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Role of Surfactants and Metal-Doped Dye Systems in Enhancing DSSC Performance Using Malachite Green and Congo Red

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Abstract:-

Dye-Sensitized Solar Cells (DSSCs) are emerging as a promising and innovative technology, offering a low-cost alternative to traditional photovoltaic systems and facilitating high-efficiency solar energy conversion. Their performance is strongly influenced by dye stability and interfacial interactions. Therefore, this study explores the use of a dye mixtures-(Malachite Green and Congo Red)—in combination with surfactants (SDS, HTAB, Brij 35), metal dopants (Co^{2+}, Tb^{3+}) and deoxycholic acid (DCA) as a co-adsorbent to enhance DSSC performance. The notable performance of HTAB and Brij 35 surfactant systems highlights their potential role in the optimization of solar energy devices.

Keywords: DSSC, performance, dye, surfactant, DCA.

Introduction:-

The increasing need for renewable energy has driven several researchers to investigate innovative methods for its generation. Solar energy is an abundant resource that can be converted into power. The DSSC is among the most efficient devices for capturing renewable energy from sunlight. Researchers have extensively investigated the use of natural and organic dyes, including blended dye systems, to enhance the light-harvesting efficiency of dye-sensitized solar cells, and have also reviewed the properties and challenges of bulk interface polymer and perovskite solar cells.**[1-8]**. A multitude of solar cell types convert sunlight into electrical energy. The solar cells with the highest photon-to-current conversion efficiency are first-generation devices made from single silicon crystals **[9]**. The problem with this solar cell is its high production and installation expenses. A multitude of researchers have concentrated on second-generation devices using semiconductor thin films to reduce manufacturing costs and improve the efficiency of first-generation solar cells, despite ongoing efficiency challenges **[10, 11]**. The third generation of solar cells include DSSCs, heterojunction cells and organic cells. DSSCs are devices that transform visible light into energy by the photosensitization of wide band-gap TiO_2 semiconductors using dye molecules. The effectiveness of the cell mostly depends on the dye used as a sensitizer. Therefore, this paper focuses on experimenting with dye combinations (Malachite Green and Congo Red) to evaluate their efficiency in DSSCs.

A prominent dye employed in this study is Malachite Green (MG), a short-chain monomethine cyanine dye, is characterized by its distinctive ionic chromophore and a conjugated system with dual resonance structures involving auxochromic nitrogen atoms. The dye's unique alternant configuration and steric interactions between its intrachain N–N phenyl groups result in a significant bathochromic shift, allowing absorption of light at extended wavelengths. The organization of the diffuse ionic cloud across the dye monolayer affects ion transport and electrolyte gradients, thereby playing a critical role in modulating electron transfer at the TiO_2/dye/electrolyte interface. Malachite Green and its derivatives have previously been tested for sensitization in solar energy systems **[12].**

Congo Red, another dye used in the current study, is an organic azo dye and the sodium salt of 3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid). It usually appears as a reddish-brown powder that is easily soluble in both water and ethanol. In renewable energy research, Congo Red has also been investigated as a sensitizer for DSSCs. Studies have shown that doping Congo Red with metal ions such as iron (Fe), cobalt (Co) and nickel (Ni) can significantly improve its light-harvesting capabilities. Notably, Fe(II)-Congo Red achieved a DSSC efficiency of 8.17%, followed by Co(II)-Congo Red at 6.13%, and Ni(II)-Congo Red at 2.65%. These improvements are attributed to the metal ions' role in enhancing electron transfer and expanding the dye's absorption range, thereby boosting solar energy conversion efficiency **[13-15].**

Dye-sensitized solar cells (DSSCs), first developed by O'Regan and Grätzel in 1991, are devices that convert light into electricity through photoelectrochemical processes. They are valued for their efficiency, ease of fabrication, cost-effectiveness and sustainability. The dye-sensitized solar cell (DSSC) is composed of a nanocrystalline TiO_2 layer sensitized with dye on a transparent conducting oxide (TCO) substrate, acting as the working electrode. A graphite layer serves as the counter electrode, and an electrolyte containing iodide/triiodide redox couples completes the cell **[16-19].**

In view of this, the study involves the synthesis of Dye System II, composed of Malachite Green and Congo Red. The dye formulation was further modified using deoxycholic acid (DCA), metal salt solutions, and surfactants.

Experimental: - Dye System-II

1. Materials Used: Materials used in the study included fluorine-doped tin oxide (FTO) glass slides, TiO_2 nanoparticles anatase , dyes such as Malachite Green and Congo Red , and various surfactants including SDS, HTAB and Brij 35. Additional reagents comprised deionized water, ethanol, glacial acetic acid, hydrochloric acid (HCl), and Triton X-100. The electrolyte system was prepared using potassium iodide (KI) and iodine (I_2) in solvents like ethylene glycol and acetonitrile. Other components included graphite pencils for counter electrode preparation, metal salts such as cobalt nitrate and terbium chloride and deoxycholic acid (DCA) as a co-adsorbent.

2. Methods:

(a) Preparation of dye mix II - For Dye Solution 19, 0.125 g of Malachite Green and 0.125 g of Congo Red were dissolved in SDS surfactant solution. The surfactant solution was prepared separately using 50 CMC of SDS. For Dye Solution 20, 90 mL of the previously prepared dye solution (containing 0.125 g each of Malachite Green and Congo Red in SDS) was mixed with 10 mL of a DCA solution. For Dye Solution 21, 1 g of cobalt nitrate ($Co(NO_3)_2$) was dissolved in SDS and then added to the dye solution containing 0.125 g of Malachite Green and 0.125 g of Congo Red in SDS. For Dye Solution 22, 1 g of terbium chloride ($TbCl_3$) was dissolved in SDS and incorporated into the dye solution consisting of 0.125 g each of Malachite Green and Congo Red in SDS. For Dye Solution 23, a mixture was prepared by combining 1 g of cobalt nitrate ($Co(NO_3)_2$) dissolved in 50 mL of SDS, 10 mL of a DCA solution (containing 0.30 g of DCA separately dissolved in 50 mL SDS), and 0.125 g each of Malachite Green and Congo Red dissolved in 50 mL of SDS. The cobalt nitrate solution was prepared separately in SDS before mixing with the dye solution. For Dye Solution 24, a mixture was prepared by combining 1 g of terbium chloride ($TbCl_3$) dissolved in 50 mL of SDS, 10 mL of a DCA solution (containing 0.30 g of DCA separately dissolved in 50 mL SDS), and 0.125 g each of Malachite Green and Congo Red dissolved in 50 mL of SDS. Similarly, Dye Solutions 25 to 30 were formulated following the same method as with SDS, but replacing it with HTAB surfactant, which was prepared separately using 100 CMC of HTAB.Furthermore, Dye Solutions 31 to 36 were prepared using Brij 35 as the surfactant, with the solution made using 100 CMC of Brij 35. DCA and metallic solution were prepared separately.

Table 1: List of Dye System II
(Malachite Green+Congo Red)

S. No.	Code	Dye Soln No.	Surfactant	DCA	Co Salt Soln $Co(NO_3)_2$	Tb Salt Soln ($TbCl_3$)
1	**D2S1**	**19**	**SDS**	*	*	*
2	**D2S2**	**20**		**Y**	*	*
3	**D2S3**	**21**		*	**Y**	*
4	**D2S4**	**22**		*	*	**Y**
5	**D2S5**	**23**		**Y**	**Y**	*
6	**D2S6**	**24**		**Y**	*	**Y**
7	**D2H1**	**25**	**HTAB**	*	*	*
8	**D2H2**	**26**		**Y**	*	*
9	**D2H3**	**27**		*	**Y**	*
10	**D2H4**	**28**		*	*	**Y**
11	**D2H5**	**29**		**Y**	**Y**	*
12	**D2H6**	**30**		**Y**	*	**Y**
13	**D2B1**	**31**		*	*	*
14	**D2B2**	**32**		**Y**	*	*
15	**D2B3**	**33**		*	**Y**	*

16	**D2B4**	**34**	**Brij 35**	*	*	**Y**
17	**D2B5**	**35**		**Y**	**Y**	*
18	**D2B6**	**36**		**Y**	*	**Y**

(b) Fabrication of the Working Electrode: The fabrication of the working electrode commenced with the cleaning and thermal treatment of fluorine-doped tin oxide (FTO) glass plates. These plates were heated at 300 °C for 15 minutes and subsequently rinsed with ethanol. To synthesize the TiO_2 paste, 2.0 g of TiO_2 nanomaterial anatase was mixed with 2 mL of glacial acetic acid and 2.0mL of ethanol. The mixture was stirred manually with a glass rod for one hour, followed by the addition of two drops of Triton-X surfactant to improve uniformity. This paste was further stirred magnetically for 24 hours to ensure complete dispersion of TiO_2 nanoparticles. The resulting paste was then applied to the conductive side of the cleaned FTO glass using the Doctor Blade method. To define the active area, three sides of the glass slide were masked with scotch tape, leaving a 1 cm^2 window for coating. The paste was evenly spread over this area and leveled with a glass rod to achieve a uniform film thickness of about 10–11 µm. After drying the coated glass at room temperature for 30 minutes, it was calcined at 500 °C for one hour to strengthen the film's adhesion to the substrate. Once cooled, the TiO_2-coated plates were immersed in dye solutions containing a mixture of Malachite Green and Congo red in a petri dish and kept in the dark for 24 hours to facilitate effective dye adsorption. Afterward, the slides were rinsed to remove unbound dye and air-dried. Finally, two sides of each slide were covered with scotch tape, exposing one side for electrical contact, thus completing the working electrode preparation.

(c) Fabrication of counter electrode - The FTO slides were first cleaned, and their conductive side was checked using a multimeter. The active surface was then coated by rubbing it with a graphite pencil, followed by heating the slide in a furnace at 350°C for 45 minutes to create the graphite-coated photo-cathode electrode. After heating, the slide was allowed to cool down to room temperature.

(d) Preparation of electrolyte- The iodide/triiodide (I^-/I_3^-) redox electrolyte, widely employed in DSSCs for its efficient dye regeneration and low recombination rate, was formulated by dissolving 0.05 M iodine (I_2) and 0.5 M potassium iodide (KI) in a solvent mixture of ethylene glycol and acetonitrile. The solution was thoroughly stirred to ensure complete dissolution and subsequently stored in a dark container to protect it from light-induced degradation.

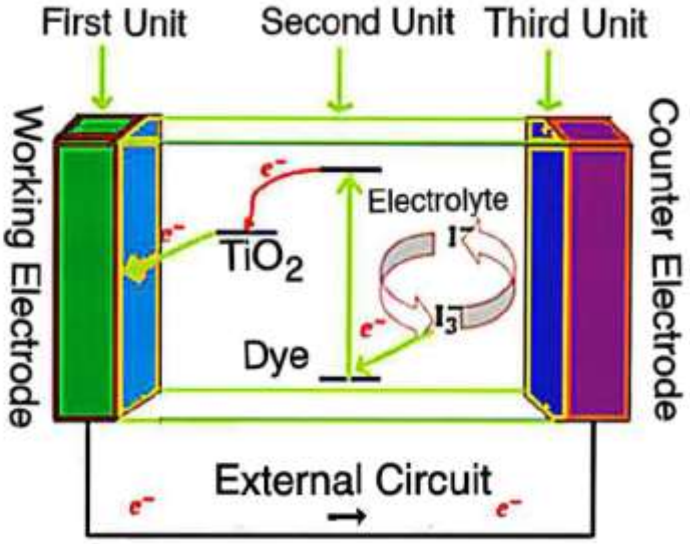

Fig 1: Structure of DSSC [24]

(e) Fabrication of DSSC - The dye was adsorbed onto the TiO_2-coated FTO glass substrate, leaving space at the edges for electrical connections. A liquid electrolyte containing the iodide/triiodide redox couple was introduced onto the dyed surface. The counter electrode was placed on top and the two conductive plates were held together using an alligator clip. Any excess electrolyte that leaked was gently cleaned with tissue paper. The assembled DSSC was then connected to an external circuit for current and voltage measurements and exposed to a light source for performance testing.

Result & Discussion: -

This section presents the spectral study and I–V curve analysis of the dye sets in System II. The spectral properties of the dyes were investigated using a UV-Visible spectrophotometer. Dye samples were prepared and analyzed in the absence of light over a wavelength range of 300 to 800 nm to evaluate their optical behavior in selected solvents

Spectral Characterization:

The findings for Dye System II, which includes a mixture of Malachite green and Congo red with **SDS** as the surfactant, reveal noticeable shifts in absorption maxima (λ_{max}) and changes in intensity (E_{max}) upon the addition of deoxycholic acid (DCA) and metal salts.

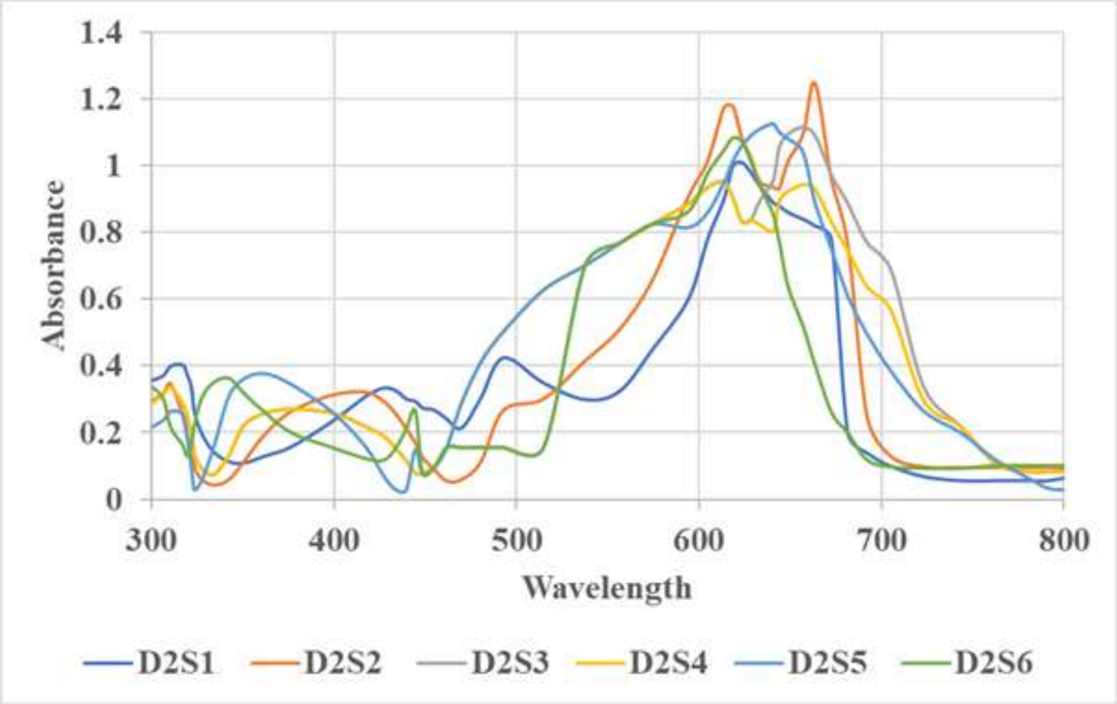

Fig 2: UV-Vis Spectra of Synthesised Dye System II – SDS

The unmodified dye-SDS system (D2S1) showed an absorption peak at 623 nm and intensity E_{max} of 1.010, serving as the baseline. Introducing DCA (D2S2) caused a clear bathochromic shift to 663 nm and increased E_{max} to 1.234, indicating that DCA may stabilize the dye environment or reduce non-radiative losses. The addition of $Co(NO_3)_2$ salt alone (D2S3) resulted in a shift to 657 nm with a moderate rise in E_{max} to 1.114, suggesting dye-metal interactions that affect the electronic structure. Similarly, $TbCl_3$ salt (D2S4) caused a shift to 656 nm, but the intensity dropped to 0.944, pointing to possible fluorescence quenching or energy transfer to Tb^{+3} ions. A combination of DCA and cobalt nitrate salt (D2S5) shifted the λ_{max} to 648 nm with E_{max} at 1.080, which could be attributed to changes in dye aggregation or solvation caused by both additives. Interestingly, the mixture of DCA and $TbCl_3$ salt (D2S6) led to a hypsochromic shift to 618 nm with E_{max} of 1.080, possibly due to strong interactions like complex formation or microenvironmental changes that altered the dye's photophysical properties.

The analysis of Dye System II incorporating **HTAB** as the surfactant reveals significant changes in both absorption maxima (λ_{max}) and intensity (E_{max}) with the addition of DCA and metal salts. The base dye system (D2H1) exhibited a λ_{max} at 623 nm and a high E_{max} of 1.428, indicating strong interaction between the dye and HTAB and stable chromophoric characteristics.

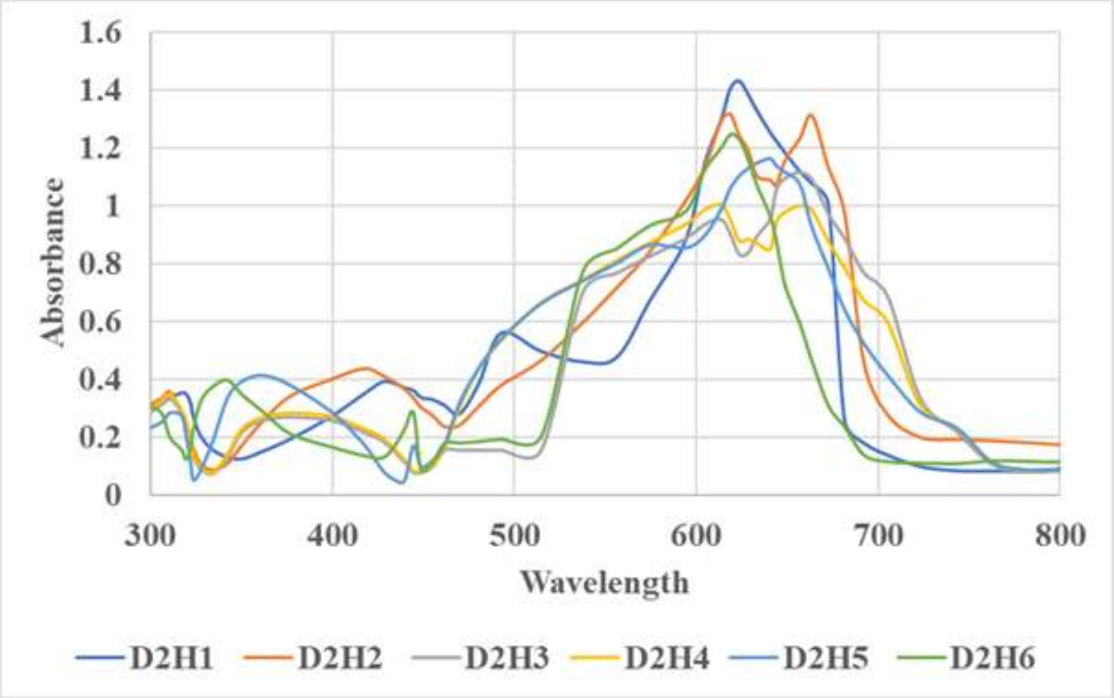

Fig 3: UV-Vis Spectra of Synthesised Dye System II – HTAB

Introducing DCA alone (D2H2) led to a slight blue shift to 618 nm and a reduction in intensity to 1.317, suggesting alterations in the dye's microenvironment that may influence solvation or aggregation behavior. When cobalt nitrate salt was added without DCA (D2H3), a pronounced red shift to 657 nm occurred, accompanied by a significant drop in E_{max} intensity to 1.114, pointing to the formation of a dye-metal complex and possible quenching due to changes in electronic transitions. A similar red shift to 658 nm and further decline in intensity to 1.010 were observed with $TbCl_3$ salt alone (D2H4), likely due to energy transfer effects or enhanced non-radiative decay. The combined use of $Co(NO_3)_2$ salt and DCA (D2H5) resulted in a λ_{max} at 640 nm and an intensity of 1.162, indicating that DCA modulates dye-metal interactions, possibly limiting aggregation or altering complexation behavior. In the presence of both terbium chloride salt and DCA (D2H6), a further blue shift to 621 nm was observed, with a moderate E_{max} of 1.242, reflecting a delicate interplay between solvation dynamics, surfactant stabilization, and metal ion coordination that influences the overall photophysical response of the dye system.

The UV-Vis spectral analysis of Dye System II—comprising a mixture of malachite green and Congo red with the nonionic surfactant **Brij 35**—revealed notable changes in both absorption maxima (λ_{max}) and intensity (E_{max}) under varying conditions involving deoxycholic acid (DCA) and metal salts.

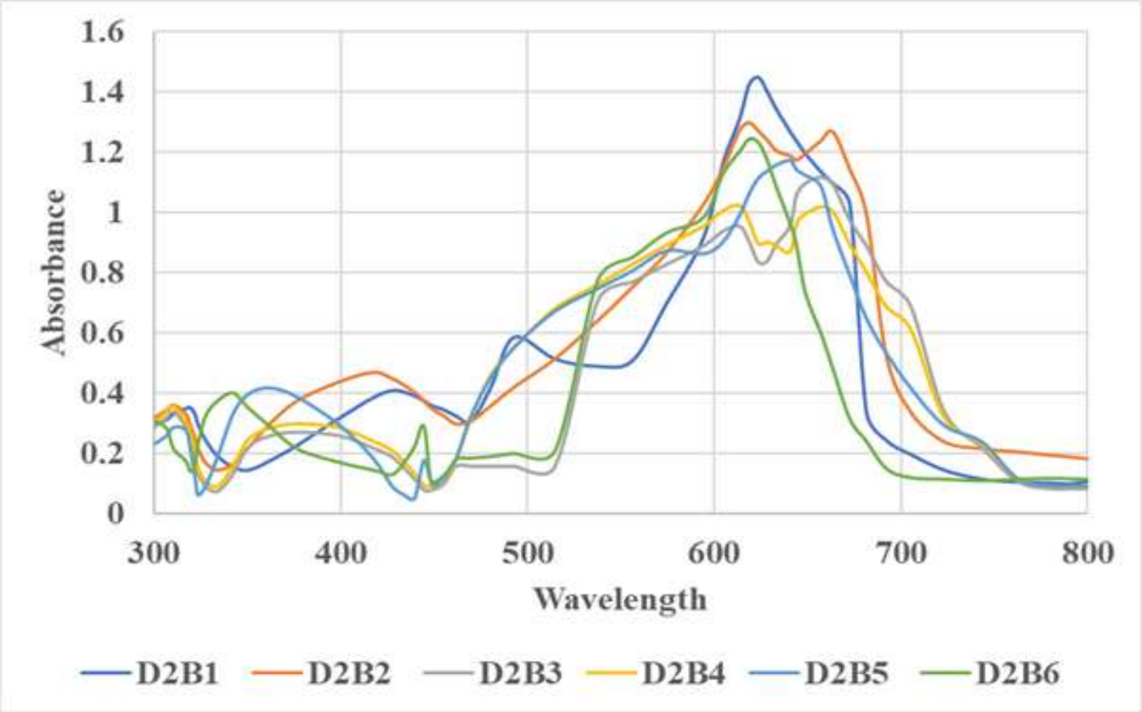

Fig 4: UV-Vis Spectra of Synthesised Dye System II - Brij 35

The base system (D2B1), without any additives, showed an absorption peak at 623 nm and a relatively high E_{max} intensity of 1.447, suggesting strong dye-micelle interactions within the Brij 35 environment. With the addition of DCA (D2B2), a slight hypsochromic shift to 618 nm occurred, along with a decrease in emission intensity to 1.296, indicating that DCA may influence dye aggregation or micellar encapsulation, possibly by altering the dye's microenvironment. The incorporation of cobalt nitrate salt (D2B3) led to a bathochromic shift to 657 nm and a marked decrease intensity to 1.115, which points to the formation of dye-metal complexes that modify the dye's electronic transitions. A similar red shift was observed with terbium chloride salt (D2B4), where λ_{max} moved to 655 nm and intensity dropped further to 1.015, likely due to energy transfer or quenching effects introduced by Tb^{+3} ions. Notably, the combined use of DCA and $Co(NO_3)_2$ salt (D2B5) produced a bathochromic shift to 642 nm and a moderate increase in intensity to 1.170, suggesting that DCA may modulate dye-metal interactions, leading to partial restoration of fluorescence. When DCA and $TbCl_3$ salt were combined (D2B6), the absorption peak shifted back near its original position at 622 nm, and the E_{max} increased to 1.230.This implies that DCA may counteract some of the quenching effects of Tb^{+3} ions, potentially by redistributing dye molecules within the micellar matrix or limiting direct metal-dye interactions. The UV–Vis spectral analysis showed peak shifts and broadening, indicating dye–surfactant interactions in line with earlier reports **[20-22].**

Overall, the results highlight that the type of surfactant significantly influences dye organization, charge transfer, and light absorption. Among the surfactants tested, HTAB and Brij 35 showed superior conditions for improving the photophysical performance of Dye System II in DSSC applications, particularly when used alongside DCA and metal dopants.

I-V Characteristics of Fabricated DSSCs:

After conducting optical characterization, DSSC modules were fabricated and evaluated for their efficiency. Performance parameters were investigated across different systems. Current-voltage (I-V) characteristics were measured using a digital multimeter to determine open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), maximum power point (Pmax), characteristic resistance (R_{CH}), fills factor (FF), and overall conversion efficiency (η). Voltage and current outputs of the fabricated DSSCs were assessed using a variable load resistor in the circuit under standard AM1.5G illumination at intensity of 100 mW/cm², V_{oc} and I_{sc} values were recorded to construct the I-V curve. Key performance indicators such as peak power current (Ipp), peak power voltage (Vpp), and peak power (PP) were calculated to derive the fill factor and conversion efficiency.

The fill factor (FF) and Efficiency of the Cell (η) were calculated using the following equations:

$$\mathbf{FF = Vpp * Ipp / I_{sc} * V_{oc}}$$

$$\textbf{Efficiency}\ (\eta) = \frac{\mathbf{FF \times I_{sc} \times V_{oc}}}{\mathbf{P_{in}}} \times 100\%$$

The I-V characterization of the dye-surfactant system using **SDS** (Sodium Dodecyl Sulfate) illustrates the impact of various additives—namely deoxycholic acid (DCA), cobalt ($Co(NO_3)_2$) salt, and terbium ($TbCl_3$) salt—on the electrochemical and photovoltaic behavior of Dye Mix II. The reference system (D2S1), consisting solely of the dye mix in SDS, shows a V_{oc} of 0.87 V, I_{sc} of 0.498 mA, a fill factor (FF) of 0.363, and a power conversion efficiency of 0.157%, with a charge transfer resistance (R_{CH}) of 1.42 Ω. This system serves as the control for comparison. Introducing DCA alone (D2S2) results in reduced performance, with a V_{oc} of 0.798 V, I_{sc} of 0.439 mA, FF of 0.34, and a lower efficiency of 0.119%.

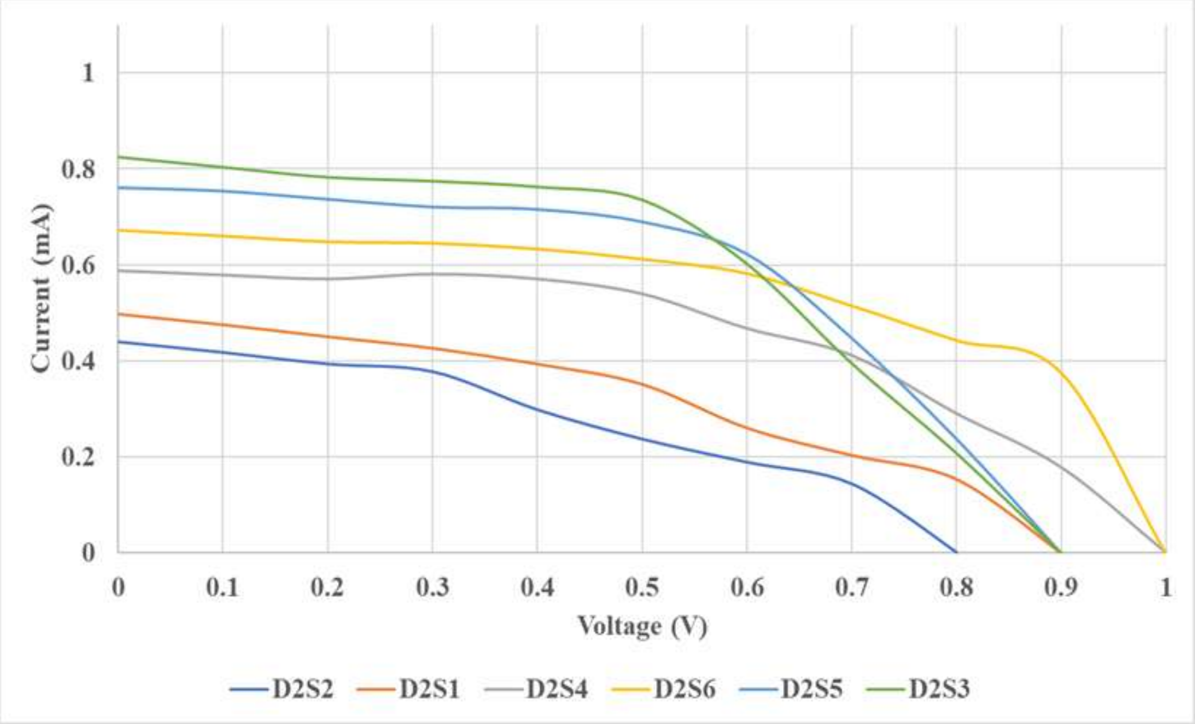

Fig 5: I-V curves for each of the DSSC tested with different Dye System II-SDS

This indicates that although DCA may aid in dye stabilization, it does not substantially enhance charge transport in isolation within the SDS medium. Conversely, the incorporation of cobalt nitrate salt (D2S3) markedly improves performance: V_{oc} rises to 0.891 V, I_{sc} increases significantly to 0.824 mA, FF improves to 0.5, and efficiency reaches 0.367%.

Additionally, a reduced R_{CH} of 0.68 Ω reflects improved charge transfer and electron mobility, likely due to the beneficial effects of Co^{+2} ions on dye regeneration. The addition of $TbCl_3$ salt (D2S4) results in the highest observed V_{oc} (0.987 V), with I_{sc} at 0.588 mA and FF at 0.496, producing an efficiency of 0.287%. This suggests that terbium, a rare-earth metal, enhances energy alignment and charge separation, though it may be less efficient in electron injection compared to cobalt.

Table 2: Electrochemical properties of Synthesised Dye System II-SDS

S. No.	Code	Surfactant	DCA	Co Salt Soln	Tb Salt Soln	V_{oc} (V)	I_{sc} (mA)	FF	η (%)	R_{CH} (Ω)
1	**D2S1**	**SDS**	*	*	*	0.87	0.498	0.363	0.157	1.42
2	**D2S2**		**Y**	*	*	0.798	0.439	0.34	0.119	2.109
3	**D2S3**		*	**Y**	*	0.891	0.824	0.5	0.367	0.68
4	**D2S4**		*	*	**Y**	0.987	0.588	0.496	0.287	1.699
5	**D2S5**		**Y**	**Y**	*	0.895	0.761	0.548	0.373	0.963
6	**D2S6**		**Y**	*	**Y**	0.991	0.672	0.541	0.36	1.359

A combined system of DCA and ($Co(NO_3)_2$) salt (D2S5) further elevates performance, yielding a V_{oc} of 0.895 V, I_{sc} of 0.761 mA, FF of 0.548, and efficiency of 0.373%, with an R_{CH} of 0.963 Ω, indicating enhanced interfacial charge transport. Similarly, the DCA and $TbCl_3$ salt combination (D2S6) achieves a V_{oc} of 0.991 V, I_{sc} of 0.672 mA, FF of 0.541, and efficiency of 0.36%. While this combination is also effective, its performance is marginally below that of the cobalt counterpart. These findings collectively highlight the significant role of metal salts—particularly in combination with DCA—in improving the interfacial charge dynamics and photovoltaic efficiency of SDS-based dye-sensitized solar cells. Notably, D2S5 system in SDS showed improved interfacial charge transport, which is linked to its low charge transfer resistance, resulting in an efficiency of 0.373%.

The I-V characterization of the dye-surfactant system using **HTAB** (Hexadecyltrimethylammonium Bromide) reveals the impact of different additives—deoxycholic acid (DCA), cobalt nitrate salt, and terbium chloride ($TbCl_3$) salt—on the electrochemical and photovoltaic properties of Dye Mix II, composed of Malachite Green and Congo Red. The base system (D2H1), consisting of only the dye mix and HTAB, showed a V_{oc} of 0.873 V, I_{sc} of 0.553 mA, fill factor (FF) of 0.365, and a relatively low efficiency of 0.176%, along with a charge transfer resistance (R_{CH}) of 2.047 Ω.

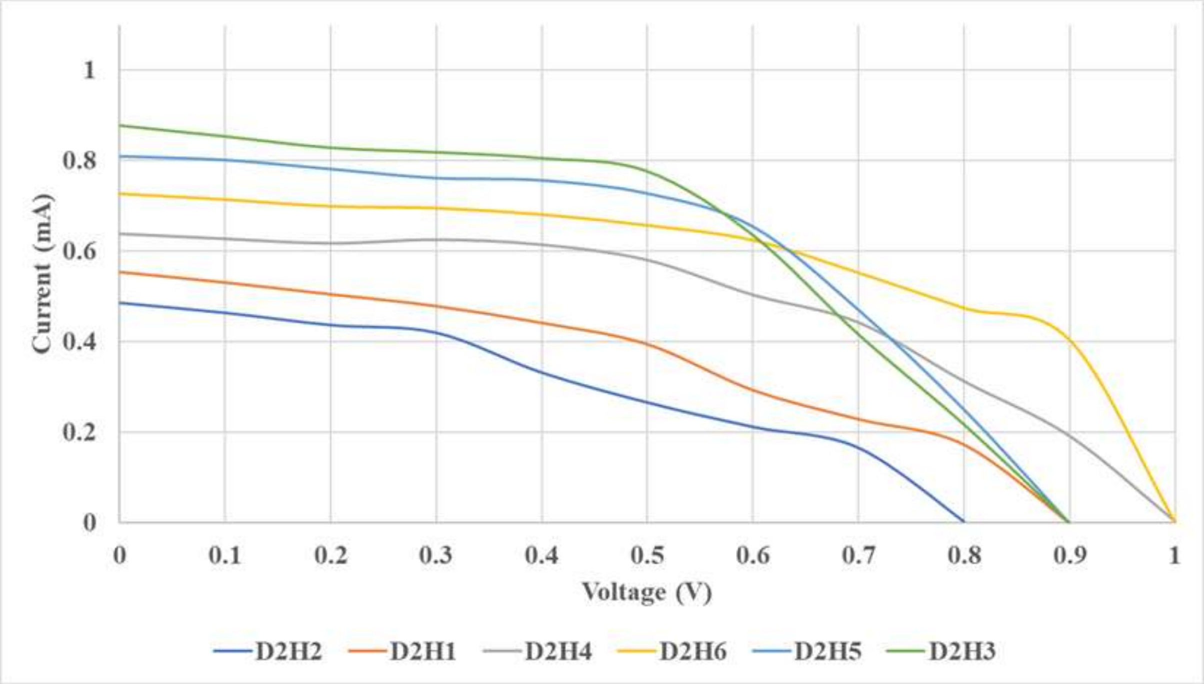

Fig 6: I-V curves for each of the DSSC tested with different Dye System II-HTAB

When DCA was introduced (D2H2), both V_{oc} and I_{sc} dropped to 0.786 V and 0.486 mA respectively, reducing the efficiency to 0.132% and increasing R_{CH} to 2.83 Ω. This suggests that while DCA may stabilize the dye, it does not significantly enhance charge transfer in the HTAB-based system when used alone. In contrast, the inclusion of $Co(NO_3)_2$ salt (D2H3) notably improved performance, increasing I_{sc} to 0.878 mA and efficiency to 0.387%, supported by a higher FF of 0.494 and R_{CH} of 3.669 Ω, indicating enhanced electron transport due to favorable metal-dye interactions.

Table 3: Electrochemical properties of Synthesised Dye System II-HTAB

S. No.	Code	Surfactant	DCA	Co Salt Soln	Tb Salt	V_{oc} (V)	I_{sc} (mA)	FF	η (%)	R_{CH} (Ω)
1	**D2H1**	**HTAB**	*	*	*	0.873	0.553	0.365	0.176	2.047
2	**D2H2**		**Y**	*	*	0.786	0.486	0.348	0.132	2.83
3	**D2H3**		*	**Y**	*	0.894	0.878	0.494	0.387	3.669
4	**D2H4**		*	*	**Y**	0.983	0.638	0.493	0.309	2.564
5	**D2H5**		**Y**	**Y**	*	0.898	0.81	0.54	0.392	3.187
6	**D2H6**		**Y**	*	**Y**	0.986	0.728	0.539	0.386	2.227

The addition of $TbCl_3$ salt alone (D2H4) resulted in the highest V_{oc} of 0.983 V and a moderate I_{sc} of 0.638 mA, leading to an efficiency of 0.309%, suggesting that rare-earth metal ions may facilitate better electron mobility and reduce recombination. Remarkably, the combination of DCA and cobalt nitrate salt in D2H5 produced the highest efficiency in the group (0.392%), with V_{oc} of 0.898 V, I_{sc} of 0.810 mA, and the highest FF (0.540), indicating strong synergistic effects between the surfactant, DCA, and metal salt. Similarly, the DCA-$TbCl_3$

combination in D2H6 achieved a V_{oc} of 0.986 V and I_{sc} of 0.728 mA, yielding an efficiency of 0.386%. These results confirm that combining DCA with metal salts significantly enhances DSSC performance, likely due to better dye alignment and reduced electron-hole recombination.

The I-V characterization of the dye-surfactant system using **Brij 35** reveals the distinct impact of various additives—namely deoxycholic acid (DCA), cobalt $Co(NO_3)_2$ salt, and terbium ($TbCl_3$) salt—on the photovoltaic behavior of the dye mixture. The base system (D2B1), comprising only Malachite Green and Congo Red in Brij 35, exhibits a V_{oc} of 0.883 V, I_{sc} of 0.519 mA, fill factor (FF) of 0.406, and an overall efficiency of 0.186%. A charge resistance (R_{CH}) of 3.21 Ω suggests moderate electron mobility in the absence of any additive.

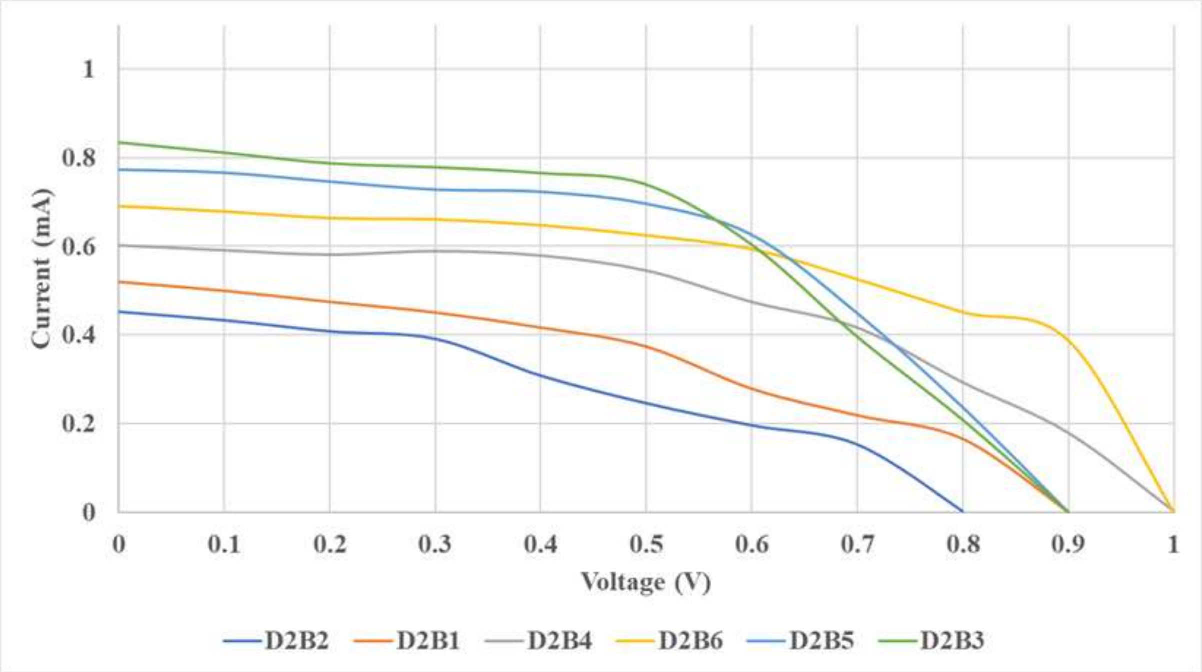

Fig 7: I-V curves for each of the DSSC tested with different Dye System II-Brij 35

Upon addition of DCA alone (D2B2), a decline in V_{oc} (0.796 V), I_{sc} (0.452 mA), and FF (0.342) is observed, reducing efficiency to 0.123%. This indicates that while DCA may assist in dye dispersion, it does not sufficiently enhance charge transfer in the Brij 35 matrix. In contrast, the addition of $Co(NO_3)_2$ salt (D2B3) significantly enhances performance: I_{sc} increases to 0.835 mA, FF to 0.494, and efficiency to 0.369%, highlighting improved dye-metal interaction and electron transport.

Table 4: Electrochemical properties of Synthesised Dye System II-Brij 35

S. No.	Code	Surfactant	DCA	Co Salt Soln	Tb Salt	V_{oc} (V)	I_{sc} (mA)	FF	η (%)	R_{CH} (Ω)
1	**D2B1**	**Brij 35**	*	*	*	0.883	0.519	0.406	0.186	3.211
2	**D2B2**		**Y**	*	*	0.796	0.452	0.342	0.123	3.061
3	**D2B3**		*	**Y**	*	0.896	0.835	0.494	0.369	3.846
4	**D2B4**		*	*	**Y**	0.984	0.603	0.491	0.291	2.730
5	**D2B5**		**Y**	**Y**	*	0.891	0.772	0.505	0.347	3.389
6	**D2B6**		**Y**	*	**Y**	0.989	0.69	0.538	0.367	2.325

The use of $TbCl_3$ salt (D2B4) yields the highest V_{oc} (0.984 V), a solid I_{sc} of 0.603 mA, and FF of 0.492, resulting in 0.291% efficiency—likely due to favorable electronic properties of Tb^{+3} ions enhancing injection and mobility. When DCA and coalt nitrate salt are combined (D2B5), further enhancement is seen, with V_{oc} at 0.891 V, I_{sc} at 0.772 mA, FF at 0.505, and efficiency reaching 0.347%, indicating a synergistic effect where DCA stabilizes the dye environment and Co^{+3} ions facilitate charge separation. The best-performing system is D2B6, which combines DCA with Tb salt. This configuration achieves the highest performance metrics: V_{oc} of 0.989 V, I_{sc} of 0.690 mA, FF of 0.538, and an efficiency of 0.367%. It also records the lowest R_{CH} (2.33 Ω), pointing to improved charge transport and minimal recombination. Overall, these results highlight the critical role of rare-earth metal doping and nonionic surfactants like Brij 35 in enhancing DSSC performance by modulating dye-environment interactions. The photovoltaic results reported for these DSSCs are reinforced by numerous experimental studies **[23-25].**

The efficiency of DSSC with Dye Mix II depends on surfactant choice and additives. Metal salts enhance electron injection and reduce recombination, while DCA improves dye dispersion. In this system HTAB and Brij 35 delivers the best performance, boosted further by cobalt and terbium salts.

Conclusion:-

This study systematically investigated the performance of DSSCs using a novel dye combination (Dye Mix II: Malachite Green and Congo Red) in the presence of three different surfactants—SDS, HTAB, and Brij 35—along with additives such as deoxycholic acid (DCA), cobalt nitrate ($Co(NO_3)_2$), and terbium chloride ($TbCl_3$). The findings clearly demonstrate that both the choice of surfactant and the incorporation of metal ions and DCA significantly influence the photovoltaic efficiency of the DSSCs. Among all the formulations, the highest power conversion efficiency (η = 0.392%) was achieved using Dye Mix II in HTAB surfactant with the combined addition of DCA and Co salt (D2H5). This superior performance is attributed to the synergistic effect where DCA enhances dye anchoring and uniform distribution on the TiO_2 surface, while cobalt ions (Co^{+3}) facilitate improved electron injection and charge transport. The HTAB surfactant likely contributes to better micellar orientation and dye-packing, which favors more efficient interfacial charge dynamics. Other combinations such as D2S5 (SDS + DCA + Co salt, η = 0.373%) and D2B6 (Brij 35 + DCA + $TbCl_3$, η = 0.367%) also exhibited notable performance, confirming the beneficial roles of rare-earth and transition metal ions in improving charge separation and suppressing recombination. In conclusion, the study highlights the effectiveness of Dye Mix II as a sensitizer system and establishes HTAB + DCA + $Co(NO_3)_2$ metal salt as the most efficient combination for enhancing DSSC performance. These results offer a promising pathway for further optimization of dye–surfactant–metal ion systems in low-cost, metal-enhanced solar energy devices.

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