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Silver-calcium-borates as better replacement for conventional organic antimicrobials in cosmetic products

A.L. Arunachalam[a], S. Induja[a], V. Parthasarathy[b] and P.S. Raghavan[a*]

[a]*Department of Chemistry, Hindustan Institute of Technology and Science, Padur, Chennai – 603 103, TN, India*
[b]*Department of Physics, Hindustan Institute of Technology and Science, Padur, Chennai – 603 103, TN, India*

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A B S T R A C T

Microbes generally develop resistance towards organic antibacterial agents like ampicillin, Sulfonamides, methicillin, etc., and progressively new drugs are being invented to replace them. Hence, replacement of organic antibacterial agents with inorganic analogues requires constant research and the present investigation reports alternatives for conventional antimicrobial agents like methylparaben, diazolidinyl urea, etc., in the cosmetic products with silver incorporated calcium borates. The chemically synthesized silver-calcium borates have been analyzed for phase purity using powder XRD analysis, nature of bonding using FTIR vibrations, and morphology using SEM. The antibacterial and antifungal studies were carried out for the novel inorganic silver-calcium borates incorporated cosmetic products. The products were also subjected to thermal & photostability studies and found to be comparable with that of commercially available products. A minimum quantity of 3 ppm of silver-calcium borate concentration was required to bring about nearly 100% bacterial reduction in the cosmetic products.

1. Introduction

The health care and cosmetic products incorporated with antimicrobial and antiviral agents play a lead role in preventing spreading of infectious disease, especially in pandemic situations. The main disadvantage of synthetic organic antibacterial compounds is the development of resistance by the microbes over prolonged exposure. For example, the *E. faecium*, *S. aureus*, *K. pneumoniae*, *A. baumannii*, *P. auruginosa* and *Enterobacter species* have developed resistance to most of the common antibacterial agents[1-2]. The inorganic antimicrobial agents, *viz.,* metal and metal oxides of silver, copper, zinc, etc., have been proved to have prolonged activity and do not develop resistance amongst the microbes[3]. The antibacterial activity of bimetallic nanoparticles of Cu-Ni against dental pathogen was reported by Argueta-Figueroa *et al.*[4] The hand-wash dispersed with silver nanoparticles was prepared and compared its antimicrobial activity with the conventional hand wash by Ahmed and his research team[5]. The antibacterial activity of silver selenide and silver sulfide nanoparticles was studied by Delgado *et al*.[6] The antifungal activity of silver nanoparticles stabilized with dextran sulphate was investigated against *Candida albicans* by Milorad and his research team[7]. Nguyen *et al.*[8] investigated the antibacterial efficiency of silver/graphene composite against the *Listonella anguillarum* and *E. coli* (Gram-negative) and *S. aureus* and *Bacillus cereus* (gram-positive) bacterial strains. The report of Diaz *et al.*[9] suggested that the nanocomposite of silver/hydroxyapatite can be used as promising biomaterials in reconstructive surgery and implant applications due to its high degree of bactericidal activity. The bactericidal effect of silver/cellulose bio-composite was analysed against multidrug-resistant strains and

* Corresponding author. Tel.: +91-44-27474262; Fax: +91-44-27474208
E-mail address: raghavan@hindustanuniv.ac.in (P.S. Raghavan)

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common bacterial strains by Garza-Cervantes *et al.*[10] Recently nanoparticles of silver and copper were used as drugs and antimicrobials in consumer products. The metallic nanoparticles possess a small size with a high loading capacity. Unlike organic antimicrobials, they possess prolonged stability[11]. However, the toxicity effect studies of these metal nanoparticles are at the infant stage and fewer research groups reported about the penetration of these nanoparticles through human skin[12].

Generally, cosmetic products contain organic antimicrobials like triclosan in hand-wash, diazolidinyl urea in body-wash, and methylparaben in face cream[13]. In the present investigation, an attempt to replace these antimicrobials with silver-calcium borates has been made. Calcium borates are highly stable, non-reactive and insoluble in both aqueous and organic solvents and none of their components were reported to be carcinogenic according to IARC, ACGIH, NTP and OSHA. They possess very low antimicrobial effects, and their antimicrobial ability can be enhanced many folds by adding silver into the calcium borate matrix[14]. The silver present in the calcium borate is not a nanoparticle, does not get leached and hence, it is expected to be safer for both the human and environment. In the present investigation, three different cosmetic products such as body-wash, hand-wash and face-cream were short-listed to evaluate their antimicrobial performance, thermal stability and photo-stability.

2. Results and discussion

2.1. Structural and Morphological studies

The XRD patterns of the CaB and Ag-CaB are presented in **Fig. 1A** and **Fig. 1B**, respectively. The CaB showed formation of CaB_2O_4(PDF: 750640) and $CaNaB_5O_9$(PDF: 780294) phases. As reported in earlier literature, the silver incorporated CaB showed $CaNaB_5O_9$ as a major phase and CaB_2O_4 as a minor phase. No additional peaks corresponding to the formation of silver compounds were observed, suggesting that the silver enters into the matrix of CaB. The FTIR spectra of Ag-CaB samples showed the presence of BO_3 groups of borates resulting in B-O bending vibration at around 710 cm^{-1} and B-O stretching vibration at around 1330 cm^{-1} (**Fig. 2**)[16]. The presence of BO_4 was inferred by B-O stretching vibration at around 950 cm^{-1}.[17] On addition of metal ions in the CaB matrix, the additional B-O asymmetric stretching was observed at around 1150 cm^{-1}.[18] The SEM image of Ag-CaB showed the formation of irregularly shaped particles in the range of 2 – 5 microns (**Fig. 3**). The particle morphology resembles that of borate glass as reported by Elfayoumi *et al*.[19]

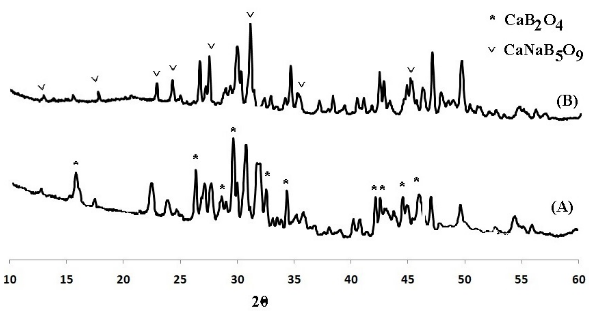

Fig. 1. XRD patterns of (A) CaB and (B) Ag-CaB calcined at 800°C

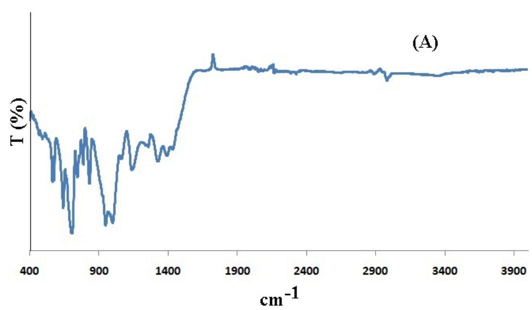

Fig. 2. FTIR spectrum of (A) Ag-CaB calcined at 800°C

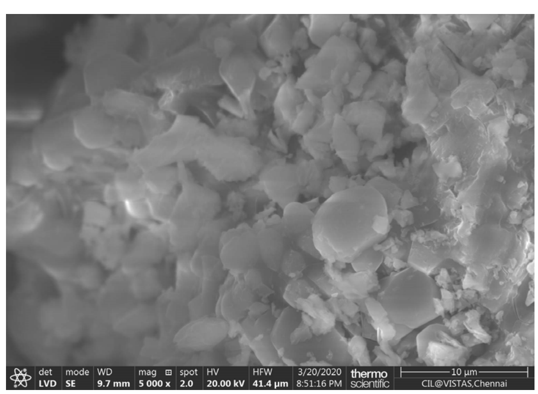

Fig. 3. SEM image of Ag-CaB calcined at 800°C

2.2. UV-Visible analysis

The commercially available sunscreen ointment absorbed between 200 and 220 nm (**Fig. 4A**), while the Ag-CaB incorporated face cream was found to absorb UV radiation of wavelength around 200 - 240 nm, with a sharp absorption at 215 nm (**Fig. 4B**). The absorption intensity for the Ag-CaB was much higher than the commercial sample. This study proves that the Ag-CaB incorporated face cream possesses not only antibacterial and antifungal properties but also protects from UV rays as compared with the commercial sample.

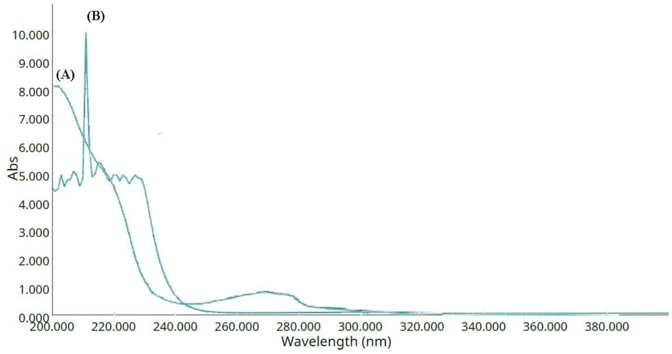

Fig. 4. UV absorption of samples (A) Commercially available sunscreen ointment and (B) Ag-CaB face-cream

2.3. Antibacterial studies

The antibacterial studies for Ag-CaB incorporated body-wash against *S. auerus* and *E. coli* were carried out to conclude its excellent antibacterial activity (**Fig. 5 and Fig. 6**), and the results are presented in **Table 1**. The blank products (without any active antibacterial ingredients) showed marginal antibacterial reduction (Entry-1), which was due to the surfactants and foaming agents present in the formulations[20].

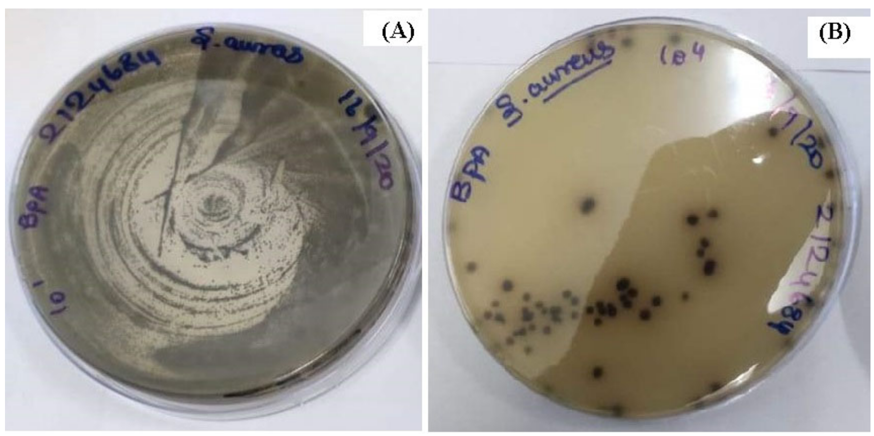

Fig. 5. Antibacterial studies against *S. auerus* over (A) Blank (B) Ag-CaB Body-Wash

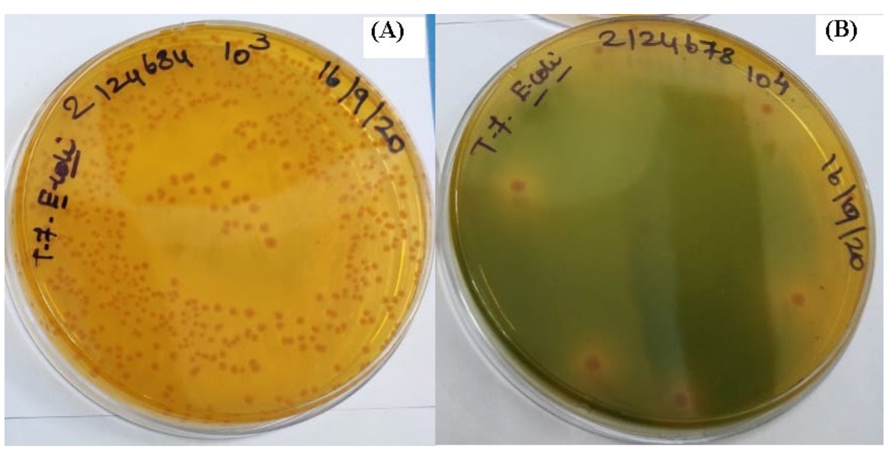

Fig. 6. Antibacterial studies against *E. coli* over (A) Blank (B) Ag-CaB Body-Wash

Table 1. Antibacterial analysis results of cosmetic products incorporated with Ag-CaB

S. No	Quantity of Product taken for analysis (g)	Ag-CaB content in 10 mL of the culture (ppm)	CFU reduction % / mL BODY WASH *		HAND WASH *		FACE CREAM *	
			S. aureus	*E. coli*	*S. aureus*	*E. coli*	*S. aureus*	*E. coli*
1.	1	--	12	15	11	15	10	14
2.	0.5	2.5	75	72	78	75	82	85
3.	1	5	87	91	88	93	92	95
4.	3	15	98	99	99	99	99	99
5.	5	25	99	100	99	100	99	99
6.	1 (Commercial product)	30 (Active ingredient)	97	98	99	99	97	99
7.	1 (After stability studies)	5	82	90	86	94	92	94

* Note: The variation of results was generally, within ± 4 units and the activity above 97% was ± 1 unit.

Initially, to find the influence of Ag-CaB on the antibacterial effect, the concentration of the products taken for analysis varied between 0.5 g and 5 g. 0.5 gram of the product (Ag-CaB = 2.5 ppm) showed around 70 to 80% CFU/mL reduction. On increasing the product content to 1 gram (Ag-CaB=5 ppm), the antibacterial effect increases to around 90% CFU/mL reduction, and on further increasing the product content to 3 g (Ag-CaB = 15 ppm), a maximum reduction of nearly 100% was observed. The comparison was made by analyzing the antibacterial effect of commercially available products (Entry-6) which showed nearly 100% CFU/mL reduction with the active ingredients of around 30 ppm. Thus, the present Ag-CaB exhibits equivalent antibacterial activity with nearly half of the concentration of active ingredient incorporated in the cosmetic products.

2.4. Antifungal studies

The antifungal studies were carried out for the prepared face cream incorporated with 0.5% of Ag-CaB against *A. brasiliensis and S. cerevisiae* as shown in **Fig. 7** and **Fig. 8**, and the results are presented in **Table 2**. One gram of the product (Ag-CaB – 5 ppm) showed relatively less CFU/mL reduction against the fungi as compared to bacterial strains. On increasing the product content, the antifungal activity was found to increase and a maximum antifungal activity of around 100% was observed for 25 ppm of Ag-CaB content (5 g of product).

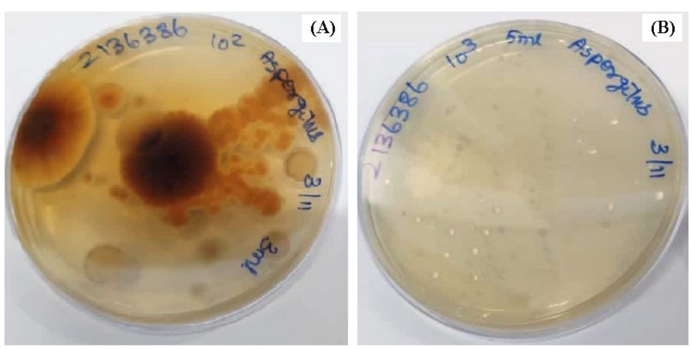

Fig. 7. Antifungal studies against *A. brasiliensis* over Ag-CaB Face cream (A) 3 g sample (B) 5 g sample

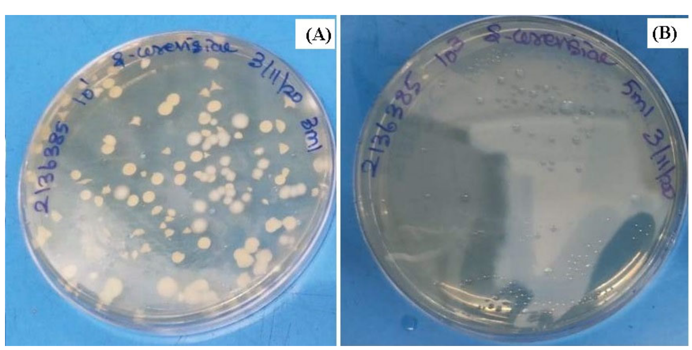

Fig. 8. Antifungal studies against *S. cerevisiae* over Ag-CaB Face cream (A) 3 g sample (B) 5 g sample

2.5. Stability studies

The cosmetic products dispersed with Ag-CaB were subjected to stability studies, in order to find the compatibility on aging. Generally, the organo-leptic properties will be studied subjecting the samples to different conditions for the cosmetic products. Thermal stability is one of the most important properties of cosmetic products. Around 50 grams of the same was taken in a clear transparent borosilicate glass bottle and placed at 5°C, 27°C and 50°C for 8 weeks. Aliquots of the samples were withdrawn and studied for 1, 3, 5 and 8th weeks. The samples were evaluated for change in color, physical homogeneity, and finally antibacterial activity.

Table 2. Antifungal analysis of face-cream incorporated with Ag-CaB

Quantity of Product taken for analysis (g)	Ag-CaB content in 10 mL of the culture (ppm)	CFU reduction % / mL FACE CREAM*	
		Saccharomyces cerevisiae	***Aspergillus brasiliensis***
1	5	62	75
3	15	85	86
5	25	97	99

* Note: The variation of results was generally, within ± 4 units and the activity above 97% was ± 1 unit.

The Ag-CaB incorporated cosmetic products were studied for photostability by subjecting around 50 grams of sample in quartz bottle and exposed to UV light (400 nm) at around 60 cm distance for 24 hours. For every 8 hours, aliquots of the sample were withdrawn and tested for color change by the visual inspection method. The stability study results are presented in **Table 3**. No phase separation in the products was observed when subjected to aging conditions under study and the products incorporated with 0.5% of Ag-CaB were found to be stable at 5°C and room temperature. But, at 50°C mild colour change was observed for face cream and hand wash, this is due to the inherent property of silver products, which are temperature sensitive. On the other hand, the body wash did not show much change in colour with the increase in storage temperature even after 8 weeks. The experiment was studied with products with less Ag-CaB content (0.1%) and the results are presented in **Table 3**. Due to the lesser concentration of the silver, the products did not show any colour change when stored at 5, 27 and 50°C, even after 8 weeks. The photo-stability studies were carried out for all the products and the results are presented in **Table 3**. The products containing 0.5% of Ag-CaB showed a very negligible colour change on exposure to UV light for 24 hours and on the other hand, the cosmetic products incorporated with 0.1% of Ag-CaB did not show any colour change. The antibacterial studies of the cosmetic products subjected to stability studies were carried out to check their antimicrobial performance on aging, and the results are presented in **Table 1** (Entry-7). The antibacterial activity was found to be nearly the same on aging in comparison with the fresh sample.

Table 3. Stability studies of cosmetic products incorporated with Ag-CaB

SAMPLE	Thermal Stability Studies * (After 8 weeks of storage)		Photo Stability Studies at RT* (27°C, 24 h)
	Temperature, °C	Visual inspection	
Face Cream Ag-CaB(0.50%)	5	A	AB
	27	AB	
	50	C	
Hand wash Ag-CaB(0.50%)	5	A	AB
	27	AB	
	50	C	
Body wash Ag-CaB(0.50%)	5	A	AB
	27	AB	
	50	AB	
Face Cream Ag-CaB(0.1%)	5	A	A
	27	A	
	50	A	
Hand wash Ag-CaB(0.1%)	5	A	A
	27	A	
	50	A	
Ag-CaB Body wash Ag-CaB(0.1%)	5	A	A
	27	A	
	50	A	

* Product Discoloration coding: A - None; B - Almost Unnoticeable; C – Slight; D – Noticeable; E – Distinct; F - Severe

3. Conclusions

The silver incorporated calcium borate was prepared, and the phases were identified using XRD analysis. The FTIR spectral analysis showed the presence of BO_3 groups and the formation of BO_4 groups on the incorporation of silver in the calcium borate matrix. The SEM images showed irregular-shaped particles in the size range of 2 – 5 microns. The antibacterial and antifungal studies of Ag-CaB incorporated products, viz., face cream, body wash and hand wash were investigated in detail. The products showed a maximum CFU/mL reduction of around 100% bacterial strains at 3 ppm of Ag-CaB, and around 100% fungal reduction at 5 ppm. The thermal stability study showed that the cosmetic products incorporated with 0.1% of Ag-CaB were stable, while photostability studies showed that the products incorporated with 0.5% of Ag-CaB were stable. The performance of the cosmetic products was better than the commercially available products with relatively less Ag-CaB content. The clinical trials on the compatibility of the products are in progress for commercialization.

4. Experimental

4.1. Materials

All the chemicals used for this experimental work were of analytical grade. Calcium nitrate and silver nitrate were procured from SD fine chemicals, India. Cetyltrimethylammonium bromide and sodium tetraborate were purchased from Merck, India.

4.2. Synthesis of silver incorporated calcium borates

The silver-incorporated calcium borates (Ag-CaB) were prepared by adopting procedures reported in the literature[14]. The typical procedure involves dissolving calcium nitrate (98%) and silver nitrate (99.5%) in distilled water to get a clear solution. To this, a small quantity of cetyltrimethylammonium bromide (99%), cationic surfactant was added and stirred till dissolution. In another beaker sodium tetraborate (Qualigens, 99%) was added in distilled water maintained at around 80°C under vigorous stirring. The mole ratio of calcium oxide, silver oxide and boric oxide was kept as 1:0.01:1. After 30 minutes, when dissolution is complete, the prepared nitrate solution was added in drops to the above reaction mixture under constant agitation to get white precipitate. Once the whole quantity was added; the contents were stirred for 1 h and allowed to settle overnight. The supernatant was decanted and tested for the presence of unreacted silver and calcium by adding sodium chloride and sodium carbonate, respectively. The precipitate was repeatedly washed with distilled water till it was free from nitrates. Then it was centrifuged and dried at 120°C for 6 h. The dried precipitate was calcined at 800°C for 30 minutes and labelled as Ag-CaB. As a control sample, the procedure was repeated without the addition of silver nitrate and the sample was labelled as CaB.

4.3. Characterization

The crystallinity and phase purity of the samples were measured by X-Ray diffraction analysis carried out using a PANanalytical powder X-Ray Diffractometer (Xpert3). The vibrations of various bonds in the sample were analyzed using Perkin-Elmer FTIR (Spectrum 2). The morphology of the samples was determined using FEI Quanta – Quattro-S scanning electron microscope. The UV-absorption of the samples was measured using Systronics UV-Visible Double beam spectrometer (Type 2202), between 200 and 400 nm.

4.4. Cosmetic product formulations

The cosmetic formulations were made by following guidelines given by Sharma *et al.*[15]A typical face cream formulation generally contains, EDTA to soften tap-water, stearic acid which forms an emulsion with water. It thickens and softens the cream and provides a cool sensation on applying it to the skin. Glycerol was generally added to trap the moisture and isopropyl myristate was used as a moisturizer and glycerol monosterate as an emulsifier. Finally, potassium hydroxide was used to neutralize to achieve a pH of 6.5 – 7. The preparation involves in 3 stages, the first stage was to prepare aqueous solutions and the second stage was to prepare the oil phase. The potassium hydroxide solution was prepared in the third stage. The first stage involves dispersing EDTA (0.2%) in double-distilled water (76.5%) at around 75°C under agitation. The oil phase was made by heating 16 % of stearic acid at around 80°C followed by the addition of 1.5 % of isopropyl myristate under constant agitation. It was further added with the glycerol monosterate (1%) and glycerol (4%) and stirred continuously for 30 minutes to form a homogeneous mixture. Then, the oil phase was added slowly into the aqueous phase under slow stirring by maintaining the temperature. Finally, Ag-CaB was added and stirred continuously for 2 hours to form a thick cream to which the required quantity of potassium hydroxide solution (0.6%) was added slowly to get a pH between 6.5 and 7. The product is given in **Fig. 9A**.

Body wash (Shower Gel) was prepared by dispersing sodium laureth ether sulfate (18% by weight) in double-distilled water (68.6%) and adding cocamidopropylbetaine (9%) slowly, without forming foam. A small quantity of propylene glycol (0.5%) and glycerol were added and stirring continued gently. In order to adjust the viscosity of the gel, sodium chloride was added (around 1.5%). Finally, the antifungal/antibacterial agent (Ag-CaB) was powdered and dispersed well for 30 minutes (**Fig. 9B**). Unlike body-wash gel, the hand-wash gel contains acrylic copolymer and no foaming agents were added. It was prepared by dissolving acrylate copolymer in distilled water followed by the addition of sodium laureth ether sulfate as a surfactant, glycerol for retaining moisture and blended. A small quantity of propylene glycol was added to add viscosity and finally neutralized with sodium hydroxide solution (**Fig. 9C**).

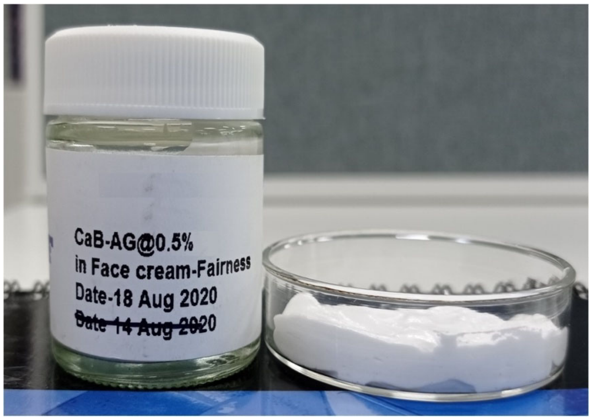

Fig. 9A. Image of Face-cream incorporated with 0.5% of Ag-CaB

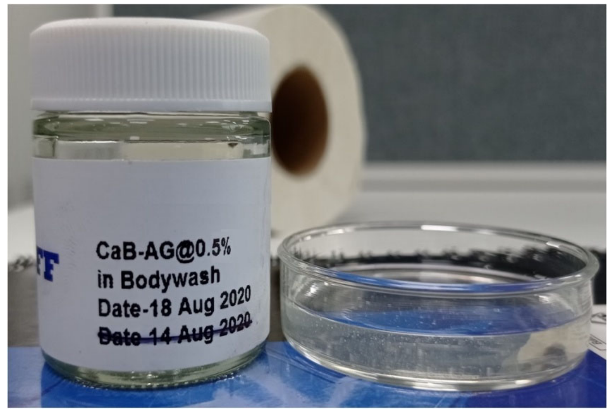

Fig. 9B. Image of Body-wash incorporated with 0.5% of Ag-CaB

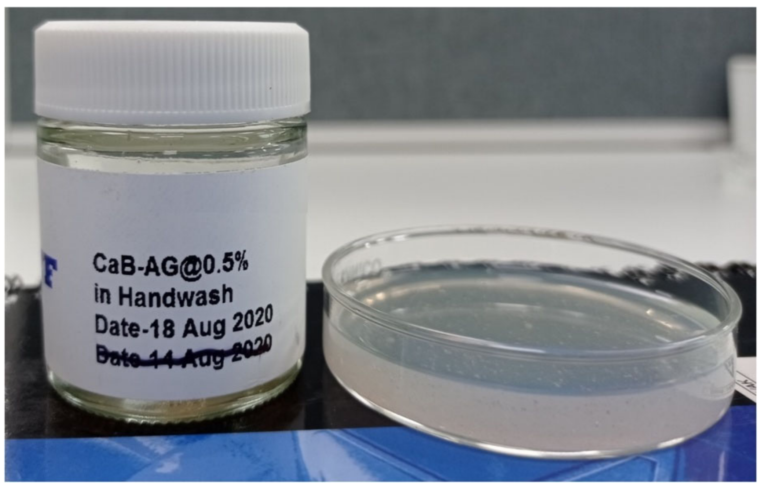

Fig. 9C. Image of Hand-wash incorporated with 0.5% of Ag-CaB

4.5. Antibacterial procedure

The antibacterial analysis of the products was carried out using the ASTM-E-2149 procedure. The bacterial strains selected were *Staphylococcus aureus* (NCIM2127) and *Escherichia coli* (NCIM 2931), with an initial concentration of 57.5×10^5 and 115×10^5CFU/mL, respectively. 1 mL of the inoculums was transferred into a clean test tube containing 9 mL of sterilized distilled water. To this, 1 g of the product was added and shaken well. After 1 hour, 1 mL from the above test tube was spread over a petriplate containing nutrient agar with the help of an 'L' rod. The petriplate was inverted and incubated for 24 h at 37°C. The procedure was repeated without adding the sample as blank. The colony-forming units (CFU/mL) were calculated in both the blank and the sample. The antibacterial activity was calculated as CFU/mL reduction percentage in comparison with blank. The experiment was triplicated for confirmation of results. Antifungal activity was studied adopting the above procedure against *Saccharomyces cerevisiae* (NCIM3287) and *Aspergillus brasiliensis* (NCIM1196) with an initial concentration of 5.32×10^5 and 8.7×0^4 CFU/mL, respectively and incubated for 5 days.

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