PREPARING BIODEGRADABLE DETERGENT FROM NEEMSEED OIL AND H.MULTIFLORUM (LAANA/LAANI) ASH

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ABSTRACT: *Considerable attention has been focused on the problems arising from chemicals coming from detergent production as well as laundry. The environmental risks associated with manufacture, use and disposal of these chemicals is of a great interest. Detergent products are used in large quantities for industrial applications. Large proportion of Faisalabad water had more than 100 ppm and more TDS which required 10% more detergent to clean. Water pH is 7 which is effective for a good wash. So the produced biodegradable detergent must be that effective to work in hard water of 600 ppm with less dosage. According to the comparison made between four of the used builders, sodium citrate and potassium citrate showed excellent biodegradability but they had low foamability and washability as compared to the other two builders. Citrates were safe to handle, non-polluting and biodegradable whereas sodium acetate was compatible with equipment surface. Sodium citrate showed good biodegradation among other builders under anaerobic conditions as the bacteria formed completely digested the microorganisms. Citrates were more effective on magnesium than calcium ions which contributed to BOD load.*

Key Words: TDS, EDTA, LAB, BAB, BOD, pH, Whiteness Index (WI), CMC, surfactant, builders.

1 INTRODUCTION

Detergents contain polar and hydrophobic groups. They replaced soaps as they are effective in both hard and soft water. The only problem was that they were not degraded by microorganisms present, which is necessary for full sewage treatment. Many rivers and streams were polluted with detergent foam. The main components of modern detergent are surfactants such as (LABS) Linear Alkyl Benzene Sulfonate, Builders, Co-Builders, Bleach, Bleach Activator, Fluorescent Brightener, Filler, Corrosive Inhibitor, Antifoaming Agents and Enzymes. Most commonly used builders such as phosphates were found to be good fertilizers as they increase growth rate of algae, so they were replaced by Ethylene diaminetetraacetic acid (EDTA) and its derivatives in present era,ethylenediaminetetraacetic acid and its derivatives have poor biological degradation and cause severe environmental problems [6]. Procter & Gamble (P&G) studied the effect of replacing petrochemical surfactants with plant based surfactants on (CO_2) gas emissions. Such a result resulted in 0.1% reduction in CO_2 emission. Plant based oleo chemicals also contain fossil fuel and also generates greenhouse gas emissions. Plant-based surfactants consumed carbon dioxide and produced oxygen. These experiments predicted that coconut based plant derivatives resulted in minimal impact on the environment. So they banned all petrochemical processing and processes like ethoxylation, which produces the cancer-causing chemical dioxane [32].Neem oil is green in colour having a bitter taste and garlic odor. It contains Limonoids that cures cancer and tumor. The Lemonoid compounds present in neem are Azadirachtin, Nimbidin, and Nimbolin Neem oil contains vitamins, calcium and fatty acids. Neem soap is good for those people who have skin diseases and cannot use soap containing Diethanolamine and Butylated toluene. It also treats the dandruff on skin [9].H.Multiflorumis botanically known as SidaFrutiosaHaloxylonCamelrun with local name ofLaana/Laani. A low shrub, from 4 to 6 inches high, of the north-western Punjab plains, distributed to Afghanistan and Baluchistan. In the settlement report of the Montgomery district Lana is mentioned as being used in the manufacturing of Barilla. Stewart in dictionary of the economic product of India, volume 4 writes" it is used in some parts for washing clothes, and it is probably this bellew states to be used by women in Peshawar valley for washing the head".[18, 15]

Parameters Effecting Biodegradability

From the some important studies carried in past, the following factors such as Water content, pH, number of microorganisms and temperature, Organic substrate bioavailability, Detergent dosage, Foam height, Mass transfer rate affected the biodegradability.

In biodegradation process initial reaction is started with supply of microorganisms in both aerobic and anaerobic conditions. For optimized biodegradation ambient conditions and sufficient water content are necessary. As water content is major factor for all biological processes. Other factors influencing biodegradability are pH and temperature. For the optimal growth macro and micro nutrients are needed. No further nutrition is required in the presence of complex organic substrate in a reaction mixture. Inhibition is mostly caused by microbes, which is the degradation of metabolite. Detergent dosage is controlled by newly developed technique by Procter and Gamble Co P&G. detergent is available in the form of pods which are concentrated detergent using low wash water. New measuring caps are also available by Tide, Era, Gain and Cheer having more defined lines and bigger numbers displayed. Bioavailability is another factor affecting the biodegradability. It limits the biodegradability. It is dependent on the mass transfer rate, dissolution rate and chemical fate. Mass transfer rate of water soluble molecules also affects the biodegradability as they can be metabolized.

2 MATERIALS & METHODS

The present experimental methodology proposes not a defined Experimental System but the experiments were performed in steps. Major work was carried at the Chemical Process Industries (CPI) & Environmental Engineering Labs of NFC Institute of Engineering & Fertilizer Research (IEFR) Faisalabad and discussed hereafter.

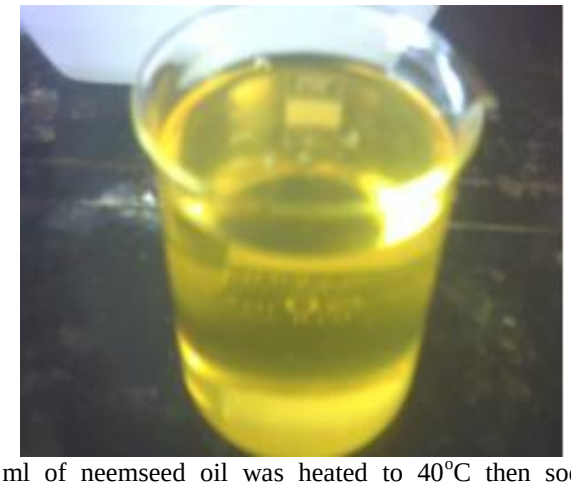
Laana/laani plants were dried in the sun and then burned in a reducing or smoky atmosphere at (500 - 700) ^{0}C to produce ash in hemispherical holes made in earth. After few hours the fire was set off by spraying water. Ash was pressed into

lumps. Neem seed sample having a moisture content of about 8.1% was obtained. An oil expeller having capacity of 15-25 kg/h was used for oil extraction, 3 phase electric motor with reduction gear as shown in Figure 1. The expeller was run at 74 RPM. Some of the properties of this oil are also given in Table 1.

Table 1: Properties of oil at (30°C)

Temperature (°C)	30°C
Iodine value (g/100g)	92.9032
Acid number (mg/g)	19.6283
Saponification value (mg/g)	187.7902
Refractive index	1.4660

Fig 1: Neem Seed Oil Expelling



30 ml of neemseed oil was heated to 40°C then sodium hydroxide solution was prepared mixed with the neem oil. About 10 ml of H_2SO_4 was added to maintain the pH between 9 to 9.5. Then H_2O_2 was added to make a homogenous mixture. 2.5g Sodium acetate (builder) and 2.5g Carboxymethyl cellulose (anti-redeposition agent) were added. The mixture was cooled and dried naturally for 3 days. After the detergent prepared was scooped out and weighted. The same procedure was repeated for 10%, 20%, 30%, 40% and 50% w/v of H.Multiflorum with sodium citrate, potassium nitrate, and sodium acetate and potassium citrate as builders respectively.

Fig 2: Photograph of Available Experimental Syste (NFC IEFR FSD)

Fig 3: Samples of Products obtained

3 RESULTS & DISCUSSION

Prior to experimental runs tap water properties were studied in detail. The sample water was collected from NFC (IEFR). Analysis of ground water were carried out in Environmental lab of NFC (IEFR). For a surfactant to be fully beneficial, it needs to be able to clean in any water hardness. Linear alkyl sulfonates loosen their detergency in very herd water. From laundering perspective compounds such as Mg and Ca are most important. Water hardness is classified by ASTM 2960-84, soft water is 35ppm, moderately hardness is 100ppm and very hard water is 260ppm.

The table 1 shows that the water sample used for washing was very hard. Due to which the risk of lime deposit, discoloration on fabrics and in interior of washing machine could result.

Table 2: Tap Water Properties

pH	7.25
Conductivity	8000µs
TDS	5600 ppm
Ca	100.75 ppm
Mg	93.00 ppm
Total hardness	639.37 ppm
Na	1570 ppm
K	36.00 ppm
Cl	1032 ppm
SO_4	1105 ppm
P value	Nil
Carbonate	Nil
Bicarbonate	976.32 ppm
Hydroxide	Nil

METHODOLOGY

Experimental runs were based on aconstant amount of 2.5g each Sodium citerate and carboxymethyl cellulose added with temperature at 40°C and pH was maintained at 9.3 respectively. H.Multiflorum concentration was changed from (10 to 60) %. Same procedure was repeated for sodium acetate, potassium nitrate and potassium citrate. The experimental methodology is shown as in Table 3.

Table 3: Methodology for Experimental Runs

Sr. No.	Types of builders	Amount of builder (g)	Temp. (°C)	Concentration of H.Multiflorum (%)
1	**Sodium acetate**	25	40	10
		25	40	20
		25	40	30
		25	40	40
		25	40	50
		25	40	60
2	**Sodium citrate**	25	40	10
		25	40	20
		25	40	30
		25	40	40
		25	40	50
		25	40	60
3	**Potassium nitrate**	25	40	10
		25	40	20
		25	40	30
		25	40	40
		25	40	50
		25	40	60
4	**Potassium citrate**	25	40	10
		25	40	20
		25	40	30
		25	40	40
		25	40	50
		25	40	60

Sodium Citrate

In this section the effect of parameters discussed in the objectives were studied by using Sodium Citrate (2.5g) as builder and the results were generated then. All the results are presented in Table 4.

Table 4 : Detergents with Sodium Citrate

H.Multiflorum Concentration (%)	BOD (mg/l)	Whitenes Index (WI)	pH	Foam height (cm)
10	20	43.21	9.3	3
20	30	49.47	9.5	3.5
30	35	50.88	9.6	3.7
40	40	50.76	9.7	4
50	30	49	9.9	3.9
60	25	47.29	10	4

Effect of H.Multiflorum Concentration on Whiteness Index

Effect of H.Multiflorum concentration on Whiteness Index at 40°C was observed and presented in Fig 4.

The Figure shows an increase in whiteness index as the H.Multiflorum concentration increases. But high concentration of H. Multiflorum causes damage due to accidental oral ingestion.

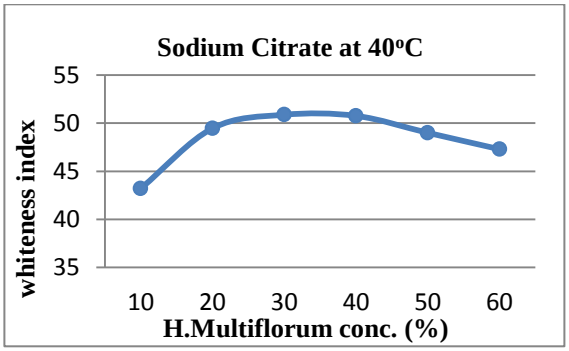


Fig 4: Effect of concentration on whiteness index

Effect of H.Multiflorum Concentration on pH

Oil and acidic components are broken down by alkali. Effect of H.Multiflorum concentration on pH was observed and the results presented in Figure 5, which shows that increasing the pH increases the hydroxide ion concentration. But very high pH damages the fabric. By increasing pH the negative charge increases resulting in good dirt removal.

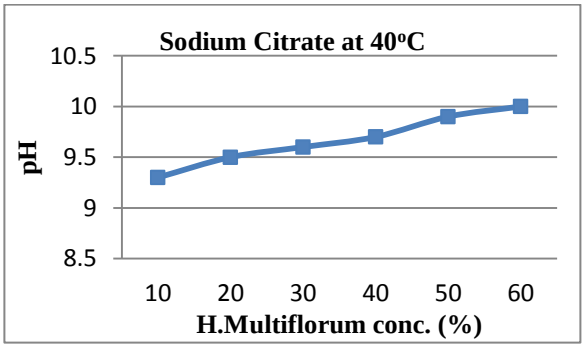


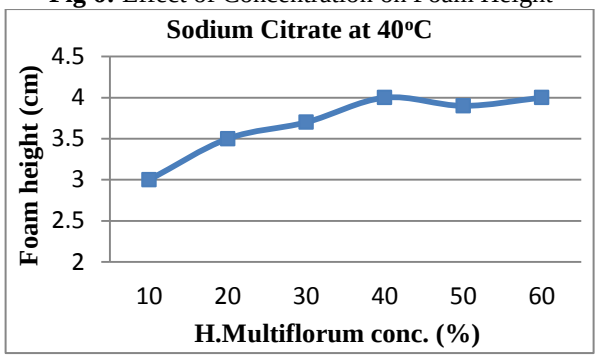
Fig 5: Effect of concentration on pH

The effect of H.Multiflorum concentration on pH of the prepared detergent was examined by this graph. The effectiveness of detergent at different concentrations was different.

Effect of H.Multiflorum Concentration on Foam Height

Foam height has been found a significant parameter in process studies, so it was also observed in present research. The effect of H.Multiflorum conc. on foam height is highlighted in Fig 6.

Fig 6: Effect of Concentration on Foam Height

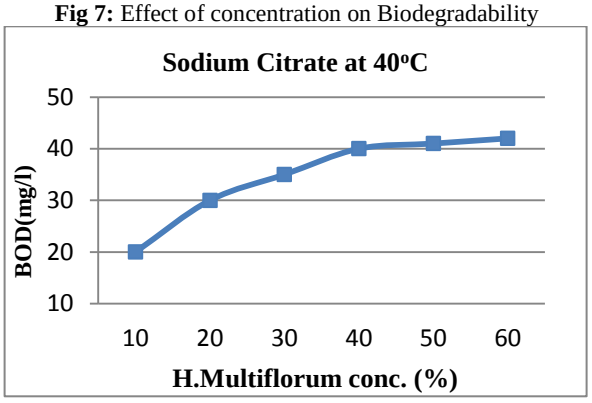


The curve reflects that height of foam increases with increasing the H.Multiflorum concentration. As a result the detergency increases as the foam action stops the redeposition of soil and grease particles.

Effect of H.Multiflorum Concentration on Biodegradability

Fig 7 shows the effect of Biodegradability as it indicates that by increasing the H.Multiflorum concentration, the Biodegradability also increases. BOD is most precise method to check the concentration of organic compounds in waste water. The dissolved oxygen for 5 days period represents the oxygen demand for respiration by bacteria.

Fig 7: Effect of concentration on Biodegradability



Sodium Acetate

The present section deals with the results obtained by using Sodium Acetate as builder. In order to study the effect of sodium acetate, it was desired to prepare detergent of a specific concentration using different concentrations of H.Multiflorum. The data was generated and shown in Table 5.

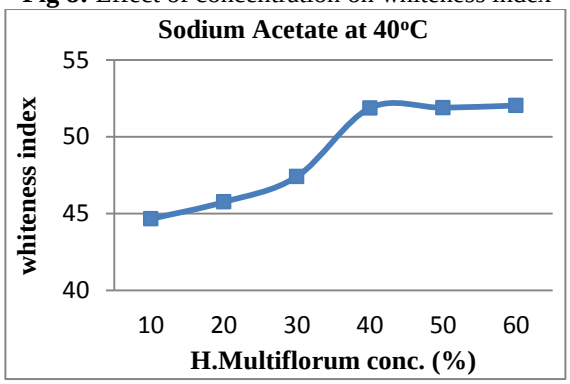
Table 5 : Detergents with Sodium Acetate

H.Multiflorum Concentration (%)	BOD (mg/l)	Whitenes Index (WI)	pH	Foam height (cm)
10	10	44.66	8.7	4
20	13	45.76	9	4.2
30	17	47.42	9.1	4.8
40	17.5	51.88	9.2	5
50	18	51.90	9.2	5.1
60	18	52.04	9.2	5.8

Effect of H.Multiflorum concentration on Whiteness Index

Similar to previous sections, first the effect of H.Multiflorum concentration on Whiteness Index was studied and a change trend was generated. The results were plotted in Fig 8.

Fig 8: Effect of concentration on whiteness index

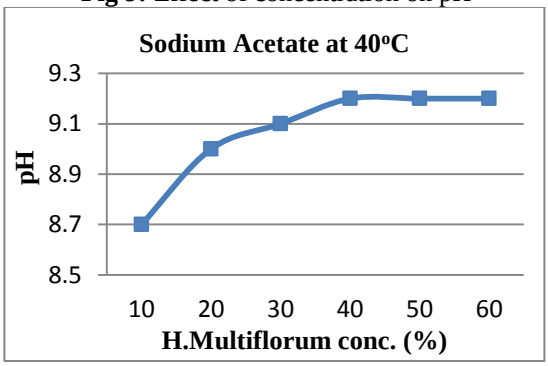


Whiteness index represents good detergency. Sodium acetate showed good results from 40 to 60 % H.Multiflorum concentration. As pH increases the alkalinity increases which causes the fabric to torn out thus reduces the whiteness index. As a result of which soil starts to redeposit on the fabric making it appear yellow. The graph indicates the increasing trend of Whiteness index with an increase of H.Multiflorum conccentration. After 40% concentration the WI remains constant which shows that washability is not improving anymore because of high concentration of H.Multiflorum. The carbonate ions present in these compounds react with water to form stable alkaline solution thus leaving more detergent for cleaning purpose. Detergents dissolves readily and detach the oil, greese and dirt more effectively from sample cloth.

Effect of H.Multiflorum Concentration on pH

The effect of H.Multiflorum concentration on pH was studied and shown in Fig 9.

Fig 9: Effect of concentration on pH

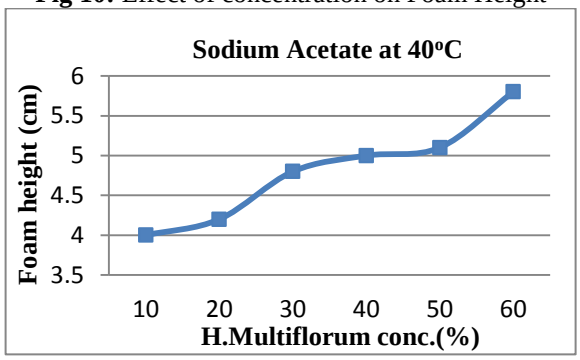


The above figure determines the effectiveness of detergent powders and their required alkalinity for standard cleaning of cloth sample in hard water. An increasing trend of pH with the H.Multiflorum concentration observed. The anti-redeposition agent as carboxy methyl cellulose (CMC) was very effective in increasing the negative charge on cloth sample that helped in repelling the soil particles which were also negatively charged.

Effect of H.Multiflorum Concentration on Foam Height

Graph The Figure 10 indicates that by increasing the concentration of H.Multiflorum, the foam height also increases.

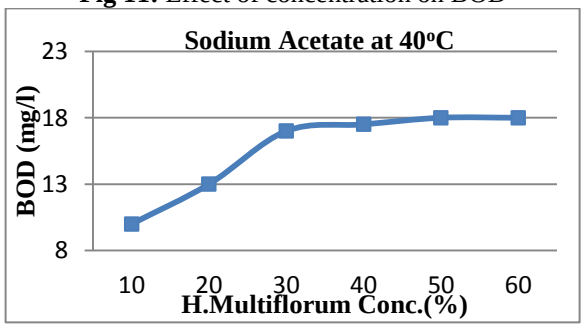
Fig 10: Effect of concentration on Foam Height



Effect of H.Multiflorum Concentration on Biodegradability (BOD)

Again the effect of Biodegradability was observed and presented in Fig 11.

Fig 11: Effect of concentration on BOD



The curve indicatesthe BOD for 5 days for sodium acetate builder. As the concentration of H.Multiflorum increases the BOD also increases. The practical interpretation of biological stabilization is based on ultimate BOD value. If the waste water contains a single organic material, correlation of 5-days BOD and ultimate BOD would be practical.

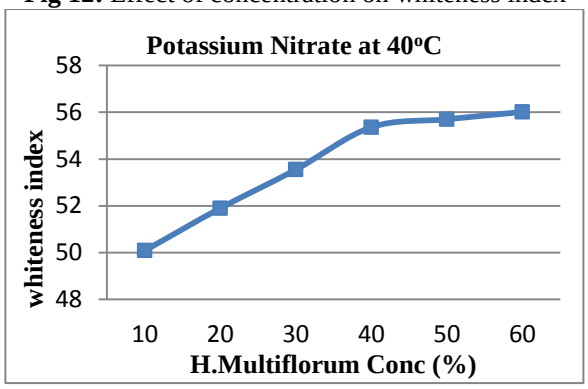
Potassium Nitrate

Again Potassium Nitrate was used as the builder due to its importance. Potassium is a key nutrient in natural mineral important to maintain life. It removes the minerals from hardwater resulting increase in effectiveness of detergent. It also acts as deflocculating agents that block the dirt from settling back on clothes while washing. Due to their no toxicity and irritancy they nonetheless contribute to eutrophication of waterways. That is why they have been banned in many countries. This section presents the effect of stated parameters by using Potassium Nitrate.

Effect of H.Multiflorum concentration on Whiteness Index

The effect of H.Multiflorum concentration on WI was again studied and pointed in Fig 12.

Fig 12: Effect of concentration on whiteness index

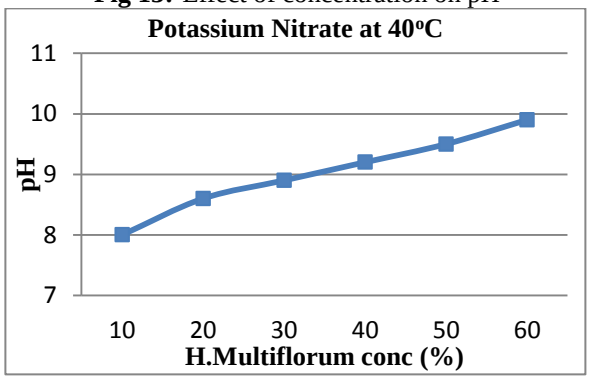


The figure indicates an increase in whiteness index for potassium nitrate even in very hard water. When effectiveness of powdered detergent was compared, it was observed that potassium detergents gave whiter samples. At lower water hardness (100-150) ppm detergents worked affectively.

Effect of H.Multiflorum Concentration on pH

The Fig 13 reflects the effect of H.Multiflorum concentration on pH for potassium nitrate as a builder.

Fig 13:-Effect of concentration on pH

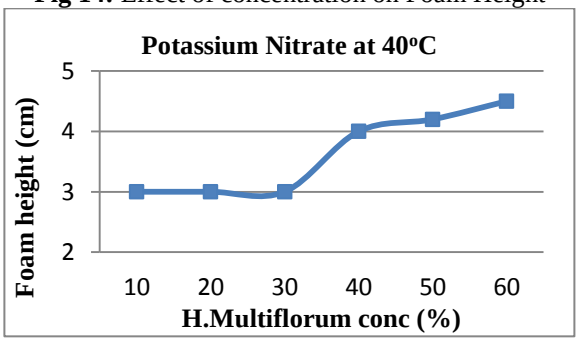


The curve shows that the increasing pH results from increased concentration of H.Multiflorum. This is because of increased alkalinity due to the increased concentration of sodium and potassium salts.

Effect of H.Multiflorum Concentration on Foam Height

The effect of H.Multiflorum concentration on foam height for Potassium Nitrate builder is shown in Fig 14.

Fig 14: Effect of concentration on Foam Height



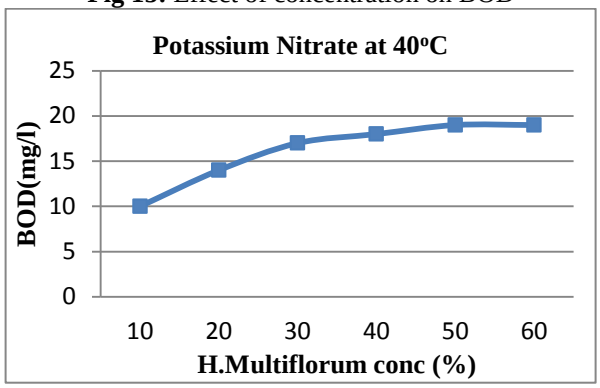
High foamability results from an optimum chain length. Chain length also changes the surface tension which results in rapid drainage of film to thickness. Graph shows an increase

in foam height for 50% concentration of H.Multiflorum resulting in good wash properties.

Effect of H.Multiflorum concentration on Biodegradability (BOD)

The trend for effect of H.Multiflorum conc. on BOD is indicated in Fig 15.

Fig 15: Effect of concentration on BOD



Above figure shows the effect of H.Multiflorum concentration on BOD for potassium nitrate. Graph shows an increase in BOD with the H.Multiflorum concentration. But it remains constant after 40% concentration.

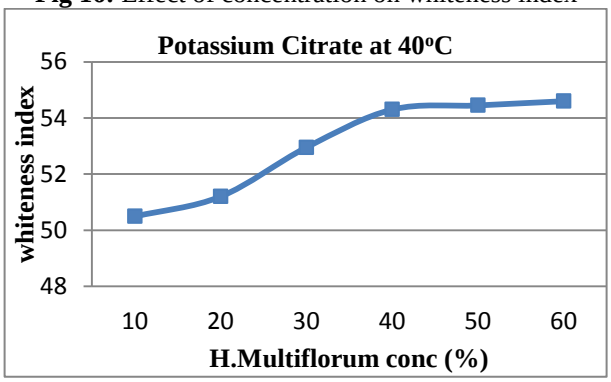
Potassium Citrate

At the end of the experimentation the results were obtained for Potassium Citrate used as builder and discussed as follows.

Effect of H.Multiflorum Concentration on Whiteness Index

The effect of H.Multiflorum conc. on WI was studied for the potassium citrate builder which gives the trend as shown in Fig. 16.

Fig 16: Effect of concentration on whiteness index

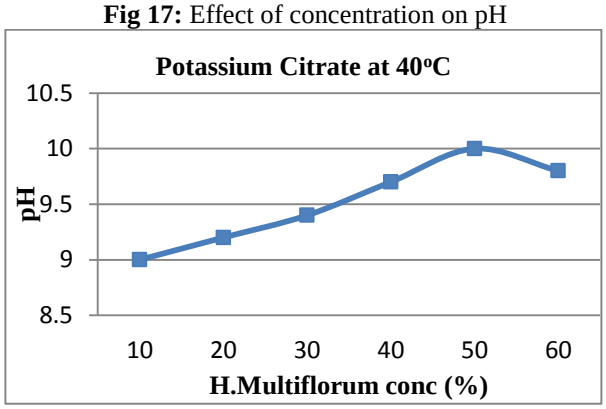


Potassium salt is considered as more water soluble than the sodium, although it is more expensive. This builder augments the cleaning ability of detergent's surfactant by removing hardness ions from the wash solution. Whiteness index increases as a result of increases h.multiflorum concentration.

Effect of H.Multiflorum Concentration on pH

The Fig. 17 shows that the buffer effect on the wash liquid maintains a desired level of alkalinity that significantly helps soil removal.

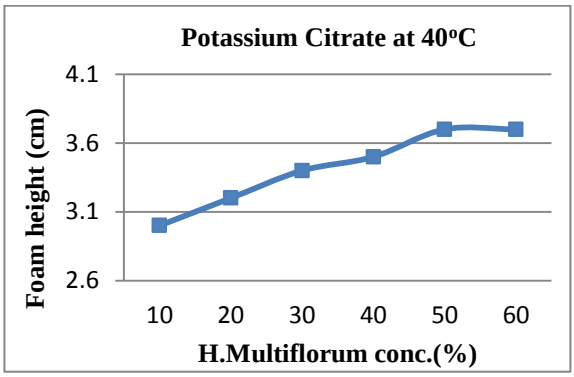
Fig 17: Effect of concentration on pH



Effect of H.Multiflorum Concentration on Foam Height

Foaming power is associated by foam height. Foam height increases due to increase in h.multiflorum concentration increases. But increases in foam height decreases the collision effect resulting in low wash ability.

Fig 18: Effect of concentration on Foam Height

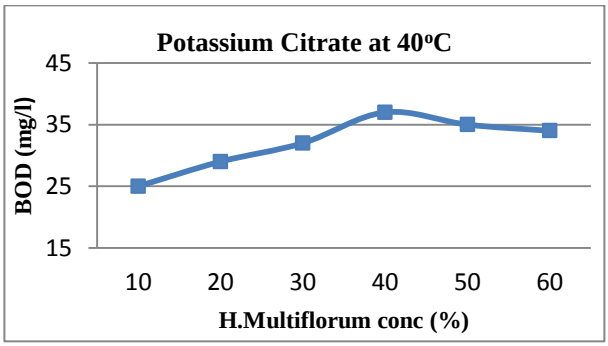


Foam height for potassium citrate was high. The Figure 18 shows an increase in foam height with H.Multiflorum concentration. Temperature was kept constant at 40°C.

Effect of H.Multiflorum conc. on Biodegradability (BOD)

The effect of H.Multiflorum conc. on BOD value is shown in Fig 19.

Fig 19: Effect of concentration on BOD

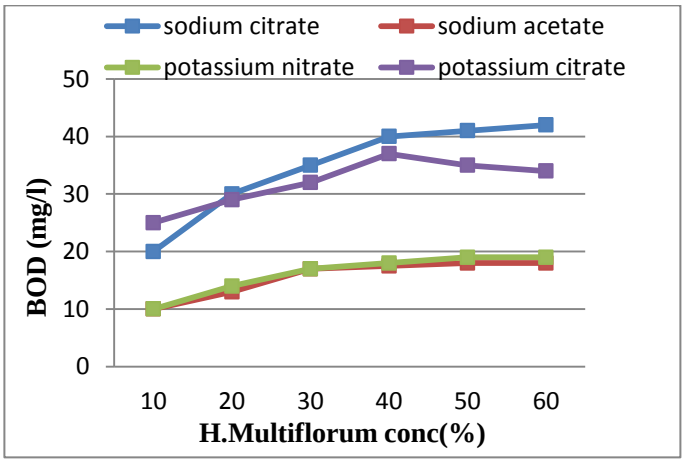


The above Figure 19 shows that the H.Multiflorum concentration affected the BOD mostly in increasing order.

4 COMPARISON OF BUILDERS ON BASIS OF BIODEGRADABILITY (BOD)

As discussed earlier Biodegradability (BOD) was the most important parameter. So a trend was made to make the comparison of all the builders used in the present research on BOD. This comparison is pointed out in Fig 20.

Fig 20: Effect of H.Multiflorum concentration on BOD of Builders



It is evident from the above figure that none of the detergent fulfilled all the good properties of a desirable detergent. According to the comparison made between four of the builders' sodium citrate and potassium citrate showed excellent biodegradability but they had low foam ability and wash ability as compared to the other two builders.

5 CONCLUSIONS

- Foam height was not so significant parameter in the present research work.
- Linear Alkyl Salfonate was compatible with all builders and Carboxymethyl Cellulose.
- Citrates were good builders for alkaline mediumas they showed good biodegradation result at 40% H.Multiflorum concentration.
- Effective cleaning was observed as foam formation by all builders at different concentrations of H.Multiflorum in 608 ppm hard water.
- Effect of concentration of H.Multiflorum on whiteness index was found significant in all cases with different builders used.
- Effect of concentration on BOD was very important and BOD changed constantly.
- The produced detergent was found in good comparison with other commercially available detergents.

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