



Treatment of Petroleum and Flowstation Wastewater using Combined Coagulants (A Case Study of Typical Oil Company Flowstation in Nigeria)

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Abstract Performance and effectiveness of single and combined coagulants in the treatment of petroleum and flow station wastewater has been studied. In this study, samples of petroleum and flowsation were treated separated with Barium Chloride, Iron (ii) sulphate, Magnesium Oxide and then with mixtures of different chemicals. Standard methods for examination of water and wastewater was used in the analysis of some important physico-chemical parameters. The results of the analysis of all the parameters in the petroleum and flow station wastewater samples treated with six different types of coagulants shows significant changes and variations in the level of virtually all the parameters in the treated samples when compared with that of the blank.

The combined chemical coagulants exhibited a high capacity to reduce the pollutants to recommended effluent limits with the mixture of Magnesium Hydroxide and Iron (ii) Sulphate been the most effective coagulants. The result revealed that average value of all selected parameters showed variation from points A to F. However, these variations are not statistically significant with F (0.068019) being less than $F_{critical}$

Keywords Petroleum, Flow station, Wastewater, Coagulants, ANOVA

Introduction

One of the greatest problems faced by the oil rich Niger-Delta part of Nigeria is the lack of clean surface and underground water. This is due to the contamination of water bodies with petroleum hydrocarbon. During well drilling, petroleum production, refining and transportation, a large amount of hydrocarbon is spilled directly on the surface of water bodies. They are wastes resulting from processes employed in petroleum industrial establishments and discharged into the environment [1]. Managing oil and gas industrial environment requires close and constant monitoring of the effluent discharges from such industries. The essence of such monitoring is to ascertain the level of compliance of such industries with the pollution control guidelines set by regulatory agencies in Nigeria such as Department of Petroleum Resources and Federal Ministry of Environment.

In flow stations, wastewater consists of water dump coming out of API tank going to the pit which may have mixed with other forms of wastewater such as, produced water after separation of oil and water, sewage water, condensed steam from heaters, overboard water from water injection and drain lines. Wastewaters from petroleum exploration and production processes represent important point sources of toxic organics in the last decade. The petroleum wastewater are complex materials of organic pollutants and most of them contented oil and grease, which clog drain pipes and causing unpleasant odours [2]. In addition, petroleum and flow station waste water also contain nitrates. Petroleum and flow station wastewater effluent will vary from one company to another, depending on the degree of water reuse, and the on-site treatment methods that are used. Effluent water is often referred to as wastewater. Such water contains fundamentally some quantity of substance in such a concentration that makes the water technically polluted [3]. The composition of petroleum wastewater and their



negative effects are summarized by Elshamy et al [4]. The analysis used to characterized the principal impurities found in petroleum and flow station wastewater are have been reported by John Pichtel [5].

However, in flow stations, petroleum wastewater can be sampled from the water outlet of oil-water separators, and this main produced water is majorly re-injected for flooding or disposed [6]. Oil water separators can be designed to treat a variety of contaminants in water including free floating oil, emulsified oil, dissolved oil and suspended solids. Presently, physical, biological and chemical methods are the different conventional methods of petroleum and flow station wastewater treatment. Coagulation, flocculation, precipitation and electrochemical methods are the common chemical techniques and the chemical treatment depends on the type of coagulants [7]. Although aluminum sulphate and ferric chloride are commonly used coagulants, its high cost have induced several investigators to search for low cost non-conventional coagulants. This paper, therefore, examined the suitability of using alternative non-conventional single or combined chemicals as coagulant for petroleum and flow station wastewater treatment.

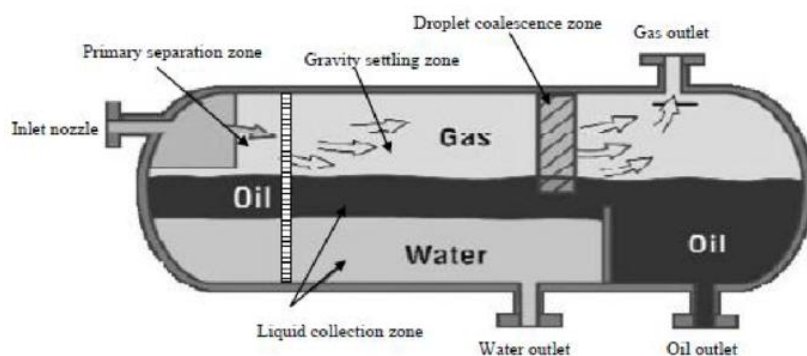


Figure 1: Three phase gravity Separator [8]

Materials and Methods

The chemical coagulants employed in this research were general purpose grade Ferrous sulphate, Barium chloride and magnesium hydroxide. Sample of petroleum wastewater used was collected from a flow station/production platform in a 20 litre jerry can, previously washed with thorough with potable water and dried. The jerry can was filled to the brim with the sample and allowed to overflow in order to remove the entrapped air. The sample sealed and transported to the laboratory for analysis. Coagulation studies were performed using jar test apparatus. Ferric sulphate, Barium chloride, Magnesium chloride and mixtures of ferric sulphate and barium chloride, ferric sulphate and magnesium hydroxide and barium chloride and magnesium hydroxide were treated with the petroleum and flow station wastewater. At the end of the chemical analysis, the clear filtrate was furthered analyzed for some important parameters using Standard for the examination of water and wastewater [9].

Results and Discussion

Table 1: Treatment of samples with single coagulants

Parameters	Blank	FeSO ₄ (5g/100ml)	BaCl ₂ (5g/100ml)	Mg(OH) ₂ (5g/100ml)	DPR Limit (offshore)	FMENV Limits
pH	5.8	6.8	7.1	9.8	6.5-8.5	6.5-8.5
BOD(mg/l)	759.17	5.82	13.12	0.68	-	-
COD (mg/l)	929.88	8.26	14.68	2.83	-	-
TSS (mg/l)	284	212	132	156	50.0	30.0
O&G (mg/l)	4124	6.27	14.13	0.73	40.0	10.0
Electrical Conductivity (microohms/cm)	22300	21300	32500	22000	-	-
TDS (mg/l)	12600	12035	18363	12430	5000	2000
Alkalinity (mg/l)	1624	300	1052	5012	-	-
Total Organic Carbon (TOC) (mg/l)	1229	2.31	5.21	0.27	-	-
Chlorides Cl ⁻	9954	9508	14507	9820	-	-

Table 2: Treatment of Samples with combined coagulants

Parameters	Blank	FeSO ₄ and BaCl ₂ (5g/100ml)	FeSO ₄ and Mg(OH) ₂ (5g/100ml)	BaCl ₂ and Mg(OH) ₂ (5g/100 ml)	DPR Limit (offshore)	FMENV Limits
pH	5.8	7.8	6.3	8.3	6.5-8.5	6.5-8.5
BOD(mg/l)	759.17	12.47	1.19	1.69	-	-
COD (mg/l)	929.88	11.97	4.95	7.04	-	-
TSS (mg/l)	284	103	160	16	50.0	30.0
O&G (mg/l)	4124	13.43	1.28	1.82	40.0	10.0
Electrical Conductivity (microohms/cm)	22300	21100	22200	26500	-	-
TDS (mg/l)	12600	11922	12543	14973	5000	2000
Alkalinity (mg/l)	1624	740	8020	2460	-	-
Total Organic Carbon (TOC) (mg/l)	1229	4.96	0.47	0.67	-	-
Chlorides Cl ⁻	9954	9418	9909	11829	-	-

Analysis of Variance (ANOVA)

Due to the wide variation in the values of the parameters obtained from the analysis of the treated samples, it becomes necessary to subject the data to statistical analysis of variance to further proof the observed variation statistically. The one-way analysis of variance (ANOVA) was used to determine whether there are any statistically significant differences between the means of the six independent (unrelated) groups.

Table 3: Summary of single and combined values of parameters

Parameters	A	B	C	D	E	F
pH	6.8	7.1	9.8	7.8	6.3	8.3
BOD	5.82	13.12	0.68	12.47	1.19	1.69
COD	8.26	14.68	2.83	11.97	4.95	7.04
TSS	212	132	156	103	160	16
O&G	6.27	14.13	0.73	13.43	1.28	1.82
EC	3.39	2.11	2.5	1.65	2.56	0.26
TDS	6.7	4.17	4.93	3.25	5.06	0.51
ALKALANITY	21300	32500	22000	21100	22200	26500
TOC	12035	18363	12430	11922	12543	14973
CL	300	1052	5012	740	8020	2460

Groups	Count	Sum	Average	Variance
6.8	9	33877.44	3764.16	58893283
7.1	9	52095.21	5788.357	1.37E+08
9.8	9	39609.67	4401.074	61165539
7.8	9	33907.77	3767.53	57519281
6.3	9	42938.04	4770.893	63707512
8.3	9	43960.32	4884.48	89721167

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	26506848	5	5301370	0.068019	0.99661	2.408514
Within Groups	3.74E+09	48	77939231			
Total	3.77E+09	53				

Where A = Ferric Sulphate (FeSO₄), B = Barium Chloride, C = Mg (OH)₂, D – Ferric Sulphate / Barium Chloride, E = Ferric Sulphate/Magnesium Hydroxide and F = Barium Chloride / Magnesium Hydroxide



The results of the analysis of all the parameters in the petroleum wastewater samples treated with six different types of coagulants are shown in tables 1 and 2. The result shows significant changes and variations in the level of virtually all the parameters in the treated samples when compared with that of the blank.

The determination of Oil and Grease presence in water is very important and necessary as a measure of oil carry over in the petroleum industry and production platforms. Increased or high presence of Oil and Grease in water is dangerous to aquatic life's. From the results obtained, all the chemicals proved effective and the percentage removal of oil and grease was very high, thereby meeting the regulatory standard.

Total Dissolved Solids (TDS) are the combination of all the organic and inorganic substances contained in the water, they are present in ionized molecular or micro-granular form. In table 1 above, there is no significant reduction in the values of TDS of the treated samples when compared with the blank with 12,600mg/l, increase is rather noted in the case of Barium Chloride (BaCl_2) (18363mg/l) and mixture of Barium Chloride (BaCl_2) and Magnesium Hydroxide $\text{Mg}(\text{OH})_2$ with an increased TDS of 14973. This could be as a result of presence of Chloride in those chemicals which subsequently forms more dissolved salts in the solution.

Total suspended solids (TSS) are solids that cannot pass through the pores of a sieve or filter paper of 2 micrometers and yet are indefinitely suspended in the water. High value of TSS will affect the aquatic organisms because this can influence the level of dissolved oxygen in the water.

The results from the table above implies that only the mixture of Barium Chloride (BaCl_2) and Magnesium Hydroxide $\text{Mg}(\text{OH})_2$ was able to reduce the total suspended solids significantly to meet the required standard, this chemical mixture reduced the total suspended solids from 284mg/l to 16mg/l, 94.4% removal.

There was increase in pH values for all the samples for Ferrous Sulphate, Barium Chloride, Magnesium hydroxide, Ferrous Sulphate with Barium Chloride, Ferrous Sulphate with Magnesium Hydroxide and Barium Chloride with Magnesium Hydroxide.

The alkalinity of water is its acid neutralizing capacity. It is the sum of the titratable bases using a standard acid. The results showed that the neutralizing capacity of each of the coagulants is highly dependent on the power of the cation present in each of the chemicals. The blank alkalinity of 1624mg/l dropped to 300mg/l after treatment with Ferric Sulphate, this is 82% reduction in the acid neutralizing power of the original sample, an indication of the presence of a weak cation and a strong anion in the composition of the coagulant.

Furthermore, the reverse was the case for Magnesium Hydroxide and the mixture of Ferric Sulphate and Magnesium Hydroxide, these produced good examples of more alkaline solutions as they increased the alkalinity from 1624mg/l to 5012mg/l and 8020mg/l, respectively.

For conductivity test, BaCl_2 seems to be highly conductive as its presence in the solution significantly increased the conductivity compared to other coagulants. For the treated samples with Barium chloride and mixture of Barium chloride with Magnesium Hydroxide, the conductivity increased from 22300microhms/cm for the blank to 32500 microhms/cm and 26500 microhms/cm respectively, while those of other samples falls in the same range with the blank with slight differences.

Another parameter worthy to be noted and whose determination is very important is the chemical oxygen demand (COD), it is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as Ammonia and nitrite. From the result, there is significant reduction in the COD values of all the analyzed treated when compared the blank. The blank COD value of 929.88 mg/l was reduced to 8.26mg/l by Ferrous Sulfate, 14.68mg/l by Barium Chloride, 2.83mg/l by Magnesium Hydroxide, 11.97mg/l by the mixture of Ferrous Sulfate and Magnesium Hydroxide, 4.95 mg/l by the mixture of Ferrous Sulfate and Magnesium Hydroxide and also reduced to 7.04mg/l by the mixture of Barium Chloride and Magnesium Hydroxide, Magnesium Hydroxide proved most effective in this area.

For the total organic Carbon (TOC) removal, all the coagulants showed very high effectiveness especially by Magnesium Hydroxide, mixture of Ferrous Sulfate and Magnesium Hydroxide and Barium Chloride with Magnesium Hydroxide, these three chemicals reduced the TOC from 1229mg/l to 0.27mg/l, 0.47mg/l and 0.67mg/l respectively.

For the Chloride ions, the removals by non-chloride Coagulants are very insignificant while the coagulants that contain chloride in them only increased the chloride ions present in the sample. This can be seen in the samples treated with Barium Chloride and the mixture of Barium Chloride with Magnesium Hydroxide, these two



coagulants rather increased the Chloride ions from a blank value of 9954mg/l to 14507mg/l and 11829mg/l respectively.

Oneway ANOVA and correlation was employed to see the statistical difference of the variables at 5% significant level and to observe associations of variables. The result revealed that average value of all selected parameters showed variation from points A to F. However, these variations are not statistically significant with F (0.068019) being less than F_{critical} (2.408514).

Conclusion

This research shows that combination of chemicals can have high efficiency in the treatment of petroleum and flow station wastewater. The chemical coagulants exhibited a high capacity to reduce the pollutants to recommended effluent limits with the mixture of Magnesium Hydroxide and Iron (ii) Sulphate been the most effective coagulants.

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