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Comparative Studies on Phosphate and Non-phosphate Biodegradable Synthetic Detergent from Lokoja Quartzite

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Abstract: Surfactants and builders are the two most important ingredients in laundry, household and personal-care cleaning products. Based on the environmental consideration various detergent builders ranging from inorganic, organic and polymeric types have been developed

Sodium metasilicate an inorganic builder is an effective and quick-dissolving non-phosphate builder in detergent formulation that can replace the sodium tripolyphosphate (STPP) which is not environmentally friendly because phosphates are excellent fertilizer for algae, bacteria, and other flora and fauna in rivers, lakes and oceans, making them bloom at very rapid rates, exhausting the oxygen supply both in the surface and in the bottom layers of water bodies, and killing fish. This phenomenon is called eutrophication. In this studies sodium metasilicate produced from Lokoja quartzite was used as a non- phosphate builder in the formulation of detergents which comprised of a mixture of 20 wt.% surface active agent (LABS) was formulated using 50 wt.% and 80 wt.% sodium meatasilicate (builder) separately, and the results of the properties of phosphate and non-phosphate detergents were compared.

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1.0 Introduction

A laundry detergent composition generally comprises six groups of substances: surfactants, builders, enzymes, bleaching agents, fillers and other minor additives such as dispersing agents, fabric softening clay, dye-transfer inhibiting ingredient, and optical brighteners [1]. All of these groups have specific toxic effects. Detergent builders play a central role in the course of washing process. Their function is largely that of supporting detergent action and eliminating calcium and magnesium ions, which arise partly from water and sometimes also from soil and fabric [2].

Surfactant efficiency is greatly reduced in hard water and surfactants do not show good performance even in softer water. Furthermore, large amounts of surfactants in detergents not only significantly increase biological demand in water but also impose heavy load on sewage works and on the environment due to their eco-toxicity. To remove Ca^{2+} and Mg^{2+} ions existing in hard water and in soils, and thus to lower the content of surfactants in the detergent formulations, detergency builders are often used in conjunction with surfactants. A potential builder should satisfy a large number of requirements including sequestering ability, alkalinity, buffer capacity, bleach compatibility, soil deflocculation, oral toxicity, skin absorption, eye irritation, effects on fish and other aquatic animals, and other environmental and economic practicability [2,3]. Examples of builders are: sodium tripolyphosphate

(STPP), sodium carbonate (soda ash), sodium silicate, Nitrilotriacetic acid (NTA), Ethylene Diamine Tetra-acetic (NTA), Ethylene Diamine Tetra-acetic Acid (EDTA), citrate and zeolites [4].

Many studies have been done for replacing STPP in the detergent compositions. Layered crystalline silicate ($Na_2Si_2O_5$) is a promising candidate since it combines a high performance per unit mass with a high degree of multi-functionality. Polymeric builders have good builder capacity and thus are frequently used, but most of them are not naturally biodegradable. zeolite A and zeolite X were more effective in cleaning than STPP and clinoptilolite at low temperatures, but zeolites increases suspended solids and may cause fouling of pipeline. It significantly increases sludge volumes in sewage treatments plants, making disposal of sludge more difficult. In addition, the surfactant in the zeolite detergent is trapped inside the zeolite and takes time to diffuse into the wash liquor. To compensate for the shortcomings as a detergent builder, an alkaline compound such as soda ash or sodium silicate is added.

Recently, to manufacture more compact powder detergents and more ecological detergents, a multifunctional builder is demanded. Layered crystalline silicate ($Na_2Si_2O_5$) is a promising candidate since it combines a high performance per unit mass with a high degree of multi-functionality [1,5].

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2.0 Experimental

2.1 Materials

Linear Alkyl Benzene Sulphonate (LABS), sodium sulphate, carboxyl methyl cellulose (CMC) and sodium hydroxide (NaOH) were of commercial grade and used as purchased. The sodium silicate, (builder) prepared from Lokoja Quartzite as reported in our previous paper [6], was used in formulation of the detergent. Deionized water was used in all experiments.

2.2 Non-phosphate Detergent Formulation

Formulation of non-phosphate builder detergent involved the preparation of aqueous NaOH, Neutralization of LABS, slurry making and drying followed by addition of fragrance.

The aqueous NaOH was prepared by dissolving 75g, 50g and 25g of NaOH pellets separately in 100ml of deionized water and manually stirred continuously to ensure complete dissolution of NaOH pellets. Each of the prepared NaOH solution was used to neutralize LABS to form a neutral detergent paste. The sodium metasilicate, sodium sulphate, carboxyl methyl cellulose and colourant were mixed in 50wt.%, 30wt.%, 10wt.% and 20wt.% respectively. The solution/mixture was then mixed with deionized water to formed slurry. The slurry was then mixed with the neutral detergent paste. The resulting mixture was stirred at 10 rpm using 73-660 mechanical stirrer to prevent formation of lumps. The resulting detergent was in an open air. The dried detergent was then sieved through a 1.2mm sieve size into powder.

2.3 Analysis of Detergent

2.3.1 Determination of Bulk density of Detergent

Bulk density of the detergent was determined using an electronic weigh balance. A container of fixed volume, weight of empty container and mass of detergent was determined. Then the bulk density was calculated from equation (1).

$$Bulk\ density(g/ml) = \frac{Mass\ of\ Detergent}{Volume\ of\ empty\ container} \quad (1)$$

2.3.2 Detergent Foamability Test

Foam is a dispersion of a gas (in this case air) in a liquid [7]. The foamabilty of the detergent is determined by the following procedure: 1.0g of detergent was dissolved in a 100ml deionized water and shaken vigorously. The initial heights of water and foam were taken respectively. Then the foam was allowed stay for 10 minutes, and the foam height recorded and the foam loss was calculated from equation (2).

$$Foam\ loss = Initial\ foam\ height - Foam\ height\ after\ 10\ minutes \quad (2)$$

2.3.3 Biochemical Oxygen Demand (BOD)

The BOD is a measure of the oxygen utilized by micro-organisms during the oxidation of organic materials [8]. The BOD of detergent was determined in the laboratory using a YSI model 57 oxygen meter, 300ml BOD glass bottles, deionized water, magnetic stirrer and dilution water were used. Dilution water was prepared by pipetting 1.5ml each of phosphate buffer, magnesium sulphate, calcium chloride and iron (III) chloride into a 5000ml conical flask containing 1.5 liters of deionized water and shake vigorously. Then the two blanks solutions were taken by filling up the BOD bottle with dilution water and labelled blank 1 and 2. Then 1g of detergent was dissolved in 100ml of deionized water and poured into BOD bottles and filled up by topping it with a dilution water. The initial oxygen demand of blanks was determined using YSI model 57 oxygen meter and the values recorded. Then both the blanks and detergent samples in BOD bottles were placed in an incubator for 5 days. After 5 days, the oxygen demand was measured. The BOD was calculated from equation (3).

$$BOD\ (mg/l) = \left(DO_b - DO_i\ \frac{Vol.of\ bottle}{ml\ sample}\right) \quad (3)$$

Where, DO_b and DO_i are the dissolved oxygen values in blank and the dilutions of the samples respectively at the end of the incubation period.

2.3.4 pH determination

Detergency normally improves with increase in pH. For Most domestic and fabric washing purposes, it is necessary to avoid too high a pH and a value around 9.5 – 10.5 is usually desirable [7]. pH of the detergent was determined by the following procedure. 1g of detergent was dissolved in 100ml of deionized water and solution stirred gently. Then pH meter model EIL 7055 was then immerse into the solution and pH reading recorded.

2.3.5 Critical Micelles Concentration (CMC)

The CMC of a non-phosphate detergent was determined employing a method of measuring a surface tension of the detergent solution in form of a film by the following procedure.
0.05g of detergent was dissolved in a 100ml of deionized water and the solution stirred. Then the frame was carefully lowered into the solution as shown in Figure 1. The frame was then withdrawn and allowed to drain and any films appearing between the upper thread and the wire ABC and DEF were punctured, the thread assumed the shape indicated in Figure 1b. Then the measurement of GH, DF and CF were taken with the transparent ruler. The procedure was repeated with weight of 0.00, 0.45, 0.85, 1.02 and 1.20g attached at point E as shown in Figure 1a. This procedure was repeated with detergent concentration of 0.0005, 0.0010, 0.0015, 0.0020, 0.0025 and 0.0030 ml/g. The value for each was recorded and graph plotted using the relationship in equation 4. A surface tension was determined from the slope of the graph, for every run, until the surface tension becomes constant and ceases to decrease with an increase in the concentration of detergent at this point is called a critical micelles concentration (CMC).

$$\frac{h^2-d^2}{d} = \frac{mg}{2\gamma} - 2a \quad (4)$$

Where,

$$AC = DF = 2a \quad (5)$$

$$GH = 2b \quad (6)$$

$$AD = CF = 2h \quad (7)$$

$$slope = \frac{g}{2\gamma} \quad (8)$$

$\gamma = surface\ tension$, $g = 9.81 m/s^2$

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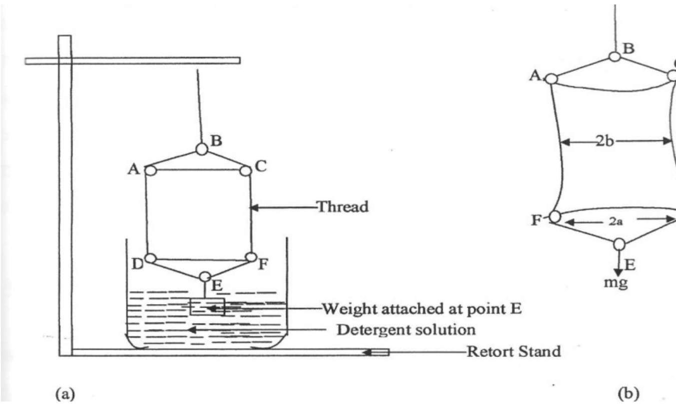

Figure 1: (a) Experimental set-up for surface tension test (b) Film formed in the detergent solution

3.0 Results and Discussion

3.1 Bulk densities of the detergent

The result of the comparative analysis of the bulk densities of the commercial (STPP) and sodium metasilicate based detergents are shown in Figures 1a and 1b. As can be seen the bulk densities of five various commercial detergents were compared with the sodium metasilicate based detergents produced at different concentration of sodium hydroxide and sodium metasilicate. From the result it can observed that the bulk densities fall within the range of 0.450 g/ml – 0.77g/ml, when these values are compared with the literature values of 0.130 g/ml and 0.60 g/ml or higher for low bulk and high bulk densities respectively [9]. In this direction, it was observed that for all concentration of sodium metasilicate, both 75% and 50% NaOH based detergents have relative the same bulk densities of about 0.60 g/ml, while 25% NaOH based detergents have the highest bulk densities of about 0.7 g/ml. In this regards, the detergents produced can be classified as a high bulk density detergents (HBDD).

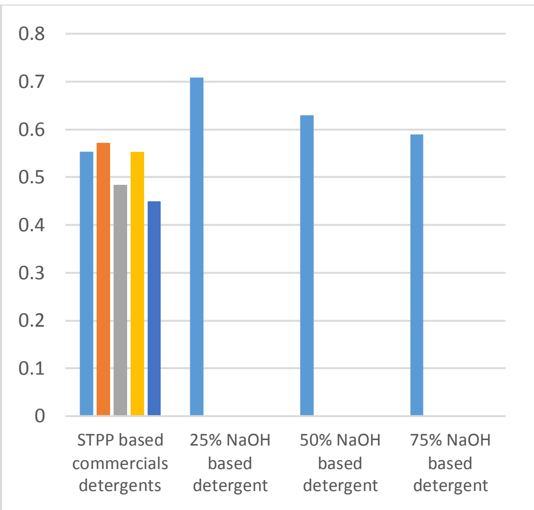

Figure 1a: Bulk density for STPP and 50g sodium metasilicate based detergents Formulated at different concentration of NaOH.

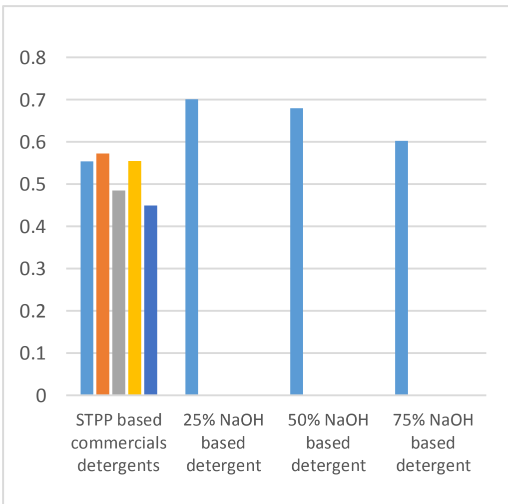

Figure 1b: Bulk density for STPP and 80g sodium metasilicate based detergents Formulated at different concentration of NaOH.

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3.2 Foamabilty test of the detergent

The results of the foamability for STPP and sodium metasilicate based detergent are presented in Figures (2a and 2b). When the results of foamability test were compared, it was observed that 75% NaOH based detergents for all concentration of sodium metasilicate generally have lowest foam loss. This is may be due to the fact that 75 % NaOH have sufficiently neutralized LABS hence, no excess of it to account for a higher foam loss. While 50% and 25% NaOH formulated detergents generally have a higher foam loss due to the fact that they have not completely neutralized LABS, hence excess of it is responsible for high foam loss.

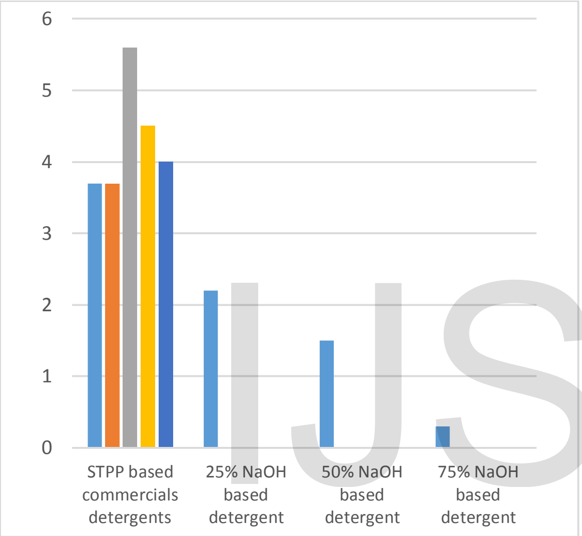

Figure 2a: Foamability Test for STPP and 50g sodium metasilicate based detergents Formulated at different concentration of NaOH.

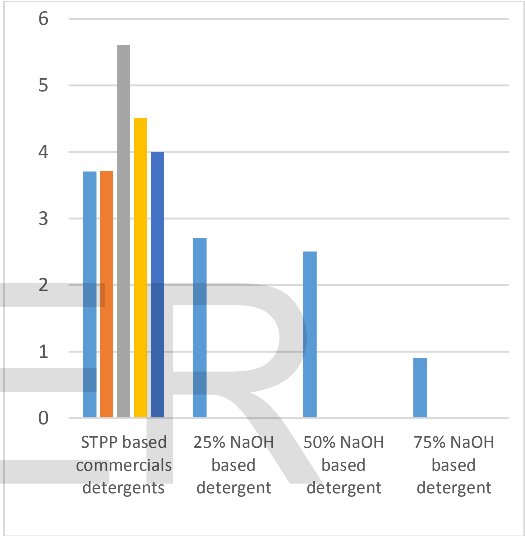

Figure 2b: Foamability Test for STPP and 80g sodium metasilicate based detergents Formulated at different concentration of NaOH.

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3.3 BOD Test

The result of BOD for five different STPP based commercial detergents were compared to the
sodium metasilicate formulated detergents as shown in Figures 3a and 3b. It can be observed that the BOD values are within the range of 0-7 mg/L as reported in Rao (1991). 75 % NaOH based detergent have the same BOD values of 3mg/L for all concentrations of sodium metasilicate. This may be due to the fact that 75% NaOH has sufficiently neutralized the LABS hence little unreacted LABS biodegrade fast. Conversely the 25% and 50% NaOH formulated detergent have higher BOD of 6mg/L. However, detergent formulated using 80 g sodium metasilicate have BOD of 3 mg/L for all concentrations of NaOH.

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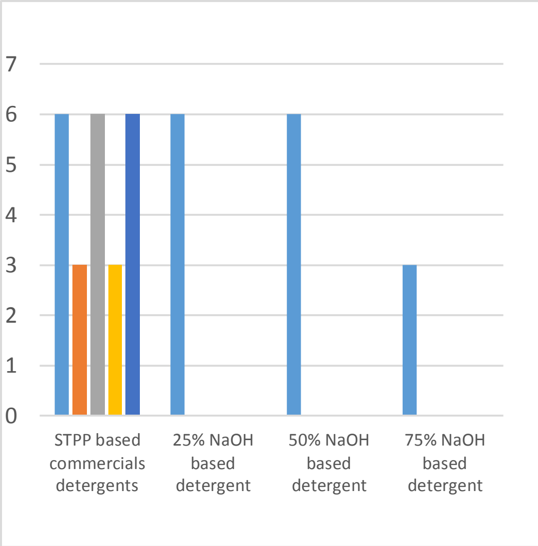

Figure 3a: BOD_5 Test for STPP and 50g sodium metasilicate based detergents Formulated at different concentration of NaOH.

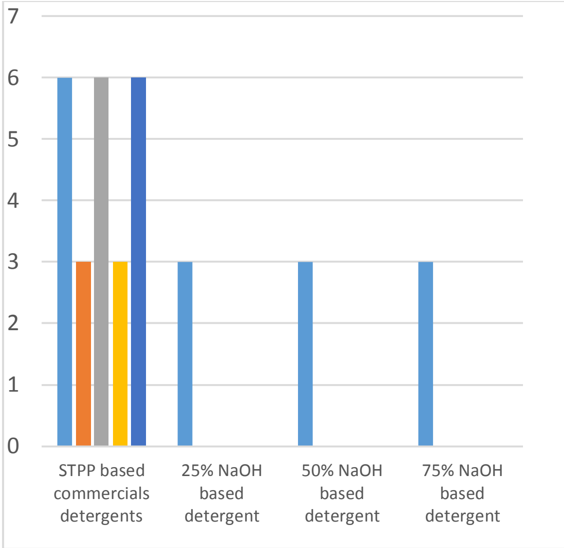

Figure 3b: BOD_5 Test for STPP and 80g sodium metasilicate based detergents Formulated at different concentration of NaOH.

3.4 pH Test

The results of the pH for STPP commercial detergents and sodium metasilicate formulated based detergent were compared in Figures 4a and 4b. When these results were compared with the reported literature values of 9.5 – 10.5. It can be observed that STPP based detergents and both the 75% and 50% NaOH based detergents for all sodium metasilicate concentration have a lower pH's and was found fall within the ranges of the literature value that meet the domestic purposes. Conversely, 25% NaOH based detergent for all sodium metasilicate concentration have a higher pH values that slightly deviated from the literature values.

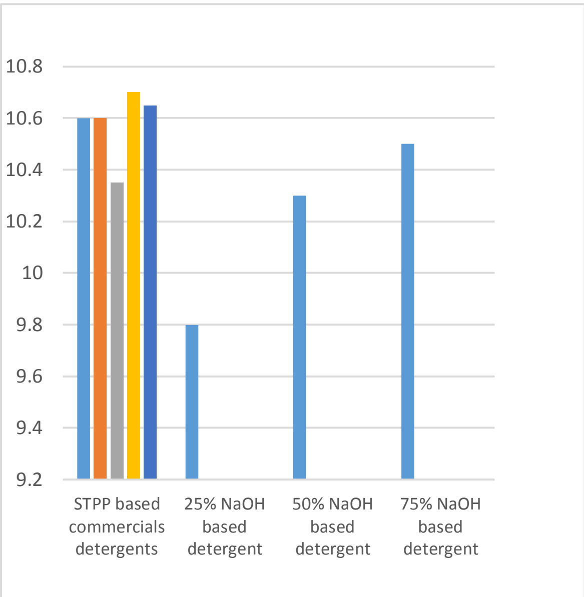

Figure 4a: pH Test for STPP and 50g sodium metasilicate based detergents Formulated at different concentration of NaOH.

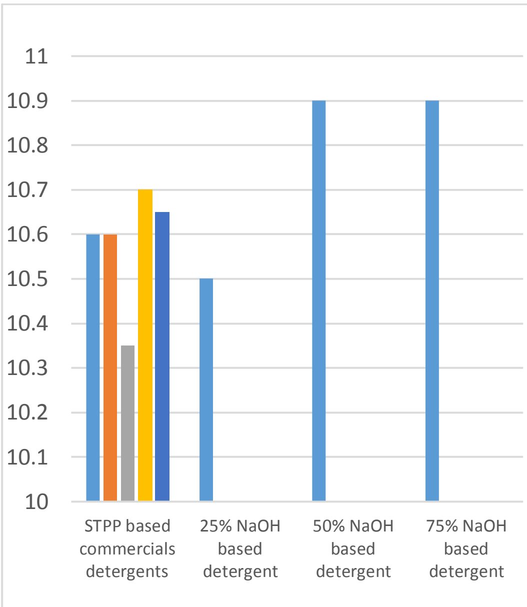

Figure 4b: BOD_5 Test for STPP and 80g sodium metasilicate based detergents Formulated at different concentration of NaOH.

3.5 CMC Test

The results of the CMC's for STPP commercial based detergents and sodium metasilicate formulated detergents were compared in Figures 5a and 5b. When these values are compared to the reported literature values in the range of 7-10 mM [10]. It can be observed that the 75% NaOH based detergents for both 50g and 80g concentration of sodium metasilicate and those detergents formulated from 80g sodium metasilicate using 50% NaOH have a CMC's values of 6.9348 mM, 8.6685 mM and 6.9348 mM respectively agrees with literature values. Conversely, 80g sodium metasilicate based detergents from 25% NaOH and 50 g sodium metasilicate based detergents from 50% and 25% NaOH concentrations with the CMC of 5.0211 mM do not agree with the literature values.

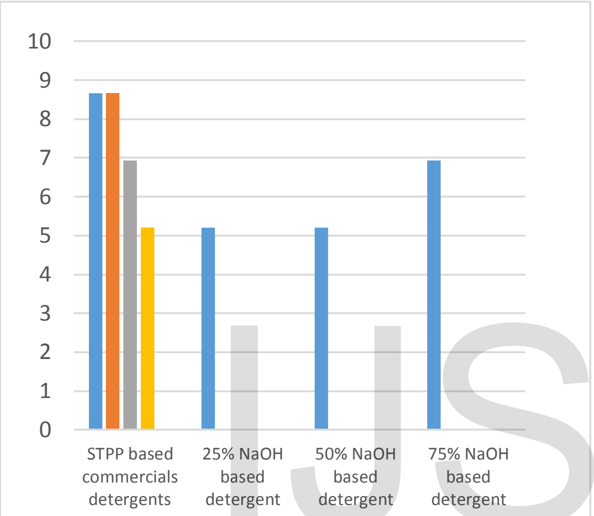

Figure 5a: CMCTest for STPP and 50g sodium metasilicate based detergents Formulated at different concentration of NaOH.

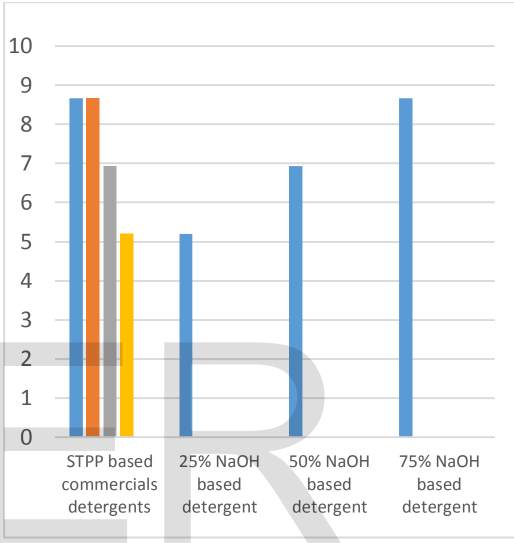

Figure 5b: CMCTest for STPP and 80g sodium metasilicate based detergents Formulated at different concentration of NaOH.

4.0 Conclusion

From the results obtained in this work it can be concluded that, the high bulk density detergents (600g/L or higher) were produced for formulated detergent. High and low foam losses of 3.5 cm and 0.1cm respectively is an indication of poor and good detergency. The BOD values of 3mg/L and 6mg/L of the detergent show fast and low biodegradation respectively. The pH values of 9.5-10.5 for 75% and 50% NaOH based detergents meets the requirement for domestic purposes. The CMC's of the detergent showed that 75% NaOH based detergents for all sodium metasilicate concentration, as well as 50% NaOH based detergent using 80g sodium metasilicate were found to be within the literature value of the range (7-10mM)

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