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Biosilica Properties from Rice Husk using Various HCl Concentrations and Frequency Sources

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Rice husk is a by-product of rice milling with more than 90% of silicon dioxide. The objective of this research was to characterize the purity and electricity as well as structure property and surface morphology of silicon dioxide depending on different concentration of chloride acid (HCl). The experimental consisted of leaching the rice husk using HCl solutions of 1%, 3%, and 5% for 2 hours and burning it at several annealing temperatures and times with temperature rate of 1 °C.min-1. The analysis included purity and morphology, structure property, and electricity of silicon dioxide using Energy-dispersive X-ray/Scanning Electron Microscopy (EDX -SEM), X-ray Diffraction (XRD), and Inductance, Capacitance & Resistanc (LCR) meter, respectively. The EDX measurement indicated that the higher the concentration of HCl, the higher the purity of silicon dioxide. Additionally, the higher the concentration of HCl led to the higher the electrical conductance, conductivity, and dielectric constant. While, the higher the frequency led to the higher the electrical conductance and conductivity but the lower the dielectric constant. Based on these electrical properties, silicon dioxide from rice husk can be applied as both an insulator and semiconductor materials on electronic devices.

Introduction

In recent years, it has been discovered that biomass as a renewable energy has a potential to be a substitute for the fossil fuels. However, one of the problems associated with its use is that if its residue is not properly managed, it can cause environmental pollution and health problem for living organisms [1]. Rice husk is one of the agricultural by-products which is produced from paddies milling. According to Central Agency Statistics, in Indonesia, 75.36 million tons of dried paddies were produced in 2015 which is an increase of about 6.37% compared to that in 2014. This development has led potentially to the production of more rice husk. Rice husk contains organic compounds such as lignin, protein, oil cellulose, hemicellulose, and other components as well as inorganic compounds such as silicon dioxide which has a chemical formula of SiO_2 as its major component [2]. When rice husk is burned, it produces about 20-25% w.t. of ash that contains over 90% of silicon dioxide and other metal oxides [3,4].

In Indonesia, rice husk is processed into biofuel. However, the residue of the combustion is

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instrumental in environmental pollution. The temperature of rice husk combustion if not controlled results in the production of rice husk ash which has crystalline silicon dioxide as its content. The World Health Organization (WHO) has pointed out that crystalline silicon dioxide is very harmful because of its cancer-producing properties. Silicon dioxide consists of two phases which are crystalline and amorphous phases and the crystalline phase comprises α-crystoballite, β-cristoballite, α-tridymite, β-tridymite, α-quartz, β-quartz, moganite, keatite, stishovite and coesite. Furthermore, Hamad and Khattab [5], have established that various temperatures of rice husk combustion can convert the phase of silicon dioxide from amorphous to crystalline.

Silicon dioxide can be extracted from rice husk by leaching process using a solvent. According to Matori K et al. [6] and Ugheoke et al. [7], a solution of chloride acid (HCl) is more effective than HNO_3 and H_2SO_4 for removing impurities of metals and for increasing the purity of silicon dioxide to about 99%. The chloride ion (Cl^-) from HCl will interact with metal ions to produce chloride salt and will be eliminated using filtration process. Although leaching process has no effect on silicon dioxide phase [6,7], acid solution is able to remove alkali metals such as calcium, sodium and magnesium, which are present in rice husk ash [8]. Masrur et al. [9] obtained an extract of silicon dioxide using HCl 3% with heating rates of 0.5 °C and 1.5 °C per minute and achieved a purity of 99.15%. Rohaeti et al. [10] obtained an extract of silicon dioxide using HCl 3% with annealing temperatures of 700 °C, 800 °C, 900 °C, and 1000 °C. Fatoni [11] produced silicon dioxide extracts using HCl 3% from two different methods which were leaching before and after burning the rice husk. Aminullah et al. [12,13] and Sa'diyah [14] produced silicon dioxide extract from bamboo leaf using HCl 3% as well as Irzaman et al. [15] extracted Ampel bamboo leaves using 1%, 3%, and 5%. Adli et al. [16], Nazopatul et al. [17], and Sintha et al. [18] extracted silicon dioxide from charcoal of baggase, rice straw, and rice husk, respectively, using HCl of 3%. In addition, Riveros and Garza [19] reported purity of silicon dioxide from rice husk was 99.98% using HCl 3% at 90°C. NaOH also used as a solvent in leaching silicon dioxide from rice husk ash as reported by Kalapathy et al. [20] and Fernandes et al. [21]. The aim of this research is to determine the purity as well as structure and surface morphology of silicon dioxide with different concentrations of HCl from Rice Husk and the electrical property using various frequency sources.

Experimental

The materials for this research comprised 32% solution of HCl, aquabides, and rice husk. Each 50 g of rice husk was made to undergo leaching using HCl of 1%, 3%, and 5% on the hotplate at 200 **°C for two hours. Then it was rinsed with hot** aquabides until the pH 7 and dried in the oven at 90 **°C for three hours. Dried rice husk was burned and the charcoal was** ashed in the furnace at 400 **°C, 950 °C, and 1000 °C with holding time of one hour, two hours, and one hour, respectively with increasing rate of 1 °C per minute. Finally, white rice husk ash was formed.**

Samples were characterized by X-ray diffractometer (SHIMADZU XRD 7000 X-Ray Diffractometer mAXima) with CuK**α λ=1.5406 Å. The angle of diffraction was scanned from 10 ° to 80 ° at a scanning rate of 0.02 ° per minute. Component of silicon dioxide was measured using EDX (JSM-6510LA Analytical Scanning Electron Microscope) and the surface morphology of samples was measured using SEM with magnification of 3500 and 10000. A thin film of gold was** spread on the samples to enhance conductivity. The electrical properties such as electrical conductance, electrical conductivity, and dielectric constant were analyzed using LCR meter (HIOKI 3532-50 LCR HITESTER) where the frequencies were scanned from 50 Hz to 5 MHz with 200 points of observed frequencies.

Results and Discussion

EDX studies

Table 1 shows the composition of silicon dioxide using EDX where the higher concentration leads to the higher purity of silicon dioxide. However, in 5% concentration of HCl, the purity of silicon dioxide tends to be lower. This is due to Si ions were interacted to Chloride ions which has high electronegativity to form salt in the leaching process. Kurama and Kurama [22] stated that the higher the concentration of HCl, the higher will be the purity of silicon dioxide. However, saturation point was attained in HCl addition which indicated that the purity of silicon dioxide using HCl of 3 M was lower than that of 2 M [22]. Additionally, Kurama and Kurama [22] and Khalifa et al. [23] reported that the higher the concentration of HCl led to the lower the impurity in the sample. Khalifa et al. [23] made it known that a significant reduction in the concentration of impurities can be achieved when the purification was undertaken with thermal annealing and acid leaching. Diffusion of impurities from the volume of silicon dioxide grains to their surface occurs during thermal annealing, then the impurities are localized and removed from this surface during acid leaching. Larbi [24] confirmed that silicon dioxide from rice husk using EDX instrument was a high silicon-rich solid more than 99.5% w.t.

SEM and XRD studies

Figures 1 to 3 show the surface morphologies of silicon dioxide using SEM with magnification of 3500 and 10000. The surface morphologies of all silicon dioxides are not uniform, although there is a tendency that the higher concentration will leads to the lower grain formation. This morphology in accordance to Fernandes et al. [25] which reported that the silicon dioxide particles from their treatments were irregular and jagged. Azmi et al. [26] also showed that silicon dioxide from rice husk were in irregular geometry. These non-uniform formations reveal that the produced silicon dioxide has amorphous phase. This result is in line with the diffraction pattern by X-ray diffraction in Figure 4 where there are no dominant peaks. This XRD pattern has similiar to study of Ikram and Akhter [27] which stated a typical XRD pattern of amorphous silicon dioxide produced from rice husk combustion. Maximum peaks of HCl 1%, 3%, and 5% are in 2θ = 21.91 °, 21.65 °, and 21.77 °, respectively, with the same hkl plane (101). These peaks in line with Fernandes et al. [25] which presented that silicon dioxide from rice husk using temperature of 800 °C has amoru phous phase. Azmi et al. [26] and Johan et al. [28] also reported silicon dioxide from rice husk at 700 – 1100 °C and 700 – 1000 °C, respectively, were in amorphous with cristobalite phase and have peaks at 2θ of 20 – 22 °.

Electrical studies

In this study, characterization of the electrical properties on silicon dioxide from rice husks aims to determine whether the produced silicon dioxide has semiconductor properties or not as well as to find out how the material behavior when given a high frequency/energy which this behavior must be in accordance to the general formula that dielectric constants are inversely proportional to the frequency. The temperature for measurements taken against frequency is at room temperature about 300 K. Figure 5 indicates the relationship between the electrical conductance and frequency at 50 Hz to 38 kHz. This electrical conductance aims to predict the direction of electron flow in the properties of electrical conductivity in the plane of geometry orientation which analyzed from XRD. The electrical conductances of silicon dioxide using HCl of 1%, 3%, and 5% were in the range of 0.0 – 0.4 S, 0.6 – 4.5 S, and 2.5 – 12.5 S, respectively. These results indicate that silicon dioxide using HCl of 3% has the highest electrical conductance, while concentration of 1% has the lowest. In addition, Figure 5 also showed that the higher the frequency, the higher the electrical conductance value.

Figure 6 shows the relationship between electrical conductivity and the frequency of the samples at 50 Hz to 38 kHz where silicon dioxide using HCl of 3% has the highest electrical conductivity than any other concentration which supported by the result on XRD which stated that silicon dioxide using HCl of 3% has the lowest oxygen atom percentage of 37.59%. This property has similiar pattern compare to conductance property with different intensity values (Y-axies). According to Srivastava et al. [29], the lower the percentage of oxygen in silicon dioxide the higher the electrical conductivity of it. In additon, the greater the frequency used in this study the higher the electrical conductivity. This is due to an electron that excites to conduction band from valence band when it gets some energies thereby leaving some holes. The greater the energy given to the material, the greater the number of electrons that move from valence to conduction band and the greater will be the number of holes created. These movement of electrons and formation of holes are proportional to the electrical conductivity, that is, the higher the number of holes the higher will be the electrical conductivity. The electrical conductivities of silicon dioxide using HCl of 1%, 3%, and 5% are in the range of 0.0 – 10^{-3} $S.cm^{-1}$, 5×10^{-4} – 5.2×10^{-2} $S.cm^{-1}$, and 1.5×10^{-2} – 7.5×10^{-2} $S.cm^{-1}$ in frequencies of 50 Hz – 38 kHz. These results showed that the conductivity values of silicon dioxide from rice husk were in the range of the semiconductor. Kwok et al. [30] stated that the range of conductivity values of semiconductor materials ranging from 10^{-8} - 10^{3} $S.cm^{-1}$.

Table 1. The chemical composition of SiO_2 using EDX

Element	% atom		
	1%	**3%**	**5%**
Oxygen	50.54	37.59	67.16
Silicon	45.76	58.70	32.16
Calcium	2.10	-	-
Aurum	1.61	3.71	0.68
SiO_2	**99.99**	**99.99**	**96.48**

Figure 1. Surface morphology of silicon dioxide using HCl of 1%

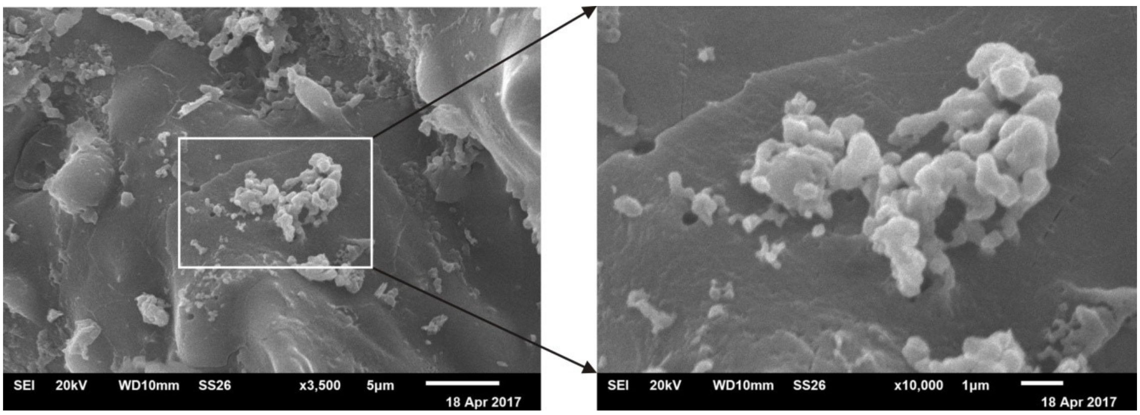


Figure 2. Surface morphology of silicon dioxide using HCl of 3%

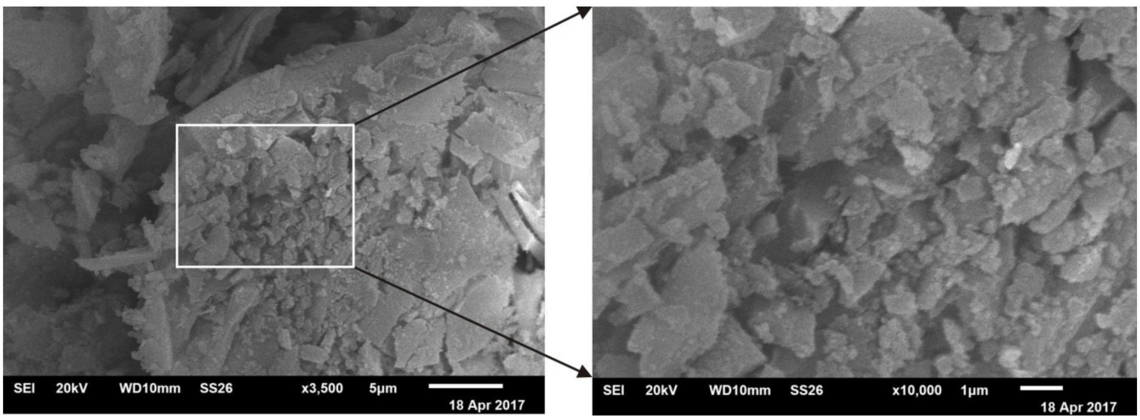


Figure 3. Surface morphology of silicon dioxide using HCl of 5%

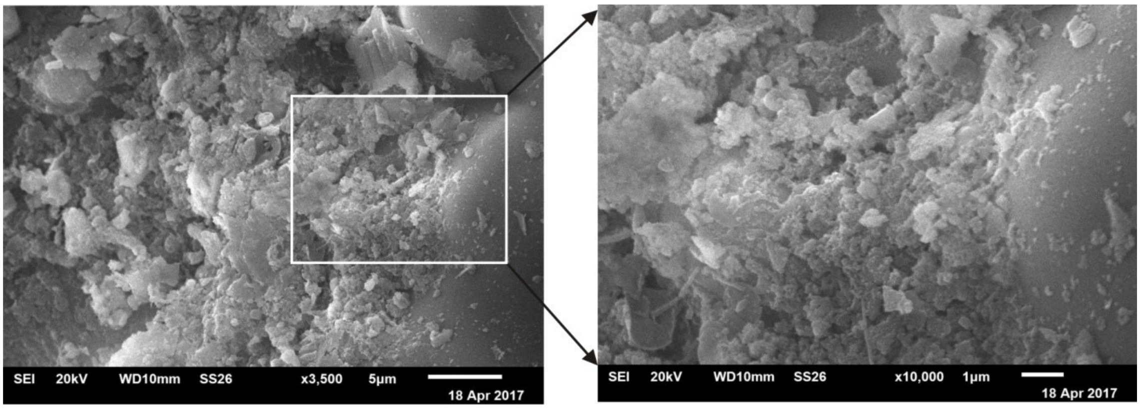


Figure 4. Diffraction pattern of silicon dioxide using HCl of 1%, 3%, and 5%

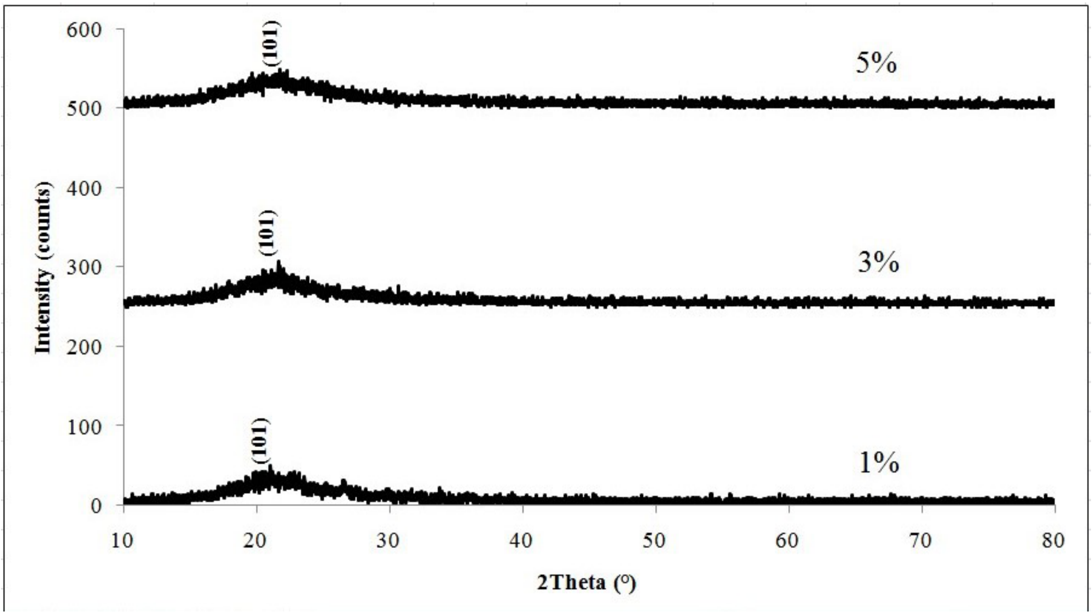
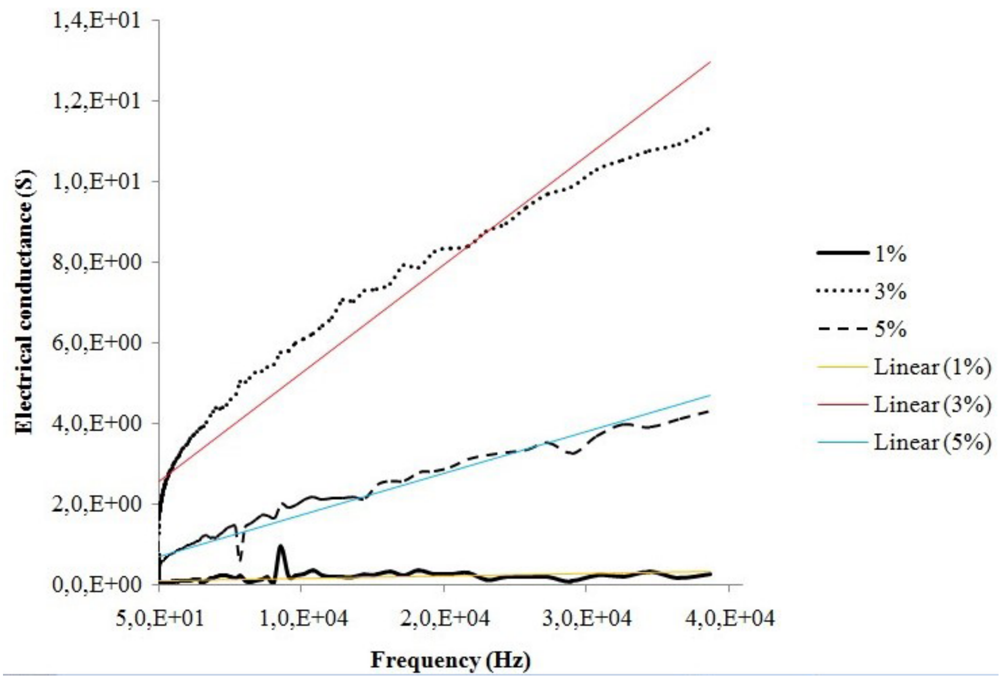


Figure 5. Electrical conductance of silicon dioxide with various frequency sources



Figures 7 and 8 show the relationship between dielectric constant and frequency of samples at 50 Hz – 680 Hz and 680 Hz - 38 kHz, respectively. From these figures show that minority elements such as aurum and calcium also vibrate which cause the formation of peaks at frequencies of 50-100 Hz. While at higher frequencies, minority elements do not vibrate so do not form peaks or it has ideal curve as described by Sze [31]. The dielectric constant values of silicon dioxide using HCl of 1%, 3%, and 5% are in the range of $1.9 \times 10^9 – 0.0$, $6 \times 10^9 – 0.0$, $8.3 \times 10^9 – 0.0$, respectively, for frequencies of 50 Hz - 680 Hz and lower than 1×10^7, $4 \times 10^7 – 1 \times 10^7$, $9.5 \times 10^7 – 1 \times 10^7$, respectively, for frequencies of 680 Hz – 38 kHz. The results in this study indicated that the higher the frequency, the lower the dielectric constant of silicon dioxide which strengthens the results of the obtained conductivity. This is as a result of their dipole orientation which cannot balance the electric field. This factor causes a drop in the net polarization of the material as each polarisation mechanism ceases to contribute, and hence its dielectric constant will drop. Fares [32] pointed out that the motion of free charge carriers is constant at a lower frequency so that the dielectric constant is constant. As the frequency increases, the charge carriers move through the dielectric and get trapped at the defect site which is causing opposite charges in the vicinity. This causes a reduction in the speed of the charge carrier and the value of the dielectric constant also reduces. Yadav et al. [33] reported that the higher frequency given, the lower the dielectric constant and this follows equation below [34],

where is dielectric constant at low frequency, is dielectric constant at high frequency, ω is angular frequency, and τ is relaxation time. In addition

Conclusion

Different concentration of HCl has an effect on purity and electricity of silicon dioxide from rice husk. The higher the concentration of HCl the higher the purity of silicon dioxide. Additionally, the higher the concentration of HCl the higher the electrical conductance, conductivity, and dielectric constant and the higher the frequency given the higher will be the electrical conductance and conductivity, however, dielectric constant decreased. In addition, these data show HCl of 3% is the optimum concentration for leaching rice husk

Figure 6. Electrical conductivity of silicon dioxide with various frequency sources

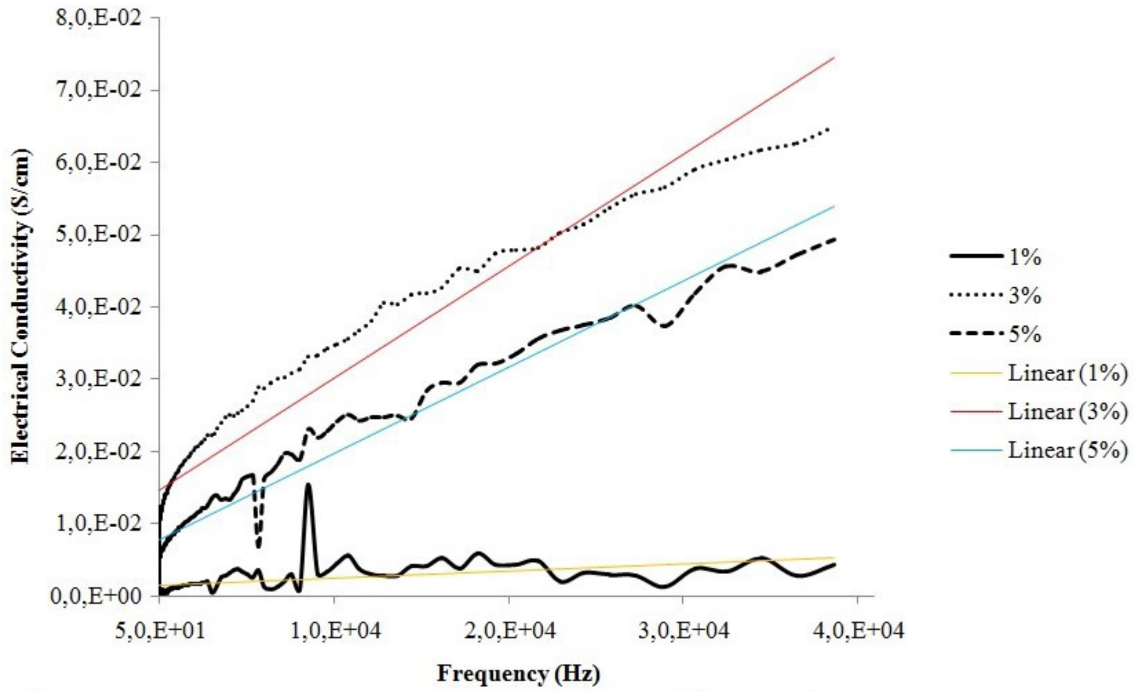


Figure 7. Dielectric constant of silicon dioxide with frequency sources at 50-680 Hz

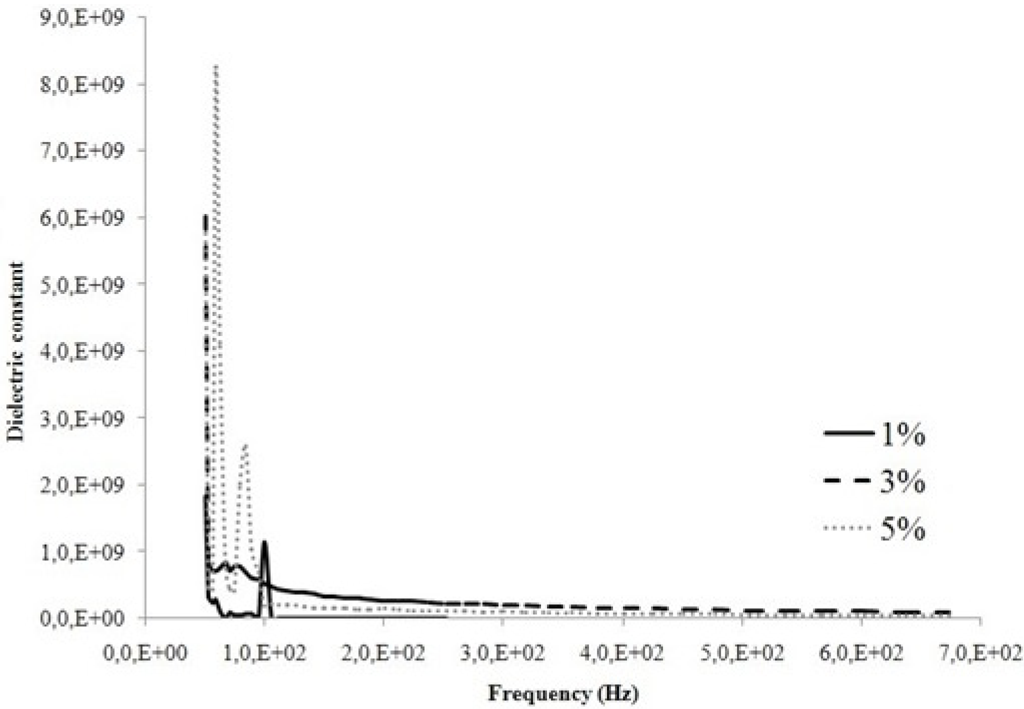
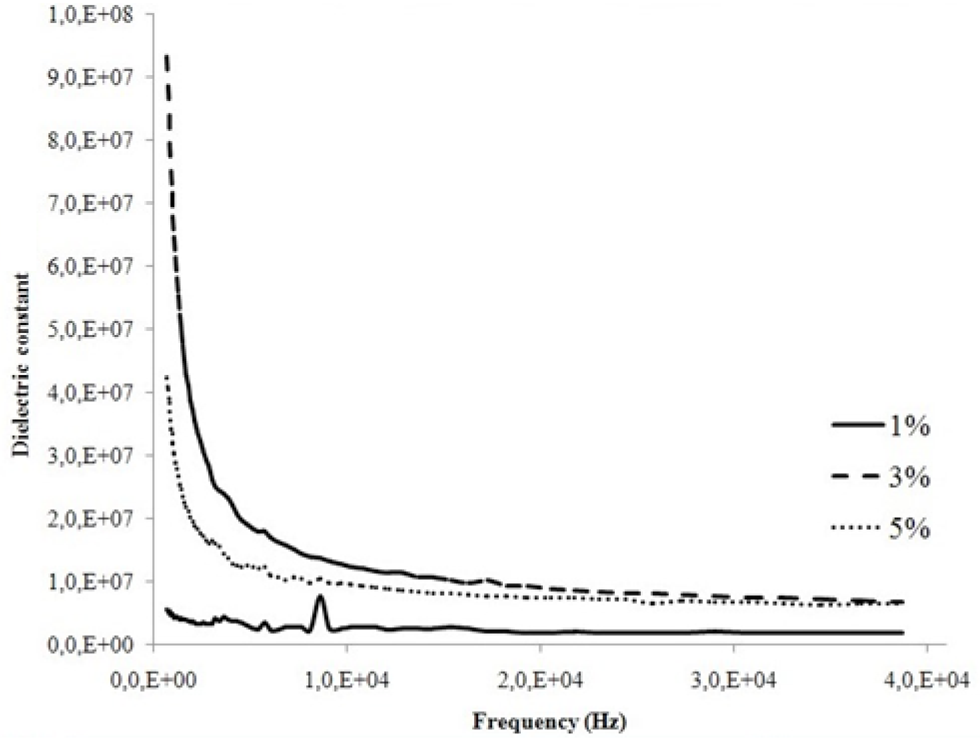


Figure 8. Dielectric constant of silicon dioxide with frequency sources at 680-38000 Hz



enhance purity and electrical properties of silicon dioxide. In addition, higher concentration than 3% results in lower purity as well as lower electrical properties. Based on these electrical properties, silicon dioxide from rice husk can be applied as both an insulator and semiconductor materials on electronic devices.

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