Silica-Cellulose Hybrid Material Application as Natural Pigment Adsorbent as Studied by Spectroscopy Method

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Silica-Cellulose Hybrid Material Application as Natural Pigment Adsorbent as Studied by Spectroscopy Method

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Abstract. Rice husk ash and nata de coco are used as the sources of silica and cellulose, both materials can be combined to form a silica-cellulose hybrid. This material can be used as the adsorbent for natural pigment or metals also for any bigger molecule like enzyme. Curcumin and chlorophyll were chosen as the probe adsorbate. This research aimed to know the characteristic of the silica-cellulose hybrid and the adsorption behavior of chlorophyll and curcumin pigments via the batch method and also as a stationary phase in TLC. FT-IR and UV-Vis analysis were involved. The research was an experimental laboratory and divided into 4 steps (1) preparation and produce silica-cellulose hybrid, (2) characterization of silica-cellulose hybrid, (3) application of the material to chlorophyll, curcumin and the mixtures, (4) analysis of surface interaction using spectrophotometer FT IR and UV-Vis. The results of this research showed the role of cellulose in changing the surface properties towards molecular interaction from both batch and thin layer experiments.

Keywords: Silica-cellulose hybrid, natural pigment, adsorbent, spectroscopy method, curcumin pigments

1. Introduction

New materials from natural biomaterials are important since there are a lot of new applications come out to demand. On the other hand, biomass, which is usually troublesome agro-waste, can be converted into something else with new properties. Designing new materials from waste products is actually challenging, while the desirable properties can be reached within the scope of chemistry. Silica material is actually common since silica is everywhere on earth. Silica is also taken and accumulated by plants and used to cover the hard-material needed by plants, beside lignin. In paddy plants, silica is bio-accumulated and stored in rice husk to be the hard place for growing rice. Naturally, some organic materials are also present but when the husk is burnt to form ash, the remaining minerals is silica with the biggest portion [1,2]. Accordingly, bio-silica is a new material that works almost the same function as silica from stones and earth.

Besides, cellulose materials are also common [3,4]. Bacterial cellulose is one type of cellulose source, which gives very high purity of cellulose without lignin from wood and other plant sources. This type of cellulose is in a high demand since the effort to separate lignin and another lignocellulose requires quite a long process. Bacterial cellulose like nata de coco is hydrolyzed or treated to reach nanodimension and can be applied for many purposes [5-7]. The combination of silica and cellulose will give new surface properties for the new materials. Moreover, the preparation via sol-gel processing yields porous materials. When silica is highly absorbing, the presence of cellulose makes the surface less polar and can be used for adsorbents as well as chemicals releasers [8,9]. Separation chemistry is based on the dynamics in the interfaces [10]. In porous media, it can be a solid-gas interface or solid-liquid interface, that the adsorption and desorption occur simultaneously according to the equilibrium constant of each adsorbate [11]. The mechanism governing separation actually relies on this equilibrium and this is the basis of separation by chromatography. Small particles dynamics on the surfaces actually was studied thoroughly by the aid of NMR relaxation and diffusion long time before [12,13]. More experiments in NMR that appear recently [14] is actually supporting the similar relaxation data on a similar sample before, which silica sol-gel was in use [15]. More experiments on the surfaces by another method actually describe the water role in adsorption systems [14,16] by the air of infrared and Raman spectroscopy, as well as computational chemistry.

In this experiment, the silica-cellulose matrix was used to adsorb and separate natural dyes, curcumin and chlorophyll dyes in polar solvents in batch as well as thin layer systems, separately or in mixture. These two pigments were chosen as the probe pigments to give information about Interactions in the Surface were followed by ultraviolet and visible as well as infrared spectroscopy. The characterization of the matrix was done also by common physical and chemical properties, and BET analysis was the additional information for describing the nature of the gels. The incorporation of cellulose and silica causes the polarity of the adsorbent to decrease so that the ability of adsorption to organic compounds can be better. Adsorbents are usually characterized before use.

Chlorophyll ($C_{55}H_{72}O_6N_4Mg$) is a green pigment in photosynthetic plants, algae and bacteria that play a role in photosynthesis and can potentially be anticancer, whereas curcumin ($C_{21}H_{20}O_6$) is a yellow compound with a molar mass of 368 g/mol, derived from turmeric rhizome and usually found in curcuminoid forms which are commonly used as antioxidants. The content of curcumin in turmeric is quite high [17]. Thin Layer Chromatography (TLC) is a method of separating mixtures from several compounds using a stationary phase and a mobile phase through thin layers [18]. The mobile phase in TLC usually consists of 1 type of eluent or several types of eluents with a certain ratio. Besides TLC, there is also a batch method. The difference in the TLC method is used to determine the effectiveness of an adsorbent in separating the mixture, while the batch is used to determine the percentage of adsorption because in this method the adsorbent is directly contacted with adsorbate in a period of time. For this research, the stationary of the TLC method was replaced by silica from rice husk ash. This research is aim to know (1) characteristic of silica-cellulose hybrid adsorbent consist of FT-IR analysis, water content, ash content, density and adsorption capacity of iodine, (2) adsorption capacity of chlorophyll, curcumin and mixture then know the effectiveness of material as a stationary phase in TLC, and (3) surface interactions from spectrophotometer FT IR and UV-Vis.

2. Methods

2.1 Chemicals and Instrumentation

The chemicals were obtained from Sigma Aldrich and E. Merck and all bench activities used pyrex glassware. Chlorophyll and curcumin as natural pigment were used to study the dynamic of silica-cellulose surface, while the R_f study was used to learn the effectiveness of the material as a stationary phase to separate both natural pigment. Methanol, ethanol, and surfactant were used as a mobile phase for TLC. Chlorophyll was obtained from K-Link factory in which the alfalfa (*Medicago sativa*) leaves was the raw chlorophyll source, with a concentration of 8000 ppm. Curcumin p.a was obtained from E. Merck, and only soluble in ethanol. During the experiment, chlorophyll used demineralized water and curcumin ethanol p.a as solvents.

The instruments used for this study were XD-1700 M, Nabertherm, and Thermolyne furnace for ashing the rice husk, magnetic stirrer of NESCO LAB MS-H280-Pro or Thermoscientific Cimarec for gelling reactions, EYELA oven, type WFO-450ND, IR -Prestige-21 (SHIMADZU) and UV-Visible Type Pharmaspec 1700 (Shimadzu). Working wavelengths of chlorophyll measurement were 400 nm and curcumin 422 nm.

2.2 Material Preparation and Characterization

The preparation was done by washing rice husk then burned to obtain charcoal grey-black color. The ash was heated again in the furnace for 1 hour. This process aims to obtain silica in an amorphous form it has a larger surface area than crystalline silica. The silica extraction process was done using NaOH to dissolve the silica in alkaline solutions. The yellow extract was clear and contains sodium silicate. The obtained filtrate will be combined with colloidal cellulose from nata de coco as a result of its hydrolysis process using a high concentration of H_2SO_4. The result of this process was a purplish gray cellulose colloid. To eliminate sulfate ion, the addition of NH_4OH was done to the mixture and then the distilled water was added. Filtering was done using a funnel to obtain a large amount of white residue. The residue was dried in the oven again. All procedure of making silica-cellulose matrix was already granted Indonesian Patent Number IDP000049626, 14 February 2018. The chemical reaction can be written as follow:

$$SiO_2(s) + 2\ NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l)$$
$$Na_2SiO_3(aq) + H_2SO_4(aq) \rightarrow SiO_2(s) + Na_2SO_4(aq) + H_2O(l)$$

After the preparation, the matrix was treated to know the physical characteristic, including water content, ash content, density, and iodine adsorption capacity, and the chemical characteristic including a functional group from the material by FT-IR. For the application, the material silica-cellulose was used to adsorb chlorophyll, curcumin molecules and the mixture of both using batch method. As much as 0.05 grams adsorbent was used in the batch method, while the adsorbate volume was 10 mL and 20 minutes contact time. After the batch process, the calculation of chlorophyll and curcumin concentration before and after adsorption was carried out through their respective linear regression equations, then the percentage of adsorption was determined. The material was also used in TLC as a stationary phase for eluting the natural pigment using some organic solvent as mobile phase and the results were compared to the commercial silica. The additional system was created using very polar eluent, the ethanolic surfactant. N-cetyl trimethyl ammonium bromide was used as the surfactant and it was dissolved in ethanol.

3. Results and Discussion

3.1 Silica-Cellulose Hybrid Material Characterization

The physical characterization of the material can be seen in table 1. Ash content shows the number of minerals contained in the adsorbent, and this high value came from silica. The absorption capacity of the iodine solution shows the adsorption ability. The low density of material showed the higher porosity which is the internal property of the material. Iodine adsorption number is also a description of a porous material. The higher the value of Iodine adsorption, the better the adsorption ability in general, which was not always the same with the other purposes.

Table 1. Physical Characterization of Silica-Cellulose Hybrid

Physical Characterization	Result
Water Content	5.69%
Ash Content	92.10%
Density	2.35 g/mL
Iod Adsorption Value	7.10%

Chemical characterization by FT-IR instrument can be seen in Figure 1. The analysis was carried out in the area 400-4000 cm^{-1}. Silica-cellulose material showed the absorption band of silanol bending vibration (≡Si-OH) at the wavenumber 1091.71 cm^{-1} and 2897.08 cm^{-1}, indicating the vibration of the silanol group of the silica surface. The addition of cellulose particles caused the appearance of the absorption peak at the 1614.42 cm^{-1} that indicated C-O vibration of cellulose.

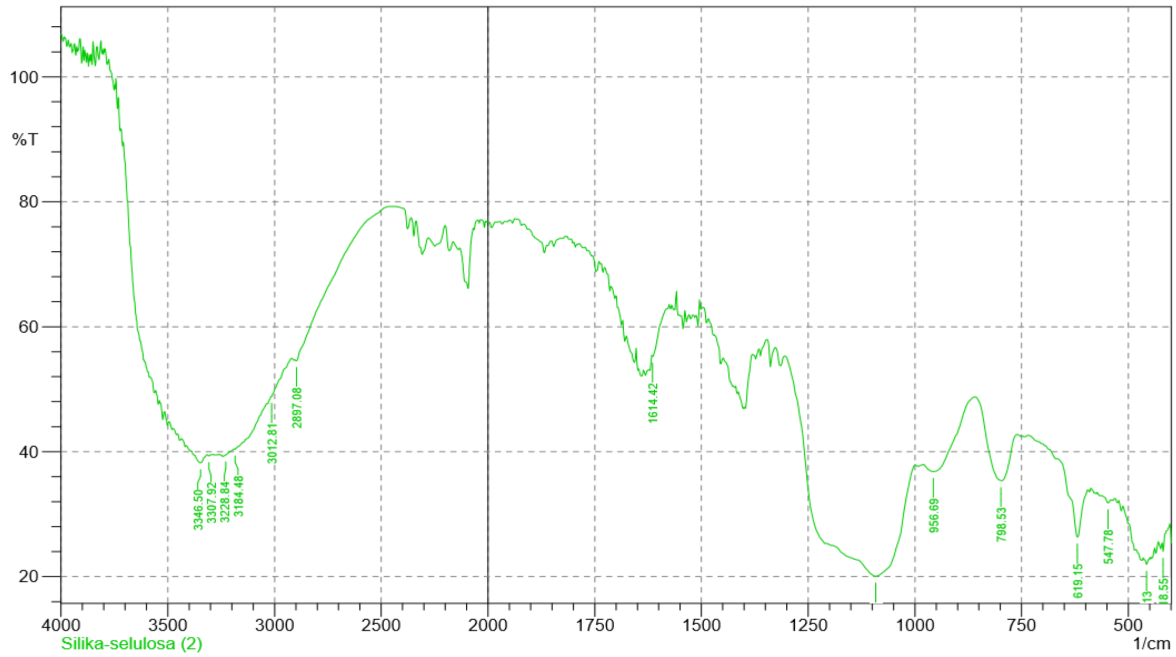


Figure 1. Spectrum IR of Silica-Cellulose Hybrid

3.2 Application as an adsorbent for chlorophyll and curcumin with batch method

Chlorophyll solution in presence of silica-cellulose hybrid material would be adsorbed physically not more than 25%. In this situation, the relatively big molecules will be attached in the inhomogeneous surface via the active sites as well as by physical entrapment. Curcumin molecules and the lower polarity, the result was lower adsorption percentage onto the silica-cellulose surface. The results can be seen in Figure 2 right and left.

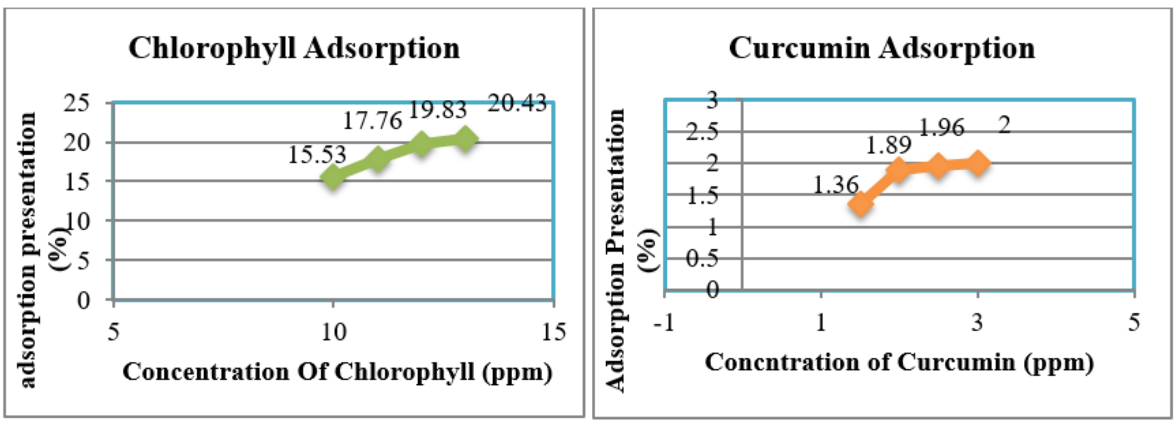


Figure 2. Graphic of Chlorophyll (left) and Curcumin (right) Adsorption Using Silica-Cellulose Hybrid material

Based on the batch results, it can be seen that silica-cellulose can adsorb both chlorophyll and curcumin. This adsorbent was slightly polar adsorbent because of the addition of cellulose during the gelling process so that the cellulose will stick to the surface of the silica and partly attached to the pores. Chlorophyll and curcumin are polar organic compounds, but the polarity of chlorophyll is higher than curcumin, with additional electron cloud from nitrogen in the porphyrin ring which is always in an excited state due to light adsorption. Chlorophyll molecule is bulkier than curcumin. There are more chances to be trapped in the pore system compared to curcumin molecules.

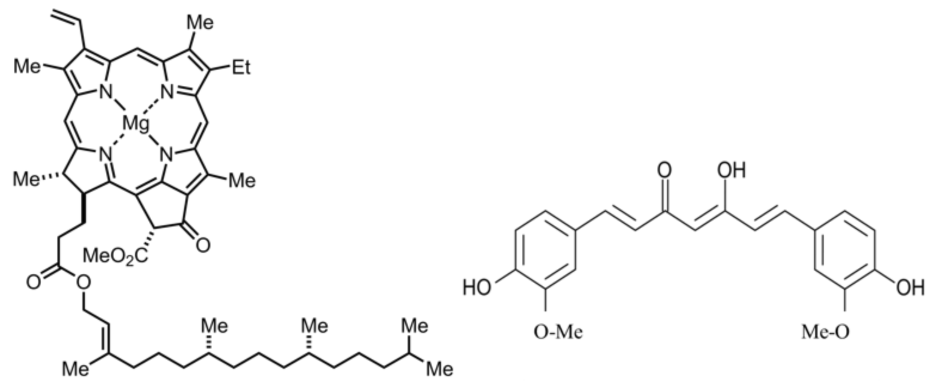


Figure 3. The molecular structure of chlorophyll (left) and curcumin (right)

Chlorophyll molecule is significantly polar because of Mg^{2+} and carbonyl groups present in the structure. The polar site must interact with nonpolar sites of the silica-cellulose surface, while the hydrophilic area in the chlorophyll structure will interact with the silica-cellulose polar part and the other way around. The average adsorption percentage of chlorophyll was 17.75%. Curcumin also has active sites capable of interacting with the silica-cellulose surface, so that curcumin can be absorbed even with a small percentage, with an average adsorption percentage 1.80%.

The adsorption of the surfaces has the tendency to increase as the concentration of chlorophyll and curcumin increases. In the constant pH and temperature, this is the sign of physical interaction occurring on the surface, while the relaxation of every species is efficient and adsorption-desorption equilibrium plays role in an efficient way too. This phenomenon was already seen from NMR relaxation experiments long time before [19]. The key information about what is occurring in the surfaces is already discussed recently using another spectroscopy method [14,20]. When the RMTD mechanism does occur in this complex surface, then the dynamic equilibrium leading to fast diffusion will take more adsorbate from the bulk pore liquid [12,21,22].

Something that cannot be excluded is the role of water molecules as a solvent, which is different in properties with ethanol. Water is more polar but it also has higher surface tension (0.072 N/m) rather than ethanol (0.023 N/m). Lower surface tension enables ethanol to move and diffuse around pore and surfaces, bringing the curcumin molecules in and out the pore systems easier than water solvent molecules. This fact lowered the adsorption and shifted the surface dynamics as well. If the chlorophyll had the same solvent than the prediction of adsorption values would be predicted lower too.

3.3. Application as thin layer material

The capacity of adsorbent to adsorb and brings natural pigments as well as to separate the mixture of both pigments can be done by thin layer chromatography (TLC) method. The silica-cellulose material was used as stationary phase with a different kind of mobile phase. Ethanol and methanol are polar solvents, and surfactant solution was also very polar and almost ionic additional adsorbate in the eluent. Both pigment chlorophyll and curcumin were eluted individually and in a mixture of both. Silica plate for thin layer chromatography was used to compare the newly made stationary phase with the commercial one which has standard properties. All results can be seen in Table 2.

Table 2. The R_f of Chlorophyll and Curcumin and their mixtures in a different solvent.

Systems	**Solvents**	**R_f Chlorophyll**	**R_f Curcumin**	**Mixture of Chlorophyll and Curcumin**
Silica-Cellulose Preparative Plates	Ethanol	0.333	0.833	Zone 1: 0.818 Zone 2: 0.545
	Methanol	0.517	0.857	Zone 1: 0.500 Zone 2: 0.167
	Surfactant in Ethanol	0.500	0.952	Zone 1: 0.845 Zone 2: 0.538
Commercial Silica thin layer	Ethanol	0.575	0.625	*no separation
	Methanol	0.444	0.555	* no separation
	Surfactant in ethanol	0.625	0.869	Zone 1: 0.833 Zone 2: 0.666

Zone 1: Curcumin
Zone 2: Chlorophyll

The separation using silica-cellulose as a stationary phase and some organic eluents as mobile phase indicated that ethanol was good in silica cellulose system. In line with the batch adsorption system, curcumin was less adsorbed than chlorophyll and the R_f was greater, both ethanol and methanol dissolved curcumin better and brought it faster and further up. Meanwhile, chlorophyll was adsorbed more in the matrix and left behind. In the mixture, the condition was similar, however, the R_f values shifted a bit. There was a competition between chlorophyll and curcumin molecules, as well as water and eluent molecules on the surface of silica cellulose. The complexity arose while the solvent molecules were leaving the surface too in the opened surface. Something critical occurred in a system with methanol as the mobile phase. The curcumin was adsorbent in the surface while actually, it dissolved well in methanol. The light molecules left surface for evaporation leaving the curcumin molecules adsorbed on the surface.

The process of separation using commercial silica shows that curcumin is lifted earlier than chlorophyll, the same result was also shown using silica-cellulose adsorbents. This showed chlorophyll has polarity greater than the curcumin. In addition, a commercial silica plate was also used to separate the mixture of chlorophyll and curcumin, but both methanol and ethanol eluents could not separate the two pigments, unlike the silica-cellulose system. This is the role of cellulose in separating organic pigments one to another. The results are somehow in line with the previous report on the silica-cellulose system [8]. Cellulose surface particle shifted the surface equilibrium and changed the whole surface polarity as well and of course the surface tortuosity.

3.4 Surface Interaction Analysis with FT-IR

While after adsorption the infrared spectrum was taken, it showed that there was a widening of the band at the wavenumbers of 3000-3600 cm^{-1} where the area indicated the presence of hydrogen bonding from O-H vibrations. This showed the dominant group on the interaction of adsorbent and adsorbate is O-H in silanol as well as the presence of water or ethanol molecules in the pores. In addition in figure showed the result of surface analysis for curcumin, the absorption band indicated the OH stretching vibration from curcumin appeared at wavenumber 3510.45 cm-1, besides that, a vibration absorption band appeared C = O and CO at wave numbers 1627.92 cm^{-1} and 1429.25 cm-1. There was also a spectrum that indicated the presence of double bond vibration C = C of molecules at wave numbers 624.94 cm^{-1} and 964.41 cm^{-1}. The change in wavenumber that occurred indicated the interaction that occurs on the surface, which is characterized by a spectrum that was previously sharp, became wider (Figure 4).

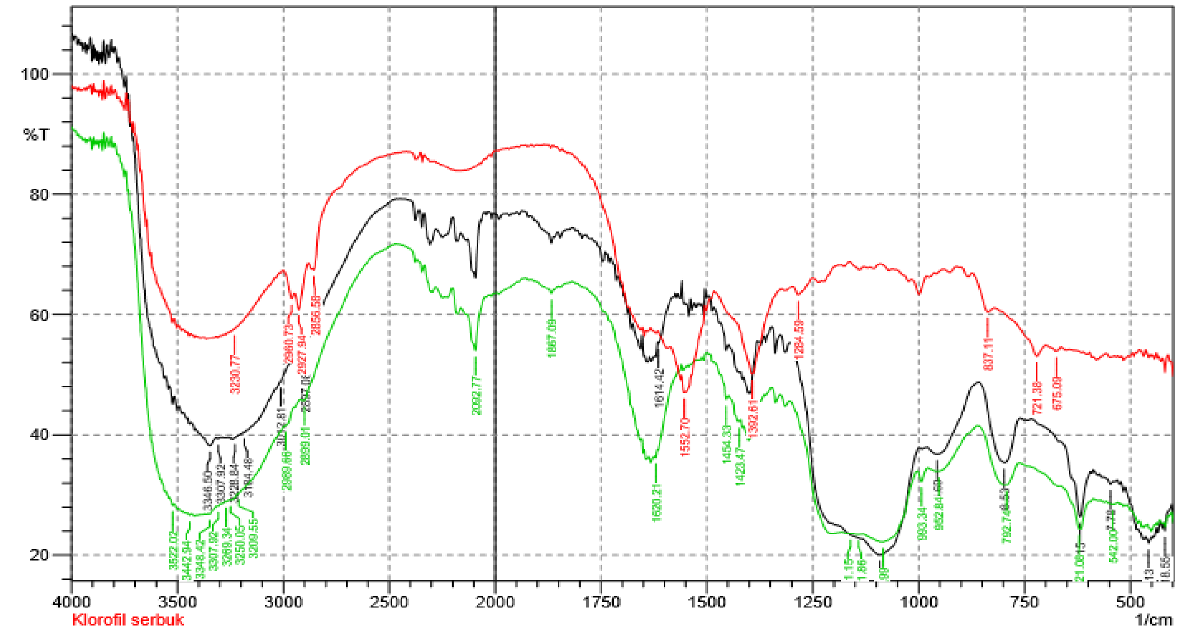


Figure 4. Combination Spectrum IR of Chlorophyll (red), Silica-Cellulose Hybrid (black), and Chlorophyll on the material (green)

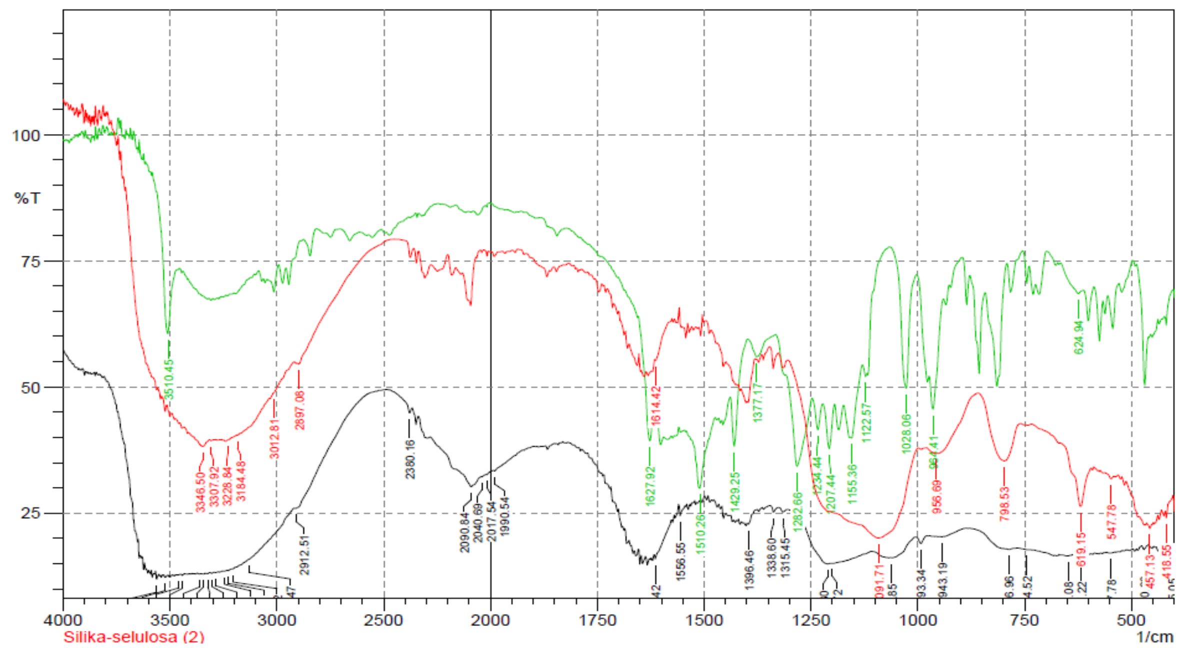
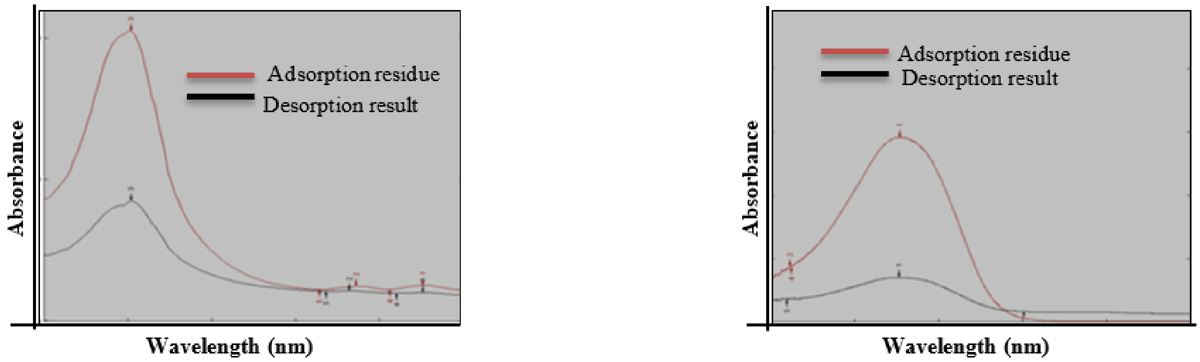


Figure 5. Combination Spectrum IR of Chlorophyll (red), Silica-Cellulose Hybrid (black), and Chlorophyll on the material (green)

The infrared spectrum shows that there is no new bond formed during adsorption or in other words, the physical adsorption or entrapment in between pores occurs. There is no new sign of new covalent bonding seen from the spectrum.

3.5 Surface Interaction Analysis with UV-Vis

The first step in this analysis was done by batch adsorption. This process was done to determine the kind of adsorption. Leaching process was done by using solvents from each adsorbate, water for chlorophyll, and ethanol for curcumin. After the adsorbate molecule released and dissolved to the solvent, further analyses were done using UV-Vis spectrophotometer with wavelength range 350-600 nm. The whole scanning was intended to get the profiles of the whole adsorption pattern in the UV-visible region. The desorption (leaching) process indicated that the physical adsorption, in which the adsorbate molecules, in this case, chlorophyll, curcumin were attached only to the surface by Van der Waals forces, so that the adsorbate be detached again quite easily, as can be seen in Figure 5.



(a) (b)

Figure 6. (a) Adsorption-Desorption of Chlorophyll, (b) Adsorption-Desorption of Curcumin

The results of the analysis with UV-Vis spectrophotometer showed that all adsorbate experienced desorption process and was characterized by its maximum wavelength that did not change. Actually, there are more analysis could be done by another method of spectroscopy to describe what is really occurring on the surface during adsorption. The more understanding of the surface behavior leads to new application procedures, the more in physical interaction or even moving into chemical properties changes. Catalysis is a new area of interest in the future.

4. Conclusion

The silica-cellulose hybrid material was made of basilica extracted from rice-husk ash, and hydrolyzed cellulose of *nata de coco* and applied to separate natural chlorophyll and curcumin pigments. The results showed surface dynamics adsorbed the pigment molecules in a different way and resulted at different retardation factors, while the solvent materials helped in desorption of both pigments as can be seen in the UV-Visible profiles. All experiments confirmed physical adsorption in silica-cellulose surface materials.

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