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SULFUR DIOXIDE AND AMMONIA GAS REDUCTION USING COCONUT CELLULOSE AND ACETYLATED CELLULOSE

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Abstract: Some adsorbent materials were employed to reduce ammonia and carbon dioxide gases. Cellulose materials from *nata de coco* and grated coconut meat were packed in a column to be used as gas adsorbent. The effect of surface modification of cellulose by acetylation in order to enhance the sorption ability and capacity was also studied. Another factor that was tested was the column length.
The characteristics of cellulose materials were done by electron microscopy, infrared spectroscopy, and physical parameters such as water and ash contents as well as iodine sorption ability. The amount of ammonia and sulfur dioxide gases absorbed by the materials were analyzed by visible spectroscopy. The results showed that the cellulose material can be good adsorbent for basic gas like ammonia as well as acidic sulfur dioxide gases. Acetylation as a method of surface modification gave the proof of better sorption for both gases but was greater for ammonia. However, the column length gave greater impact in ammonia compared to sulfur dioxide. This study provides a better explanation of dynamics at surfaces, in the search for better adsorbents.

Keywords: *adsorption, ammonia, cellulose, cellulose acetate, sulfur dioxide*

INTRODUCTION

Air pollution is a serious problem in global community. Increasing activities of modern people, industrial processes, energy consume and higher life style, all contribute significantly to the air pollution [1]. Usual gas pollutant can be neutral enough like carbon dioxide but other can be hazardous like ammonia and sulfur dioxide. In presence of moist, ammonia will form ammonium hydroxide and sulfur dioxide will turn into sulfuric acid. Several attempts have been done to minimize gases produced by chemical processes. Making catalytic converter to change hazardous gases into milder ones is one of the popular attempts. However these methods produce also hazardous wastes and byproducts.
As a “green material”, cellulose attracts attention because of the wide variety of application, mostly due to its pure cellulose content. In nature, cellulose can be found in huge amount in plants as the main part of wood. The form of cellulose in plants varies, mostly is mixed with lignin. Mango bark consists of 36.5 % cellulose besides 49.5 % lignin [2], which makes the cellulose difficult to extract. However, there are some other sources of cellulose which are abundant and pure in nature, such as the fiber of *nata de coco*. This *nata* is made of coconut water and the fermentation is done by the aid of *Acetobacter xylinum* in slightly sweet and acidic medium [3, 4]. Coconut meat is the other relatively pure cellulose source from coconut fruit. The oil content can be separated easily by solvent extraction.
The surface of cellulose consists mostly of polar hydroxyl groups, and it is also covered by moist. This enables good interaction in the surface area between polar particles in the surroundings and the polar surface. Sorption ability of cellulose is the key property to be utilized in this research, in order to reduce “bad” gases as the waste products of fuel combustion as well as in many industrial processes. The surface behavior determines the separation of molecules exposed to the surface, depending on uniqueness of interactions of each [5]. When a molecule possesses more than one functional group, then more possibility in pattern of surface attachment must be considered. When more than one types of molecules present together on a surface, then complexity in approaching and leaving the surface arises. In this way, separation of compounds like in chromatography processes can be well thought-out.
Actually some physical aspects of the interaction in small scale or in molecular level can be well described by the aid of modern instrumentation such as nuclear magnetic resonance (NMR). In this method, molecular relaxation and diffusion of the probe nuclei, usually protons, on surfaces informs the sorption behavior on surface [6]. Sorption process and phenomena on surfaces are the key concepts of the gas reduction system. The physical sorption which was investigated using NMR experiments indicated a surface dynamics that enables particles to interact with surface in a special mechanism [7]. While some materials with very high surface area are usually porous, the sorption in porous media system can be considered for cellulose in these systems. Gas molecules and small particles can undergo very fast diffusion due to inner pore space in combination with surface properties. Other investigations also revealed the effect of polarity of the small particles to the surface dynamics [8].
In recent decades, several investigations concerning the cellulose sorption ability have been done. Sorption of water, methanol, and benzene vapors on cellulose surface and its standard isotherm has been reported [9]. Another study of NO_2 gas sorption using

mango bark powder and neem bark dust showed good sorption capacity yet they are not a pure cellulose form [10, 11]. Removal of carbon dioxide from ambient air has also been done using amine-modified nanofibrillated cellulose [12]. Further investigation studied single component and binary CO_2 and H_2O sorption of the material [13]. Interaction between CO_2 and amine groups on cellulose surface can be explained by acid-base properties. The slightly acidic CO_2 will be adsorbed by the basic amine groups. Beside CO_2 and NO_2, there are ammonia and sulfur dioxide gases polluting the atmosphere. Ammonia is mainly released from fertilizer industries while sulfur dioxide is emitted from fossil fuel combustion. Several methods have also been applied to reduce ammonia concentration such as air scrubbing techniques [14], and biotrickling filter-denitrifying bioreactor [15].

The study of cellulose acetate as an adsorbent for several chemicals has been reported, but less common for hazardous gases. Nonwoven membrane of cellulose acetate has been used to adsorb heavy metal ions Cu^{2+}, Hg^{2+}, and Cd^{2+} in water [16]. This study stated that the adsorbed ions are easily desorbed by addition of ethylenedinitrilotetraacetic acid solution. Another investigation showed that cellulose acetate was capable of adsorbing cyclic compounds, such as cycloalcohols, cycloethers, amino acids, heterocyclic aromatic compounds, and nucleosides [17]. The suggested sorption mechanism was inclusion of those compounds into micropore in cellulose acetate. The use of modified cellulose acetate as an adsorbent has also been reported. Polyaniline-modified cellulose acetate membrane has been introduced as an ion exchange material of AuI_2^- complex [18]. These investigations indicated that cellulose acetate can be used as a green material for pollutant removal.

In this work, the sorption ability of coconut cellulose and cellulose acetate to reduce ammonia and sulfur dioxide gases was studied. The simple and abundant material can meet more important application as environmental friendly adsorbent. Utilization of this cheap material can be one of the benefits of this research regarding gas pollution in the future. On the other hand, the chemistry underlying this research is very simple and can be understood by many. Moreover, the method for gas sorption can also be useful as a part of chemistry education, which must include environmental issues in the future.

EXPERIMENTAL

Adsorbents preparation

The first part was the cellulose and cellulose acetate material preparation, as well as the making of the columns for gas sorption experiments. There were two sets of samples, the original cellulose from *nata de coco* and its acetylated surface. The other set was the grated coconut meat and its acetylated surface.

The second part was the gas sorption experiments. The cellulose and cellulose-acetate from *nata de coco* were used for ammonia gas sorption, while sulfur dioxide sorption experiments were carried out on grated coconut meat and its acetylated surface.

All chemicals for the experiments were from Merck and Sigma Aldrich. The raw material was pure cellulose fiber from *nata de coco*, and cellulose from grated coconut meat from which the coconut oil was already cleaned by *n*-hexane solvent *via* continuous extraction. Both of the cellulose materials were dried at 70 °C in oven several hours and then crushed in order to reduce particle size to 50 mesh. These materials are porous by nature. This original cellulose was also characterized by the water and ash content as well as the iodine adsorption.

Surface modification was made by dissolving 5 g of each cellulose material in 100 mL of glacial acetic acid at room temperature for 90 minutes before the addition of sulfuric acid and some more glacial acetic acid. The temperature was made 35 °C for another 90 minutes under magnetic stirring. The mixture was then filtered, and the solid part was then dissolved in 30 mL anhydride acetic acid, stirred at 35 °C for another 90 minutes. The mixture was again filtered and the white solid was washed with water before drying process in the oven at 45 °C for 24 hours. The acetylation can be monitored from the infrared spectra. Acetylation reaction can be written as follows:

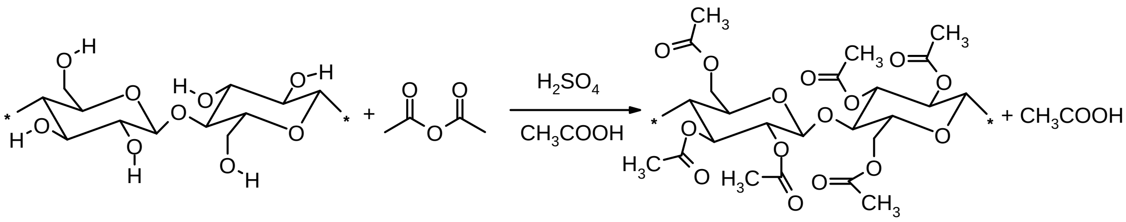


Figure 1. *Acetylation reaction of cellulose*

Gas sorption experiments

The sorption experiments were done for the *nata* and grated coconut meat systems as well as for acetylated cellulose from both types of cellulose, by passing the ammonia or sulfur dioxide gas through a column filled with the material. The elution of ammonium gas was done by connecting the source of the gas from one end and trapping the gas remained by immersing the other end of the column in a solution of 0.5 % boric acid. The length of column and duration of elution were varied. To the final solution, phenol-sodium nitroprusside and basic buffer were added to make a blue colored complex which can be analyzed using UV-visible spectrometry. The chemical reaction of the process can be seen in Figure 2:

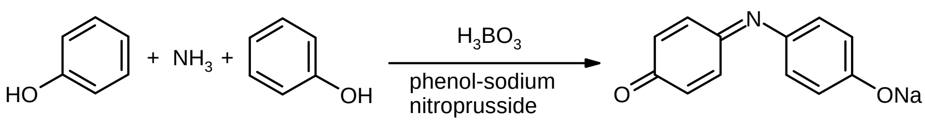


Figure 2. *Development of blue colored complex for ammonia detection*

The second type of sample was grated coconut meat and its acetylated cellulose. For this system, through the similar packed column, the sulfur dioxide gas was released and flowed to the end of column where it was captured by a solution of 35 % hydrogen peroxide. The sulfur dioxide was made by reacting sodium thiosulphate with hydrochloric acid. The analysis was done using turbidimetry since the white solid of barium sulfate formed is proportional to the amount of the sulfur dioxide gas according to the following basic reactions:

$$Na_2S_2O_3\ (s) + 2HCl\ (aq) \rightarrow 2NaCl\ (aq) + S\ (s) + SO_2\ (g) + H_2O\ (l)$$

$$SO_2\ (g) + H_2O_2\ (aq) \rightarrow H_2SO_4\ (g)$$

$$H_2SO_4\ (aq) + BaCl_2\ (aq) \rightarrow BaSO_4\ (s) + 2HCl\ (aq)$$

RESULTS AND DISCUSSION

Adsorbent material

The original cellulose from *nata de coco* or coconut meat has different surface texture even though the surface chemistry was similar. Cellulose is the main material for both coconut meat and *nata de coco* and other carbohydrate like galactomannan gives no impact since the functional groups on surfaces are the same. However, the coconut meat has empty oil pockets after oil extraction using *n*-hexane solvent. The empty holes seen in the material were the dried oil pockets which made the surface area even bigger. *Nata de coco* has fine fibers and the density depends on the length of the fermentation. Originally the surface is polar covered by water and slightly acidic due to the medium used for the *Axetocater xylinum*. Coconut meat cellulose was the adsorbent for sulfur dioxide gas while *nata de coco* was made for ammonia gas. Both were acetylated and the sorption abilities of each sample were compared. The figures from scanning electron microscopy showed the different surface appearance as can be seen in Figure 3.

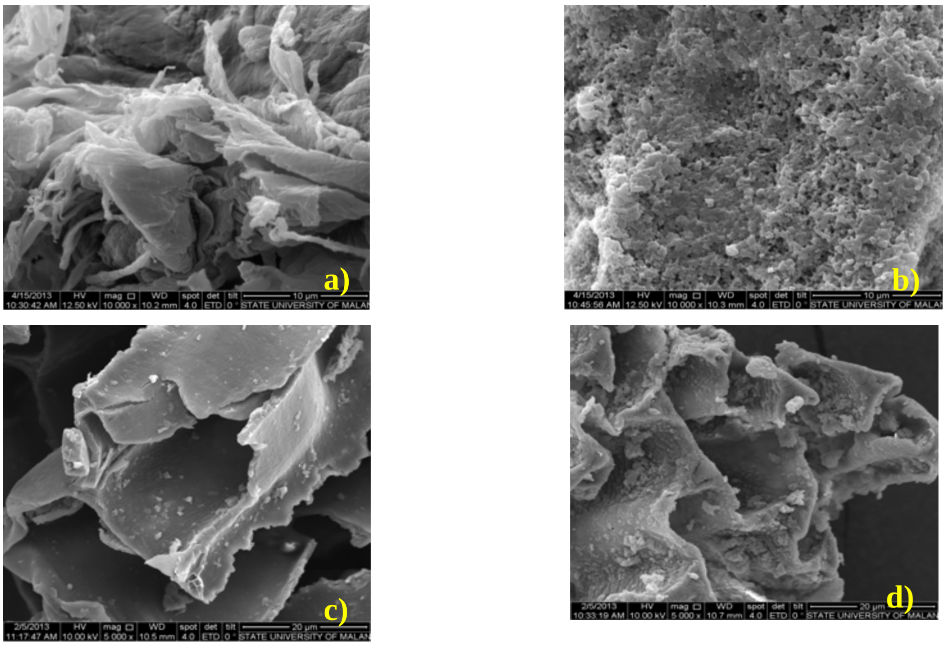


Figure 3. *The surface of:*
original (a) and modified (b) nata de coco (at 10,000x magnification) and
original (c) and modified (d) shredded coconut meat (at 5,000x magnification)

From the texture difference in acetylated cellulose, the porous media could be claimed. However, *nata* cellulose fiber was very tight entangled and this made the sorption process hard. The inner surface of the cellulose could not be reached by the adsorbate molecules in solution unless swelling process occurred. On the other hand the acetylation process makes the surface more porous as can be seen in the Figure 3. The "swelling" of the network could be done during acetylation process. The pores formed by acetylation were clear too, and the dimension might reach as small as nanometer scale. Moreover, the esterification process would make the surface "hairy" in molecular level due to additional functional groups (ester group $–COOCH_3$) attached on the surface. The sorption process would be optimum while the inner surfaces were better accessed *via* the pores from outside. The same appearance could be found in coconut meat cellulose. The acetylated surface was rough and porous. This fact made the porous media surface dynamics discussed before [19]. The fast diffusion in porous media is more or less a physical interaction with no strong bonding in the surface of the pores. However, the mechanism would be partly applicable before the gas molecules could be trapped permanently in the pore system.

Figure 4 showed infrared spectra of both original cellulose as well as acetylated cellulose

a

b

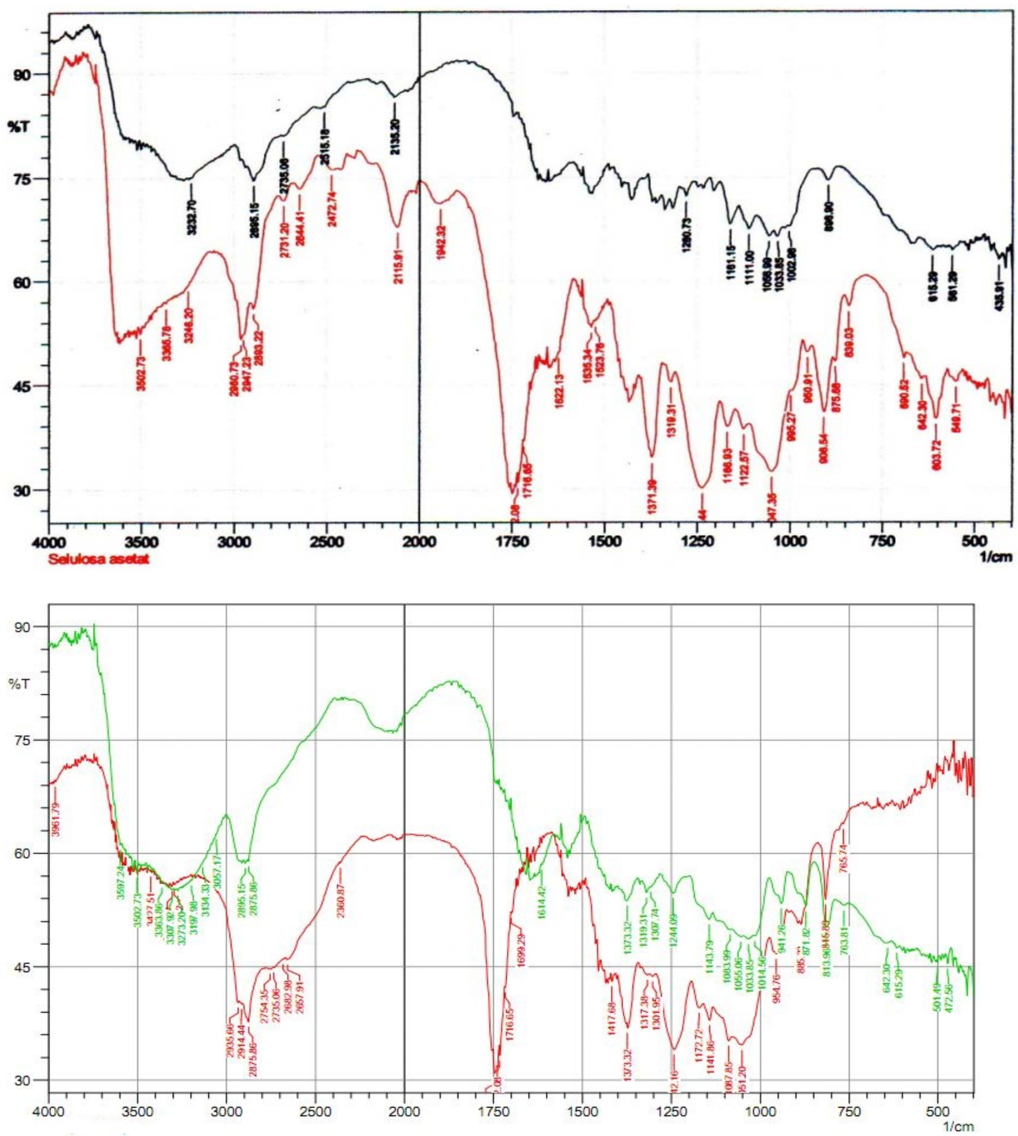


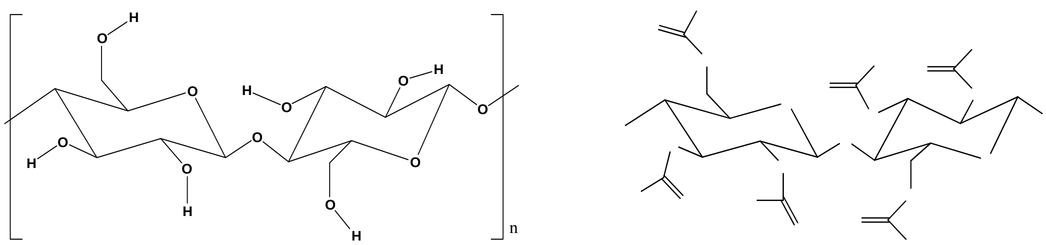
Figure 4. *IR-spectra of cellulose (black and green) and cellulose acetate (red) of nata de coco (a) and grated coconut meat (b)*

The difference between the adsorption bands around 1700 cm^{-1} arose from the ester bond formed. This can be the proof of acetylation reaction. It occurred both in cellulose material from *nata de coco* as well as coconut meat cellulose.
The physical characterization of the material can be described by water and ash content as well as iodine sorption ability as can be seen in Table 1. Iodine adsorption is the general term to describe sorption ability of adsorbent and the quality of potential sorption process. Both types of samples showed increase in water content after acetylation. The moist could be the polar contribution for the surface while the iodine adsorption was related to the pore system formed.

Table 1. *Chemical characterization of cellulose material*

Parameter	System	Before acetylation [%]	After acetylation [%]
Water content	*Nata de coco*	8	28
Ash content	NH_3 sorption	1	0
Iodine sorption ability		2.74	4.11
Water content	Grated coconut meat	7	16.5
Ash content	SO_2 sorption	2.0	1.0
Iodine sorption ability		5.997	14.778

The molecular structure of cellulose and cellulose acetate are shown in Figure 5. The active sites enable the surface to adsorb polar molecules in gaseous or aqueous phase where water molecules also play an important role. The surface of cellulose acetate has more active sites due to oxygen atoms at carbonyl groups from the ester functional group. Moreover relatively higher water content indicated wet and polar surface area for acetylated cellulose. This type of material can be a good adsorbent for polar gases like ammonia and sulfur dioxide. In this case, the porous media dynamics cannot be applied in simple way due to the complexity in the surface. Not only gas but also water layer plays significant role in the sorption process. Part of weak binding energy of the adsorbate molecules in the surface active sites must be considered besides the hydrogen bonding occurring between ammonia and sulfur dioxides molecules with water molecules.



a *b*

Figure 5. *The molecular structure of cellulose (a) and cellulose acetate (b)*

Gas reduction experiments

The sorption experiments gave indication of more surface interaction than only physical entrapment of gases in the porous media in the column. The acetylated cellulose adsorbed the gases more than the original cellulose in both ammonia and sulfur dioxide systems. The cellulose acetate had more active sites in the surface compared to the original cellulose, indicated by active methyl ester group (-$COOCH_3$) on the surface (Figure 5). The acetyl part was also very polar rather than the hydroxyl groups in the original cellulose. The presence of terminal oxygen atoms which contained two lone-pair electrons would bring the relatively negative charged sites on the surface which in turn would play role in the sorption process. In connection with van der Waals interactions, the intra- and intermolecular hydrogen bonding between hydroxyl groups must be taken into account in the adsorbent-adsorbate interactions. With a more complex surface, cellulose acetate would bind adsorbate molecules stronger.

Moreover since the polarity is higher, the acetylated surface tends to be hygroscopic, adsorbing moist in greater amount. The water contents of *nata* and also grated coconut meat were less than the acetylated cellulose as shown in Table 1. The surfaces were covered by moist, and this moist coverage could be a fixed layer of water ready for molecular distribution. The iodine sorption ability which is usually connected with surface area increased after acetylation in *nata de coco*. Coconut cellulose showed sharp increase in iodine sorption value after acetylation indicating that the ability of surface changed by acetylation. The complexity in the surface would arise from the different chemical condition on surface, or in other words the active sites would play important role. The interaction was more efficient in the modified surface.

The cellulose acetate membrane in other system can sieve cyclic compounds due to the pore entrapment of the membrane body [17]. The small gas molecules like carbon dioxide and sulfur dioxide, in our case, cannot be considered only physically entrapped in the confinement. However the presence of water layer on pore surfaces might adsorb the molecules in longer retention time before releasing them back to the pore liquid or pore space. The fast diffusion within the surface area could be considered. The water content of the material was also the sign of hygroscopic properties in the material, which in turn, helped the sorption process. The acetylation process made the surface "hairy" and adsorbed water molecules more as can be seen in the water content (Table 1).

The ammonia had the tendency to have basic properties especially when associated with water molecules in the system, while the sulfur dioxide was certainly more acidic as this oxide would form sulfuric acid in presence of water. The increase of adsorbed ammonia sharp up to more than 90 % in the acetylated cellulose compared to the original cellulose (Figure 6). The sulfur dioxide absorbance in the cellulose acetate was around twice the amount at the pure cellulose surface.

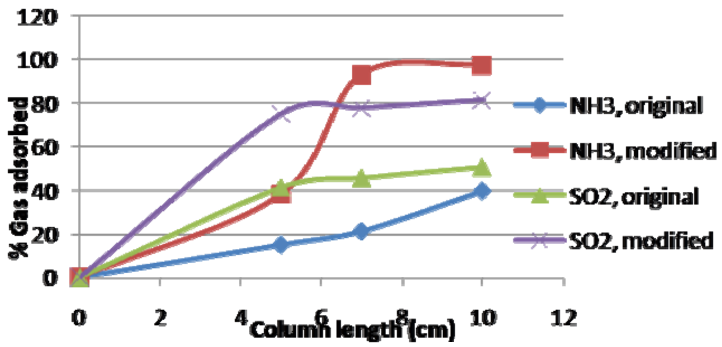


Figure 6. *The sorption of NH_3 and SO_2 by the adsorbents*

The pores in the surface could give more surface area for partition of the gases. The moisture layer in the surface area acts as stationary phase for the gas molecules to dissolve. The ambient air acts as mobile phase when compared to separation process in chromatography. The returning molecules to the gas phase from the moist layer might lead to particular mechanism discussed previously [7, 8, 19]. The gases released from the surface undergo surface diffusion mechanism in which the speed is enhanced. However, pore entrapment will reduce the amount of gases reaching the end of the column.

The column length which is proportional to the amount of adsorbents indicated the interaction of adsorbate molecules and surface. The ammonia system consistently gave increased gas sorption as the column was made longer, while in the case of sulfur dioxide sorption, the increase was not too high suggesting physical interaction reached equilibrium. Physical entrapment of the gas was also considered. Sorption process reduces the amount of both gases differently depending on the internal properties of the adsorbate as well as the surface properties.

CONCLUSION

Some types of adsorbent material based on natural cellulose have been made for gas reduction application. The seeking of better materials for gas reduction in the environment was one of the aims for better future. Materials based on cellulose from coconut meat and *nata de coco* were employed to adsorb ammonia and sulfur dioxide gases. The surface modification by acetylation in fact changed surface texture and also increased the ability of the material to adsorb gases. Ammonia gas was adsorbed in greater amount compared to sulfur dioxide, both in cellulose as well as acetylated cellulose.

The sorption mechanism of gas particles on some other types of surfaces is being investigated. Suitable isotherms for sorption behavior can be a good description for the gas-sorption models in the future, aiming on fabrication of cheap and green materials for gas reduction purposes.

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