Formulation and Evaluation of Sunscreen containing Zinc Oxide (ZnO) Nanotubes

(prepared by Chemical etching process)

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Abstract

Zinc oxide (ZnO) nanotubes have gained attention in the field of sunscreen due to their unique properties. In this article, we focus on the characterization of multiwalled zinc oxide (MWNTs) synthesized by Chemical Etching method. The morphology of MWNT is characterized by scanning electron microscopy (SEM). The SEM micrographs are used to analyze the morphologies of the nanostructures. The UV Visible spectrophotometer has been implemented in examine the in-vitro efficacy of sunscreen, which was discovered to be between of 6.97 to 7.24, which is good for skin pH of all formulations of cream were shown pH nearer to skin required, but pH formulation. The results show that zinc oxide nanotube-based sunscreen is a promising alternative to traditional sunscreens, potentially providing enhanced sun protection and improved cosmetic characteristics. Based on the formulation, sunscreens may offer improved aesthetics in contrast to the marketed sunscreen products, potentially providing enhanced sun protection and improved cosmetic characteristics. Therefore, it is preferable to combine various sunscreen agents with physical sunscreen in order to increase the level of protection.

Keywords: Nanotubes, zinc oxide, Sunscreen, UV. Radiation.

FORMULATION OF SUNSCREEN

Introduction

A variety of electromagnetic radiation is produced by the sun, our nuclear furnace at the heart of our solar system, some of which is necessary for life as we know it on planet. Although we are most aware of the visible light from the sun, the only light that is visible with the unaided eye, there are a few numbers of kinds of light we cannot see. One of these is infrared light, which is responsible for heating our planet. Another is ultraviolet light which is responsible for sunburn and suntan and increases the risk of basal cell carcinoma and malignant melanoma. Ultraviolet light is artificially divided into three ranges:

UVA is radiation inside 320-400 nm range, UVB is radiation inside 290-320 nm range, UVC is radiation inside 100-290 nm range

UVC is totally blocked by the ozone layer in the upper atmosphere of the Earth. The ozone layer blocks some of the UVB and all of the UVA passes through the ozone layer. Generally, UVB has been blamed for sunburn, but some studies indicate that UVA may also cause skin damage.

Sunscreens are cosmetic formulations that block UV rays. Sunscreens are assigned sun protection factors, or SPF, ratings that are supposed to indicate the level of protection from UV radiation. A multiplier known as the SPF rating indicates how long a person can comfortably spend in the sun. An SPF-15 sunscreen, for instance, should enable a person whose exposed skin burns in five minutes to spend fifteen times as long—or seventy-five minutes—in the sun without becoming burned.

The UVA radiations (320–400) that make up the UVR that reaches the earth's surface get through the ozone layer and induce sunburn and accelerated aging of the skin by inhibiting immunological function. Although the ozone layer blocks UVB radiations (290–320 nm) to some extent, sunburn may still result from them. The ozone layer completely blocks UVC radiation, which is measured

between 100 and 290 nm. Therefore, a better choice to increase the level of protection is to add another sunscreen agent in addition to physical sunscreen.. [1]

Some active ingredients in sunscreen

Benzyl salicylate and salicylate derivatives. One of the first sunscreen agents. It provides UVB protection, but not UVA. It is not soluble in water and can be used in waterproof formulations. It is often used in combination with other ingredients. One of the derivative compounds is known as homosalate.

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PABA (p-aminobenzoic acid). This compound was extensively used in many formulations; however, it was not water soluble and needed to be used in alcohol-based solutions, it would discolour fabrics, and many individuals experienced or developed allergic reactions to it.
Most sunscreen lotions are now PABA free. Butyl methoxydibenzoylmethane and related compounds. Also known as Parsol 1789 and Parsol A is an effective UVA blocker. Oxybenzone is a related compound.

Zinc oxide and titanium dioxide are two inorganic compounds that are insoluble in most liquids. These block the UV radiation because their preparations are opaque to light. Sunscreen lotions containing these are normally white opaque ointments on the skin. Each of the active ingredients provides an SPF factor related to its concentration in the sunscreen. Increasing the concentration of the ingredient should also increase the SPF rating of the sunscreen.

PREPARATION OF SUNSCREEN

Ingredients/ materials

Cetyl alcohol (also called as 1-hexadecanol), Benzophenone-3 (also called as oxybenzone) Ethylhexylmethoxycinnamate (also called as octyl methoxycinnamate), (Mixture of Zinc oxide and Titanium Dioxide), Stearic acid, Glycerin, Triethanolamine, Water, distilled or deionized, Stearyl dimethicone silicate crosspolymer and Cyclopentasiloxane, Beaker 150 mL, 2 Beakers 400 mL, Thermometer, 110°C, Stirring rod, Water bath, Beaker tongs.

Procedure

Place a 150-mL beaker on a balance and weigh it. Fill the 150-mL beaker with the weights of the ingredients listed in your assigned formulation from Table 1: cetyl alcohol, benzophenone-3, ethylhexylmethoxycinnamate, stearic acid, glycerin, and stearyl dimethicone silicate crosspolymer. Heat the beaker with the organic combine in a water bath until all the ingredients have meltedNote: Never melt cosmetic components over a direct flame or high heat as they might scorch or break down if heated much higher than water's boiling point. Fill a 400 mL beaker with 78 g of water. To the water, add 1.0 g of triethanolamine. Stir. Raise the temperature of the water solution to between 80° and 85°C.

After the water solution has reached a temperature between 80° and 85°C, remove it from the heat and slowly pour the melted cetyl alcohol, benzophenone-3, ethylhexylmethoxycinnamate, stearic acid, glycerine, and stearyl dimethicone silicate cross polymer mixture into the water a little at a time, stirring constantly. It may be helpful to hold the 400-mL beaker using a pair of beaker tongs. (Note: You can remelt the "organic mixture" by heating it momentarily in the water bath if it has solidified.) Your emulsion will be lumpy or the ingredients may not form an emulsion if you pour too quickly or do not stir. Stirring continuously will result in a homogeneous, smooth paste. Put the sunscreen cream in the beaker and label it before letting it cool.

FORMULATION OF ZINC OXIDE (ZnO) NANOTUBES

Introduction

ZnO is a wide band gap semiconductor, the band gap width is about 3.37 eV, the electron binding energy at room temperature is 60 meV [2], and generally presents a hexagonal wurtzite structure. ZnO semiconductor materials have good physical properties (conductivity, piezoelectricity, photoelectricity, etc.) [2-5] and chemical properties (stability, gas sensitivity, etc.), so they have widely used in optoelectronics [6], solar cells [7-8], sensors [9], field emission [10], piezoelectric [11] and catalysis [12], etc. So far, the synthesis methods of preparing ZnO nanomaterials have made great progress, mainly including the vapor deposition method [13-14], template method [15-16] and hydrothermal method [17-18]. The products synthesized by these methods have good crystallization, high purity, and controllable particle size, but these methods have more or fewer disadvantages that are difficult to overcome, such as the harsh preparation conditions of the vapor deposition method (requires high temperature, a certain gas atmosphere or high vacuum). In addition, the instrument is expensive, time-consuming to operate, the template method is less independent (need to be used with other methods), and the hydrothermal method has a long preparation cycle. Therefore, it is necessary to find a preparation method that can overcome the above disadvantages and is easy to produce on a large scale. Compared with other methods, galvanostatic deposition technology has many advantages, such as mild reaction conditions, simple equipment, high deposition rate, environmentally friendly one friendliness, and controllable morphology [19-24It has been heavily applied to the preparation of one- dimensional ZnO nanorod arrays.

In recent years, ZnO nanotubes have emerged as a popular subject of study due to their unique hollow structure and high surface area compared with nanorods and nanowires, which can greatly improve the application efficiency in sensors, solar cells, photoelectronic and other aspects. At present, the methods of preparing ZnO nanotubes are mostly alkali chemical etching [25-27]. ZnO nanocolumns can be etched into tubes using alkali chemical etching, but the etching effectiveness

is too poor, and it takes some time to etch all the way to the bottom of the nanotubes. At the same time, the etching intensity is strong enough to directly etch the bottom of the nanotubes, thus increasing the surface area of the nanotubes to a greater extent, which can improve the optical and photoelectrochemical properties of nanotubes and get a certain improvement in the sensor, ultraviolet light detector, solar cell.

The growth of ZnO nanorods arrays on substrates can be obtained either using vaporus phase syntheses or in solutions [28]. The former requires expensive equipment, high temperatures and time-consuming procedures [29,30] whereas the latter is easy to perform at low temperatures [31]. The most popular methods for creating ZnO nanorod solutions include hydrothermal growth [32-33], the method of electrochemistry [34] or by the process of wet chemical synthesis [35].

PREPERATION OF ZINC OXIDE (ZnO) NANOTUBES

Materials

Zinc nitrate hexahydrate (Zn(NO3)2, hexamethylene tetramine (C6H12N4) and potassium hydroxide (KOH). the three-electrode system are used as the test instruments. Among them, the opposite electrode in the three-electrode system uses a platinum sheet, the reference electrode uses the standard Ag/AgCl electrode (filled with saturated KNO3 solution), and the functional electrode is ITO conductive glass.

Preperation of ZnO nanorods

First, 0.01mol/L zinc nitrate solution was prepared and electrodeposited with a three-electrode system for 60 s under constant potential -0.1V to prepare the ZnO seed layer, which was rinsed washed with ultra-pure water and put into the oven to dry. Then 0.02 mol/L Zn (NO3)2 and 0.02 mol/L C6H12N4 were mixed to prepare 100 mLof mixed solution. The dried ZnO seed layer was deposited in a three-electrode system of 1.25 mA under constant current for 5400 s. After the

deposition was completed, the prepared film was rinsed washed with ultra-pure water and put into the oven to dry to obtain ZnO nanorods.

Preperation of ZnO nanotubes by Chemical etching Method

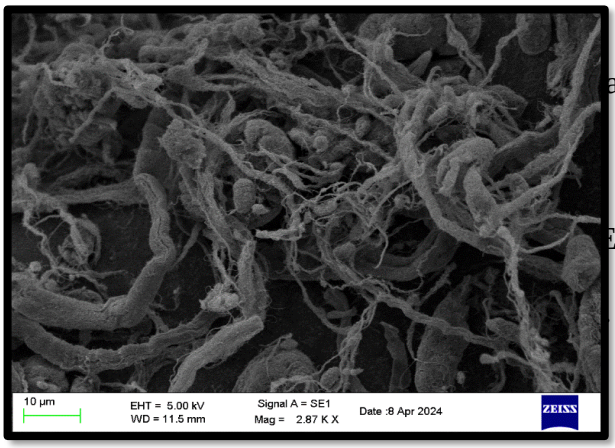
Weigh 2.02 g of KOH into a beaker, add 100 mL of ultra-pure water, and stir well. Then, the prepared ZnO nanorods were placed in potassium hydroxide solution and etched in a water bath at 80 °C for 60 min. The obtained sample is rinsed with ethanol and put into the oven to dry.

CHARACTERIZATION OF ZINC OXIDE (ZNO) NANOTUBES

Scanning Electron Microscopy (Sem)

Information about the sample, including as its exterior appearance (texture), chemical composition, and the orientation and crystalline structure of the components that make up the sample, can be found in the signals that result from electron-sample interactions. In the majority of applications, a 2D image that shows the spatial variations in these attributes is created after data are gathered over a predetermined portion of the sample's surface. Conventional SEM methods can be used to examine areas with widths ranging from about 1 cm to 5 microns in a scanning mode (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). Analyzing specific point locations on the material with the SEM is another capability; this method is particularly helpful for semi-quantitatively or qualitatively assessing chemical compositions, crystalline structures, and crystal orientations.

Using a method called scanning electron microscopy (SEM), one can examine the morphology of synthesized zinc oxide nanotubes. The SEM micrographs for raw MWNTs synthesized by Chemical Etching method, raw MWNTs which have been subjected to air oxidation and raw MWNTs which have been subjected to air oxidation and acid purification (as well as covalent functionalization) have been shown. The SEM micrographs for raw MWNTs synthesized by Chemical Etching method clearly show huge forests of MWNTs Fig., lending support to the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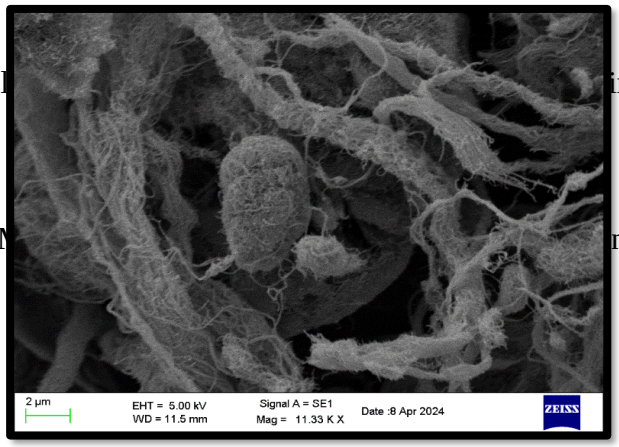
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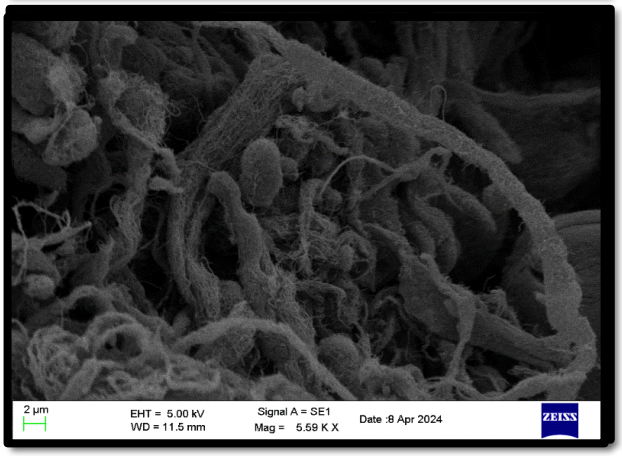
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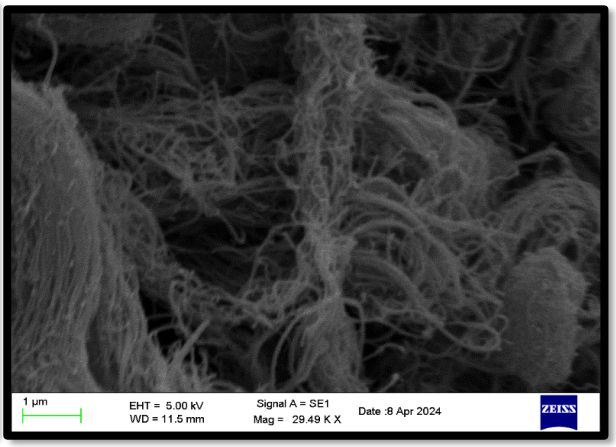
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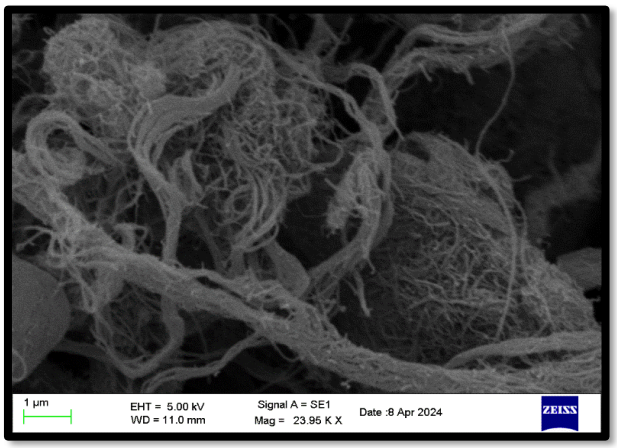
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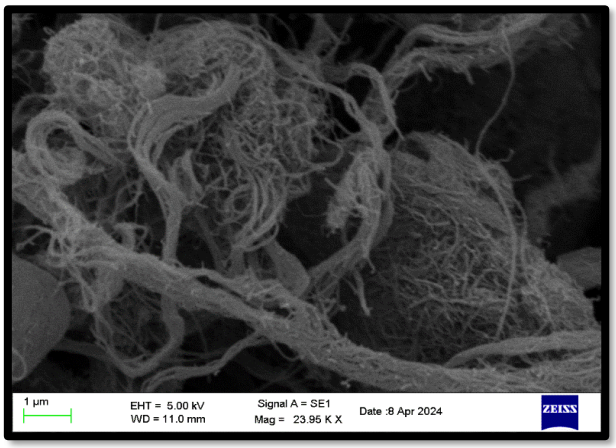
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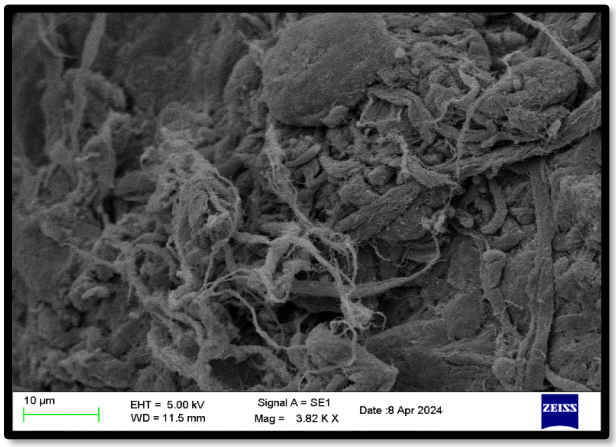
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EVALUATION OF ZINC OXIDE NANOTUBES BASED SUNSCREEN CREAM

Physical evaluation parameter

Colour: To determine the colour of the compound, 0.2g of the material was placed against white background in diffuse day light, viewed by eye and its colour should be determined accordingly.

Odour: To determine the odour of the compound, 0.4g of the material was placed in a 5cm diameter watch glass, left for 15 minutes and these after the air above the sample was inhaled slowly and repeatedly. Determining the smell as non-existent, weak, distinct, or strong and describing the sensation as fragrant, fruity, musky, or rotten allowed us to determine the strength of the odour.

Determination of pH: Using a digital pH meter, sunscreens' pH was measured. After 1 g of the formulation was dissolved for 2 hours in 100 ml of freshly made distilled water, pH was determined. Ensuring that the pH of the sunscreens generated matches the pH of the skin after a 24-hour usage was the aim of this investigation. Three checks were made on the results, and was recorded.

Determination of Viscosity: The Brookfield viscometer was used to test viscosity, with the proper number of spindles (SPL3) selected. A 50 ml beaker was used to hold 50 g of preparation until the spindle groove was dipped and the rpm was set. Sunscreen viscosity was measured at 5, 10, 20, 50, and 100 rpm. The viscosity was computed using the factor obtained from the reading. The Brookfield viscometer measures viscosity in centipoise (cP) or millipascal-seconds (mPa•s).

Spreadability: The spreadability of Sunscreens were found to have a therapeutic effect. The two sides took the prescribed amount of time in seconds to slip off when the proper amount of sunscreen was put in between them and under the load directions. Spreadability was defined as the amount of time it took to separate two slides in less time.

The formula for calculating it is: $S = M \times L/t$

Where, M = weight tied to the upper slide, L = length of glass slide,

T = time taken to separate the slides

Stability Testing: Stability testing of prepared formulation was conducted at room temp, studied for 7 days. And then the formulation was studied at 45 ±1°C for 20 days. The formulation was kept both at room and elevated temperature and observed on 0th, 5th, 10th, 15th, and 20th day for all the evaluation parameters.

Determination of sun protection factor (SPF)

The sun protection factor (SPF), which is the UV energy needed to produce a minimal erythema dose (MED) on protected skin divided by the UV energy needed to produce a MED on unprotected skin, is typically used to quantify the effectiveness of a sunscreen. The lowest time interval or dosage of UV light irradiation necessary to cause a modest, noticeable erythema on unprotected skin is known as the minimal erythemal dose (MED). The product is more successful in preventing sunburn the higher its SPF.

In vitro sunscreen effectiveness was assessed using a UV Visible spectrophotometer. A 0.10 percent (w/v) solution of sunscreen cream in ethanol was made by dissolving 0.050 g of sunscreen cream in 50.0 ml of ethanol. Between 290 and 320 nm, aliquots of each sunscreen were scanned at 5 nm intervals. SPF was calculated using the equation below. Three times each sample was analysed.

$$\text{SPF} = \text{CF} \times \sum_{290}^{320} \text{EE}(\lambda) \times \text{I}(\lambda) \times \text{A}(\lambda)$$

Whereas, CF= Correction factor; EE= Erythemogenic effect;

I= Intensity of solar light of wavelength; A= Absorbance

Wavelength (λ nm)	EE×I (normalized)
290	0.0150
295	0.0817
300	0.2874
305	0.3278
310	0.1864
315	0.0839
320	0.0180

Microbial Test: The formulated sunscreen was inoculated on the plates of agar media by cup plate method. The plates were placed in to the incubator and are incubated at 37°C for 24 hours. After the incubation period plates were taken out and check the microbial growth.

RESULT AND DISCUSSION

Determination Of Physical Parameters

Table no. 1: Physical Parameters

Sr.No.	Parameter	F1	F2	F3
1.	Colour	Whitish	Whitish	Whitish

2.	Odour	Rose like	Rose like	Rose like
3.	Appearance	Good	Good	Good
4.	State	Semisolid	Semisolid	Semisolid
5.	Texture	Smooth	Smooth	Smooth
6.	Washability	Washable	Washable	Washable

Discussion: From the above observation, we can conclude that all has all the ideal physical characteristics.

DETERMINATION OF pH

Table no 2: Determination of pH

Sr.No.	Days	F1	F2	F3
1.	Initial days	5.93	7.10	7.10
2.	7 Days	6.82	6.97	7.12
3.	15 Days	6.97	6.83	7.24

Discussion: - For fifteen days, the base formulation was subjected to the pH test. It was discovered that the cream's pH ranged from 6.97 to 7.24, which is ideal for skin. All of the cream formulations' pH values were shown to be closer to the pH needed by the skin, although not exactly. Long-term pH restoration is shown by formulations f1, f2, and f3, while formulation f3 show stable pH.

DETERMINATION OF VISCOSITY

Table no. 3: Determination of Viscosity

Sr.No.	Observation
F1	21613mPa•s
F2	21442mPa•s
F3	20131mPa•s

Discussion: -Viscosity tests were performed. From the observation formulation F1 and F2 had slightly high viscosity and it is found that the F3 had appropriate viscosity like cream.

SPREADABILITY TEST

Table no. 4: Spreadability Test

Washability parameter	F1	F2	F3
Spreadability	24.47 ±0.4	22.35±0.5	26.33±0.3

Discussion: From the above observation, the formulation F3 shows desired spreadability than F1 and F2. One cycle is completed by placing the product at -10°C for 24 hours and then at room temperature (25°C) for 24 hours.

STABILITY TESTING

Table no. 5: Stability testing

Parameter	F1	F2	F3
Thermal Stability	No oil separation	No oil separation	No oil separation

Discussion: From the above observation, the formulation F1 to F3 shows no oil separation.

DETERMINATION OF SPF

Table no. 6: Determination of SPF

Wavelength (nm)	EE(λ)×I(λ)	F1		F2		F3	
		Abs(λ)	EE(λ)×I(λ)×Abs(λ)	Abs(λ)	EE(λ)×I(λ)×Abs(λ)	Abs(λ)	EE(λ)×I(λ)×Abs(λ)
290	0.0150	1.843	0.02764	3.2733	0.49099	2.995	0.0449
295	0.0817	1.448	0.1183	3.4743	0.28385	4.739	0.3872
300	0.2874	0.837	0.2405	0.9246	0.266099	1.735	0.4997
305	0.3278	1.423	0.4665	1.0413	0.34133	2.964	0.9716
310	0.1864	0.872	0.1625	3.1486	0.58689	1.925	0.3588
315	0.0839	1.205	0.1009	2.8856	0.023961	1.975	0.1653
320	0.0180	1.294	0.0233	3.0563	0.054946	2.839	0.0511
		TOTAL: - 1.139		TOTAL: - 1.606		TOTAL: - 2.4786	
		SPF: - 11.39		SPF: - 16.06		SPF: - 24.786	

Discussion: From the above observation and calculation, it was found that the formulation F3 had highest SPF than the F1 and F2.

Microbial test:

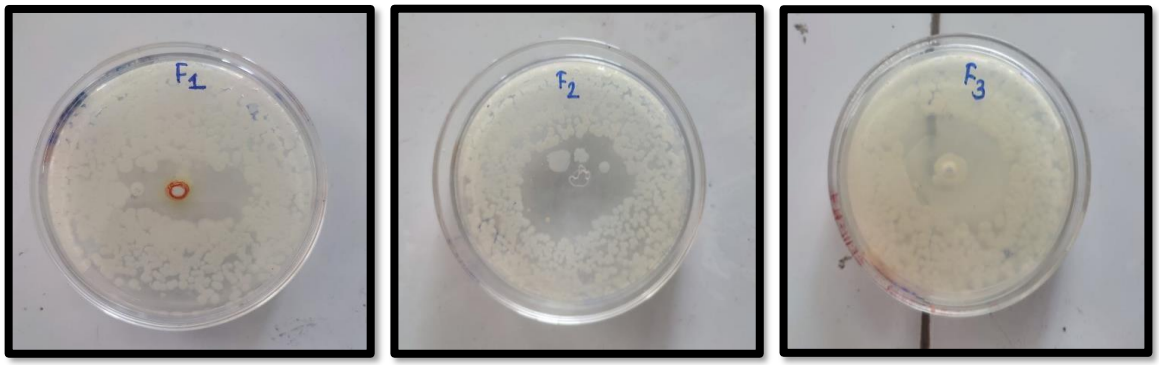

Table no 7: - microbial test

Discussion: The Most apparent acute benefit of currently available sunscreen is the prevention of sunburn from UVR exposure. This effect has been suggested to be both a benefit and a potential and concern. The obvious benefit is the prevention of sun burn that may reduce the risk of non-melanoma and perhaps melanoma skin cancers because severity and frequency of sun burn.

CONCLUSION

As Zinc oxide (ZnO) nanotubes-based Sunscreen was formulated by using Chemical Etching method. Zinc oxide (ZnO) nanotubes have gained attention in the field of sunscreen due to their unique properties. These nanotubes offer several advantages over traditional sunscreen ingredients like titanium dioxide and micronized zinc oxide particles. ZnO nanotubes can effectively scatter and absorb UV radiation, offering more protection against both UVA and UVB rays. Depending on the formulation, zinc nanotube sunscreens may offer improved aesthetics compared to the marketed sunscreen products. They may be less likely to leave a white cast on the skin and feel lighter as compared to normal marketed sunscreen.Zinc has a higher capacity to permeate skin cells and function as a wound healer than zinc oxide, which provides better protection against sunburn and cataracts. Nanotube create a physical barrier on the skin and surface effectively scattering and absorbing both UVA and UVB rays. Nanotechnology allows collagen building ingredient to work where they can tighten and thicken skin. For example, which implies that

product works better and more efficiently also it improve how a product looks and feel. Due to shape of nanotube, it blocks the skin pores and due to its cylindrical shape reflection of UV radiation are higher than normal sunscreen. It also improves the penetration of zinc oxide into skin.

In summary, zinc nanotube-based sunscreens offer a promising alternative to traditional sunscreens, potentially providing enhanced sun protection and improved cosmetic characteristics.

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