EFFICIENCY OF DEGREASING BY DISHWASHING DETERGENTS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
Consumption of agents for manual and machine washing of dishes is constantly increasing. Although the growth of the use of dishwashers is evident, hand dishwashing is still dominant in our region. A good dishwashing detergent must effectively remove food residues and degrease the surface of dishes, made of different materials, while the surfaces of washed dishes should remain smooth, shiny with a pleasant smell of freshness. The requirements of consumers-users of these funds are, in addition to the listed basic functions, also practicality of handling and dosing, pleasant smell and mild action on the hands and acceptable price. The aim of this paper is to examine the degreasing efficiency of commercial detergents from our market on four types of fats. In addition to commercial dishwashing detergents, whose composition is known only roughly indicated in the producer declaration, was tested a laboratory prepared sample with exactly known composition. All tests of the degreasing ability of dishes with different types of impurities were performed under the same conditions with a change in the concentration and type of detergent, and according to the method used by some industrial detergent manufacturers. It was found that in addition to the concentration of detergent in the washing solution, the degreasing efficiency is affected by the type and concentration of surfactants, as well as auxiliary components that are part of the product.

KEYWORDS: degreasing; fat; dishwashing detergents; surfactant

INTRODUCTION

Liquid detergents play a very important role in our daily lives for personal care, household surface care and fabric care. Due to faster dissolution than powder detergents and easier dosing, liquid detergents are gaining more and more popularity [1].

Detergents can be classified as hard surface cleaners, laundry detergents, and dishwashing detergents according to their application.

Liquid dishwashing detergent is defined as an aqueous solution of a mixture of surfactants, in combination with other specific materials whose function is to increase the foam, stabilize and homogenize the formulation, and provide adequate viscosity [2]. Commercial products of liquid dishwashing detergents are foaming mixtures of surfactants (about 20%) and various additives (about 80%), most of which are water. Primarily used for washing glasses, cutlery, plates, kitchen utensil and other dishes.

Mixtures of anionic, nonionic and amphoteric surfactants are mainly used in the production of detergents in order to improve the cleaning performance and the ability to have a beneficial effect on the skin of the hands. Anionic surfactants, in waters of high hardness, lead to the deposition of divalent ions Ca^{2+} and Mg^{2+}, thus reducing the ability to clean with detergent. For this reason, amphoteric and nonionic surfactants are added, the combination of which increases temperature stability and the ability to thicken without the use of thickeners [3]. Amphoteric surfactants are characterized by gentleness to eyes and skin, very low toxicity, biodegradability, foam stability and water solubility, emulsification, temperature stability, hard water resistance and degradation by oxidation and reduction resulting from molecular structure [4]. Liquid detergent formulations are usually based on sodium salts and surfactants due to their low cost and high capacity to increase viscosity [5].

The surfactant properties used in these products should have the following characteristics: reduction of surface tension, good ability to wet and foam, non-toxicity and biodegradability, mild and harmless effect on the skin and mucous membranes, emulsifying ability, ability to disperse impurities and possibility of easy application.

The ability to clean detergents is attributed to the specific structure of surfactant molecules, which consists of hydrocarbon chains (hydrophobic part) attached to the active group (hydrophilic part). The removal of dirt from dishes is caused by the affinities of the hydrocarbon chain to dissolve grease (dirt) and hydrophilic groups for dissolve in water.

Many detergents suppress the growth of various bacteria that can cause odor, skin infection, food poisoning, intestinal diseases and other diseases. One study was conducted to determine the antibacterial efficiency of different brands of commercial dishwashing detergents on two tested microorganisms E. coli and Staphylococcus aureus and was confirmed in four samples [6].

Detergents represents the second largest category of products in the Middle East whose total annual consumption is estimated at about 700,000 tons [2].

MATERIALS AND METHODS

The experiments have been carried out in Laboratory for organic and inorganic chemical technology at the Faculty of Technology, University of Banja Luka. This research consists of examining the influence of different types of commercial dishwashing detergents on the degreasing efficiency.

Nine commercial samples of detergents were obtained from the domestic market and one sample of detergent was prepared in the laboratory (Figure 1). A series of solutions of different concentrations (5 g/L, 10 g/L, 20 g/L, 50 g/L and 100 g/L) was prepared from these dishwashing detergents.

Figure 1. Detergents: laboratory prepared sample (left) and commercial (right)

In order to examine the influence of the type and concentration of components present in the detergent on the degreasing effect, six formulations were prepared, shown in Table 1.

Table 1. Composition of formulations

Type of component (%)	Formulation I	Formulation II	Formulation III	Formulation IV	Formulation V	Formulation VI
anionic surfactants (AS)	10	10	3	7	10	10
amphoteric surfactants (AMS)	7	3	7	10	3	3
nonionic surfactants (NS1)	3	7	10	3	7	-
nonionic surfactants (NS2)	-	-	-	-	-	7
auxiliary component (NaCl)	-	-	-	-	2	-

The degreasing effect was examined on the following fats: fat from roasting a pigs (F1), homemade processed fat (F2), restaurant fat (F3), and fresh unused fat (F4), showed on Figure 2.

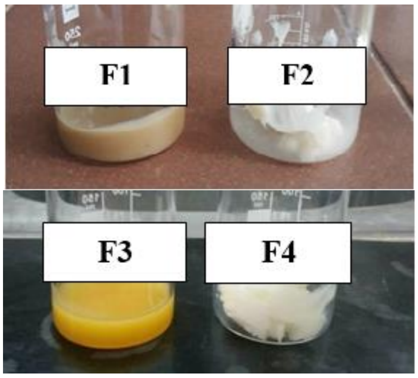


Figure 2. Fat samples

Physico-chemical characteristics of detergents and greases were determined and that characteristics are shown in the Table 2.

Table 2. Examined characteristics of detergent and grease samples

Characteristic of detergent	Characteristic of fat
Content of anionic surfactants (%)	Iodine number (g/100g)
Content of NaCl (%)	Peroxide number (mmol/kg)
Dry residue (%)	Acid number (mg KOH/g)
Content of total surfactants (%)	Index refraction on 20 ºC
Other surfactants (%)	
Density on 20 ºC (g/mL)	

Determination of the content of anionic substances in the sample was performed by two-phase titration, by dissolving the detergent sample, from which an aliquot was taken and 15 mL of chloroform and 10 mL of mixed indicator (dimidium bromide and disulphine blue) were added and titrated with benzenthonium chloride solution. The appearance of a gray-blue color of the lower phase of the solution mean end of titration.

The chloride content of the detergents was determined by dissolving the precise mass of the sample in a 50% solution of acetone, with an indicator of potassium chromate and titration with a solution of silver nitrate until the first deviation from the pure yellow color of the solution (light brown).

The dry residue was determined by drying the exact mass of the sample in an oven at 105 °C to constant weight, and weighing after cooling in a desiccator.

From the difference between the content of dry residue and the content of sodium chloride, the value of total surfactants was obtained. By subtracting the content of anionic substances from the total surfactants, the value of other surfactants is calculated. The density was determined by thermostating the sample at 20 °C and reading the density values using a hydrometer.

A certain mass of the sample was dissolved in chloroform, Hanus reagent was added, mixed carefully and left in a dark place for 30 minutes to make the reaction of addition. Potassium iodide solution and distilled water are then added. Titration is performed with sodium thiosulfate solution until a yellow color appears when starch is added, shake vigorously and titration continues, until a blue color of the solution appears.

The peroxide number was determined by dissolving the exact mass of the fat sample in a mixture of glacial acetic acid and chloroform (3:2) and then adding 0.2 mL of saturated KJ solution. After stirring, distilled water and starch as an indicator are added to the flask and titrated with 0.1 M $Na_2S_2O_3$ solution until the blue color is lost.

The determination of the acid number is based on dissolving the exactly known mass of the fat sample in a neutralized mixture (diethyl ether: 95% ethanol = 1: 1) and titrating with 0.1 M KOH solution, with the phenolphthalein indicator until a pink color appears. The refractive index was determined at a temperature of 20 ˚C using an Abbe refractometer.

The detergent solution is thermostated at 43 ºC. The grease sample is also thermostated for one hour at a temperature of 60 ºC and after reaching the set temperatures, about 3 g of grease is transferred to the beakers and 50 mL of detergent solution is added. The beaker with its contents is thermostated in a water bath (memmert) for an hour at 60 ºC, after which about 5 g of paraffin is added and these beakers are placed again on the water bath so that the paraffin melts faster (about 15 minutes). When all the paraffin has melted, the beakers are placed in the refrigerator in order to make the best possible separation of the aqueous phase from the fat that has not been removed and is located on the surface of the solution. The aqueous phase is decanted and the solid phase-paraffin cake is washed with ethanol and dried in an oven at a temperature of 60 ºC, to constant weight, cooled and weighed. Subtracting the mass of paraffin from the mass of the dried residue gave the mass of unremoved fat. When the mass of unremoved fat is subtracted from the initial mass of fat, the mass of fat removed by this degreasing process is obtained. Based on that, the degreasing efficiency is calculated:

$$Degreasing\ efficiency\ (\%) = \frac{m_1 - m_2}{m_1} * 100 \quad (1)$$

m_1 – weight of fat sample, (g) and
m_2 – weight of unremoved fat, (g).

RESULTS AND DISCUSSION

The results of this research are presented in tables and graphs through diagrams. Table 3 shows the results of the analysis of the tested fats.

Table 3. Results of phisico-chemical properties of fat samples

Characteristic	Fat			
	F1	F2	F3	F4
Iodine number (g/100g)	56.716	56.256	54.920	48.210
Peroxide number (mmol/kg)	0.871	1.794	1.810	0.516
Acid number (mg KOH/g)	1.077	0.178	2.394	0.764
Index refraction on 20 ºC	1.4687	1.4741	1.469	1.472

The value of the iodine number is lower in fresh fat (F4) compared to the fats used. Determining the iodine number gives an insight into the degree of unsaturation of a fat. Fats with a high content of unsaturated fatty acids have an iodine number greater than 130, and those with a lower content less than 80.

Fresh and carefully purified fats and oils have a low acid number because they contain very small amounts of free fatty acids. Standing increases the content of free fatty acids, and thus the value of the acid number increases. As can be seen from the table, the value of the acid number for fat F1 and F3 is higher due to the presence of water and various impurities as well as the higher number of uses. Free acids are formed as a result of hydrolysis, ie cleavage of triglycerides in the presence of water, so according to this fact, the fat F3 has the highest acid number because it is a used fat that has repeatedly come into contact with water.

The peroxide number of quality edible oil is zero and usually remains low under normal storage conditions. As the peroxide number indicates the degree of rancidity of some fat, fat F3 and F4 were used for prepare food, the obtained higher values are expect.

The refractive index is a parameter that is characteristic for certain groups of oils or fats, because it depends on the composition of fatty acids and can be used to identify fats and oils. The obtained results are in accordance with the properties of the used fats.

Table 4. Results phisico-chemical properties of detergent samples

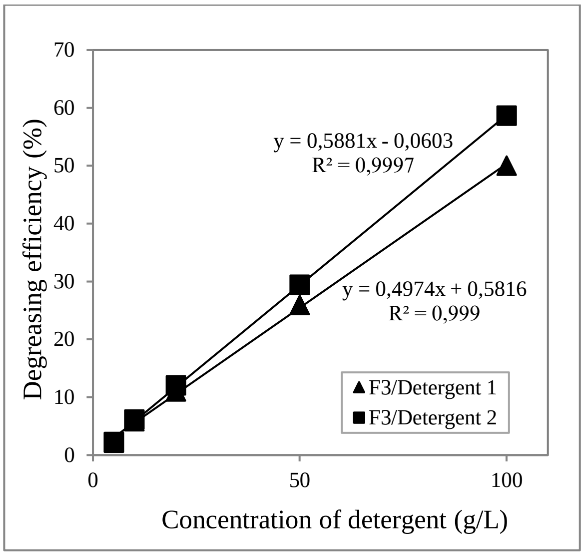
Characteristic	Detergent									
	1	2	3	4	5	6	7	8	9	10
Content of anionic surfactants (%)	4.28	6.59	8.97	5.94	8.97	4.01	10.89	5.84	4.77	12.85
Content of NaCl (%)	3.40	1.46	1.30	2.36	0.51	2.19	0.54	1.01	1.95	1.68
Dry residue (%)	12.70	14.42	15.74	14.14	18.19	7.71	17.04	13.61	9.79	22.10
Content of total surfactants (%)	9.30	12.96	14.44	11.78	17.68	5.52	16.50	12.60	7.84	20.42
Other surfactants (%)	5.02	6.37	5.47	5.84	8.71	1.51	5.62	6.77	3.07	7.58
Density on 20ºC (g/mL)	1.059	0.955	1.020	1.035	1.030	1.030	1.030	1.020	1.025	1. 030

The content of total surfactant is very different and ranges from 5.52% to 20.42%. However, the highest content of active substance does not necessarily mean that this sample will work best on fat and will give the best degreasing efficiency. In addition to anionic surfactants, detergents contain other active substances (amphoteric and nonionic surfactants) which are also responsible for removing fat during the degreasing process.

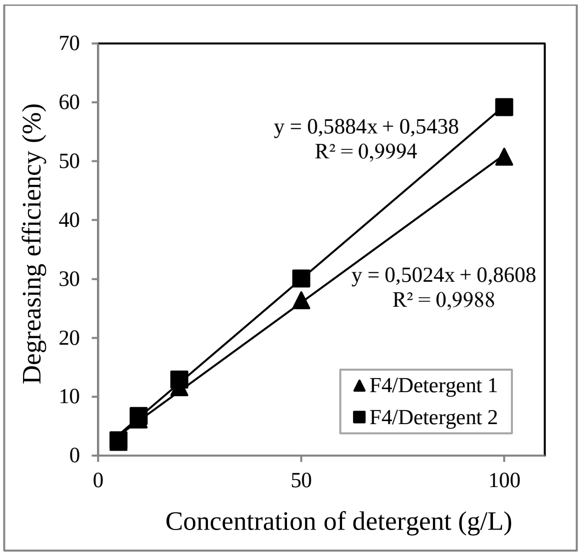
In order to increase the viscosity and reduce the cost of these formulations, NaCl is added to liquid dishwashing detergents, and the thickening effect depends on the concentration of surfactants. By higher content of NaCl compensated for the lower content of active substance.

The content of the basic active substance in these products is not limited by standard and regulations. However, in order to fulfill the basic function of these products, a certain minimum content is necessary, which depends on the type of active substance and the content of other components, and this is defined by each manufacturer in the development phase.

The Figure 3 show the dependences of the fat removal efficiency on the detergent concentration. Degreasing efficiency values increase with increasing detergent concentration for both types of fat: F3 and F4. The dependence of degreasing efficiency on detergent concentrations is a linear function, which is confirmed by their correlation factors.



a) F3



b) F4

Figure 3. Dependence of degreasing efficiency on detergent concentration

Detergent 2 shows a greater ability of removing the mentioned fats than detergent 1 of the same concentration, while the difference in the degreasing efficiency of these fats with a solution of the same detergent is very small (less than 1%).

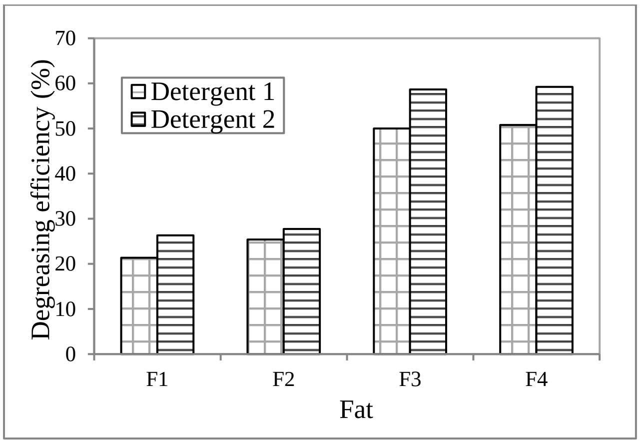


Figure 4. Efficiency of removal fats by detergent 1 and 2 (c=100 g/L)

F3 and F4 fats are much better removed with detergents 1 and 2 than other fats: F1 and F2, which show twice the values of degreasing efficiency (Figure 4).

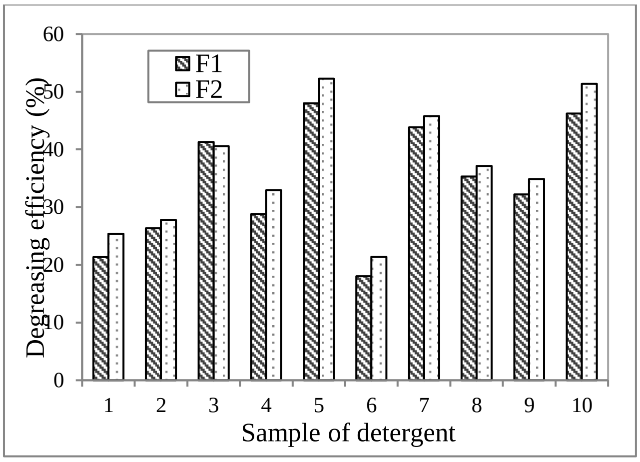


Figure 5. Dependence of degreasing efficiency and type of detergent (c=100 g/L)

All tested detergent samples show a stronger effect on F2 fat than on F1, due to the presence of mechanical impurities present in the F1, which is presented by Figure 5. The Figure 6 shows the dependences of the degreasing efficiency of F1 and F2 fat on the concentration of anionic surfactants (AS) and total surfactants (TS).

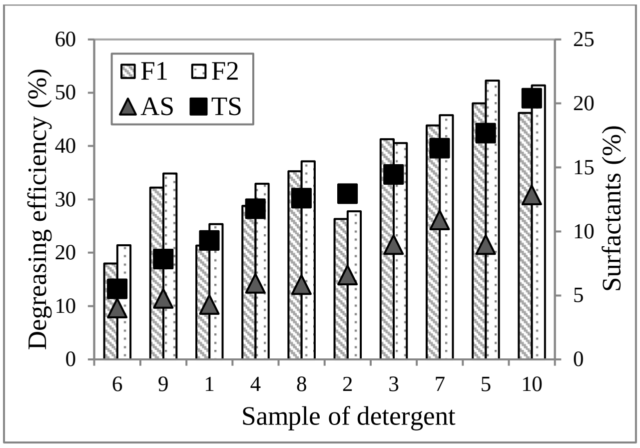


Figure 6. Influence of surfactants concentration on fat removal

From this diagram, it is clear that the content of surfactants present in the detergent affects the efficiency of fat removal. The growth trend of degreasing efficiency agrees with the growth trend of total surfactants and while with the growth trend of the concentration of anionic surfactants in detergents it shows less agreement. The concentration of anionic surfactants in detergent samples is not the main factor in the degreasing process because the presence of other active substances (nonionic and amphoteric surfactants) play a significant role in the fat removal process. For the same value of the concentration of anionic surfactants, sample 5 achieves better degreasing efficiency compared to sample 3 thanks to the other active substances present in it.

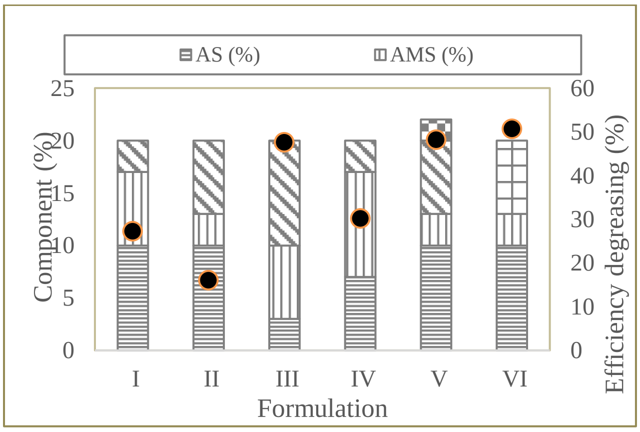


Figure 7. Efficiency degreasing fat F4 by laboratory detergent formulations

The laboratory sample of detergent (sample 10) has the highest content of total surfactants, but not the best washing effect, which means that the type of surfactant plays a major role in the degreasing process.

Figure 7 shows the influence of the composition of the prepared detergent formulations on the degreasing efficiency.

At the same concentration of anionic substance in detergent formulations (I and II), a stronger effect of degreasing is shown by a formulation with a higher concentration of amphoteric active substance. A higher nonionic surfactant content and a lower anionic surfactant content, along with the same amphoteric surfactant content in III lead to a significant increase in degreasing efficiency compared to I because in the micelles of ionic surfactants, there are also forces that tend to destroy the micelles, which are created due to the repulsion between the hydrophilic polar groups of the same charge. The presence of salt affects the degreasing efficiency because it reduces the repulsive forces of polar groups of surfactants. Due to the suppressed dissociation, the critical micellar concentration decreases and the micelle size increases, thus increasing the ability to remove fat, which can be seen from the degreasing efficiency values of formulations II and V. The formulation of detergent with ethoxylated fatty amide (NS1) leads to easier removal of fat than the combination containing a nonionic surfactant with a glycerine group (NS2).

CONCLUSIONS

Degreasing efficiency depends on the concentration and composition of the detergent. The described method is very selective because other factors such as: different temperatures and process time, mechanical action in removing grease from the contaminated surface and rinsing with water, influencing the degreasing efficiency, are constant during the experiments. The degreasing effect would be much higher if these effects were taken into account and it would be more difficult to assess the degreasing ability of the tested detergents.

The tested dishwashing detergents show different ability to remove grease, and the concentration of removed fat is directly proportional to the concentration of detergent.

REFERENCES

[1] I. Bozetine, T. Ahmed Zaıd, C.E. Chitour, and J.P. Canselier, „Optimization of an alkylpolyglucoside-based dishwashing detergent formulation“, *Journal of Surfactants and Detergents*, vol. 11, no 4, pp. 299-305, 2008.

[2] Y.A. El-Shattory, A.M.G. El-Mawla, H.A.A. El-Hamide, “Improved manual dishwashing liquid detergent compared to that produced by multinational companies in egyptian market”, *Egyptian Journal of Chemistry*, vol. 61, no. 4, pp. 651 – 659, 2018.

[3] M. Dai, J. Guo, X. Xue, and Y. Feng, „Preparation and investigation of high efficiency antibacterial liquid dishwashing detergent“, *Transactions of Tianjin University*, vol. 25, pp. 322–329, 2019.

[4] T. Kalak, K. Gasior, D. Wieczorek, and R. Cierpiszewski, „Improvement of washing properties of liquid laundry detergents by modification with N hexadecyl-N,Ndimethyl-3-ammonio-1-propanesulfonate sulfobetaine“, *Textile Research Journal*, pp. 1-15, 2020.

[5] A. Bratovcic, S. Nazdrajic, A. Odobasic and I. Sestan, „The influence of type of surfactant on physicochemical properties of liquid soap“, *International Journal of Materials and Chemistry*, vol. 8, no. 2, pp. 31-37, 2018.

[6] R.B. Cabalza, “Comparative analysis on the effectiveness of the different brands of commercialized dishwashing liquids, *Scholars Academic Journal of Biosciences*, vol. 4, no. 6, pp. 544-548, 2016.

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