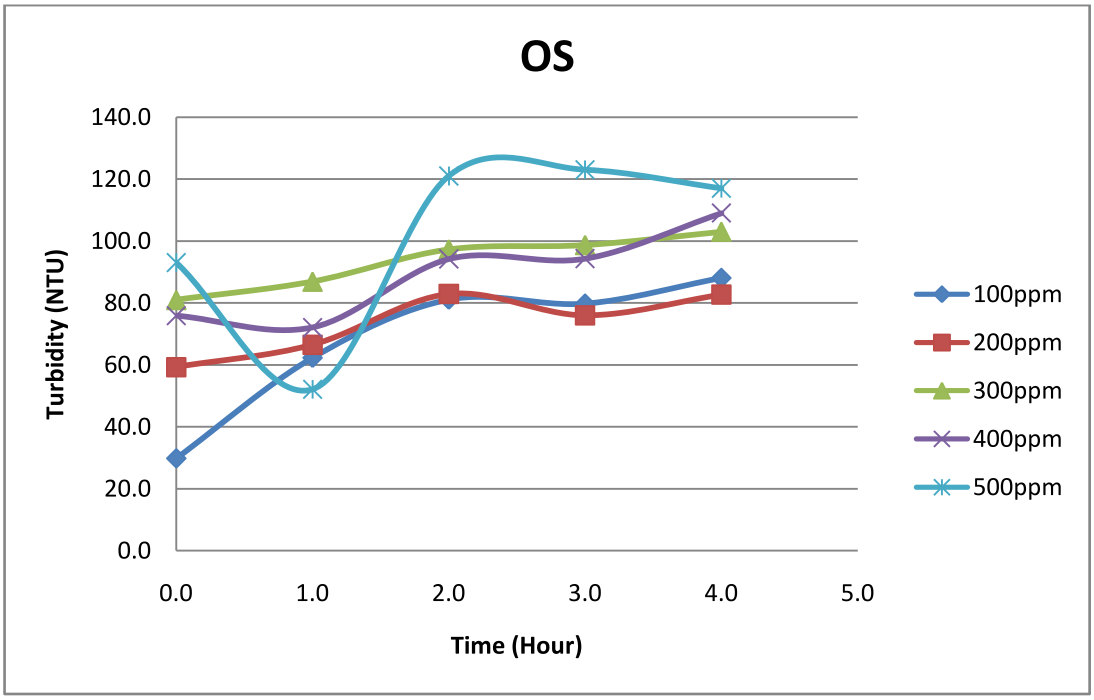


Figure 25: Performance of Orthosipon Staminus within Different Concentration

Figure 27 shows the performance of Orthosipon Staminus when using as inhibitor to mitigate silicate scale. When using 500 ppm of Orthosipon Staminus, the turbidity for 0 hour is 93.0 NTU, then decrease to 52.1 NTU at 1 hour, but increase back to 121.0 NTU at 2 hours and it kept increase until 4 hours. After reduced the concentration to 30 ppm, the value of turbidity at 0 hour is 81.0 NTU and increase to 103.0 NTU at 4 hours. At 100 ppm of inhibitor, it shows the same trend with 300 ppm when the value of turbidity is increasing from 0 hour to 4 hours.

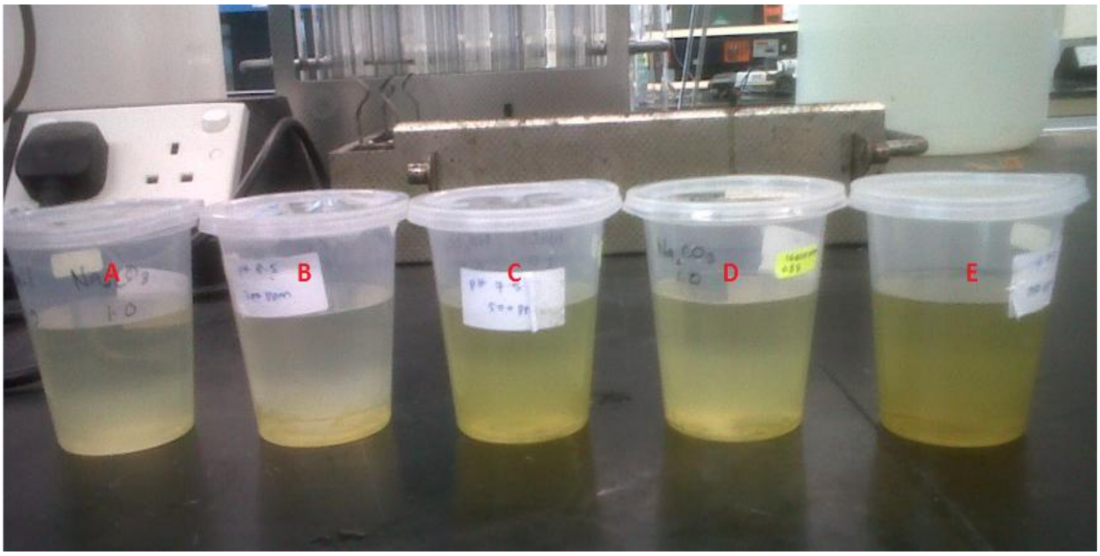


Figure 26 : Samples of Orthosipon Staminus at 0 hour

Table 9 : Samples Description

Sample	Description
A	100ppm of OS
B	200ppm of OS
C	300ppm of OS
D	400ppm of OS
E	500ppm of OS

Figure 24 above shows the five samples with different concentration of Orthosipon Staminus. The colour of samples is darker when the concentration of inhibitor is high.

Table 10: Turbidity Values of Centella Asiatica

	Turbidity				
Time (Hour)	100ppm	200ppm	300ppm	400ppm	500ppm
0.00	45.50	56.70	53.40	50.00	51.10
1.00	49.40	66.20	87.00	63.40	125.00
2.00	56.80	73.40	78.60	73.60	85.00
3.00	63.10	98.10	72.30	71.00	73.30
4.00	65.90	95.50	76.00	73.20	79.60

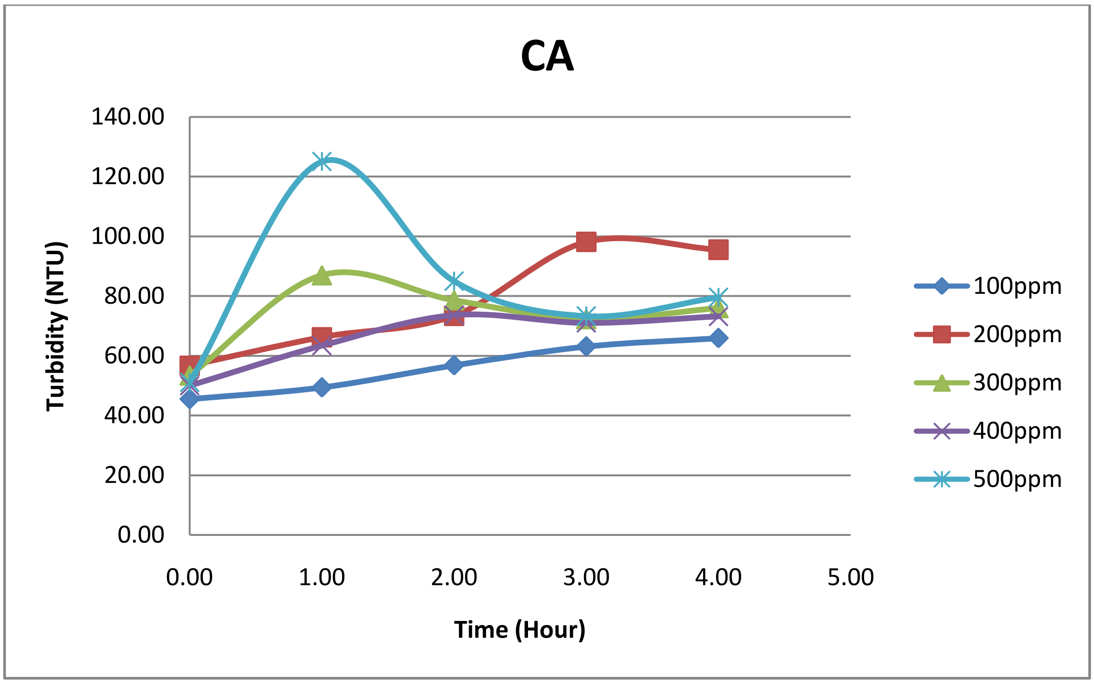


Figure 27: Performance of Centella Asiatica within Different Concentration

Figure 29 is the graph showing the performance of Centella Asiatica as inhibitor. 100 ppm of inhibitor initially used for the test and give 45.50 NTU of turbidity value at 0 hour. As the time passes, turbidity value is increasing and gives 65.90 NTU at the final hour. When using 400 ppm of inhibitor, the initial value is 50.0 NTU, and final value is 73.20 NTU. The turbidity value drastically increase from 51.10 NTU to 125.0 NTU after using 500 ppm of inhibitor, but decrease back to 85.0 NTU at 2 hours.

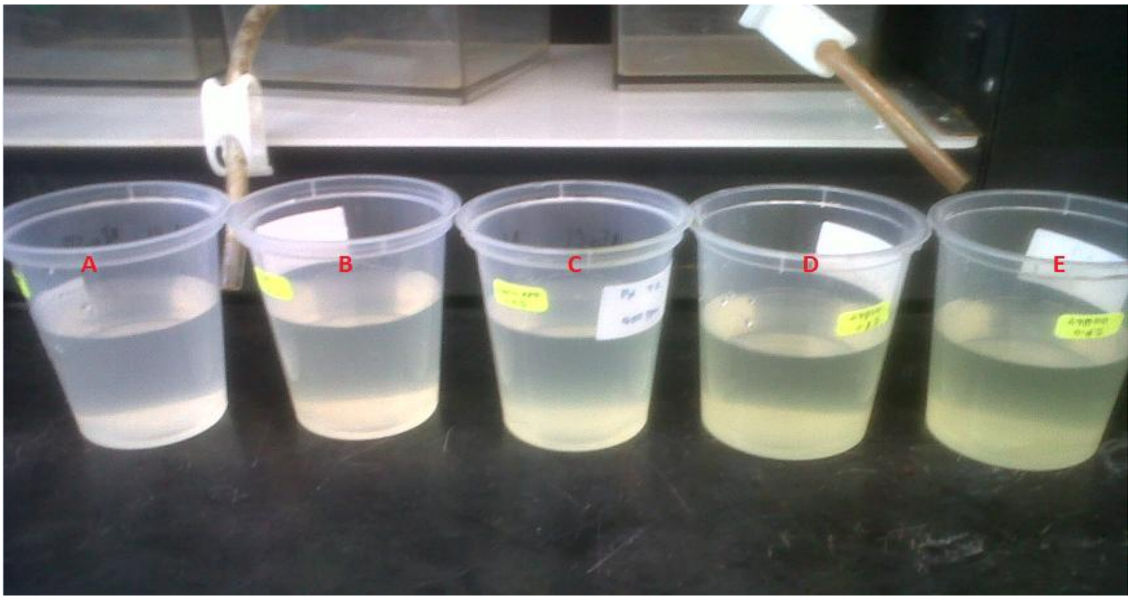


Figure 28: Samples of Centella Asiatica at 0 hour

Table 11: Samples Description

Sample	Description
A	100ppm of CA
B	200ppm of CA
C	300ppm of CA
D	400ppm of CA
E	500ppm of CA

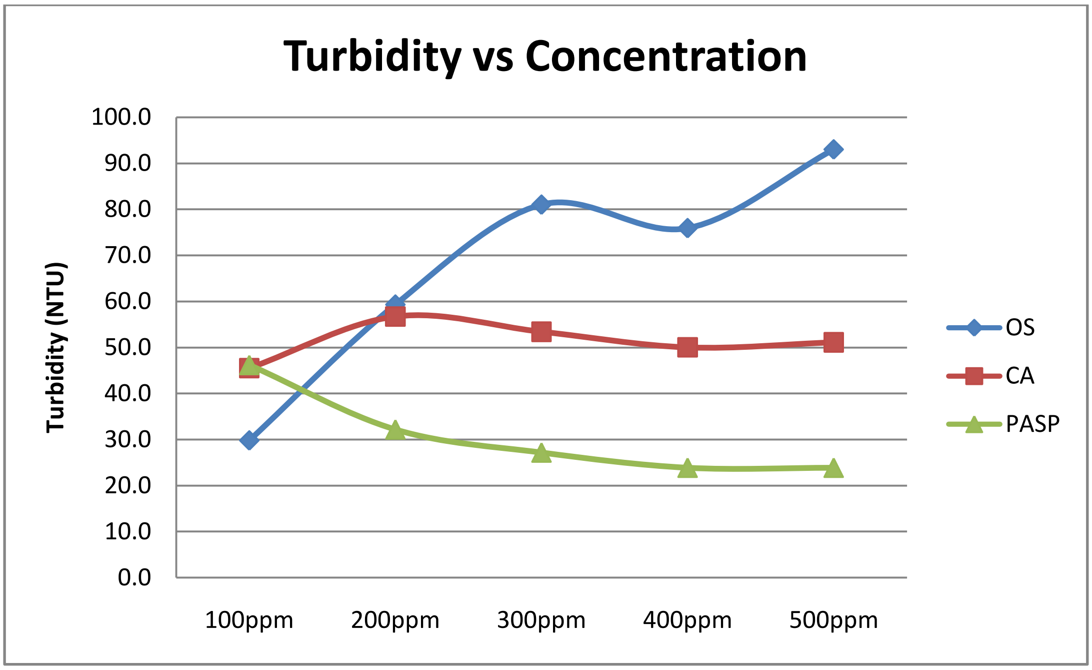


Figure 29: Performance of Centella Asiatica, Orthosipon Staminus and PASP at 0 hour

Figure above shows the effect of turbidity with respect to concentration for three different inhibitors at 0 hour. PASP inhibitor shows the decreasing of turbidity value when the concentration of inhibitor is increasing from 100 ppm to 500 ppm. Meanwhile, turbidity value for Centella Asiatica inhibitor is increase when concentration is changed to 200 ppm, but decrease back when using 300 ppm, 400 ppm and 500 ppm of inhibitor. For Orthosipon Staminus inhibitor, the value of turbidity drastically increases from 100 ppm to 300 ppm, but it decrease when using 400 ppm of inhibitor and increase back at 500 ppm concentration.

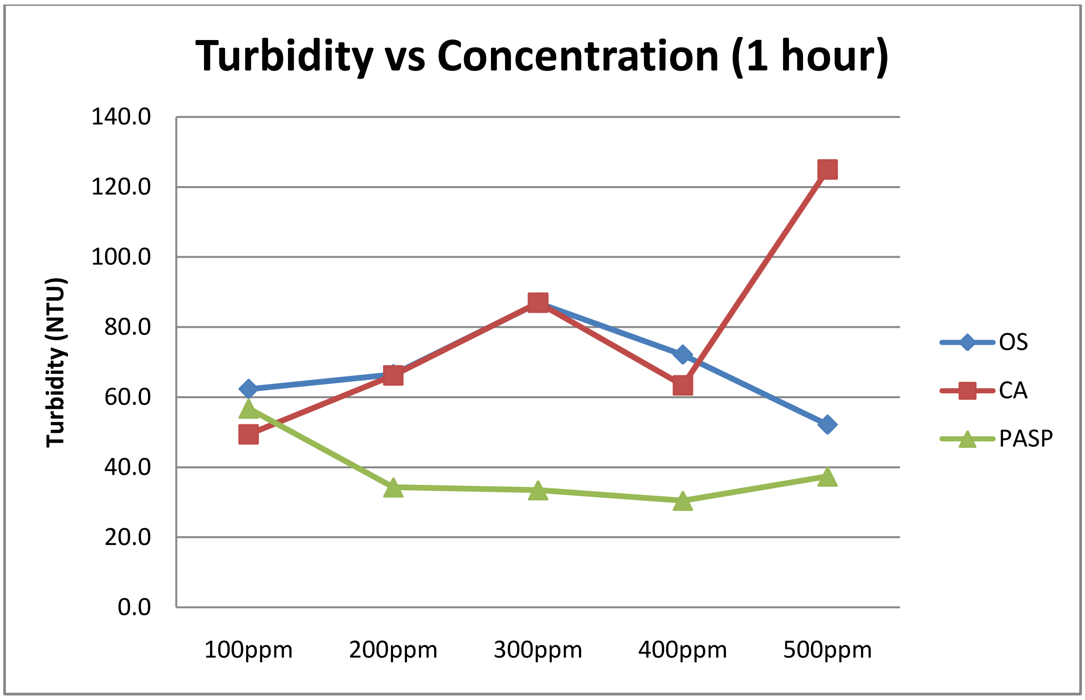


Figure 30: Performance of Centella Asiatica, Orthosipon Staminus and PASP at 1 hour

Figure 32 shows the turbidity versus concentration of inhibitor at 1 hour for three types of inhibitor. Centella Asiatica inhibitor gives the lowest value of inhibitor at 100 ppm, then increases at 200 ppm and 300 ppm , but decrease at 400 ppm and then increase again at 500 ppm. Turbidity value of Orthosipon Staminus inhibitor is highest at 100 ppm, increase at 200 ppm and 300 ppm, but decreases at 400 ppm and 500 ppm concentration. Turbidity value of PASP inhibitor drastically decreases when using 200 ppm and slowly decreases at 300 ppm and 400 ppm, but increases when using 500 ppm.

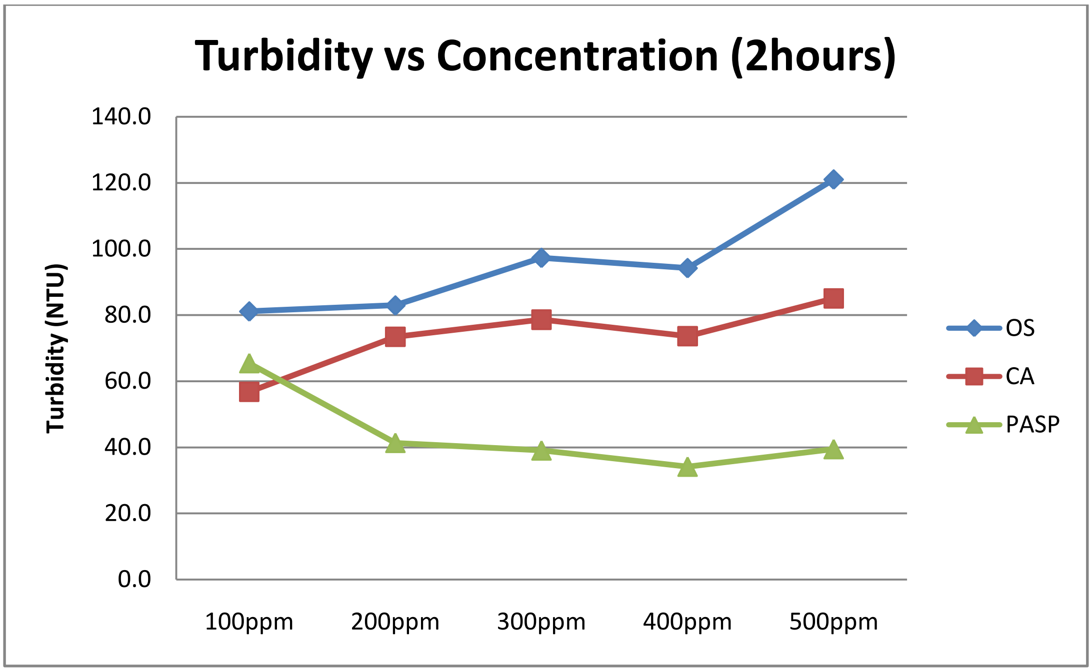


Figure 31: Performance of Centella Asiatica, Orthosipon Staminus and PASP at 2 hours

When the reaction time is increase to 2 hours, as shown in figure 456, the turbidity trend of PASP inhibitor is just same as 1 hour's trend. Both of Orthosipon Staminus and Centella Asiatica inhibitor's turbidity value is increasing when the concentration is increases.

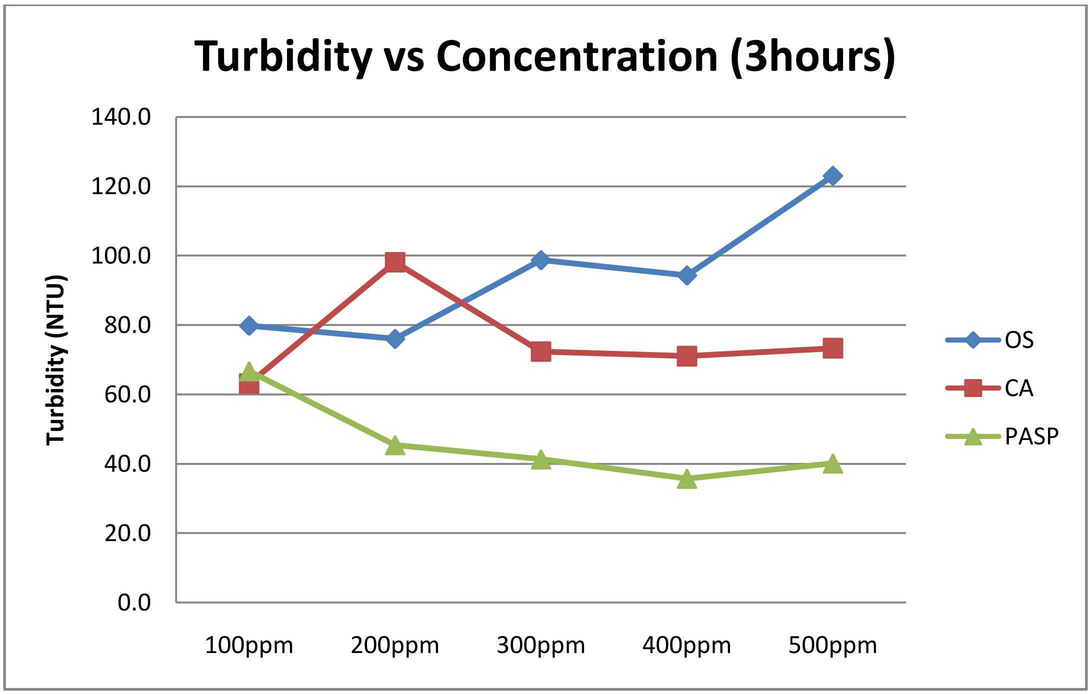


Figure 32: Performance of Centella Asiatica, Orthosipon Staminus and PASP at 3 hours

PASP's turbidity value is kept decreasing as the concentration is decrease until 400 ppm and then increase at 500 ppm. CA inhibitor's turbidity value increase at 200 ppm, then decrease at 300 ppm and 400 ppm and finally increase a bit at 500 ppm. OS inhibitor's turbidity value is increasing with respect to concentration.

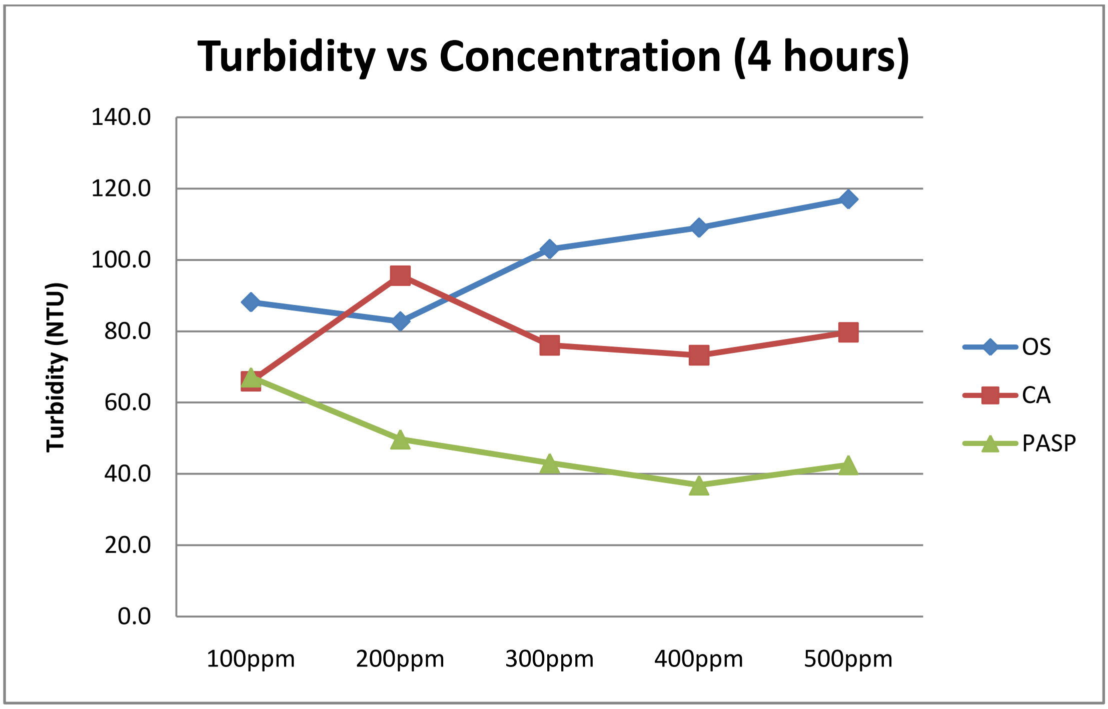


Figure 33: Performance of Centella Asiatica, Orthosipon Staminus and PASP at 4 hours

The test finally carried out at 4 hours as shown in figure 56. Turbidity's trend for all inhibitors is likely as for 3 hours.

B. Discussion

After introduced inhibitor to the formation solution, it should slow down the reaction and decrease the turbidity value. However, when tested with Centella Asiatica and Orthosipon Staminus, the reaction is not getting slower and turbidity value is increase. So, a result is contradicted with the hypothesis of inhibitor to slow down the scale formation.

The contradictions in results obtained can be explained because of misconception of knowledge. Apparently, this experiment had been performed with invalid selection of testing concentrations thus leading to unreliable outcomes gained. The concentrations used are unsuitable as they are considerably high for this test therefore not validating the objective of this test that is to determine the performance of Centella Asiatica and Orthosipon Staminus to mitigate silicate scale.

From figures above, it can be seen that Centella Asiatica show better inhibition effect compare to Orthosipon Staminus at all concentrations tested. This situation happened might possibly due to simple components compositions contained in tested inhibitor, thus leads to insufficient interactions being formed to inhibit silicate scale formation, due to this, both Centella Asiatica and Orthosipon Staminus might need additional chemical process in order to enhance its composition function as improves scale inhibitors. Improved components might influence their inhibiting potential to be higher than as obtained in recent studies.

Quality of extracted inhibitor is also assumed to be one of main interests in ensuring reliability and acceptability of outcome obtained. The colour of inhibitor might affect the reading of turbidimeter. Turbidity is a measurement of how cloudy water appears. Technically, it is a measure of how much light passes through water and it is caused by suspended solid particles that scatter light. So, very green colour of Centella Asiatica and Orthosipon Staminus might disturb turbidimeter reading.

On the other hand, PASP displayed very high inhibition efficiency compare to both of Centella Asiatica and Orthosipon Staminus because it is a commercialized scale inhibitor which present in industry. Its efficiency should be undeniably far better than other inhibitor tested. Outcomes for PASP obtained in this experiment are considered valid as it shows high effectiveness to mitigate silicate scale.

Errors and inaccuracies are inevitable in every experiment. Inaccuracy of measurements is the most predicted human error to be experienced in this test as lots of measuring involved such as weighing powder samples. Besides, machinery errors such as error of turbidimeter to read the turbidity also effect the overall outcomes of this experiment.

CHAPTER 4

Conclusion and Recommendations

4.1 Conclusion

The speed and tendency of silicate scale formation is highly depends on the pH value. If the pH value is higher, then the speed of reaction and tendency is high. The silicate scale obviously will happen during ASP flooding, which contain alkaline surfactant and cannot be ignored. So, inhibitor is produced to slow down or stop the formation process.

The performance of inhibitor can be measured by using different concentrations. When the concentration is high, then inhition capability is increasing.

Centella Asiatica and Orthosipon Staminus are selected as candidates of green inhibitors at early stage of the project. They are examined in order to identify their inhibition capability and potential towards formation of silicate scale through static test. Their performances are evaluated comparatively to commercialized green inhibitor which is PASP. Both green inhibitors have the potential to be further studied as an alternative for silicate scale inhibitor.both of them shows the potentials to be effective inhibitor through laboratory tests. Advances researches and extensive studies on Centella Asiatica and Orthosipon Staminus are needed to further explore their potential.

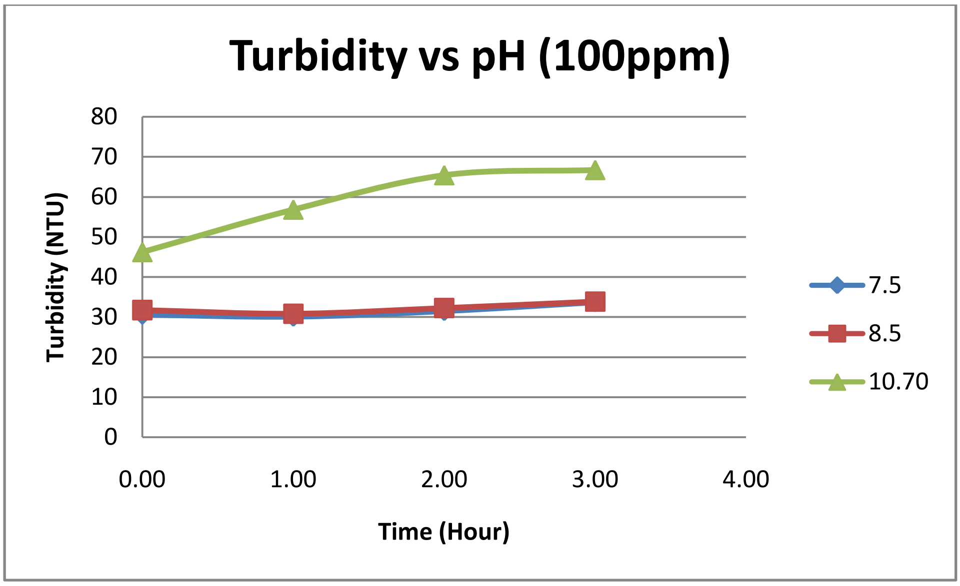
4.2 Recommendations

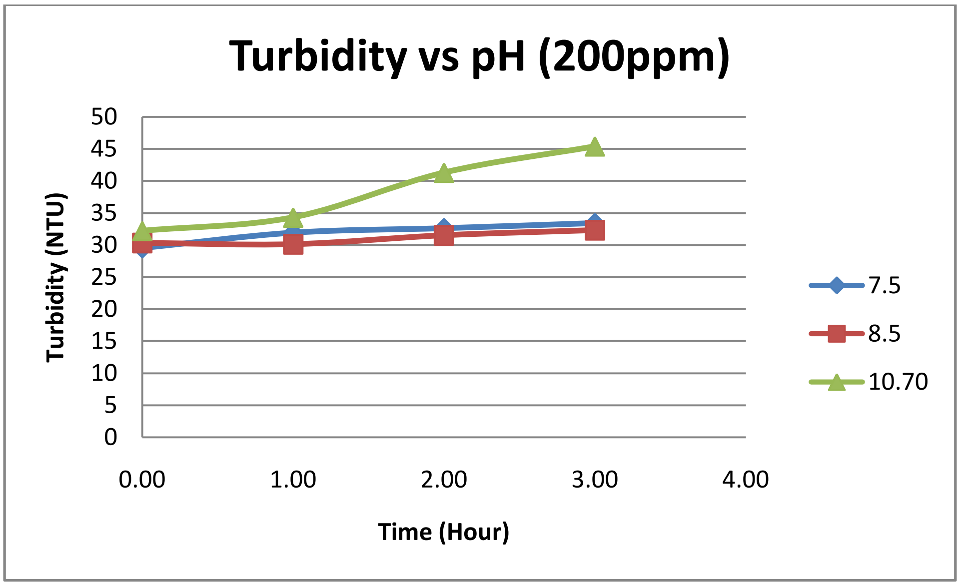
Recommendations for further study their potentials as silicate scale inhibitor are as below:

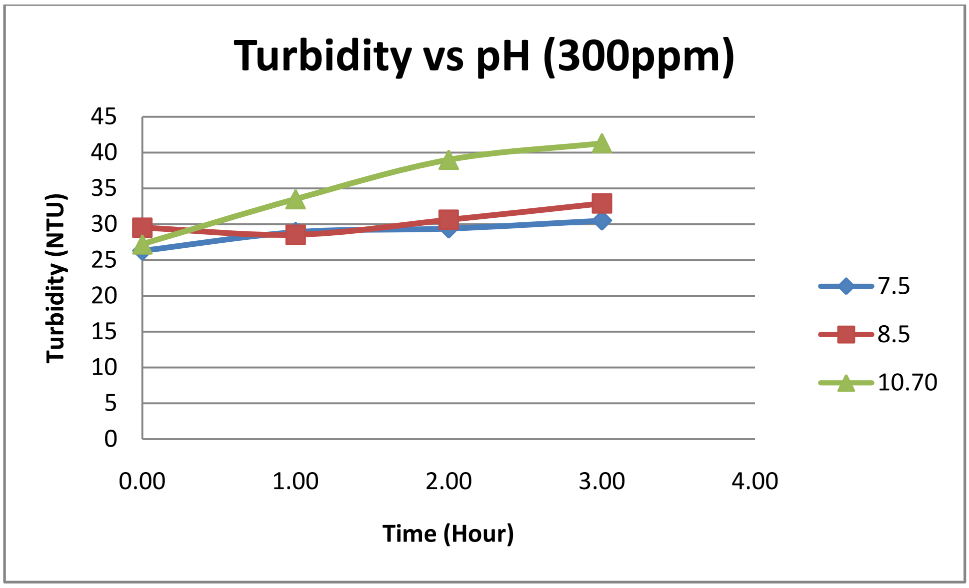
- Perform studies and researches on the active inhibiting components in Centella Asiatica and Orthosipon Staminus in order to acknowledge and enhanced their potential as green inhibitors.
- Find the exact concentrations for Centella Asiatica and Orthosipon Staminus extracts to inhibit scaling which helps in finding Minimum Inhibitor Concentration of both of them in Dynamic Tube Blocking Test.
- Find methods to clear the colour of Centella Asiatica and Orthosipon Staminus extract.
- Instead of using turbidimeter, other equipments should be use such as spectrophotometer to measure the reaction of silicate scale.

- Besides Static Test, Dynamic Tube Blocking Test should also carry out to measure the performance of inhibitor.
- Compare the commercial green inhibitor such as PASP with conventional inhibitor to set a benchmark of performance to produce competitive green scale inhibitor in future.

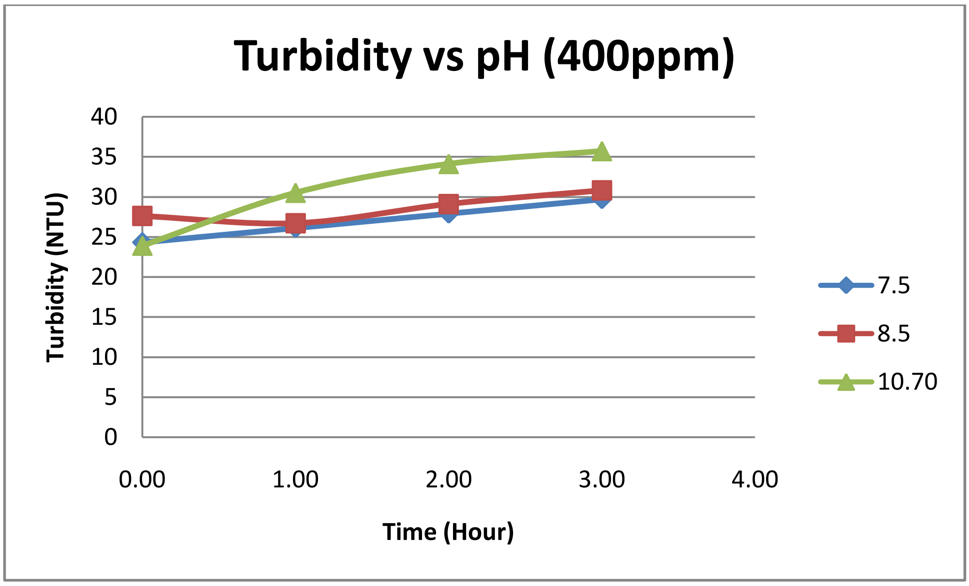
Appendix


Turbidity vs pH (100ppm)
Turbidity (NTU)
80
70
60
50
40
30
20
10
0
0.00
1.00
2.00
3.00
4.00
Time (Hour)
7.5
8.5
10.70

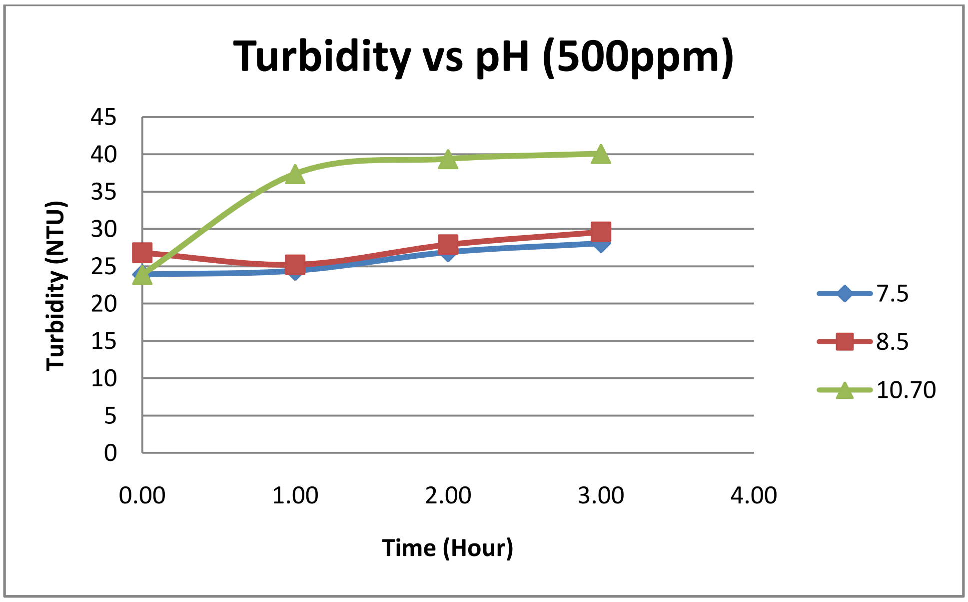

Turbidity vs pH (200ppm)
Turbidity (NTU)
50
45
40
35
30
25
20
15
10
5
0
0.00
1.00
2.00
3.00
4.00
Time (Hour)
7.5
8.5
10.70



Turbidity vs pH (300ppm)
Turbidity (NTU)
45
40
35
30
25
20
15
10
5
0
0.00
1.00
2.00
3.00
4.00
Time (Hour)
7.5
8.5
10.70



Turbidity vs pH (400ppm)
Turbidity (NTU)
40
35
30
25
20
15
10
5
0
0.00
1.00
2.00
3.00
4.00
Time (Hour)
7.5
8.5
10.70



Turbidity vs pH (500ppm)
Turbidity (NTU)
45
40
35
30
25
20
15
10
5
0
0.00
1.00
2.00
3.00
4.00
Time (Hour)
7.5
8.5
10.70

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