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ORIGINAL ARTICLE

Remediation of Oil and Gas Sewage Effluents Using Physical Treatments

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ABSTRACT –The industrial effluents from the oil and gas industry contain harmful contaminants that bring detrimental effects to the aquatic life and human population. The primary concerns are the high value of Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), turbidity and heavy metal content such as ferum and copper in the effluents, which did not comply with the Environmental Quality Act (1974) Industrial Effluent (Regulations) 2009 of Malaysian Department of Environment (DOE). This research aims to study the efficiency of natural bio-coagulants in treating the industrial effluent from the oil and gas industry. The industrial effluent sample was treated by using two natural biocoagulants F.A and F.B and three commercial treatment agents (bio-solvent, alum, and poly aluminium chloride (PAC)). Different beakers consisting of 7.5 wt% of each agent were added into 1.5 L of wastewater sample and left for a week without mechanical assistance. For the second stage, only F.A and alum were used during the experiment. By using five different weight percentages: 2.5%, 5.0%, 7.5%, 10.0%, and 12.5%, the treatment agents were added into 100 ml of wastewater and left for a week without any mechanical assistance. Then, the samples were analyzed for each of the five parameters. The results showed F.A is the best agent in COD treatment, with 41% reduction; followed by alum with 36%, PAC with 26% and bio-solvent with 22% reduction, respectively. The obtained results also showed that F.A and alum are at optimum performances at 7.5 wt%. The F.A and alum efficiency are deteriorating when the dosage is below and above 7.5 wt%.

KEYWORDS
Natural bio-coagulants, industrial effluents, environment, alum, COD reduction.

INTRODUCTION

Malaysia's oil and gas industries are a critical sector of growth for the entire economy and contribute approximately 20% of the country's total gross product in recent years (US Energy Information Administration, 2017). However, rapid activities in oil and gas industries generate industrial effluents with harmful contaminants that bring adverse effects to aquatic life and human populations. Hence, it is vital to ensure the industrial effluents are well treated to protect both ecological and human health (Pinzón-Espinosa & Kanda, 2020). The Malaysian Department of Environment has imposed a stringent standard limit for effluent discharged. The discharge effluents must adhere to the Environmental Quality Act (1974) Industrial Effluent (Regulations) 2009 that covers physical, chemical and biological parameters (Awang et al., 2019; Environmental Quality Act, 2009).

In the oil and gas sector, tonnes of production are being generated daily. The drilling equipment and machinery are also regularly utilised in each batch of the production process. Water and detergents are used in cleaning all the drilling equipment involved in the production. The discharged water will then be discarded as sewage effluent to the temporary effluent tank before releasing to the environment. Even so, the oil and gas industrial player will have to face the problem on the discharged effluent, as it does not comply with the standard limit for effluent discharged imposed by the Malaysian Department of Environment. The effluents contain hazardous materials in high volumes that can alter the parameters of the environment especially Chemical Oxygen Demand (COD), Total Suspended Solid (TSS), water turbidity and heavy metals. Besides, some of the chemicals are known to be acutely toxic, carcinogenic and endocrine-disruptors which is known to be detrimental to public health and the environment (Pitchel, 2016). The installation of a new wastewater treatment plant to treat this industrial effluent will incur an extra cost which is not feasible during this economic downtrend. Thus, it is important to find a feasible alternative which can be the potential treatment for minimizing the number of certain parameters in the industrial effluents before being discharged to the environment (Cui et al., 2020; Paiman et al., 2020; Sahebi et al., 2020; Shamaei et al., 2020)

Natural and commercial or industrial agents are two significant products that are continuously being used in the water treatment sector. Both have some distinct properties and effectiveness that play an important role in coagulation and adsorption processes. In this exploratory work, three types of industrial coagulants and two natural-type ones were used as a treatment agent. Alum, poly aluminium chloride (PAC), and bio-solvent will represent the commercial agents; while Formulation A (F.A) and Formulation F.B as natural ingredient agents. Aluminium Sulphate [$Al_2(SO_4)_3$] or mostly known as alum, is a common type of treatment that usually acts as a coagulant in the water industry (Hussaini Jagaba, 2018).

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Due to its speciality and low cost, alum is constantly being used in the reduction of Chemical Oxygen Demand (COD) and turbidity levels. PAC coagulant has been used and developed in water treatment since ancient times. By using a particular method and specific reactor technologies, PAC can be utilized through the hydrolysis of aluminium chloride solution (Abdo et al., 2020). This coagulant has been widely utilised for COD and turbidity analysis. Apart from its capability of assisting in the rapid flocculation process, it has good performance at low temperatures. Bio-solvent is a water-based product that is used widely in various industrial applications. It is normally used as a cleaning agent and is also known as a degreaser. F.A and F.B are natural bio-coagulants that come from the same source. These two agents were developed by using seafood waste as the main constituent. Both are insoluble in water and organic solvents but readily soluble in acidic solution. The advantages are their biodegradability, non-toxicity, as well as a linear cationic polymer of high molecular weight (Muruganandam et al., 2017; Oladoja, 2015). Due to their many specialities and attractive properties, this type of seafood waste is chosen as an adsorbent material for the effective removal of wastewater. Moreover, seafood waste formulation can produce flocs of better quality, namely, larger flocs and faster settling velocity (Najib Razali et al., 2019).

This study discovers the efficiency of natural ingredients (seafood waste) in treating the sewage effluent from the oil and gas sector. The treatment focusing on reducing the levels of COD, TSS, turbidity and heavy metals (Fe, Cu), as these are the main parameters concerning the above-mentioned industry.

MATERIALS AND METHODS

Materials

An approximate amount of 10 L of raw sewage samples from cleaning activities was collected from an oil and gas company sewage located in Kemaman, Terengganu. The samples were collected twice for analysis purposes and analysed with 30 parameters before treating it with commercial and natural agents. Bio-coagulant agents used in this treatment were F.A and F.B. F.A is prepared by mixing acid, water and seafood waste according to the prescribed ratio. Similarly, F.A is prepared by using seafood waste powder. These two agents were formulated by using a natural bio-coagulant (seafood waste) as their constituents. Commercial agents used in this analysis were bio-solvent, alum, and poly aluminium chloride (PAC). An amount of 1 L of liquid bio-solvent or known as industrial degreaser using microbes was purchased from Isnas Resources Sdn. Bhd.; while 15 L of PAC was acquired from i-Chem Solution Sdn. Bhd. As for the alum powder, the agent was purchased from Train Aid Global Sdn. Bhd. (HmBG).

Preparation of Agents

Natural and industrial agents were prepared beforehand. Alum powder was used as one of the industrial agents in this assay. According to work, the desired concentration of alum solution is 5,000 mg/L (Abu Hassan et al., 2009). An amount of 5 g of alum powder was slowly added into 1 L of distilled water, where it proceeded with rapid stirring for 15 minutes. The prepared 1 L of alum coagulant was stored in a beaker for further use. PAC and bio-solvent were used directly, as both were already in liquid form. Agents from natural bio-coagulants and commercial treatment were prepared at 7.5 wt%. The 7.5 wt% dosage is selected because it is the optimum dosage to treat industrial effluent according to the previous study (Najib Razali et al., 2019).

Sample Treatment

Five beakers were placed according to their designated agents. An estimated 1.5 L of raw industrial effluent samples were poured into each beaker. Each treatment agent at 7.5 wt% was added into the 1.5-L sample and left for a week without any mechanical assistance to simulate the real environment process from the oil and gas industry The samples are positive control in this experiment where that is known to produce results. Each sample is replicate 3 times. The total volume required from each agent for each sample is 112.5 mL and the total volume for each sample is 1.6125 L (1.5 L effluent and 112.5mL of agent). Then, the samples were analyzed from 30 parameters where the primary concern is from five parameters, which are COD, TSS, turbidity, ferum, and copper. For the second analysis, only F.A and alum solutions were used during the experiment. By using five different weight percentages (2.5 wt%, 5.0 wt%, 7.5 wt%, 10.0 wt%, and 12.5 wt%), the treatment agents were added into 100 ml of wastewater and left for a week without any mechanical assistance. This method was to simulate the real situation in the underground tank which sewage water was collected before releasing to the environment.

Analytical Analysis

The analysis for the treated sewage sample was carried out in the Central Lab of Universiti Malaysia Pahang. Parameters of COD, TSS, turbidity and heavy metals (ferum, copper) were analyzed. Table 1 shows the experimental method used in this analysis (Laboratory, 2018).

Table 1. Experimental analysis method.

Parameters	Test Method
COD (Chemical Oxygen Demand)	CENLAB/WI/CHEM-TM/005 (In-House method based on APHA 5210B)
TSS (Total Suspended Solids)	APHA 2450 D
Turbidity	In-House Method based on APHA 2130B
Heavy Metal (Ferum)	In-House Method based on APHA 3010
Heavy Metal (Copper)	In-House Method based on APHA 3010

EXPERIMENTAL RESULTS

Suitable methods for treating industrial effluent samples collected from oil and gas industry companies have been studied and analyzed by using commercial and natural treatment agents. Since the main concern with this industry is the high value of Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), turbidity, and heavy metal content of ferum and copper, for instance, these parameters have been used as indicators in this work.

Characterisation of Oil and Gas Sewage Effluent

Characterising the oil and gas sewage effluent is important to be conducted before a further investigation can be performed to understand the nature and behaviour of the coagulants. It is also important, as it would explain the reason behind its response toward specific treatment that is adopted in this study. The waste emulsion was compared with the Standard A and Standard B water quality parameter limits set by the Department of Environmental Malaysia (DOE), Environmental Quality (Industrial Effluents) Regulations 2009. Discrepancy and comparison of the focused parameters are discussed in this chapter. Besides, from the comparison, it will provide a standard guideline to be compared with the treated wastewater.

Table 1. Characterization of Oil and Gas Sewage Effluent

No	Parameter	Unit	Water Quality Standards		O&G Sewage Effluent
			A	B	
1	Chemical Oxygen Demand	mg/l	50	100	3390
2	Total Suspended Solids	mg/l	50	100	59
3	Colour (Turbidity)	mg/l	100	200	501
4	Iron (Ferum)	mg/l	1.0	5.0	5.26
5	Copper	mg/l	0.2	1.0	3.21
6	pH	-	6.0-9.0	5.5-9.0	6.1

Chemical Oxygen Demand (COD) Reduction

All-natural and commercial agents used in the treatments had the same weight percentage of 7.5 wt%. Based on Figure 1, the Chemical Oxygen Demand (COD) content in the raw sample had exceeded the Standard B requirement, with a value of 3,390 mg/L. However, four out of five treatments showed a reduction in COD level but still unable to meet the Standard B requirement, which is 200 mg/L. The highest COD reduction was recorded by F.A agent, with a value of 2,000 mg/L (approximately 58.7% reduction). Alum was identified as the second highest COD reduction, with a value of 2170 mg/L (36% reduction). Poly aluminium chloride (PAC) had achieved a 22% reduction, followed by the bio-solvent, with a value of 2,660 mg/L (21.5% reduction). F.B did not demonstrate any reduction and as shown in Figure 1, the COD value had increased significantly compared to others.

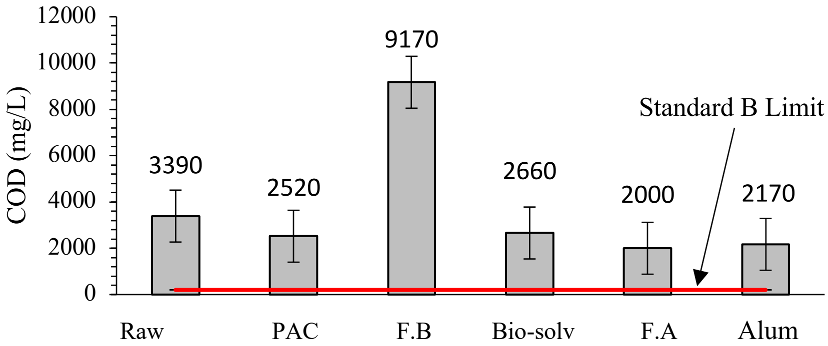

Figure 1. Graph of COD value (mg/L).

Based on Figure 2, the level of COD for raw sewage samples was exceeding the Standard B requirement, with a value of 1,098 mg/L. As shown in Figure 1, the Standard B limit for COD is 200 mg/L. In this second stage of COD analysis, only two agents were used, which are F.A and alum solution. These two agents were prepared at different percentages (2.5 wt%, 5 wt%, 7.5 wt%, 10 wt% and 12.5 wt%), and poured into 100 mL of raw sample. The experiments were left for a week without any mechanical assistance. The highest reduction for F.A had occurred at 7.5 wt%, with a COD value of 509 mg/L; while for alum solution, the highest reduction was recorded at 12.5 wt%, with the COD value of 745 mg/L. The lowest reduction obtained for F.A was at 10 wt%, as the value increased significantly to 1,153 mg/L. At this point, the COD value had exceeded the raw sample value of 1,098 mg/L. The occurrence might due to the utilization of improper methods in analyzing the TSS value; the value was supposed to be reduced as others did. For alum agent, the lowest COD value was at 5 wt%, with 520 mg/L. Figure 2 portrays that F.A had shown better reduction than alum solution at 2.5 wt%, with the COD values being 761 mg/L for F.A and 807 mg/L for alum respectively. At 5 wt%, F.A had greater reduction than alum, with their values of 520 mg/L and 852 mg/L, respectively. At 7.5 wt%, alum seemed to have decreased better than the previous dosage, achieving a 29.05% reduction. Although the value decreased, it still did not surpass the reduction value of F.A at 53.4%. At 10 wt%, alum had a better reduction value of 746 mg/L; while that of F.A had raised to 1,153 mg/L. At 12.5 wt%, alum appeared to be better than F.A, showing their reduction values at 32.15% and 28.6%, respectively. Although the agents did not pass the Standard B limit, both alum and F.A were steadily reducing the COD value from the raw sample. The reduction pattern for both agents fluctuated, as F.A had provided good reduction results only at points 2.5 wt%, 5 wt%, and 7.5 wt%; a sudden increment was observed at point 10 wt%. Then, the COD value dropped at point 12.5 wt%, with 784 mg/L. Meanwhile, the COD value for alum had initially slowly increased but began to drop steadily until it reached point 12.5 wt%. Sewage with high F.A dosage contains highly positive-charged particles in excess based on conductivity reading (2.72 mS/cm), which makes them repel each other, thus lowering the possibility for them to be attracted to the negatively charged particles inside the waste emulsion. For alum conductivity reading (0.02 mS/cm), the higher the dosage, the higher the chances are that the positively charged particles can settle down with the negatively charged ones. At this point, the chemical compound inside the waste emulsion used less oxygen to break the organic matter, as the organic matter will instead be attracted to the positive charge particles (Najib et al, 2019).

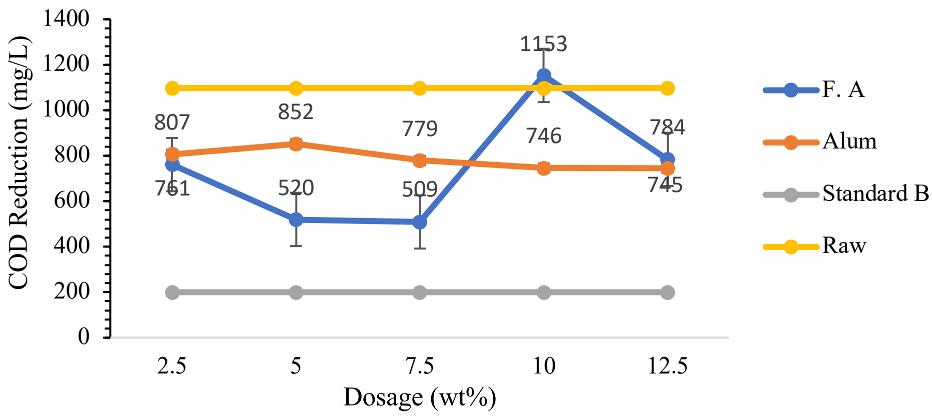

Figure 2. Effect of dosage on COD reduction.

Total Suspended Solid (TSS) Reduction

Figure 3 shows that the Standard B limit for the presence of Total Suspended Solid (TSS) is 100 mg/L. Thus, it can be concluded that the raw sewage sample had passed the regulation rules with its COD level of 59 mg/L. The highest reduction was acquired at 18 mg/L by using a commercial agent: alum solution. The use of F.B had recorded the second-highest reduction, with success in reducing 69.49% of TSS value from the raw sample.

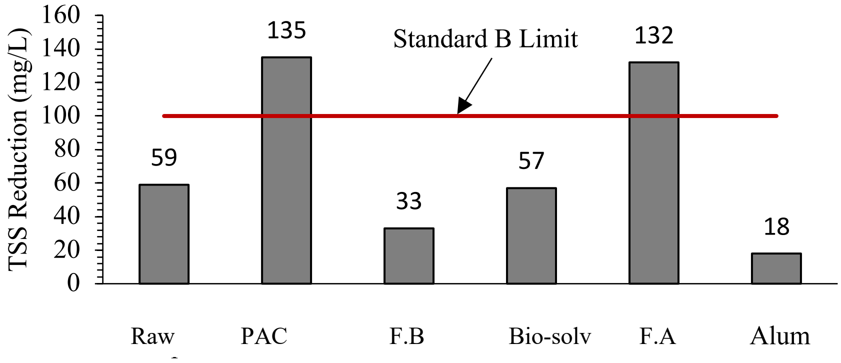

Figure 3. Graph of Total Suspended Solid (TSS) (mg/L).

Another agent that had accomplished in reducing TSS value was bio-solvent. Although the amount reduced was only 3.4%, bio-solvent appeared to be better than F.A, in which the latter had increased the amount rapidly to 132 mg/L. This value surpassed the Standard B limit and this might due to the state of F.A, as the agent was a powder-form substance thus it cause cloudy in the sample. For poly aluminium chloride (PAC), the value also exceeded the Standard B limit with 135 mg/L due to increasing cloudy in the sample. According to Pe & Salle (2016), Alumn can further reduce TSS value. It has a better coagulation performance and can develop stable flocs, even at low temperatures. The flocs are produced from having greater coagulant concentration, as it will generate many cation particles. As a result, it can be concluded that all agents, except for F.A and PAC which is cause sedimentation in the sample, have aided in lowering the TSS value.

Colour (Turbidity) Reduction

From Figure 4, the value of colour presence for raw sewage samples had exceeded the Standard B limit, with 501 mg/L. All treatment agents were observed to have the ability in reducing the colour value of the sample. The highest reduction was recorded from an alum solution, with 10 mg/L. During the experiment, alum appeared to be the first agent that showed a fast reduction mechanism compared with others, as the sewage sample became clear in just three days.

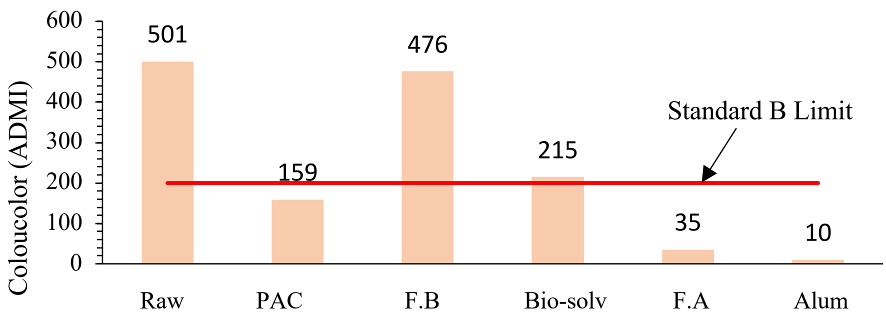

Figure 4. Graph of colour (turbidity) reduction.

Referring to Figure 5, the alum solution had achieved a 98% reduction, which is close to a 100% reduction. This reduction level was followed by F.A with 93%, PAC with 68.26%, bio-solvent with 57.09%, and F.B with 4.99%. F.B was recorded as the lowest reducing agent for colour reduction, while G-Treat A demonstrated much better performance, with a 93% reduction. Bio-solvent and PAC also did well in lowering the colour amount in the sample, which passed the Standard B limit of 200 mg/L. This is happened due to all coagulation and adsorption happened in a week. The substance in the sewage turns to sedimentation in the bottom of the beaker. Thus, it causes clear and clean solution.

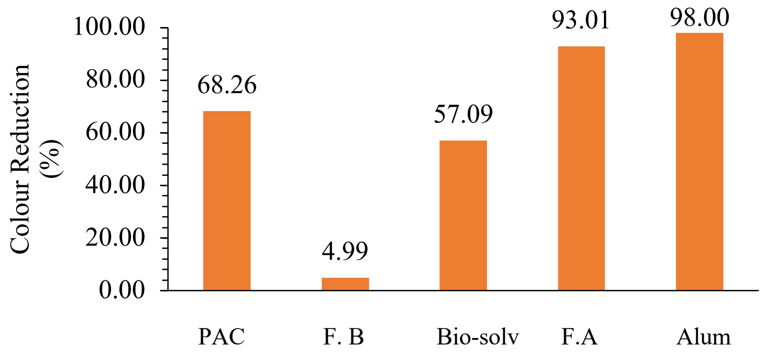

Figure 5. Graph of colour reduction (%).

Heavy Metals (Ferum) Reduction

According to Figure 6, the presence of an iron element in the raw sewage sample had surpassed the Standard B limit, with 5.26 mg/L. Figure 6 displays that the Standard B requirement for heavy metal Fe is 5 mg/L. For natural coagulant, F.A had met the expectation with almost 90% reduction of iron present in the solution. Then, bio-solvent became the second agent that had succeeded in reducing the iron amount from 5.26 mg/L to 3.99 mg/L. Following that are alum and F.B, with reduced levels of more than 20% and 6%, respectively. Polyaluminium chloride (PAC) seemed to be the only agent that exceeded the Standard B limit, with a value of 13.77 mg/L. All commercial and natural agents were observed to obey the regulation rules, except for PAC coagulant. In this analysis, F.A appeared to be better than alum in decreasing the amount of heavy metal Fe in the sewage sample. Based on the results, it showed that all these coagulants had ion exchange characteristic therefore the positive and negative ions coagulated and reduce heavy metals ions concentration in the samples. F.A also had adsorbent characteristic since seafood waste had amino and hydroxyl group. Stronger interaction involves ion direct transfer between ferum ions to seafood waste active component (Razali et al, 2010).

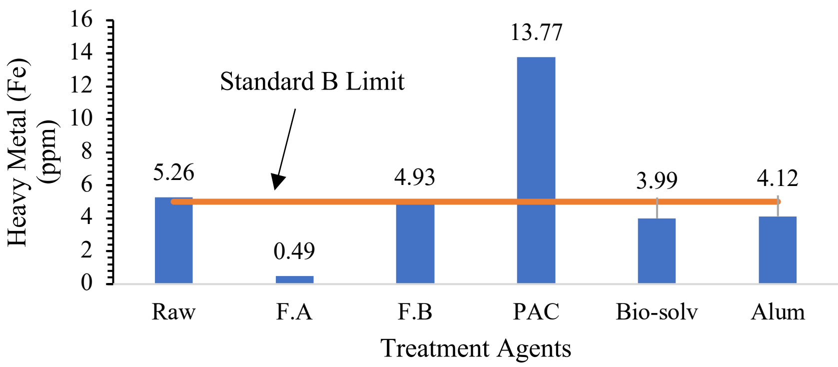

Figure 6. Graph of heavy metal Fe reduction.

Heavy Metals (Copper) Reduction

The graph in Figure 7 shows the level of reduction of heavy metal Copper (Cu) using F.A, F.B, PAC, bio-solvent, and alum. Based on the above-mentioned graph, the use of both F. A and alum solution had shown a similar amount of reduction, which was below 0.1 mg/L. The results obtained from Central Lab, Universiti Malaysia Pahang, showed that the value was unable to be detected, as it was below 0.1 mg/L. For the reduction of copper level, bio-solvent showed superior performance than F.B in lowering the value of heavy metal Copper (Cu) in the sewage sample. Bio-solvent was able to reduce the amount of copper from 3.21 mg/L to 2.2 mg/L; while for F.B, the amount was reduced from 3.21 mg/L to 2.58 mg/L. As predicted, PAC did not show any reduction to the copper value in the sample. The metal value had increased from 3.21 mg/L to 3.99 mg/L. Thus, F.a and alum were chosen as the best agents in lowering the levels of heavy metals in this experiment. Based on the results, it showed that all these coagulants except PAC had ion exchange characteristic therefore the positive and negative ions coagulated and reduce heavy metals ions concentration in the samples. F.A also had adsorbent characteristic since seafood waste had an amino and hydroxyl group. Stronger interaction involves ion direct transfer between heavy metals ions with seafood waste active component (Razali et al, 2010).

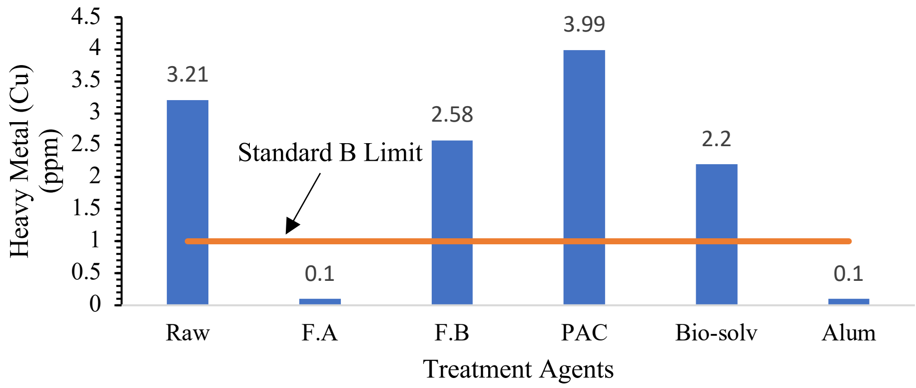

Figure 7. Graph of Copper (Cu) reduction.

CONCLUSION

The study shows that F.A and F.B are comparable to the commercial coagulants in reducing the level of Chemical Oxygen Demand (COD), Total Suspended Solid (TSS), turbidity and heavy metal content of ferum and copper. Based on the results, F.A is the best coagulant in terms of COD, turbidity, ferum and copper reduction. F.A able to reduce 3 parameters (turbidity, ferum and copper) beyond the standard B limit imposed by the Malaysian Department of Environment. Even though F.A showed the highest reduction in COD removal yet the value is relatively higher compared to the standard B limit. On the contrary, the efficiency of F.B is the highest in terms of Total Suspended Solid (TSS) reduction. Since these parameters are main environmental concerns, Both formulation A and B can be utilized, as they are proven to be one of the effective natural bio-coagulants that can be used for treatment in the oil and gas industry. This research also proves that 7.5 wt% of F.A and alum is the optimum dosage to treat the industrial effluents from the oil and gas industry. However, further research needs to be conducted to increase the efficiency of natural bio-coagulants (Formulation A and B) in reducing particularly the COD value as both coagulants cannot reduce the parameter below the Standard B limit.

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