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RESEARCH PAPERS

Characterization of M-curcumin complexes (M= Cu, Co, Ag) in turmeric rhizome as sensitizer candidates in dye-sensitized solar cell (DSSC)

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Abstract: This experimental research aims to characterize the complex compound M-curcumin (M=Cu, Co, Ag) based on turmeric (*Curcuma longa Linn*) rhizome as a candidate for photosensitizer in solar cells. The basic material used for manufacturing the M-curcumin complex compound in this study was curcumin from turmeric rhizome extract added to Cu^{2+}, Co^{2+}, and Ag^{+} metal ions. The results of the synthesis of the M-curcumin complex were characterized by FTIR and Uv-Vis spectrophotometers. The FTIR spectrophotometer test showed a curcumin compound in the viscous curcumin extract, characterized by an absorption wave number corresponding to the curcumin compound. In the M-curcumin complex, the bond between the metal and the ligand only appears in the Co-curcumin complex at the absorption number of 498.77 cm^{-1}. The results of the UV-Vis spectrophotometer test showed that the maximum wavelength absorption in curcumin extract was 430 nm (abs = 0.688), Cu-Curcumin complex λmax 300 nm (abs = 2.573), Co-curcumin complex λmax 425 nm (abs = 1.067), and complex Ag-Curcumin λmax 430 nm (abs = 1.36). The UV-Vis and FTIR characterization showed that the Co-curcumin complex has good potential compared to the organic compounds (curcumin) and can be used as an alternative *photosensitizer* in solar cells.

Keywords: Curcumin, M-Curcumin Complex (M=Cu, Co, Ag), DSSC Solar Cell.

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INTRODUCTION

The need for energy, which continues to increase along with the increase in population, causes a crisis of energy sources [1,2]. The search for economical and environmentally friendly energy grows towards renewable sources. One alternative energy source currently being developed is solar energy which can be converted into electrical energy using solar cells by directly converting solar radiation into a source of electrical energy [3].

Solar cells are a technology that converts light energy (*photons*) from sunlight into electron charges that flow in a semiconductor junction so that they can produce an electric current. The development of solar cells is divided into three generations, where dye-based solar cells *or* Dye-*Sensitized Solar Cells* (DSSC) are the third generations of solar cells. It has attracted considerable interest because of its relatively low cost, easy fabrication, high efficiency, and compatibility with flexible substrates [4].

This DSSC-based solar cell is formed by four constituent components, including semiconductor electrodes (TiO_2), dye *sensitizers*, redox mediators, and counter electrodes (usually inert metals, such as Pt) [5]. DSSC has a working principle that can convert visible light into electrical energy based on the wide band gap sensitivity of the semiconductor. The bond between dye molecules and the absorption spectrum with TiO_2 as a surface are important parameters for determining cell efficiency, so cell performance depends on using dye as a sensitizer [1].

The use of dyes as sensitizers can be derived from synthetic or natural dyes. In general, the dye sensitizers in DSSC-type solar cells are *ruthenium complex synthetic compounds* such as N719, N3, and *black dye*, where the highest efficiency with these synthetic dyes can reach 10-11% [6]. However, synthetic dyes have drawbacks, including limited availability, being less economical, taking a long time, and containing heavy metal elements [7]. Alternative natural dyes are used as dye sensitizers to overcome these problems. Natural dyes have good alternative substances when applied as sensitizers because they contain molecules that can absorb light, such as beta-carotene, curcumin, chlorophyll, and anthocyanins found in fruits and vegetables.

Many studies have been carried out on using natural plant dyes, including curcumin extract from a rhizome as a photosensitizer [8], which resulted in an efficiency of 1.37%, curcumin extract from turmeric rhizome, [9] which resulted in an efficiency of 0.63%. Although natural dyes have economic advantages, are easy to process, easy to obtain, and environmentally friendly, the highest level of efficiency that natural dyes can achieve is still low, which is below 4% [10]

One factor that affects the efficiency of DSSC is the ability of dyes to absorb light at certain wavelengths. Efforts to increase the absorbance of light can be made by sensitizing semiconductors with transition metal complexes. Transition metal complexes that are capable of acting as photosensitizers are complexes with metals that are in a low oxidation state, have low electronegativities, and have excess electron densities such as Cu(II), Co(II), Pt(II), Fe(II), and Mn (II) caused by the additional electron density of the s-bond ligand [11]. In curcumin compounds, there are ketone groups and hydroxyl groups. Both electrons in this group can interact with metals to form complex compounds with electronic transitions that are at the excitation level $\pi \rightarrow \pi^*$, n→ n*, n→ π^*. In complex compounds, the contribution of s-donors and π–acceptors provides overall stability of the complex compound. It is expected to widen the absorbance region in visible light waves, thereby increasing the value of DSSC efficiency.

MATERIALS AND METHODS

Research Tools and Materials

The equipment used in this study included: UV-Vis spectrophotometer, FTIR spectrophotometer, beaker, measuring cup, dropper pipette, stir bar, balance, Erlenmeyer, measuring flask, blender, *magnetic stirrer*, separatory funnel, spatula, and *hot plate*.

The materials used in this study included: Turmeric, 96% ethanol, n-hexane, ethanol pa (Merck), $CuCl_2.H_2O$, $Co(NO_3)_2.6H_2O$, $AgNO_3$, filter paper, tissue, clear plastic, and aluminum foil.

Research procedure

1. The method of extraction of Curcumin from Turmeric Rhizomes

   extraction method used is Maceration. As much as 1 kg of turmeric rhizome is washed thoroughly with water, peeled, cut into small pieces, and thin. The cut rhizomes were then dried at room temperature for 3×24 hours.

   The dried turmeric rhizome was then macerated with 96% ethanol with a ratio of 1:10. Maceration was carried out for 3×24 hours in a closed glass container and protected from direct sunlight. Furthermore, the extraction results were filtered to obtain the filtrate. After obtaining the filtrate, liquid-liquid extraction was carried out using n-hexane solvent. Liquid-liquid extraction was carried out using n-hexane solvent with a ratio of 1:1, and the shaking process was carried out for ± 15 minutes. The ethanol phase was taken from the liquid-liquid extraction and then stored in a dark bottle.
2. Synthesis of M-Curcumin Complex

   A total of 0.1 mol of solid $CuCl_2 .2H_2O$ was dissolved in 25 mL of ethanol solvent pa. The metal complex solution was then mixed with a dye diluted with ethanol solvent pa, and the two solutions were combined in a ratio of 1:1. The mixture was stirred for 4 hours using a *magnetic stirrer.* The same method was carried out for the Co and Ag metal complexes.
3. Characterization Stages
   a. UV-Vis Spectrophotometer

      Put 1 drop of curcumin sample and M-curcumin complex in a 4cc cuvette, then dilute it with ethanol solvent up to the boundary mark and scan it to obtain the maximum wavelength of the sample.

   b. FTIR Spectrophotometer

      The curcumin sample and M-curcumin complex were dripped onto the KBr plate to form a thin film. Then the plate was inserted into the sample holder on the FTIR tool. Computer operation is performed to bring up a graph of the functional group of the material being tested.

RESULTS AND DISCUSSION

Extraction curcumin

Extraction is conducted in four stages, preparation, extraction maceration, liquid-liquid, and concentration. Preparation conducted with cleaning, peeling, and chopping the sample becomes rush small to expand the surface touch sample. At stages of Maceration, added solvent 96% ethanol was with a ratio of 1:10. Election solvent ethanol based on the compound easy curcumin late in polar organic solvents and have the same polarity compared with other organic solvents such as methanol and ethyl acetate [12]

Stage extraction liquid used different solvents with characteristic polarity with sample n-hexane to interest curcumin major and reduce substance impurity. In stage concentration, the organic fraction is heated at 60-70 ° with the goal that the alcohol still contained in the extract evaporates. Extract curcumin colored yellow-orange. After the concentration, the obtained extract is thick, weighing 0.66 grams. Extract the thickness obtained called substance color (*dye*) Figure 1.

Figure 1 . Extract thick curcumin.

Synthesis compound M -Curcumin complex

Synthesis M-Curcumin complex originates from an extract of thick mixed curcumin with variation solution metal that is the copper of $CuCl_2.2H_2O$, cobalt from $Co(NO_3)_2.6H_2O$, and silver from $AgNO_3$. Solution metal each made 0.1 M with use solvent ethanol pa Next third solution the respective metals are mixed with substance color (extract thick curcumin) with a ratio 1:1.

When mixed, substance color and solution metal copper produce the color green old for Cu-Curcumin complex, color red concentrated for mixture Co-curcumin complex, and color yellow-orange for Ag-Curcumin complex. After mixing, an M-curcumin complex is formed and stirred for 4 hours using a *magnetic stirrer* with the purpose of the substance color with complex metal could bound with good form M-Curcumin complex. Stirring was conducted in the closed system to avoid evaporation from the solution. The longer the mixing process, resulted happening changes in color in each complex; that is, for solution Cu-Curcumin complex colored green concentrated, the solution Co-curcumin complex colored red-brown, and the dissolved Ag-Curcumin complex colored yellow (Figure 2).

Figure 2 . Synthesis M -Curcumin complex

Characterization of curcumin and the M -curcumin complex

Spectra UV-Vis absorption is a method of analysis of compounds that use ultraviolet radiation and light looks. Principle-based UV-Vis Spectro is happening transition capable electronics excite electrons from empty orbitals [13]

UV-Vis spectrometry works to determine structure qualitatively from compounds containing a group absorber or chromophore. A chromophore possibly happens in transition electronics, that is, the movement of electrons from the circumstances base to a higher energy level [14]. On extract curcumin, absorption long the resulting waves of 430 nm with absorbance the highest was 0.688. Curcumin reported its peak absorption at 420 nm, derived from the existence of diarylhepatanoid conjugati where electron excitation of n→π * on ab 290 long wave between 280-400 nm indicate group conjugated heteroatom chromophore as group carbonyl [16].

In the M-Curcumin complex, we obtained a long uptake wave by 300 nm for the Cu-Curcumin complex with an absorbance of 2.573, 425 nm for Co- curcumin complex, with an absorbance of 1.067 and 430 nm for Ag-Curcumin complex with the absorbance of 1.36. UV-Vis spectra results for compound organic and after conducted synthesis compound complex no found change score uptake long significant wave. However, the same wave exists in length with different score absorbance in each compound complex curcumin. It shows that wide absorption in the M-curcumin complex absorbs photons bigger in length, almost wave same.

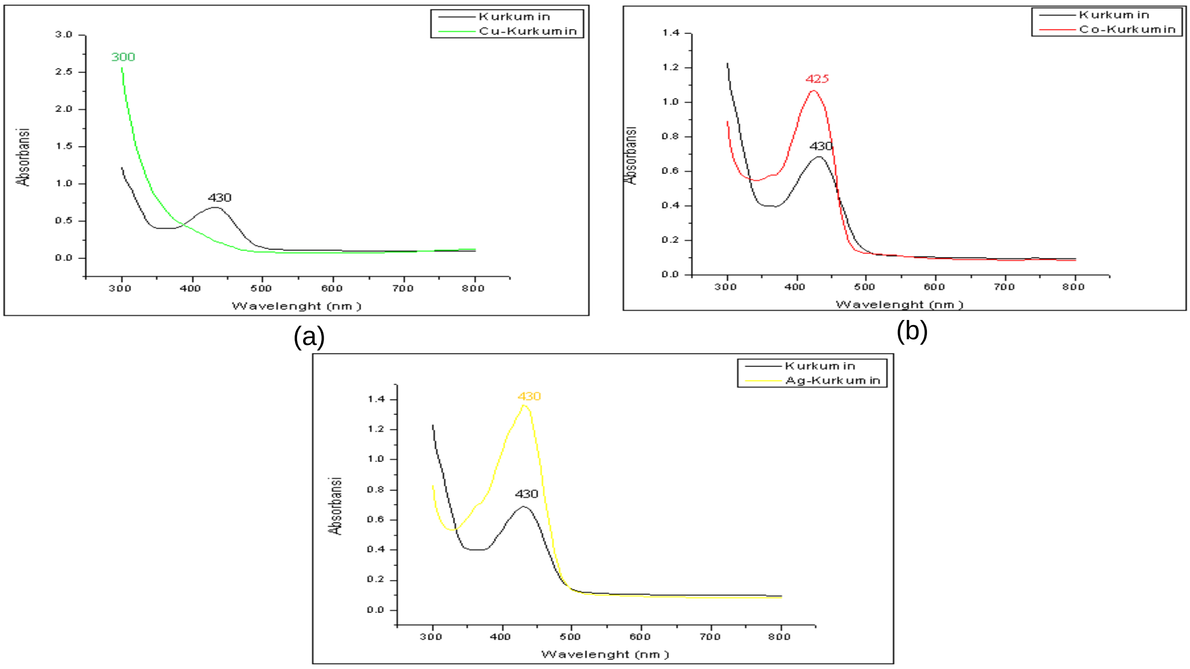
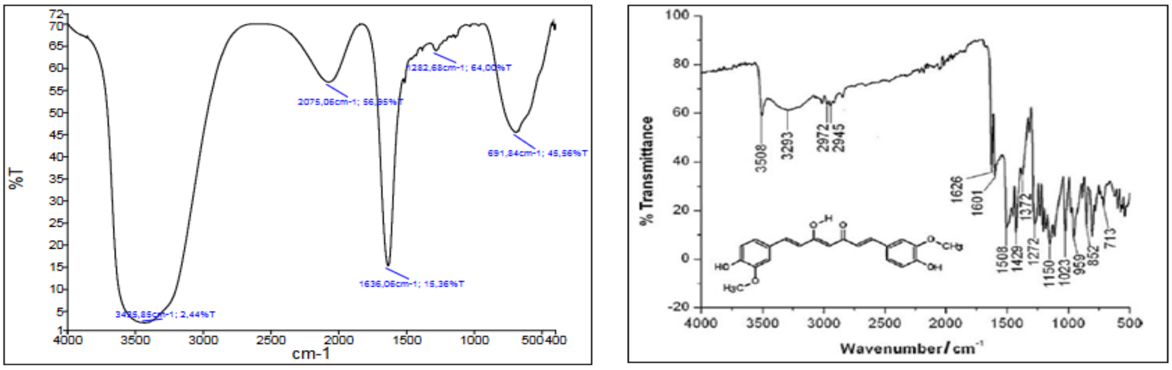


Figure 3 . Absorbance spectrum compound M-Curcumin complex ; (a) Cu-Curcumin, (b) Co-Curcumin, and (c) Ag-Curcumin

Characterization results with Spectro infrared (Figure 3) on extracted curcumin are shown in figure 4. Peak wide in area uptake number wave 3435.85 cm^{-1} indicates it exists hydroxyl O-H *stretching* on the ring aromatic [17]. Peak sharp at 1636.06 cm^{-1} indicates strain alkene C=C and carbonyl C=O (carbonyl). Stretch tape on numbers waves 1282.68 cm^{-1} indicates phenolic bond C-O. Cis-CH bonds in the aromatic ring are detectable in numbers wave 691.84 cm^{-1} [18].

Absorption FTIR analysis results number wave compound curcumin in research this own similarity uptake number wave with results study from Mohan *et al*. (2012), namely in the area uptake number waves 3508 cm^{-1}, 1626 cm^{-1}, 1272 cm^{-1}, and 713cm-1. The study from Mohan *et al* . (2012) has an area of sufficient absorption many and varied so that group detected function more many compared with results from the research. It could cause a difference in the solvent used and concentration from the tested sample try.

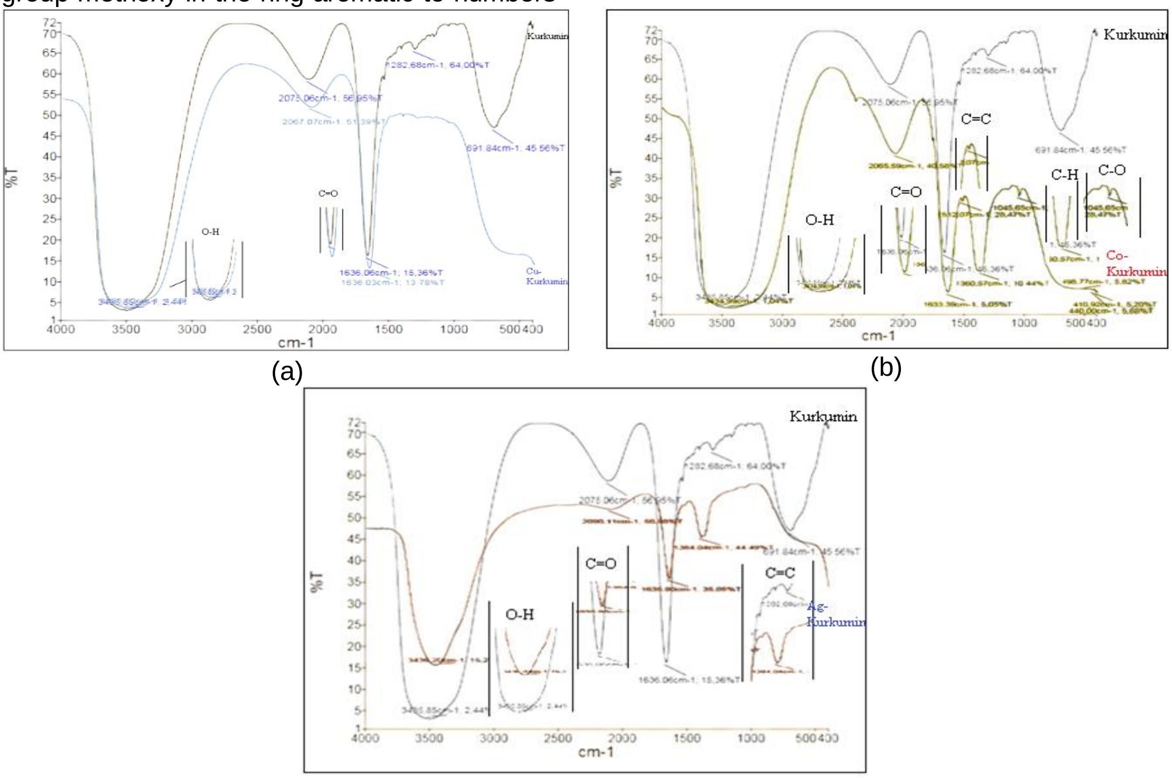


(a) (b)

Figure 4. FTIR spectrum of curcumin compound (a) results in research, (b) study literature

On the results of FT-IR spectrophotometry of the compounds, the M-Curcumin complex on the Cu-Curcumin complex identified exists bond O-H *stretching* in the area uptake wave 3435.52 cm^{-1}, and the C=O, C=C bonds *stretching* on absorption wave 1636.03 cm^{-1} (Figure 5). In the Co-Curcumin complex, a bond exists on the cluster OH *stretching* in the area uptake wave 3434.99 cm^{-1}. The bond C=O, C=C *stretching* on absorption wave 1633.39 cm^{-1}, aliphatic *bending* CC-C bonds on absorption wave number new 1512 cm^{-1} [19], enol C-OH bond on absorption wave just 1360.57 cm^{-1}, C-O-C bond *stretching* on the group methoxy in the ring aromatic to numbers wave new 1045 cm^{-1} and the M-O bond at wave new 498.77 cm^{-1}. According to Lestari (in Barik, 2007) [20-21], ties between the metal ligands will appear in waves 500-600 cm^{-1}.

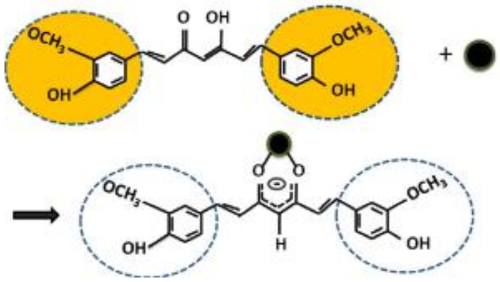
Hatamie et al., 2012 predict possible interaction Between curcumin and metal form complexation metal-ligand, where metal could interact with group hydroxyl attached to the two rings and the halves ditone on the second ring. In the Ag-Curcumin complex identified bond OH *stretching* in the area uptake wave 3436.2 cm-1, bond C=O, C=C *stretching* on absorption wave 1635.9 cm $^{-1}$, and the enol C-OH bond on absorption wave 1384.04 cm-1.



(a) (b)

(c)

Figure 5. FTIR spectrum of the M-curcumin complex; (a) Cu-Curcumin, (b) Co-Curcumin, and (c) Ag-Curcumin



Sheme 1. Possibility scheme interaction among molecule curcumin with metal.

Result analysis on the compared Cu-Curcumin complexes with study theoretical, in big part group function, no appears on the FTIR result (Table 1). Besides that, in the Cu-Curcumin complex, no show exists change in area uptake waves. For example, in clusters, the O-H *stretching function* is at 3435.52 cm $^{-1}$, whereas compound curcumin is on absorption wave 3435.85 cm $^{-1}$.

Different cases with Co-Curcumin complex and Ag-Curcumin complex where based on FTIR spectra results on the Co-Curcumin complex show existing uptake number new waves in CC-C *bending* (aliphatic), C-OH *bending* (enol), COC *stretching*, and MO bonds stretching. And for the Ag-Curcumin complex identified the uptake number of a new wave on the enol C-OH bond. A decline in percent transmittance from compound curcumin to complex curcumin shows that almost the whole missed frequency absorbed by compounds [22], as well as appearance score uptake number new wave, signifies that has happening binding Among metal ion complex with organic compounds (Scheme 1).

Table 1. FTIR results of curcumin and the M-curcumin complex

Group Function	Literature (Mohan et al., 2012)	Number Wave (cm $^{-1}$)			
		Curcumin	Cu-Curcumin	Co - Curcumin	Ag-Curcumin
O-H *stretching* (phenol)	3508	3435.85	3435.52	3434.99	3436.2
C=O *stretching*	1626	1636.06	1636.03	1633.39	1635.9
CC-C *bending* (aliphatic)	1508	–	–	1512.07	–
C-OH *bending* (enol)	1372	–	–	1360.57	1384.04
CO *stretching* (phenol)	1272	1282.68	–	–	–
C-O-C *stretching* (*out-of-plane bending of* CH_3)	1023	–	–	1045.65	–
Aromatic CCH	713	691.84	–	–	–
M-O *stretching*	468	–	–	498.77	–

CONCLUSION

Characterization results compound M-Curcumin complex (M= Cu, Co, Ag) based rhizome turmeric (*Curcuma Longa Linn*) as candidate photosensitizer. It has enough potential good based on the characterization of the results if compared with the organic compound course, where the use of Co-curcumin complex is better compared to complex metal other.

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