Spectroscopy for Characterization and Application of Silica-Cellulose Biomaterials, a Brief Review Article about Analytical Methods

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Abstract. Biomaterials and the making is one of the emerging topics in the field of material science since most are porous medium and their surfaces have so much ability to be utilized. Active sites on the surface can hold desired materials which range from small ions, molecules up to bigger biomolecules. However, method development for analyzing this ability is always needed depending on the purposes. Spectroscopic methods are useful to describe the material as well as surface activity or molecules mobility in the adsorbed phase. Interaction governing dynamics in the interface can be accessed indirectly. In this brief review paper, various spectroscopy methods are employed to characterize the biomaterials from silica/silica cellulose, as well as to test the applications in the field of the purpose. UV-Visible and infrared spectroscopy as well as SEM/TEM analysis are used, GC/MS analysis can also detect the volatiles from the surface, more insight from other methods would be presented to make good an assessment of this type of biomaterials in a certain application area.

Keywords: Silica, silica-cellulose, spectroscopy, characterization, application

1. Introduction
Material science is emerging nowadays in modern society since the demand on materials with specific purposes is also increased exponentially. Some materials have a natural origin, from living things from plants and animals, which are usually compatible with other specific function in biological systems. The “bio” attribute refers to life-related materials, organic material which is different from inorganic materials in chemistry point of view. Biomaterials have mostly carbon, hydrogen, oxygen, and some halogens, some metals like calcium and magnesium and view heavy metals like iron. However, there are now synthetic biomaterials with more varieties in composition, made of special demand for replacement materials in the living body. This way biomaterial can be defined in the wider sense, not always directly connected to the biological system but potentially related to such system must be taken into account.

Materials from natural origin sometimes are referred to as biomaterials too. In the field of material science, organic materials sometimes refer to biomaterials, to differentiate from inorganic materials.
Organic materials including polymers or bio-composites consist of more carbon, hydrogen, oxygen, nitrogen and sometimes halogens. While biomass is also related to biomaterials since some biomaterials can be converted to biomass. The applications of biomaterials are always related to the biological systems, which are related to the properties of biological materials. Therefore, the applications are examined by analytical methods in biological systems.

As materials, the scientific description is done using the characterization of the materials, as well as to explain the proper work displayed by the materials in the functional applications. In this case, method development is needed for the examination of the hypothesis, for the characterization of materials as well as in the application area. When the materials are used in agriculture, then the methods would be the agriculture methods, and also for another area of interest. And since the biomaterials can be applied to a wide range of applications, the method development as well as a wide and varied, depending on the emphasis of their applications [1-2].

There are certain emphases in biomaterials analysis [3]. Characterization must be on the first row of analysis, which includes physical and chemical properties, mechanical characterization, until surface characterization. The surface characterization attracts almost all attention in materials in biological systems since most applications of biomaterials rely on surfaces. Surface modification using chemicals was reported so many times [4–7] for many biological materials. Adsorption on silica surfaces by organic molecules was studied thoroughly [8]. Including to biomaterial topics, biocompatibility, in vivo and in vitro analysis, would attract much attention. Computational analysis is now also in demand, not only for characterization for the materials but also for the weak interatomic forces present in between biomaterials in biological systems [9] besides another emphasis on such systems [5,10].

In this paper, a biosilica-nanocellulose hybrid material is used to be the topic of discussion. This material is based on two natural materials, silica and cellulose. The silica itself is extracted from rice husk, which is actually valuable biomass from agro-waste that can be converted chemically. Cellulose from nata de coco is actually bacterial cellulose which is made of coconut water in the presence of sugar by the aid of Acetobacter xylinum. This type of cellulose is a very high purity of cellulose [11,12] by nature without the presence of lignin. Silica has the properties of adsorbing [13–15] and but cellulose has more similarity to organic materials [16,17]. Combining both silica and cellulose will give new surface properties that can be utilized for equilibrating more organic materials [18,19]. Utilizing surface can be the key for successful adsorption and desorption purposes, as already discussed thoroughly in many basic experiments in porous media study [20–23]. The insight from NMR experiments can be applied in many areas of material applications. During 20 years of time, the relaxation NMR study of small particles including solvent on the interface of porous media has been studied and similarly reported [23,24]. Most of the applications rely on the polar surface [19,25–27].

2. Methods
The chemicals were obtained from Sigma Aldrich and E.Merck which were all pro analysis grade. The glassware used during experiments were pyrex and Duran glasses. The instruments used for this study were XD-1700 M, Nabertherm, dan Thermolyne furnace for ashing the rice husk, magnetic stirrer of NESCO LAB MS-H280-Pro or Thermoscientific Cimarec, EYELA oven, type WFO-450ND, IR - Prestige-21 (SHIMADZU) and UV-Visible Type Pharmaspec 1700 (Shimadzu).

The raw material for silica is rice husk ash, which contains silica from bioaccumulation from earthly silica. The silica was taken by base-extraction via the sol-gel method as modified from the common procedure [28]. The source of cellulose was untreated nata de coco from the local market and was made flakes after drying. The cellulose flakes were the hydrolyzed in acid condition for some hours up to nanocellulose were obtained, and the suspense was used in the gel phase of the silica sol-gel making process. This enabled the small particle of cellulose trapped in silica surfaces during gelling. This method was granted Indonesian patent Number IDP000049626, 14 February 2018. This is the best condition of the silica-cellulose making and followed for many types of applications. The original chemical reaction for silica formation can be written as follow:
SiO_2(s) + 2NaOH(aq) → Na_2SiO_3(aq) + H_2O(l)
Na_2SiO_3(aq) + H_2SO_4(aq) → SiO_2(s) + Na_2SO_4(aq) + H_2O(l)

The resulting white gel material was actually a SiO_2 hybrid with nanocellulose which are actually porous materials. Porous materials have the property if very high surface area and can be a place for adsorption, immobilization, entrapment and many other applications. Cellulose particles entrapped in this matrix shifts the surface property a bit and can be followed to reach some applications. This way, examinations for each application must be done too. With good understanding about the matrix, the suitable application can be considered better, rather having some applications in mind without adequate knowledge about the matrix. Some applications were tested for the materials. As adsorbents for organic dyes or heavy metals, as a separating agent for some natural pigments, as gas releaser in tritrophic interaction. The methods used were taken from the specific area of applications.

2.1. Method for characterization

Methods for characterization employed were for physical properties, water, and ash content, Iodine adsorption number, Scanning electron microscopy, infrared and ultraviolet-visible spectroscopy. The Brunauer-Emmet-Teller (BET) analysis was used to describe the porosity of the materials as well as the adsorption isotherm since all sol-gel technique results in porous media.

In application area, the heavy metal calculation was done by atomic absorption spectroscopy (AAS), natural and chemical pigments by ultraviolet and visible spectroscopy; infrared was used as well to see the adsorbed chemicals, thin layer chromatography is one of topical application which is relatively easy and clear. Variations of heavy metals as well as dyes components (Rodhamine B and Tartrazine) concentration were done to get a description of what occurs in the interface. The concentration of heavy metal ions, in this case, Cd^{2+} ion were also varied, to get the same description of the interface indirectly, as for dye molecules. To check the concentration changes, atomic spectroscopy was employed for heavy metals and visible spectroscopy for dye molecules in their maximum adsorption wavelengths (553 nm for rhodamine B, and 429 nm for tartrazine). All sets of experiments used a batch method using a certain amount of silica as well as silica-cellulose (0.05 grams), let it in contact with 10 mL of metals or heavy metal solutions and then filtered. The number of metal ions and dyes were calculated afterward.

For gas releaser, gas chromatography and combined by mass spectrometry was employed to detect the gasses escape from the surface interface. The silica cellulose sample was made bio-attractant by adsorbing some compounds to the surface that can attract insects. Through previous experiments, it was known that some chemicals cues play a role in the tritrophic interaction between host, insect pest, and parasitoid [19,29], in agriculture applications of this material. Chemical cues released from silica-cellulose matrix were detected by gas chromatography and also bioassay using olfactometer.

3. Result and Discussion

The gels were basically made by silica extraction from rice husk ash (Figure 1a) by sodium hydroxide solution. The filtered Sodium silicate was actually a clear solution (Figure 1b) while after gelling by acidification including cellulose incorporation by giving cellulose suspension (Figure 1c), the gel is obtained and purified to give the white powder (Figure 1d) which were ready for application. This sol-gel processing is actually modified from the simple one [28] and was already granted Indonesian Patent [30].

The journey from silica in rice husk ash and cellulose from nata de coco to make a hybrid biomaterial which is ready for many applications actually brings so many interesting facts that can be controlled and analyzed chemically. The surface formation of this type of porous materials is the key concepts for more applications in many areas which needs surface dynamics. This does not yet include the area of active chemistry from the surface, such as catalysis.
Silica surface actually adsorbing and this is well known. The cellulose incorporation into the silica was done to change the surface to be more adaptive to more organic components [17]. To shift the surface properties was also done by giving some surfactant (Figure 1, the most right one) since surfactant molecule tends to be ionic [31]. The surfactant is also known as a template in silica mesoporous making, as the regular pore size should be achieved [32]. Surfactant changes the surface while attached into silica surface and play its role to separate polar or very polar molecule [8,33,34].

There are some methods to follow sol-gel processing from the nature of solidification. By relaxation nuclear magnetic resonance The surface formation can be followed by the sudden change of spin-lattice as well as spin-spin relaxation time of the probe nuclei [35] in an NMR experiment. Silica from rice husk ash undergoes similar situation, the extracted silica in sodium silicate will be gelled again in better condition. The addition of acid to lower pH made the nucleation of the system more dominant; then the base addition makes the growth occurs faster, while the network formation once started. Once the porous media is formed, the surface characterization can be done too. Some paper use the vibrational spectroscopy such as infrared or Raman spectroscopy to assign the vibrational mode in the surface.

3.1. The characterization of silica and silica cellulose.

Physical characterization was done to the gels to compare the physical condition of the materials before applications, as can be seen in Table 1. The density of materials can be related to the pore system, the porosity as well as the distribution, as usually discussed by BET method [36–38]. For some applications, certain biomaterials must be described from the porous system point of view. The surface pore wall contributes greatly to the surface properties and affinity for the adsorbate molecules, and also solvent molecules.

Table 1. Physical characterization of silica and silica cellulose materials

| Materials                | Density (g/cm³) | Water content (%) | Iodine adsorption number (%) |
|--------------------------|----------------|-------------------|------------------------------|
| Silica-Cellulose         | 1.60           | 0.70              | 3.30                         |
| Silica-cellulose-surfactant | 2.26         | 0.90              | 3.80                         |

Brunauer-Emmet-Teller (BET) method is based on nitrogen adsorption on a certain solid wall of porous media, and the pore diameter, as well as the surface area, would be calculated indirectly. The BET theory is applicable to multilayer adsorption system which is slightly different with Langmuir derivation. Moreover, the biological system unlikely relies on one monolayer adsorption. Table 2 shows the pore systems of silica cellulose materials compared to the one with surfactant added during gelling. It is also related to the inter-connectivity of the pore system, as also discussed by NMR relaxometry [39] recently. However, NMR porous media has been widely used since before, due to the large surface wall.
with a certain mechanism of molecular adsorption [40,41] in empty or half empty pores. The solvent molecules also play a role in adsorption in the interface since the solvents also have a tendency to interact with active sites in the surface with a typical mechanism. The dynamics on surfaces is important to many areas of applications, including catalysis.

### Table 2. BET result of silica and silica cellulose

| Sample                  | Pore Diameter (nm) | Pore surface area (m²/g) | Pore Total Volume (cc/g) |
|-------------------------|--------------------|--------------------------|--------------------------|
| Silica-cellulose        | 4.74606            | 54.178                   | 6.428 x 10⁻²             |
| Silica-cellulose-surfactant | 4.79726            | 36.959                   | 4.433 x 10⁻²             |

Another spectroscopy method to characterize materials is infrared spectroscopy. This method is based on the adsorption of energy around the infrared region (300-750 nm), which is actually weak compared to the ultraviolet and visible region. This energy would excite the molecule to have a vibration in entire bonding. The vibrational modes will adsorb energy in a certain amount depending on the reduced mass of atoms bonded together. That is why the infrared spectrum is strongly related to functional groups of organic molecules, from their adsorbed energy [42,43]. Infrared is useful to assign chemical components in material science.

Mostly all functional groups present in the surface would be detected, and also adsorbed molecules. Vibrational spectroscopy is becoming important to describe the vibrational modes possible within materials [43,44]. Near-infrared materials are more beneficial due to its ability to see the lost energy in the matrix. Some validation methods were also reported in relation to near-infrared measurements [45–47]. In silica and silica cellulose materials the silanol groups are clear and also the cellulose carbonyls appeared (Figure 2).

![Infrared spectra](image)

**Figure 2.** Infrared spectra of silica gel (blue), silica cellulose (grey), silica cellulose with surfactant (black) and the surfactant CTMABr alone (green)

The hydroxyl groups will have the tendency of hydrogen bonding. That is why the band is usually broad, around 30120 cm⁻¹ and other vibrational –OH bands appear elsewhere (3246.2; 3311.78; 3336.85; 3367.71) cm⁻¹. The x-axis is the wave number in cm⁻¹ while the y-axis is the % Transmittance. Peaks around 1103.28 cm⁻¹ indicated asymmetric stretching vibration of Si-O-Si. Around 948.98 cm⁻¹ is bending vibration from Si-O. The unclear 470.63 cm⁻¹ – 418.55 cm⁻¹ indicated rocking vibration of Si-
O in Si-O-Si. In the spectrum of silica-cellulose some weak signs of –OH appear in its place, from the cellulose as well (3600-3200) cm\(^{-1}\). Stretching vibration –OH Silica appear at wavenumbers 3367.71 – 3219.19 cm\(^{-1}\), and 3346.50 – 3242.34 cm\(^{-1}\) in silica cellulose. The silanol groups seen on silica samples disappeared or got smaller compared to others in silica cellulose.

The spectrum of silica gel and Silica-cellulose are different to the one using a surfactant since the peaks from surfactant itself appear strongly, means the vibrations occur freely on the surface of the gels. There are some typical adsorption bands arising from -C-N of surfactant N-CTMABr. Around 2924.09 cm\(^{-1}\) is typical for the polar head of the molecule, which is N-CH\(_3\). Around wave number 2854.65 cm\(^{-1}\) is stretching vibration of symmetrical and asymmetrical –CH, from the long chained surfactant N-CTMABr. When the surfactant can be seen clearly then it is a sign that their vibrations are free and the molecules can help to separate other compound molecules in the mixture.

Another useful technique to see vibrations is Raman spectroscopy [48–50] which is based on scattered part of adsorbed light by materials. Raman spectroscopy is a complement to Infrared since what cannot be revealed by infrared can be seen by Raman spectroscopy. More important is that hydroxyl group does not make trouble to vibrational measurement. That is why the study of water solvent in confined porous media, such as the silica and cellulose matrix can be done [51,52]. More work in the infrared assignment of bound protein and other material for light harvesting were well explained already [53,54]. The work of chemicals adsorbed on the surface must be considered in the context of water solvents as well. Dynamics on surfaces which can be well assessed by NMR relaxation spectroscopy can also be detected and explained by Raman scattering.

![Figure 3. Surface morphology of silica cellulose material, 100,000 times magnification](image)

Also important to describe the morphology of materials, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are usually employed. Both methods rely on secondary electrons from surfaces irradiated by an accelerated electron beam to illuminate samples, which in turn give kind of image about the surface textures [55,56]. SEM and TEM are widely used in material science, which needs information about the morphology of the surface in good magnification, sometimes achieving 1 million times or more. In the TEM method, the electron beam transmitted through the ultrathin layer of the sample, giving an image like an optical microscope, while in the TEM method a particular area of the surface is scanned by the electron beam. The electron beam interacts with the surface, generating signals and topographical information about the surface. In Figure 3, the surface morphology of silica cellulose gels can be depicted. The green arrows showed the pore diameter seen
from the image. The globular cellulose particle randomly mixed with similar shape silica from rice husk ash after gelling and the width of the pores was below 100 nm. SEM and TEM methods are usually combined by Energy Dispersive X-ray spectroscopy (EDX) to enable the instrument to inform about the chemical elements present in the sample [50,57]. The use of X-Ray in this type of analysis is actually invasive to the structure of samples due to the high energy involved, but the information given is quite important. Another X-Ray method is X-Ray Diffraction Spectroscopy, which exactly the best method to show crystallinity of the material [50,57,58]. XRD is used excessively in material science to describe the formation and collapsing crystal structures of the samples. Most inorganic materials need XRD method to describe the structure. However, most of the biomaterials are not crystalline so that this method is rarely used.

One other common method to describe materials is thermo-analysis [59–61], in which the change of heat makes the materials change too. One the chemical bonds break, the reducing mass followed by very fine analytical balance would be the sign. When the sample is a mixture of compounds than the way the crystal collapse or the covalent bonds break will be typical for each compound. One uses also standard samples for this analysis. This method still has some types due to possible variation possible to follow the material changes. Some organic and inorganic samples rely on this method to explain their structures.

3.2. Application of Silica-cellulose Material

The application of this biomaterial can be developed due to its surface ability to interact with other molecules. In this case, the other molecules can be organic molecules, dyes, toxins, even bigger molecules like enzymes and protein, for future development. On the other hand, the metal-molecules, metal ions, and particle, anything inorganic can be possible as well to be removed by utilizing the surface properties of biomaterials. The test for it can be the routine work of spectroscopy methods, including ultraviolet-visible spectroscopy.

Adsorption application of silica-cellulose gel was done to separate chemical dyes, in this case, Rhodamin B (red color, sometimes used as food coloring agent) and tartrazine (yellow, food coloring agent) can be the probes in their working wavelengths, where the calibration curves were made. The adsorption capacity was then calculated. From the result, it was known that the presence of surfactant did give effect in adsorption of both rodhamine and tartrazine. Originally both were not well attached to the surface of silica-cellulose, while the organic molecules would look for polar surfaces to be adsorbed. The presence of the surfactant in the surface increase the ability of surface to interact with adsorbate molecules. Increasing the concentration of both dyes also increase the adsorption of all in the surface. this is the sign of physical interaction in which solvents, as well as adsorbate molecules, have the tendency of super-diffusivity in pore walls of the porous media [40,41,62]. In physical interaction or physical entrapment in the pore system, the attachment would long for sometimes only before desorption and adsorbed back to pore wall with different orientation [22]. The profiles of both adsorptions can be seen in Figure 4.

![Figure 4](image-url)

**Figure 4.** Rhodamine B and Tartrazine adsorption on silica cellulose and silica cellulose surfactant
More complexity arise on the interface when the two dyes were mixed together. There must be a kind of competition for the surface from both tartrazine and rhodamine M and also the huge amount of water molecules in the system. In silica cellulose system the tartrazine adsorption was higher than rodhamine B, while at the previous condition tartrazine alone or rhodamine alone adsorbed in similar concentration ~20% (Table 3). The “winning” position of tartrazine in this competition continued in the silica cellulose surfactant, in which stronger interaction can occur by the presence of a surfactant. It was also interesting that both dyes adsorbed much higher than the gel without surfactant. Tartrazine molecules have a partial negative charge due to lone pair electrons from oxygen atom it has.

Table 3. Adsorption of rhodamine and tartrazine in the mixture in silica-cellulose and silica-cellulose with surfactant surfaces

| Adsorbent       | Adsorbate     | Initial concentration (ppm) | Final concentration (ppm) | Adsorption (%) |
|-----------------|---------------|------------------------------|---------------------------|----------------|
| Silica-Cellulose| Rhodamine B   | 3.44                         | 3.40                      | 1.31           |
|                 | Tartrazine    | 6.66                         | 5.16                      | 22.50          |
| Silica-Cellulose-Surfactant | Rhodamine B | 3.44                         | 0.61                      | 82.33          |
|                 | Tartrazine    | 6.66                         | 0.00                      | 100.00         |

The other part of the adsorption system tested for this biomaterial was the probe ion Cadmium(II) from its nitrate salt using the batch method. In this case, there was another party playing role in the solid-liquid interface: the anion nitrate. Nitrate ions consist of more oxygen in addition to the nitrogen atom and negative charge of it. The concentration of both metals were varied and the analysis was done by atomic absorption spectroscopy. This method is powerful to inform the amount of metal ion irrespective the anions and other particles present in the system. The metal-containing particles would be atomized by burning in high temperature to release metal atom in the gaseous state [63,64]. The adsorbed energy by atom is typical and proportional to the concentration. That is why the adsorbed cadmium can be analyzed by atomic spectroscopy. The working wavelength of cadmium (II) ion is 228.8 nm upon which the calibration curve was made, following the Beer’s Law.

As like rhodamine and tartrazine, the silica cellulose with surfactant holds more Cadmium (II) ion more than the gels without surfactant. This is also understandable since the biomaterials tend to have organic properties while the metal species is purely ionic. Also the sample tendency towards giving more ions on the surface in high concentration, the adsorption also increases before leveling off.

Figure 5. Cadmium (II) adsorption profiles of both materials
The important application of this biomaterial is the use of its surface [65]. Dynamics in the solid-liquid interface or solid-gas interface govern the functions of the silica-cellulose matrix [26]. In the tritrophic interaction followed by analytical chemistry, the real wounded lignin-cellulose biomaterial of the paddy stem was actually imitated [19,66], [67]. The best material found was silica from rice husk ash and gelled together with nano-cellulose from nata de coco [30]. Within this phenomenon, bio-attractant for brown planthopper was actually tested. The formula was put in plastic vials ready for the experiment in the paddy field. Some glued paper in the surrounding showed the number of parasitoids trapped in the glue (Figure 6). Actually, some chemicals escaped from the interface and fly off as the sign of planthopper attack for its parasitoid. There also some method to analyze the released gas from the surface materials. Olfactometer was used for the bioassay for this experiments [66]. The other analytical method was gas chromatography followed by mass spectrometry.

![Figure 6](image)

**Figure 6.** Plastic vials with bio-attractant based on silica-cellulose material (left), and the application in a real situation as the source of volatiles that attracted parasitoid (right) [19]

Since the natural system was imitated, the released gas can be tested using gas chromatography. Some chemicals were chosen, a mixture of \( n \)-hexane, \( n \)-heptane, and \( n \)-hexadecane was adsorbed in the material and gave off those back to the air, as detected by the GC/MS (Figure 7).

![Figure 7](image)

**Figure 7.** The chromatogram of free (black) and adsorbed \( n \)-hexane, \( n \)-heptane, and \( n \)-hexadecane mixture (pink) from RTX-5 column, after 1 day of exposure [26].
3.3 Material science and environmental approach
Biomaterials as modern and mostly new-man-made materials can attract more scientist to get involved. The young scientists including the ones doing their study must be aware of ethics most of the time since the chemistry people know how to create new materials the same as to damage natural equilibrium. At the moment an eco-reflective education is needed to aim environment awareness and wider view about human beings as a part of nature [68,69]. Chemistry education plays important role in future material science. When education can be more environmentally aware, then the “green curriculum” must be hardly considered.

4. Conclusion
Spectroscopy, together with some other analytical chemistry methods using modern instrumentation is powerful to describe biomaterials, from the materials themselves (the characterization) and the applications which are mostly related to the biological system. Characterization of material can be done from the start of the process, i.e. following the material making, up to the use of biomaterial in the application system. In the area of application, several steps and types of examination can be done from an analytical chemistry point of view too. That is why the definition of biomaterial that is bound to a biological system (Merriam Webster Dictionary and others) must be put in a wider sense.

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Acknowledgments
This result was founded by research technology and higher education ministry, Indonesia under batch Fundamental Research Scheme 2014-2016, together with National Research Incentive (INSINAS) from Research and Technology Ministry during 2012-2014, and also Dwi Ismiatul Fauziah and Setyowati Dwi Yulandari, Setya Ayu Aprilia for kind assistant in producing part of the data from laboratory work as well as fieldwork.