“Mitigating the Impact of Hard Water: Developing Effective Cleansing Formulations”

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1. Introduction

Groundwater is a major source of freshwater on earth, supporting a wide range of human activities and vital ecosystems [1]. It plays a critical role in providing water for agriculture, industry, and households. Unfortunately, the rapid growth of cities and industries has led to increased pressure on groundwater resources, resulting in overuse that is gradually degrading water quality. This degradation is exemplified by the rising hardness of groundwater, a significant environmental concern that requires global attention [2]. Water hardness, a frequent topic of discussion when it comes to water quality [3], is defined as the concentration of divalent cations, primarily calcium and magnesium ions, within a given water source. It is typically quantified in milligrams per liter (mg/L) [4]. According to general guidelines, water is classified as soft if it contains between 0 to 60 mg/L of calcium carbonate, moderately hard between 61 to 120 mg/L, hard between 121 to 180 mg/L, and very hard if it exceeds 180 mg/L of calcium carbonate [5].

Globally, hard water is common throughout the world, it’s affecting over a third of the United States, nearly half of Western Europe, more than half of England, and significant portions of countries like Iran, Sri Lanka and Indonesia [6]. This widespread occurrence is largely due to the geological characteristics of these regions. Areas rich in limestone, chalk, and gypsum deposits often exhibit higher levels of water hardness [7] Hard water can present challenges in daily life, particularly in terms of cleansing. The presence of calcium and magnesium ions in hard water reacts with soap, resulting in a 'scummy' residue and reduced lathering ability. This interaction also affects the performance of surfactants by causing precipitation, altering micelle behavior, and potentially changing the solution's composition [8]. Furthermore, studies have also shown that washing the skin with hard water is one such environmental factor purported to the development of atopic dermatitis [9].

Recognizing the need for innovative solutions to mitigate the negative impacts of hard water, this research employs a scientific approach to develop effective cleansing formulations. To address this challenge, we analyzed the calcium content of several groundwater sources throughout Indonesia and formulated a range of cleansers, and we evaluated the effectiveness of each formulation to address the challenges caused by hard water, potentially offering a more comfortable and efficient cleansing experience for people worldwide.

2. Materials and Methods

Materials

Disodium EDTA (Nouryoun, USA), Tetrasodium Glutamate Diacetate (Nouryoun, USA), Sodium Laureth Sulfate (TaiDong C&S, Korea), Sodium C14-16 Olefin Sulfonate (AK Chemtech, USA), Disodium Laureth Sulfosuccinate (Miwon Commercial Co., Ltd, Korea), Potassium Laureth Phosphate (Solvay, China), Cocamidopropyl Betaine (Miwon Commercial Co., Ltd, Korea), Cocamide MEA (TaiDong C&S, Korea), Phenoxyethanol (Galaxy Surfactants Ltd, India), Sodium Chloride (Samchun Pure Chemical, Korea), Citric Acid (Jungbunzlauer, Austria)

Preparation of Cleansing Formulation

The test samples were developed utilizing four different anionic surfactants in combination with two chelating agents. The chelating agents that used were Disodium EDTA and Tetrasodium Glutamate Diacetate. Several combinations were tested as summarized in Table 1. The chelating agent and surfactants were dissolved in water at 75-80°C and mixed well with the agimixer for 5 minutes. Then Sodium Chloride, Phenoxyethanol and Citric Acid were added and mixed well for 5 minutes. The formulas were degassed until a clear appearance was formed.

Table 1. Composition of test samples

Ingredient	1A	1B	2A	2B	3A	3B	4A	4B
Disodium EDTA	0.05	-	0.05	-	0.05	-	0.05	-
Tetrasodium Glutamate Diacetate	-	0.05	-	0.05	-	0.05	-	0.05
Sodium Laureth Sulfate	6.75	6.75	-	-	-	-	-	-
Potassium Laureth Phosphate	-	-	6.75	6.75	-	-	-	-
Sodium C14-16 Olefin Sulfonate	-	-	-	-	6.75	6.75	-	-
Disodium Laureth Sulfosuccinate	-	-	-	-	-	-	6.75	6.75
Cocamidopropyl Betaine	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Phenoxyethanol	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Sodium Chloride	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Cocamide MEA	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Citric Acid	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Water	To 100	To 100	To 100	To 100	To 100	To 100	To 100	To 100

Calcium Measurements

Several groundwater samples from Indonesia which listed in Table 2 were used as both the baseline control and the solvent to investigate the impact of test cleansers on water hardness. First, the initial hardness of these control samples was measured. Then, the same groundwater samples were diluted with a 10% concentration of different test cleansers. Finally, the hardness of these diluted solutions was measured again, and the change from the initial baseline was analyzed to determine the effect of the cleansers on calcium ion levels and overall water hardness.

Table 2. Groundwater samples in Indonesia

Groundwater Source Area in Indonesia
Jakarta Water (JW)
Lampung Water (LW)
Bali Water (BW)
Makassar Water (MW)

Cleansing Performance Evaluation

The cleansing performance of each test samples were measured immediately after the application of dust to assess its instant pore cleansing effect. Dust cleansing is conducted by using artificial sebum and dust as the dirt and assessed by Scpectrophotometer and Dermatoscope. From spectrophotometer, the ΔE value is measured. ΔE is a color difference metric that is used to quantify the difference between two colors in the CIE Lab color space. ΔE is measured on a scale form 0 to 100, where 0 is less color difference and 100 indicates complete distortion. Cleansing ability of a test sample can be seen by the ΔE value which means the test sample has removed the dirt and return the color value of the skin to the initial value before given the dirt.

Foam Characteristic

Foam characteristics were analyzed with a Dynamic Foam Analyzer (DFA). A 0.1% test sample solution was prepared to determine its effect on hard water. After loading 20 ml into the instrument's prism column, the DFA measured and reported bubble count, size, maximum height, and the time to reach it. These measurements provided insight into the test sample's effects.

3. Results

Calcium Reduction in Water Hardness

Various formulations of the test sample were created and assessed to find the most effective surfactant and chelating agent combination for reducing water hardness levels throughout Indonesia. Test samples 2A and 2B proved to be the most effective in lowering water hardness in several Indonesian regions as details shown on Table 3.

Table 3. The Level of Water Hardness in Indonesian Regions After Treatment

Groundwater	Control	1A	1B	2A	2B	3A	3B	4A	4B
JW	26.78	21.01	15.66	0	0	14.42	19.36	19.78	17.30
LW	97.32	76.40	81.32	0	0	77.47	75.50	73.39	80.46

BW	26.91	21.01	15.66	0	0	14.42	19.36	19.78	17.3
MW	42.54	36.46	33.71	0	0	37.24	45.86	33.71	33.32

Cleansing Performance

The effectiveness of different test samples in removing dust was assessed using a spectrophotometer, and the results were summarized by ΔE values. Test samples 2A (ΔE = 0.1) and 2B (ΔE = 1.56) demonstrated the best dust removal performance, with values approaching zero, signifying nearly complete dust elimination.

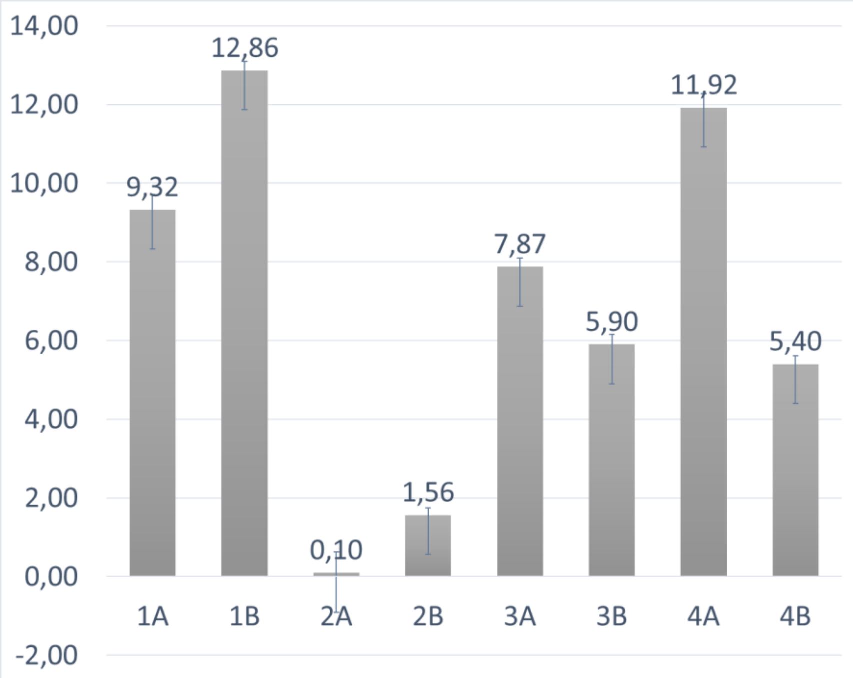


Figure 1. The ΔE of all test samples

	Before	Dust Applied	After
1A			
1B			
2A			

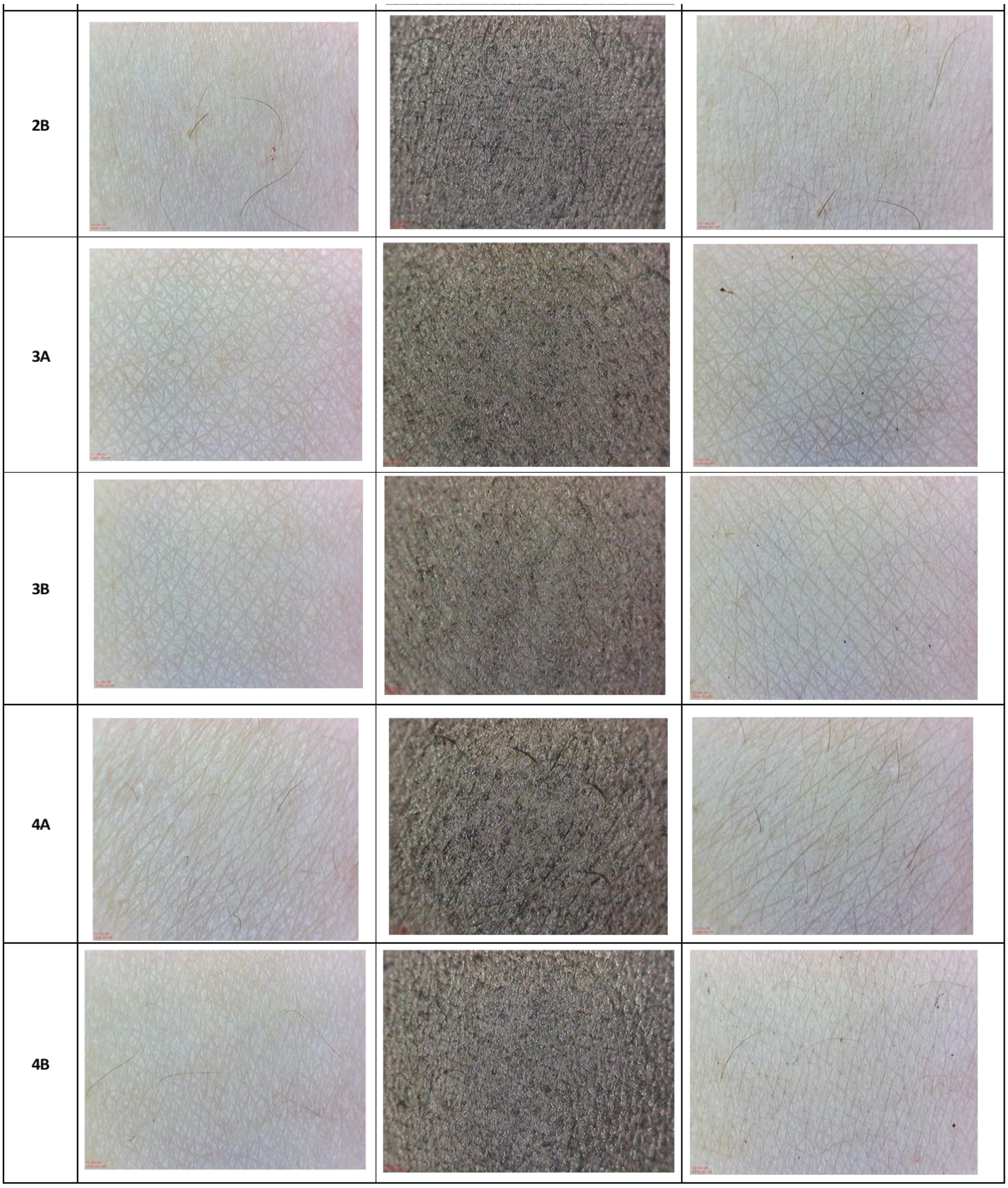
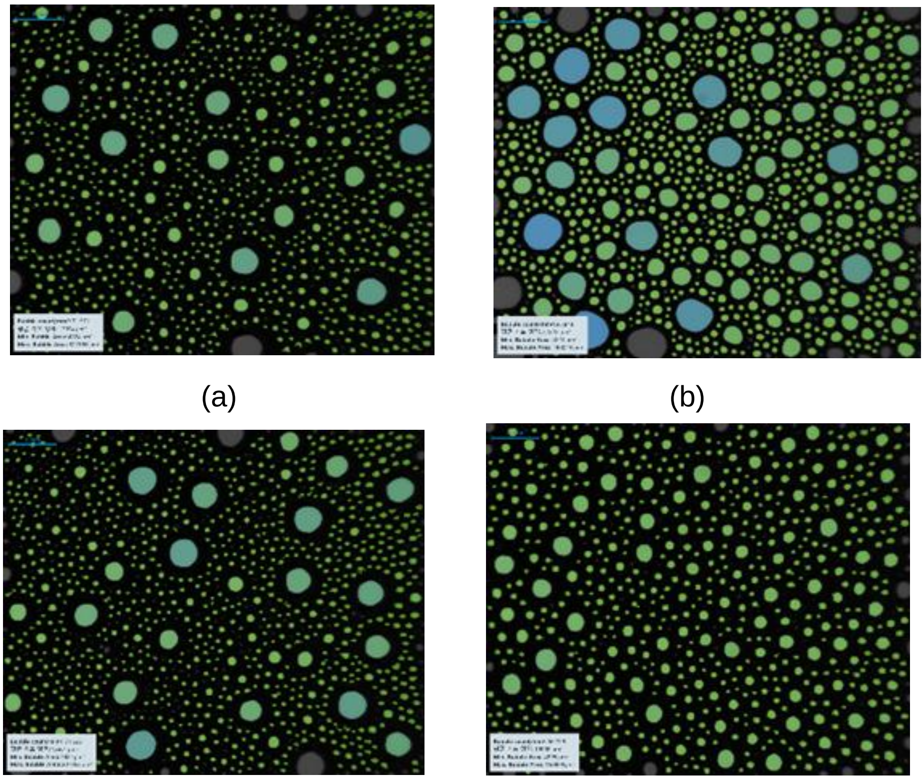


Figure 2. Comparison of dermatoscope image for dust removal

Foam Characteristic

Considering the superior calcium reduction in water hardness and cleansing performance across all tested samples, sample 2A emerged as the most effective. Consequently, the foaming characteristics of sample 2A were then evaluated across all the previously examined groundwater sources in Indonesia.



(a) (b) (c) (d)

Figure 3. The foam structures of test sample 2A with hard water from (a) Jakarta Water (b) Lampung Water (c) Bali Water (d) Makassar Water.

4. Discussion

The findings of this study highlight the effectiveness of our cleansing formulation in addressing water hardness. Previous research has established that anionic surfactants help reduce calcium levels because their negative charge enables them to attract and bind with the positively charged calcium ions found in hard water. When anionic surfactants bind with calcium, they form complexes that trap these ions, thereby decreasing the concentration of free calcium ions and enhancing cleansing performance and minimize the possibility of irritating the skin. Additionally, chelating agents are well-known for their ability to bind calcium and form very stable complexes with those metal ions, preventing them from interacting with other substances and forming precipitates.

In this study, we tested several anionic surfactants, including Sodium Laureth Sulfate, Potassium Laureth Phosphate, Sodium C14-16 Olefin Sulfonate, and Disodium Laureth Sulfosuccinate. The chelating agents used were Disodium EDTA and Tetrasodium Glutamate Diacetate. Our findings revealed that samples 2A and 2B, which utilized Potassium Laureth Phosphate (PLP) as the main surfactant and Cocamidopropyl Betaine (CB) as the secondary surfactant, achieved the greatest reduction in calcium compared to other anionic surfactants. The addition of an amphoteric surfactant was intended to compromise any potential decreases in foaming and cleansing performance which is caused by water hardness. The cleansing performance reveal that samples 2A and 2B exhibit lower ΔE values compared to the other samples, with sample 2A demonstrating the best performance. Consequently, sample 2A was tested for its foam properties with various groundwater samples, and the results indicated that the foam characteristics were generally uniform in size, suggesting a more stable foam.

The stable foam is likely due to the presence of amphoteric surfactants, which are especially effective at maintaining foam structure. Previous study indicates that amphoteric surfactants exhibit the strongest synergistic effects when used in combination with anionic surfactants [10]. This synergy means that the blend of surfactants delivers better interfacial and colloidal properties than each surfactant alone, leading to improved cleansing efficiency. Moreover, amphoteric surfactants can help reduce adverse interactions between PLP and hard water by enhancing foaming behavior. In addition, amphoteric surfactants-particularly Cocamidopropyl Betaine possess strong anti-irritant properties when paired with anionic surfactants, remain unaffected by water hardness, and generate excellent, stable foam in both soft and hard water conditions [11].

5. Conclusion

In conclusion, the development of a cleansing formulation may be capable of reducing the calcium level in water hardness which can potentially address some of the challenges associated with hard water usage. The promising results obtained with the combination of Disodium EDTA, Potassium Laureth Phosphate and Cocamidopropyl Betaine for potential applications in cleansing products for people worldwide.

Acknowledgments
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